

## BETA-ALUMINA ELECTROLYTE FOR USE IN SODIUM/SULPHUR BATTERIES

### PART 1. FUNDAMENTAL PROPERTIES

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#### Summary

This paper is the first of a two part review which aims to summarise recently published material on sodium beta alumina relevant to its use as an electrolyte in sodium/sulphur batteries. An overall objective is to relate the practical aspects of manufacturing and using  $\beta$ -alumina tubes (Part 2) to its basic materials science (Part 1) and to show how solid state chemistry and ceramic technology each play an important role in determining the properties and durability of  $\beta$ -alumina electrolyte.

In this first Part we consider the latest structural data on sodium beta alumina and discuss how variable stoichiometry is accommodated. The role of dopants is reviewed and the stability and phase relationships of both the pure binary system and doped  $\beta$ -alumina are summarised. Recent electrical conductivity measurements on single crystal and polycrystalline sodium beta alumina are discussed and it is shown why the non-stoichiometric composition  $(\text{Na}_2\text{O})_{1+x} \cdot 11\text{Al}_2\text{O}_3$  has a higher conductivity than the stoichiometric phases  $(\text{Na}_2\text{O})_{1.0} \cdot 11\text{Al}_2\text{O}_3$  and  $(\text{Na}_2\text{O})_{2.0} \cdot 11\text{Al}_2\text{O}_3$  on either side of it.

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#### Introduction

The discovery of the remarkable ability of  $\beta$ -alumina to conduct sodium ions with diffusion coefficients of  $\sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at 600 K, reported by Yao and Kummer in 1967 [1], effectively inaugurated a new branch of science — solid state ionics. Since that time the investigation of fast ion conductors (or “superionics”) has developed rapidly and there have been several international conferences on the subject [2 - 4]. This activity stems partly from scientific interest in a new phenomenon and partly from the potential technological importance of  $\beta$ -alumina as a solid electrolyte in the sodium/sulphur battery. The concept of this high temperature battery, which is now well known, was proposed by Weber and Kummer in 1967 [5]. These two papers by Kummer and his colleagues at the Ford laboratories must now be regarded as classics as they introduced both a new branch of science and a

new, potentially important, battery technology. Since that time sodium/sulphur battery development programmes have been pursued vigorously in USA, Japan, France, Germany and the U.K.

There have been a number of reviews of the literature concerned with  $\beta$ -alumina [6 - 8], but since the most recent of these the subject has moved forward rapidly and the present paper seeks to incorporate the new published information to facilitate appreciation of  $\beta$ -alumina in its role as the electrolyte in sodium/sulphur batteries. It is not intended to cover the literature comprehensively; rather, selected references will be cited to illustrate the scientific principles involved and the procedures which have been adopted for the fabrication and use of  $\beta$ -alumina electrolyte.

Even with these constraints applied, the volume of literature is large and, hence, the review has been divided into two parts. This part is devoted to the fundamental properties of sodium beta alumina (related compounds with sodium replaced by other ions are not included) and the second part (to be published in a later issue) will deal with technological aspects of the manufacture and use of the material as an electrolyte in sodium/sulphur batteries. An objective of the whole review is to relate the practical and engineering problems associated with this application to the basic materials science of  $\beta$ -alumina.

### Structure of $\beta$ -alumina

Sodium beta alumina, of general formula  $\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3$ , occurs principally in two crystalline forms designated (for historical reasons [6])  $\beta$ - and  $\beta''$ - $\text{Al}_2\text{O}_3$ . A characteristic of the  $\beta$ -alumina type materials is that neither compound normally exhibits an exact stoichiometry and this doubtless contributes to the high ionic mobilities for which they are valued. The stoichiometric variability is achieved by means of a number of structural devices which will be discussed in the following Sections. Some fundamental structural parameters of the two compounds are given in Table 1. Each of these compounds is built up from a common structural unit: slabs of spinel-like structure containing four layers of close-packed oxygen ions in cubic stacking extend normally to the  $c$  axis. The slabs are separated from each other by relatively open regions containing the sodium ions and one quarter as many oxygen ions as usual. These act as rigid inter-slab spacers between two aluminium ions, *viz.*, Al-O-Al units. (Fig. 1). The "spinel slabs" contain the aluminium ions distributed among the octahedral and tetrahedral interstices of the close-packed oxygen layers.

Ionic conduction occurs by diffusion of sodium ions exclusively within the open planes perpendicular to the  $c$  axis. In both compounds the conduction planes are 11.3 Å apart. The  $\beta$ - $\text{Al}_2\text{O}_3$  unit cell is made up of two spinel slabs ( $2 \times 11.3$  Å) with a mirror plane between them [9], while  $\beta''$  has three slabs in its unit cell ( $3 \times 11.3$  Å) which are related by a three-fold screw axis [10].

