Comments on *High-resolution electron microscopy images of defects in Mg- and Li-stabilized β″-aluminas* by J.-O. Bovin.

By L. C. DE JONGHE, *Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Materials Science and Engineering Department, University of California, Berkeley, California 94720, USA*

Abstract

A recent paper [Bovin (1979). *Acta Cryst.* A35, 572–580] reported the analysis of lattice images of faulted sodium β″-alumina, and proposed to relate the observed faults to the degradation of this electrolyte during use in the sodium/sulfur battery. In this paper, it was stated that a previous report misinterpreted the lattice images of a related fault. It is pointed out that the earlier conclusions concerning the nature of the fault are not in error, and that published and unpublished work by a number of workers on degradation of sodium β″-alumina solid electrolytes does not support the proposed degradation mechanism.

In a recent paper, Bovin (1979) compared calculated and actual images for some planar faults in sodium β″-alumina solid electrolyte. He stated that De Jonghe (1977*a*, 1979) misinterpreted the lattice image of electron-beam-induced faults of the type reported by Bovin.

The nature of electron-beam-induced defects in sodium β″-alumina was reported independently by De Jonghe (1977*a*) and Matsui & Horiuchi (1977). Matsui & Horiuchi made their observations with a high-voltage–high-resolution electron microscope under conditions where the charge density approximation holds, making the lattice-image correspondence straightforward. Those conditions were not satisfied with certainty by De Jonghe and the choice of correspondence then had to be arbitrary. This type of lattice imaging is the real-space equivalent of a g.R experiment, and permits one under certain conditions to determine directly fault displacement vectors. The comparison of calculated and actual images reported by Bovin (1979) can certainly extract more detailed information from the lattice images, provided the instrument transfer characteristics are of sufficient quality and the specimen characteristics and diffraction conditions are accurately known. Bovin, as well as Matsui & Horiuchi, could indeed determine the lattice-image spatial correspondence reliably, showing that the labeling choice by De Jonghe (1977*a*) was inappropriate. A properly labeled image is shown in Fig. 1 here. Contrary to Bovin's assertion, however, the conclusions reached by De Jonghe about the nature of the spinel-like defect are not in error since they do not depend on an absolute lattice-image correspondence – as is evident from even a cursory reading of the text. The discussion clearly points out that the fault is a result of the loss of a conduction plane. An identical inclusion was also reached by Matsui & Horiuchi.

The feature of importance for the defect is the sequence of the oxygen planes in the direction perpendicular to the conduction planes of the layered β″-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 Fig. 1 that the sequence after loss of a conduction plane has to be ···*ABCA B′ CABCABCD B′ BC*···, leading to a *B′−B′* sequence, *i.e.* a spinel-like intergrowth. However, Bovin finds that according to his calculations and images 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 Fig. 1 shown here with this conclusion. In fact, both types of defect, *B′−B′* and *C′−A′*, can occur, as reported by Matsui & Horuchi. This is not unexpected considering the variety of possible planar faultings occurring in sodium β- and β″-aluminas, as described by Stevens (1976) and De Jonghe (1977*b*). The difference between the *B′−B′* and *C′−A′* defects is that the former avoids the electrostatic problem by a shear, while the latter 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, as is also suggested by the work of Matsui & Horiuchi.

Detailed interpretation of the local lattice images remains at present somewhat speculative. Retained oxygens and
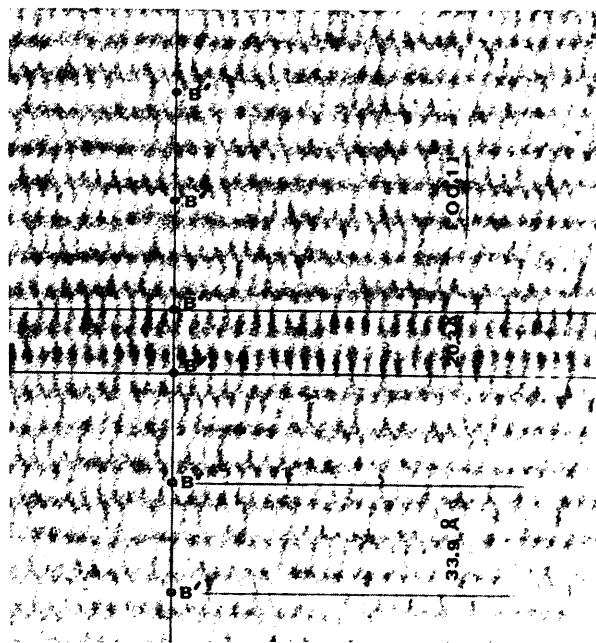

Fig. 1. (00.3, 10.3) lattice image of a fault resulting from a conduction-plane loss in a sodium β″-alumina thin foil. The conduction planes are labeled in accordance with the image correspondence determined by Matsui & Horiuchi (1977) and Bovin (1979). Only conduction planes of one type, *B′*, have been labeled. According to this image, the intergrowth defect clearly has a spinel-like structure:···¹*CA B′ CABCABCA B′ CA*···.

