Title

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Author

De Jonghe, Lutgard C.

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Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

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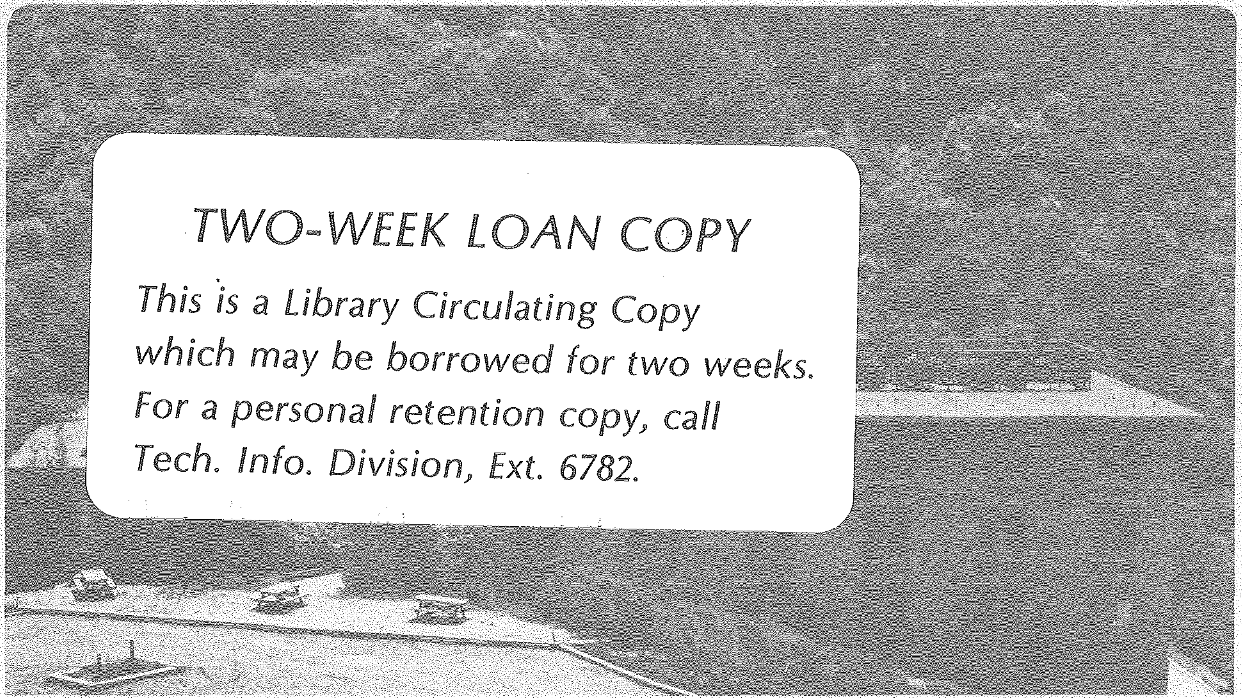

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Materials and Molecular Research Division

Lawrence Berkeley Laboratory

and

Department of Materials Science and Mineral Engineering

University of California

Berkeley, California 94720

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Electron beam induced defects in sodium-β" alumina were studied by De Jonghe (1977a) by means of lattice imaging. No detailed calculations were formed comparing the theoretical lattice images with the actual ones. Spacial correspondence of the lattice images to the real crystals, therefore, had to be assigned arbitrarily. This type of lattice imaging is the real space equivalent of a $\vec{g}.\vec{R}$ experiment, and permits under certain conditions to directly measure fault displacement vectors. Bovin (1979), in a recent paper, has analyzed multibeam lattice images of faulted sodium-beta" aluminas, matching actual images with calculated ones. Such procedures can certainly extract more information from the lattice images, provided the instrument transfer characteristics are of sufficient quality. Bovin, in his calculations, could indeed reliably determine the general correspondence between image contrast and crystal position, and he justly pointed out the proper assignement of dark image contrast to the conduction plane in beta" alumina (1977a). A corrected image for the faults reported by De Jonghe (1977a) is shown in Figure 1 here. It should, however, be pointed out that the conclusions reached by De Jonghe about the nature of the spinel-like defect are not affected by the labeling choice: it was not concluded that a conduction plane runs to the spinel-like intergrowth, as is evident from a cursory reading of the text; in fact, the discussions clearly point out that the fault is the result of a loss of a conduction plane.