TABLE 1  
Structural parameters of sodium beta aluminas

Compound	Lattice	Space group	Lattice parameters (Å)
$\beta$	Hexagonal	$P6_3/mmc$	$a = 5.59, c \sim 22.6$
$\beta''$	Rhombohedral	$R\bar{3}m$	$a = 5.59, c \sim 33.9$

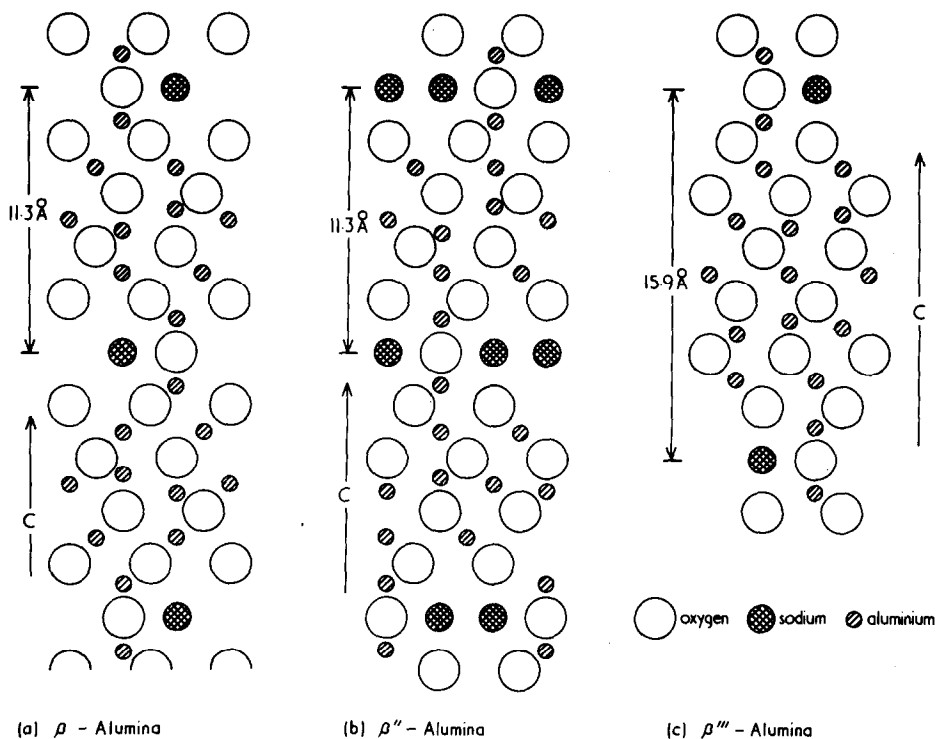
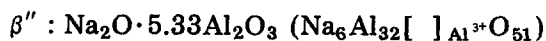


Fig. 1. Crystal structures of  $\beta$ ,  $\beta''$  and  $\beta'''$   $\cdot \text{Al}_2\text{O}_3$ ; projections of structures on  $11\bar{2}0$ . Sizes of atoms approximately to scale.

### Accommodation of variable stoichiometry

The idealized compositions of the two compounds as deduced from the structures outlined above are:



with the formula unit for  $\beta''$  revealing the existence of one cation vacancy per unit cell in the spinel blocks. If we write  $\beta$ - $\text{Al}_2\text{O}_3$  as  $\text{Na}_3\text{Al}_{33}\text{O}_{51}$  it is seen at once that  $\beta''$  is formed from  $\beta$  by replacing one  $\text{Al}^{3+}$  ion in the spinel block by three extra  $\text{Na}^+$  ions in the conduction plane.

The  $\beta$  compound is found normally to contain excess sodium oxide compared with the idealized formula, *viz.*,  $(\text{Na}_2\text{O})_{1+x} \cdot 11\text{Al}_2\text{O}_3$  with  $x$  being between 0.2 and 0.3.

In principle this excess can be accommodated either by forming  $\text{Al}^{3+}$  vacancies in the spinel block, as suggested above for  $\beta''$  alumina, or by placing extra  $\text{O}^{2-}$  ions in the conduction plane. Neutron diffraction studies [11] have shown that the occupation of the mirror plane is more complicated than originally thought. The excess  $\text{Na}^+$  is neutralized by interstitial  $\text{O}^{2-}$  ions in the conduction plane which are pinned by Frenkel defects ( $\text{Al}^{3+}$  vacancies and associated  $\text{Al}^{3+}$  interstitials) in the spinel block (see Fig. 2). This results in a linear defect of formula  $\text{V}_{\text{Al}}\text{Al}_i-\text{O}_i^{2-}-\text{Al}_i\text{V}_{\text{Al}}$ , where  $\text{V}_{\text{Al}}\text{Al}_i$  is the Frenkel defect attached through an interstitial oxygen in the conduction plane to its mirror image in the next spinel block. This composite defect will have two  $\text{Na}^+$  ions associated with it.