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 β''-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, Feldman & Millet (1979) and Virkar & Viswanatan (1979) indicate that degradation is initiated from the sodium-ion exit electrode interface. While the formation of the blocking intergrowth due to Na_2O loss indeed produces very significant stresses, other surface flaws such as preexisting microcracks are likely to be of more significance. At present, the initiation of breakdown in sodium β- and β''-alumina is still poorly understood. Current work by Buechele, Feldman & De Jonghe (1979) seems to indicate that intrinsic degradation is not a likely cause of failure initiation. Rather, it appears that effects such as impurity deposition at the electrochemical interfaces may dominate the breakdown initiation.

References

BOVIN, J.-O. (1979). *Acta Cryst.* A35, 572–580
BUECHELE, A., FELDMAN, L. & DE JONGHE, L. C. (1979). Unpublished work.
DE JONGHE, L. C. (1977a). *Mater. Res. Bull.* 12, 667–674.
DE JONGHE, L. C. (1977b). *J. Mater. Sci.* 12, 497–502.
DE JONGHE, L. C. (1979). *J. Am. Ceram. Soc.* 62, 289–293.
DE JONGHE, L. C., FELDMAN, L. & MILLETT, P. (1979). *Mater. Res. Bull.* 14, 589–595.
MATSUI, Y. & HORIUCHI, S. (1977). *Proc. Fifth Int. Conf. on High Voltage Microscopy, Kyoto,* 1977, pp. 321–324.
STEVENS, R. (1976). *J. Mater. Sci.* 11, 1911–1918.
VIRKAR, A. V. & VISWANATAN, L. (1979). *J. Am. Ceram. Soc.* 62, 528–529.

Compensation of excess intensity in space group *P2*.

By G. D. NIGAM, *Department of Physics, Indian Institute of Technology, Kharagpur 721302, India* and A. J. C. WILSON, *Department of Physics, University of Birmingham, Birmingham B15 2TT, England*

Abstract

Earlier work on *P2* made simplifying assumptions. The resulting restrictions are now removed, and the expected intensity of a general reflexion is shown to be

$$\Sigma \left[1 - 2aJ_1(4\pi as)/(C - 4\pi a^2)s \right],$$

where Σ is the sum of the squares of the moduli of the atomic scattering factors, a is an average atomic diameter, J_1 is the usual Bessel function, s is $(2 \sin \theta)/\lambda$, and C is the area of the face of the cell perpendicular to the twofold axis. The expected value is altered for the special groups of reflexions $h = k = 0$ and $l = 0$, h and k even.

Introduction

Wilson (1964) showed that symmetry elements not producing systematic absences produced instead ripples in reciprocal space that modified the expected (mean) intensity of reflexion. He treated the space group *Pm* in some detail, and indicated how the idea of inaccessible volume could be applied to other symmetry elements, such as 2 and $\bar{1}$. Nigam (1972) considered the space groups *P2* and *Pmm2*; his treatment of the former involved some simplifying assumptions, roughly equivalent to replacing the actual unit cell by a cylinder having the same *c* (twofold) axis and cross-sectional area equal to that of the *C* face. As will be seen below, this procedure is unnecessary.

Since atoms are of finite diameter, the minimum distance between a pair related by a twofold rotation axis is equal to the diameter. This will vary with the type of atom, but for the present purpose it may be assumed that all that are in contact across the axis have the same average diameter a. The x and y coordinates of the atoms, instead of being distributed with approximately uniform probability over the whole cross section of the unit cell, as assumed by Wilson (1949), are excluded from cylinders of radius a surrounding the twofold axes passing through 00, $0\frac{1}{2}$, $\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}$, the area available to them being thus $C - 4\pi a^2$ instead of C. Integration over this restricted area, required in the evaluation of the expected intensity, is readily seen to be equivalent to integrating first over the whole cross section and then subtracting the integral over the interior of the excluded cylinders.

Calculation

By the use of trigonometric identities Nigam's equation (2) can be written

$$I = \Sigma + 2 \sum_{i}^{\frac{1}{2}N} f_i^2 \cos 4\pi(hx_i + ky_i)$$

$$+ 4 \sum_{i \neq j}^{\frac{1}{2}N} f_i f_j^* \cos 2\pi(hx_i + ky_i) \cos 2\pi(hx_j + ky_j)$$

$$\times \cos 2\pi l(z_i - z_j). \qquad (1)$$