The feature of importance to the defect is the sequence of the oxygen planes in the direction perpendicular to the conduction planes of the layered beta" alumina lattice. This sequence of oxygen planes can be written as ABCA B' CABC A' BCAB C' ABC... where A, B, and C stand for oxygen layers in the spinel block, and A', B', and C' symbolize the sodium ion conduction plane. It is clear from Figure 1 that the sequence after loss of a conduction plane has to be:

...ABCA B' CABCABCA B' BC...

leading to a B'——B' sequence, i.e., a spinel-like intergrowth. However, Bovin finds that according to his calculations and iamges the sequence is...AB C' ABCACABC A' BC... leading to a C'——A' sequence, i.e., a faulted spinel-like intergrowth. It is not possible to reconcile Figure 1 shown here with this conclusion. Perhaps both types of defects, B'——B' and C'——A', can occur. This would certainly not be unusual considering the variety of possible planar faultings occurring in sodium-beta and -beta"aluminas, as described by Stevens (1976) and by De Jonghe (1977b). The difference in the B'——B' defect and C'——A' defect is that the first one avoids the electrostatic problem by a shear, while the latter one avoids it by a cooperative diffusional jump of Al^{3+}. Conceivably, the defects C'——A' might be favored over the B'——B' defect at lower rates of formation and higher temperatures.

Detailed interpretation of the local lattice images seems at present somewhat speculative. Although De Jonghe labeled the faults "spinel intergrowths," it was not implied that the defects had a perfect spinel structure. No diffusion is involved in the formation of a B'—— B' intergrowth. Retained oxygens and other point imperfections undoubtedly complicate the fault structure and cloud the interpretation of local fringe details.

Bovin proposes that the profuse formation of spinel-like defects may account for the degradation of sodium-beta" alumina in operating sodium/sulfur cells. It is difficult to see how such defects can be formed when long range oxygen ion transport is necessary. Instead, recent experiments by De Jonghe et. al., (1979), and by Virkar, et. al., (1979), indicate that degradation is initiated from the sodium ion exit electrode interface. While the formation of the blocking intergrowth indeed produces very significant stresses, as can be deduced from foil fractures in heavily faulted specimens such as shown in

Figure 2, other surface flaws such as preexisting cracks, are likely to be of significance. At present, the initiation of breakdown in sodium-beta and beta" alumina is still poorly understood. Current work by Buechele et al seems to indicate that intrinsic degradation is not a likely cause of failure initiation. Rather, it appears that impurity deposition at the electrochemical interfaces, may dominate the breakdown initiation.

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Lutgard C. De Jonghe
Staff Senior Scientist
Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Associate Professor in Residence
University of California, Berkeley 94720

FIGURE CAPTIONS

Figure 1: (00.3, 10.3) lattice image of a fault resulting from a conduction plane loss in a sodium-β alumina thin foil. The conduction planes are labeled in accordance with the image correspondence determined by Bovin (1979). Only conduction planes of one type, B', have been labeled. According to this image, the intergrowth defect has a spinel-like structure: ... CA B' CABCABCA B' CA ... XBB790 15072

Figure 2: Thin foil fractures resulting from profuse Na_20 loss and subsequent faulting, stimulated by the electron beam. Interestingly, the sodium-β" alumina behaves as a micro-composite of which the spinel blocks are the hard members. XBB799 11593