Consideration of the conduction plane of  $\beta$ - $\text{Al}_2\text{O}_3$  (Fig. 3) shows that there are three possible positions for the sodium ions [9]:

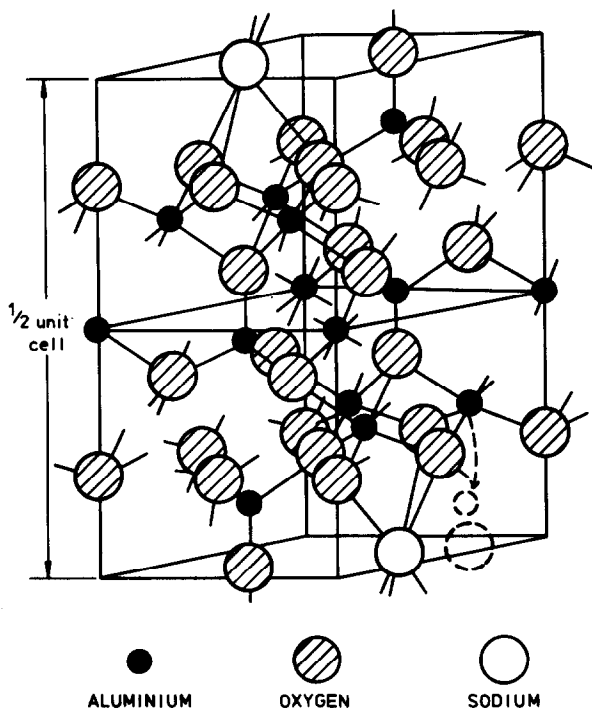


Fig. 2. The aluminium Frenkel defect which pins charge compensating oxygen ions in the basal plane of  $(\text{Na}_2\text{O})_{1+x} \cdot 11\text{Al}_2\text{O}_3$ .

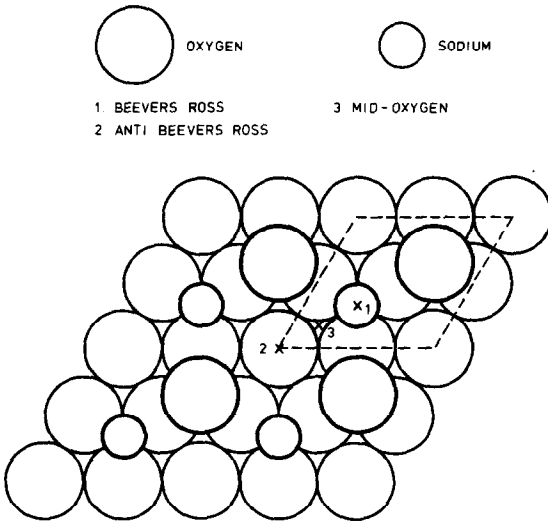


Fig. 3. Conduction plane of  $\beta$ -alumina. The dashed line shows the cross section of a unit cell. The  $c$  axis is perpendicular to the paper. Light circles are atoms on planes above and below the conduction plane.

- (1) Beevers-Ross site,
- (2) anti Beevers-Ross site,
- (3) mid-oxygen site.

In  $\beta$ - $\text{Al}_2\text{O}_3$  of composition  $(\text{Na}_2\text{O})_{1.27} \cdot 11\text{Al}_2\text{O}_3$  it has been shown [9] that the sodium ions are distributed 0.75 near to the Beevers-Ross site and 0.25 near to the mid-oxygen site. The neutron diffraction studies [11] reveal that the excess  $\text{Na}^+$  ions are associated with interstitial oxygen ions located near the mid-oxygen sites. When the sizes of the two types of ions required to populate the three types of site are taken into account (Fig. 4) it becomes evident that the filling of the conduction plane with ions will impose a sodium-rich limit on the structure as long as the linear defect revealed by the neutron studies remains the sole charge-compensation mechanism. It is

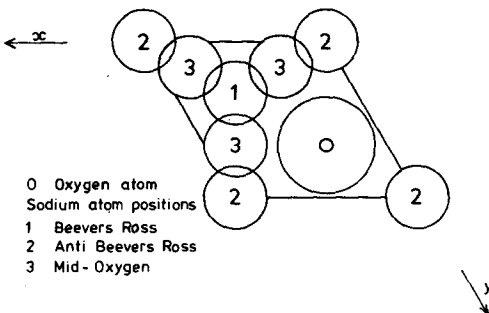


Fig. 4. Conduction plane of  $\beta$ -alumina with sodium and oxygen ions drawn to scale.

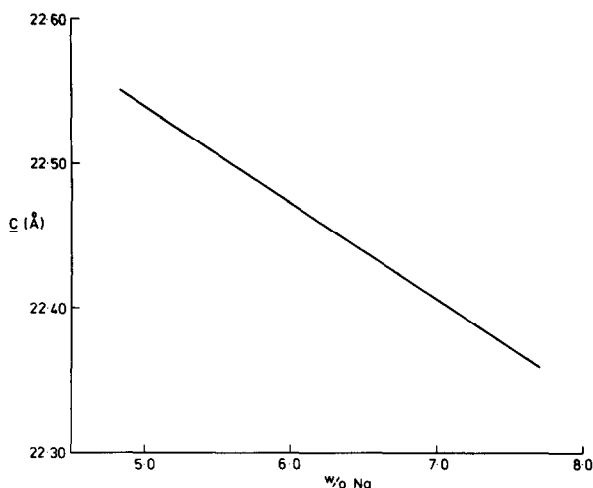


Fig. 5. Variation of the  $c$  axis of  $\beta$ -alumina with sodium concentration.

scarcely surprising therefore that during experiments designed to maximise the soda content of single crystals of  $\beta$ - $\text{Al}_2\text{O}_3$  [12] a composition close to  $(\text{Na}_2\text{O})_{2.0} \cdot 11\text{Al}_2\text{O}_3$  was obtained. (This composition is also close to the sodium-rich limit implied by the phase diagram.) As the sodium concentration of the crystals increases so the crystal  $c$  axis contracts (Fig. 5), doubtless due to the decrease in electrostatic repulsion between neighbouring spinel blocks. Evidently, a similar relationship between  $c$  axis and sodium content obtains for  $\beta''$ - $\text{Al}_2\text{O}_3$  [13].