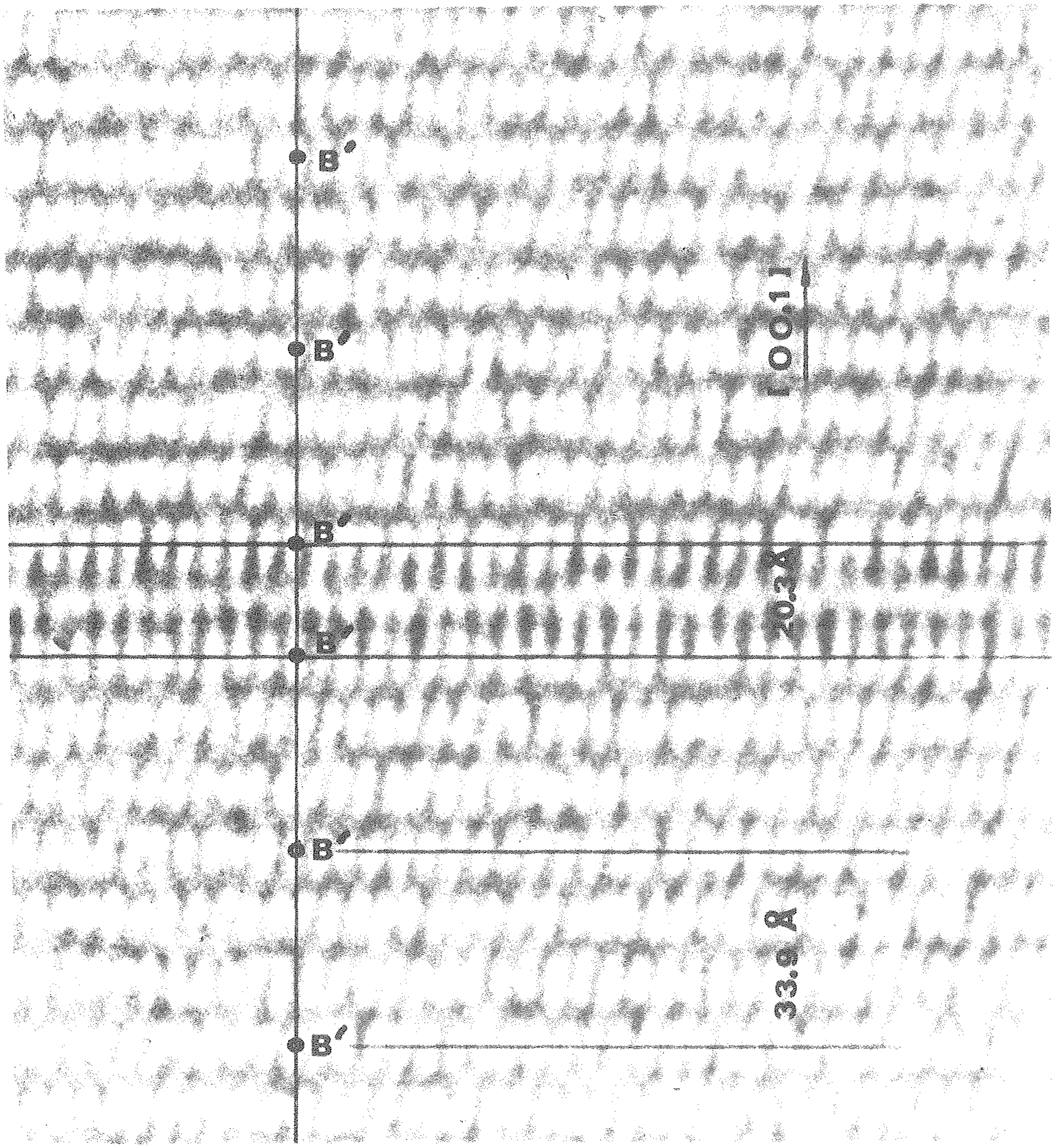

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Figure 1.