Towards the sodium-rich end of the range implied by Fig. 5, structural modifications probably occur. N.m.r. studies [14] have prompted the suggestion that some of the  $\text{Na}_2\text{O}$  present is incorporated at a site distinct from that occupied by sodium ions in normal  $\beta$ -alumina, and ionic exchange experiments [15] have pointed to the possible existence of a non-labile component in the sodium inventory of high soda ceramic. The results of a structure determination of soda-rich  $\beta$ - $\text{Al}_2\text{O}_3$  [16] are awaited with interest.

The high mobility of  $\text{Na}^+$  ions in the conduction plane of  $(\text{Na}_2\text{O})_{1+x} \cdot 11\text{Al}_2\text{O}_3$ ,  $x = 0.2 - 0.3$ , stems from the large number of possible  $\text{Na}^+$  sites between the Al-O-Al 'spacer units' which separate the spinel blocks. The migration of cations from site to site is an activated process, with a moderate activation energy to pass from the Beever-Ross to the anti Beever-Ross sites. Loss of disorder by a move either to a high stoichiometric limit  $((\text{Na}_2\text{O})_{2.0} \cdot 11\text{Al}_2\text{O}_3)$  or to a low one  $((\text{Na}_2\text{O})_{1.0} \cdot 11\text{Al}_2\text{O}_3)$  should seriously modify the ionic transport processes of the material. The complex chemistry and crystallography of the conduction plane in these compounds is a fascinating subject which remains to be unravelled in detail.

When contemplating the possible means for supporting variations of stoichiometry of  $\beta$ - $\text{Al}_2\text{O}_3$ , due consideration must also be given to the syn-

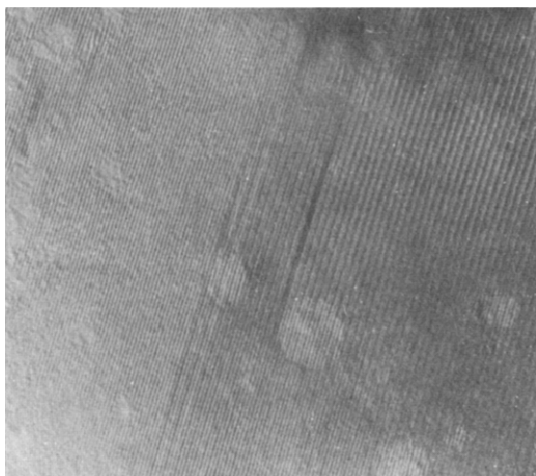


Fig. 6. Lattice image of  $\beta$ -alumina showing coherent intergrowth of  $\beta$  and  $\beta''$   $\text{Al}_2\text{O}_3$ .

tactic intergrowth of polytypes. The intergrowth of  $\beta$  and  $\beta''$  (as in Fig. 6) has been reported on numerous occasions [17 - 19] and it seems that, for magnesium doped material at least [20], the incorporation of mixed period intergrowths provides an alternative or additional means of varying the sodium inventory of  $\beta$ -aluminas. It is unlikely that syntactic intergrowth could provide the sole means of accommodating the observed non-stoichiometry [21].

### Doping

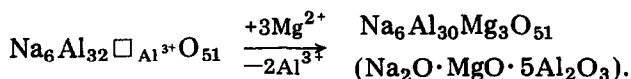
$\beta''$ - $\text{Al}_2\text{O}_3$  is well known to possess a higher conductivity than  $\beta$ - $\text{Al}_2\text{O}_3$  and, on this account, is preferable as an electrolyte. There are two structural factors which may contribute to its enhanced conductivity:

(1) In  $\beta''$ - $\text{Al}_2\text{O}_3$  the principal sodium ion sites, which correspond to the Beavers-Ross and anti Beavers-Ross sites, are crystallographically equivalent; the activation energy for diffusion is therefore lower and more cation sites are available for occupancy.

(2) The  $\beta''$  structure is stabilised by the addition of  $\text{Mg}^{2+}$  or  $\text{Li}^+$  ions which substitute for  $\text{Al}^{3+}$  ions in the spinel blocks. Charge stability is maintained by the filling of cation vacancies in the spinel block and by the elimination of interstitial oxygen ions from the conduction plane. This removes a barrier to  $\text{Na}^+$  ion diffusion.

The relative importance of these two factors in contributing to the high conductivity of the  $\beta''$  phase is not yet well established.

The substitution of  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  in the spinel block leads finally to the fully substituted compound  $\text{Na}_2\text{O} \cdot \text{MgO} \cdot 5\text{Al}_2\text{O}_3$  which was shown by Bettman and Peters [22] to have the  $\beta''$  structure with  $a = 5.614 \text{ \AA}$  and  $c = 33.85 \text{ \AA}$ .



Other compounds are known in the  $\text{Na}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3$  system which have related structures. For instance, the compound  $\text{Na}_2\text{O} \cdot 4\text{MgO} \cdot 15\text{Al}_2\text{O}_3$ , referred to as  $\beta'''$ -alumina [23], has the structure shown in Fig. 1(c) in which the spinel slab between conducting planes is made up of six close-packed layers of oxygen ions, rather than four, separated by mirror planes 15.9 Å apart. This has the hexagonal structure with  $a = 5.62$  Å and  $c = 31.8$  Å ( $2 \times 15.9$ ) and is therefore a "2 block" unit cell, analogous to  $\beta$ - $\text{Al}_2\text{O}_3$ . There is also some evidence for the existence of a rhombohedral compound analogous to  $\beta''$ -alumina and comprising three spinel blocks of six oxygen layers each [23]. This compound, designated  $\beta''''$ , has a lattice parameter of 47.7 Å ( $3 \times 15.9$ ).

Takabatake and Fukatsu noted that these six oxygen layer structures are not found in the binary  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$  system, but only in the  $\text{MgO}$  containing ternary [24]. To explain this they proposed that in the 6 layer structures the central four layers of oxygen ions remain intact, containing only  $\text{Al}^{3+}$  cations, while the  $\text{Mg}^{2+}$  ions are incorporated between the conducting layer and the immediately adjacent oxygen layers in tetrahedral cation sites. They also reported that the less stable compound  $\text{Na}_2\text{O} \cdot 2\text{MgO} \cdot 13\text{Al}_2\text{O}_3$  had a spinel type structure with five oxygen layers between the conducting planes. However, the only structural investigation bearing on this matter provides evidence to the contrary; a neutron refinement of the magnesium-stabilized  $\beta''$ -alumina structure [11] reveals that the magnesium is confined almost entirely to the  $\text{Al}(2)$  site — that is within the interior of the spinel block.

### Transmission electron microscopy

The contribution made by transmission electron microscopy (t.e.m.) to the understanding of the complex details of the crystal structure of  $\beta$ -alumina has already been referred to during the discussion of the origins of the non-stoichiometry. Local changes in structure, such as intergrowths and stacking faults, are not visible to X-rays or neutrons and for information about these use has been made of the t.e.m.

The interpretation of bright field images has been supported by electron diffraction evidence to reveal the coherent intergrowth of  $\beta$ - and  $\beta''$ - $\text{Al}_2\text{O}_3$  [17, 18] and by many-beam calculations to display the structure directly (Fig. 7) [25]. In this way stacking faults have been characterized [19] and it has been shown how defects in the crystal structure of magnesia-containing  $\beta$ -alumina (for instance spinel blocks of seven or eleven oxygen layers) can lead to effective blocking of  $\text{Na}^+$  conducting planes [26]. A complicating factor in the study of  $\beta''$ - $\text{Al}_2\text{O}_3$  has been the demonstration that irradiation by the electron microscope beam can cause  $\text{Na}_2\text{O}$  expulsion from the struc-



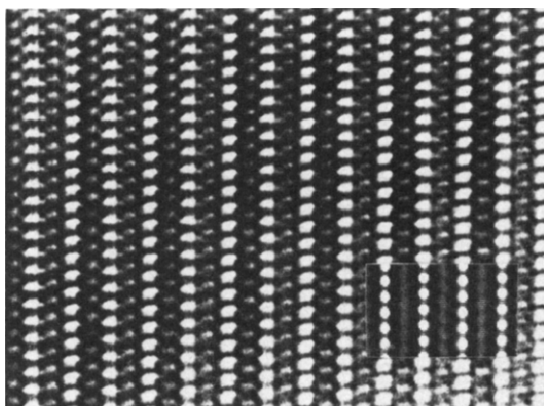


Fig. 7. Transmission electron micrograph, with computed image inserted, of  $\beta$ -alumina. Beam along  $[11\bar{2}0]$ . (After Humphreys *et al.*, ref. 25.)

ture followed by coalescence of adjacent spinel blocks to form one wider block [27]. Such artefacts complicate the detailed interpretation of the micrographs in terms of the non-stoichiometry of  $\beta''$ - $\text{Al}_2\text{O}_3$  and its stability in use, but the contribution made by t.e.m. to the understanding of  $\beta$ -alumina electrolyte is nevertheless substantial.

From the range of structural information that has been gathered it is evident that  $\beta$ -alumina, like so many ternary compounds, exhibits quite complex and subtle crystal chemistry with syntaxy, oriented intergrowths, and long range ordering of defects being prominent features. Values of  $x$  in the formula  $(\text{Na}_2\text{O})_{1+x} \cdot 11\text{Al}_2\text{O}_3$  most commonly lie between 0.2 and 0.3, allowing a high proportion of nominal sites in the conduction plane to be vacant. The 'excess' 0.2 - 0.3  $(\text{Na}_2\text{O})$  in undoped  $\beta$ - $\text{Al}_2\text{O}_3$  is accommodated by a complex defect involving an oxygen interstitial and a pair of Frenkel defect aluminium ions, while in magnesium stabilized  $\beta''$ - $\text{Al}_2\text{O}_3$  the charge compensation mechanism involves the substitution of magnesium for aluminium within the spinel blocks. In the case of magnesium-doped  $\beta$ -aluminas a contribution may also be made by intergrowth of spinel slabs with other than 4 oxygen layers per slab.