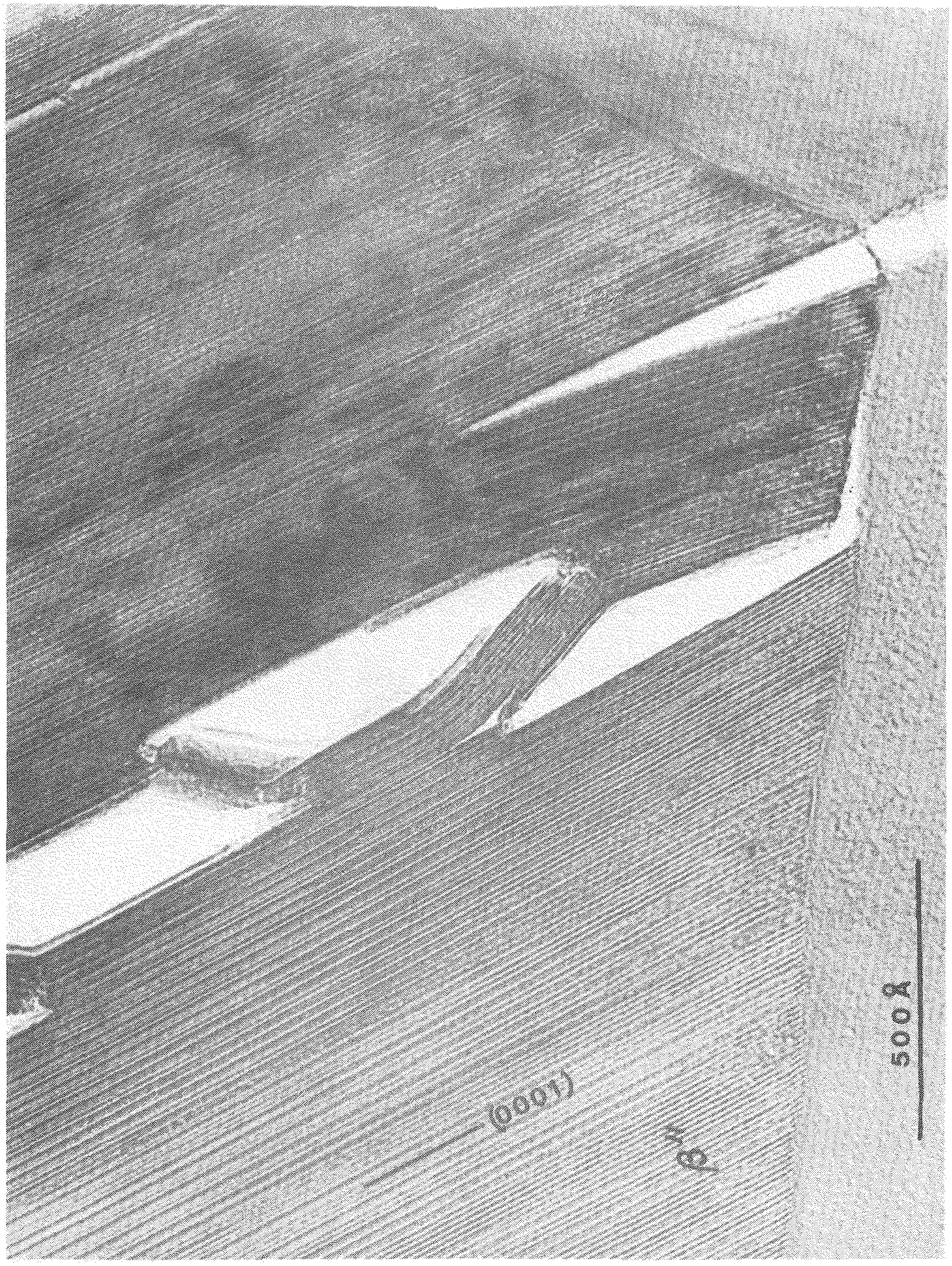

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Figure 2.