### Stability and phase relationships

$\beta$ - $\text{Al}_2\text{O}_3$  is normally produced at temperatures  $>1650^\circ\text{C}$ , where its dissociation pressure is considerable. The ease with which  $\beta$ -alumina loses  $\text{Na}_2\text{O}$ , together with its existence over a range of stoichiometry, and a tendency to form metastable states and mixed crystals, are factors which complicate the experimental determination of its phase diagram. In the case of  $\beta''$ - $\text{Al}_2\text{O}_3$  the picture is further confused by the fact that  $\text{MgO}$  and  $\text{Li}_2\text{O}$  additions are known to stabilise the structure.

The evidence pertaining to equilibria in the system  $\text{NaAlO}_2/\text{Al}_2\text{O}_3$  was reviewed by de Vries and Roth in 1969 [28]. The  $\beta''$  phase was shown to exist over the composition range  $\text{Na}_2\text{O} \cdot 5.33\text{Al}_2\text{O}_3$  to  $\text{Na}_2\text{O} \cdot 7\text{Al}_2\text{O}_3$  (*i.e.*, soda deficient) and to disproportionate at  $1550^\circ\text{C}$  to  $\beta\text{-Al}_2\text{O}_3$  and  $\delta\text{-NaAlO}_2$ ; above  $1550^\circ\text{C}$  only the  $\beta$  phase is stable and this is invariably soda-rich with respect to the formula  $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ . At lower temperatures de Vries and Roth were unable to decide whether  $\beta\text{-Al}_2\text{O}_3$  is stable or metastable with respect to  $\beta''$ . They constructed, therefore, two feasible phase diagrams, corresponding to the two cases. Liebertz subsequently made an experimental investigation of the  $\text{NaAlO}_2\text{-Al}_2\text{O}_3$  phase diagram [29] and found that both  $\beta$  and  $\beta''$  phases existed between 85 and 90 mole %  $\text{Al}_2\text{O}_3$ , with the  $\beta$  phase stable above  $1550^\circ\text{C}$  and the  $\beta''$  phase stable below this temperature.

A rather different conclusion was reached by Le Cars, Théry and Collongues as a result of their own equilibria measurements [10, 30]. While agreeing that the transformation  $\beta'' \rightarrow \beta$  is complete above  $1550^\circ\text{C}$ , they found that, on cooling, this transformation is not reversible and that at lower temperatures it is the  $\beta$  phase which is stable, with the  $\beta''$  phase being metastable at all temperatures in the pure binary system. Their phase diagram is shown in Fig. 8. While it seems likely that this diagram is substantially correct, the question as to whether  $\beta''\text{-Al}_2\text{O}_3$  is metastable in the  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  system is not of great practical importance, as the phase is normally produced in the presence of  $\text{MgO}$  or  $\text{Li}_2\text{O}$  which stabilise it, even at temperatures as high as  $1700^\circ\text{C}$  [31]. A remarkable fact, upon which all the phase diagrams agree, is that the composition  $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$  lies outside the domain of stability of the  $\beta$  phase which is therefore always soda-rich. In fact, all the evidence suggests that there is very little difference in the composition of the pure  $\beta$  and  $\beta''$  phases, both existing between  $\text{Na}_2\text{O} \cdot 5.33\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O} \cdot 8.5\text{-Al}_2\text{O}_3$ .

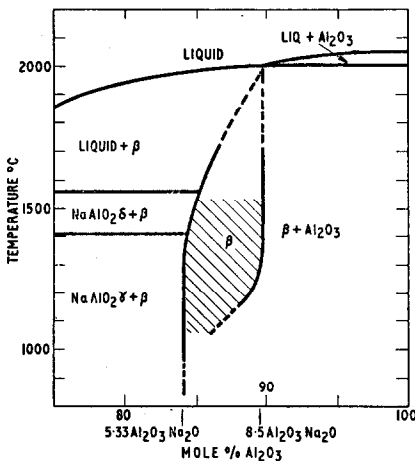


Fig. 8. Phase diagram of  $\text{NaAlO}_2\text{-Al}_2\text{O}_3$  (after Y. Le Cars *et al.*, ref. 10).

It has been suggested recently [32] that the instability of  $(\text{Na}_2\text{O})_{1.0} \cdot 11\text{Al}_2\text{O}_3$  is due to a large departure from local electroneutrality. Application of Pauling's rules [33] indicates that there are aggregations of positive charge at the centre of the spinel slabs and negative charge at its outer limits (*i.e.*, the walls of the conduction planes). Hence, the observed departure from stoichiometry in  $(\text{Na}_2\text{O})_{1+x} \cdot 11\text{Al}_2\text{O}_3$  is seen as an attempt to achieve improved local electroneutrality. Certainly,  $(\text{Na}_2\text{O})_{1.0} \cdot 11\text{Al}_2\text{O}_3$  can only be prepared by an indirect route [34] through silver beta alumina and hydrogen beta alumina as intermediate steps, and seems to be metastable. At the other extreme of the known range of existence,  $(\text{Na}_2\text{O})_{2.0} \cdot 11\text{Al}_2\text{O}_3$ , the process of charge compensation in the plane may have proceeded beyond the optimum distribution of electrostatic charge, and forceful means of preparation are again required [12]. The local electroneutrality concept provides a sensible explanation of the apparent preference of  $\beta$ -alumina for an intermediate stoichiometry with partial occupancy of sites in its crystal structure.

The role of  $\text{Li}^+$  and divalent cations ( $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Cd}^{2+}$ ) in stabilising the  $\beta''$  structure, and therefore increasing the conductivity of  $\beta$ -alumina ceramic, has been studied in some detail [31, 35]. The significant fact is that the cations which stabilise the  $\beta''$  structure are those which are capable of occupying octahedral or tetrahedral sites in the spinel lattice. In contrast  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ , which are incapable of entering the spinel block on account of their large ionic radii, and which also tend to form the magnetoplumbite structure in the corresponding ferrite systems, are found not to stabilise the  $\beta''$ - $\text{Al}_2\text{O}_3$  phase but to favour  $\beta$ - $\text{Al}_2\text{O}_3$ . Boilot and Théry conclude that impurity cations of radius  $< 0.97 \text{ \AA}$  substitute for  $\text{Al}^{3+}$  ion in the spinel blocks and stabilise  $\beta''$ - $\text{Al}_2\text{O}_3$ , while large cations show no such tendency [35]. All the divalent cations of size  $< 0.97 \text{ \AA}$  are transition metals, of potentially variable valency except for  $\text{Mg}^{2+}$ ; it is for this reason that  $\text{MgO}$  and  $\text{Li}_2\text{O}$  are the preferred additives to  $\beta$ - $\text{Al}_2\text{O}_3$  in preparing a good ionic conductor with no electronic contribution.

The function of additives in stabilizing one  $\beta$ -alumina phase or another depends upon their incorporation into the structure at the sintering stage. A structural study [36] has shown that if lithium is inserted into the  $\beta$ - $\text{Al}_2\text{O}_3$  structure at a later stage, by ion exchange, then it is accommodated in the conduction planes rather than in the spinel block and does not bring about the formation of  $\beta''$ - $\text{Al}_2\text{O}_3$ . Impurity cations larger than  $0.97 \text{ \AA}$  radius, which substitute into the conduction plane, impede the migration of  $\text{Na}^+$  ions and can cause a serious reduction in ionic conductivity. The alkaline earth cations, in particular, are deleterious to  $\beta$ -alumina as an ionic conductor [37].

### Electrical conductivity

The remarkable aspect of  $\beta$ -alumina which makes it so interesting from both a scientific and technological viewpoint is that although its melting point is around  $2000 \text{ }^\circ\text{C}$  the  $\text{Na}^+$  ion mobility is already so high at  $350 \text{ }^\circ\text{C}$

that it is possible to draw an ionic current of several hundred mA/cm<sup>2</sup>. At the same time the material is virtually an electronic insulator.

### *Techniques*

The measurement of reliable electrical conductivity data for ionic conductors by d.c. methods poses certain experimental problems. It is necessary to provide a source of sodium ions at the positive electrode and a sink at the negative electrode without introducing polarisation effects. For measurements at 300 - 400 °C the source must be either a fused salt or metallic sodium, both of which introduce handling difficulties. The use of 4 point d.c. measurements avoids polarisation effects, at the expense of introducing restrictions on specimen geometry, which must now be in the form of bars rather than discs. These problems may all be circumvented by the use of a.c. techniques with standard blocking electrodes [38, 39]. At the same time, from the frequency dependence of the conductivity, it is possible to deduce the bulk and grain boundary contributions to the overall specimen resistance. The conductivity of single crystals of  $\beta$ -alumina has also been measured by an induced torque technique [40] in which contact difficulties are avoided by inducing eddy currents in a single crystal placed in a rotating magnetic field.

### *Single crystal conductivity*

The a.c. technique has been applied to  $\beta$ -alumina by Hooper [38] who made measurements both on single crystals of the  $\beta$  phase and on polycrystalline, two-phase ( $\beta + \beta''$ ) ceramic specimens. With a single crystal a plot of  $\log \sigma T$  vs.  $1/T$  was a straight line, whose slope gave an activation energy for Na<sup>+</sup> ion conduction of 0.13 eV. The resistivity of single crystal  $\beta$ -Al<sub>2</sub>O<sub>3</sub> was 4.7  $\Omega$  cm at 300 °C, compared with a value of around 1  $\Omega$  cm for  $\beta''$  single crystals. The polycrystalline ceramic specimens had an overall resistance which contained a contribution from the bulk ( $R_B$ ) and the grain boundaries ( $R_{GB}$ ). By analysing the impedance and corresponding admittance plots (Fig. 9 inset) it was possible to separate out the bulk phase conductivity  $G_2$ . The measured activation energy (0.15 eV) was close to that for single crystals, but the resistivity at 300 °C was considerably higher (15.4  $\Omega$  cm) even though the specimen was two phase  $\beta + \beta''$ -Al<sub>2</sub>O<sub>3</sub>. As seen in Fig. 9, the grain boundary contribution to the total electrolyte resistance is negligible above 250 °C. By contrast, for specimens of pure  $\beta''$  polycrystalline material the bulk conductivity still exceeds that of the grain boundaries, even at 350 °C [41].

As would be expected from consideration of the construction of the conduction planes, the conductivity of  $\beta$ -alumina is a function of composition. At the sodium-rich limit, (Na<sub>2</sub>O)<sub>2.0</sub> · 11Al<sub>2</sub>O<sub>3</sub>, the conductivity of a single crystal is an order of magnitude less than for the normal, non-stoichiometric composition (Fig. 10) [12]. In addition, it is found that the activation energy for conductivity at both high [12] and low [34] stoichiometric limits is far greater than for the non-stoichiometric material (see Table 2).

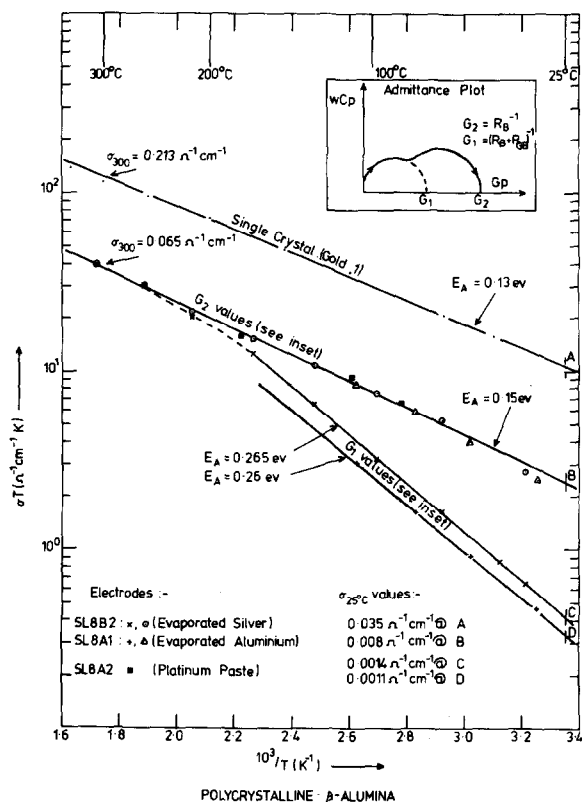


Fig. 9. Electrical conductivity of  $\beta$ - $\text{Al}_2\text{O}_3$  (after A. Hooper, ref. 38).

It has been suggested that the dependence of conductivity on composition of non-stoichiometric  $\beta$ -alumina is due to the inhibition of an interstitialcy mechanism by a short range ordering process among the mobile ions and compensating defects [42]. Two dimensional order/disorder phenomena involving the atoms in the conducting plane are well established [43] and the influences of the composition dependence of these mechanisms on the transport properties of  $\beta$ -alumina promise to be rather subtle.

Vibrational studies of  $(\text{Na}_2\text{O})_{1.0} \cdot 11\text{Al}_2\text{O}_3$  [44] indicate that a totally ordered state is available at low temperatures, but that above 100 K even stoichiometric  $\beta$ -alumina displays dynamic cation disorder.

Early theoretical models of transport processes in  $\beta$ -alumina suffered from the deficiency that they were developed for the stoichiometric 1:11 composition, whereas the material upon which measurements are customarily made is the non-stoichiometric 1.25:11. The recent microscopic interstitialcy diffusion mechanism put forward by Wolf [45] deals with  $(\text{Na}_2\text{O})_x \cdot 11\text{Al}_2\text{O}_3$ , for  $x \neq 1$  and is shown to be in agreement with the occupation probabil-

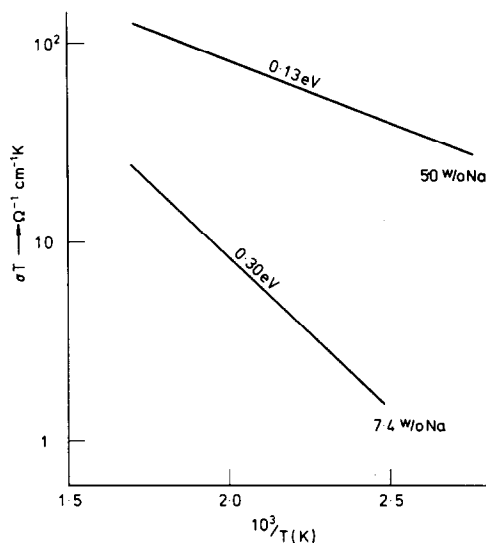


Fig. 10. Electrical conductivity of soda-rich  $\beta$ - $\text{Al}_2\text{O}_3$ .

TABLE 2

Activation energies of ionic conductivity

Composition	$E_{\text{act}}$ (eV)	Reference
$(\text{Na}_2\text{O})_{1.0} \cdot 11\text{Al}_2\text{O}_3$	0.62	34
$(\text{Na}_2\text{O})_{1.25} \cdot 11\text{Al}_2\text{O}_3$	0.13	12
$(\text{Na}_2\text{O})_{2.0} \cdot 11\text{Al}_2\text{O}_3$	0.30	12

ities established by neutron diffraction [11] for the alternative conduction plane sites (1, 2 and 3 in Fig. 3). With the aid of this model the ratio of the radio tracer diffusivity to the charge diffusivity (the Haven ratio) was determined for various sizes of associated regions around the charge compensating interstitials. The Haven ratio was found to increase with increasing temperature, in agreement with the measurements made by Kim *et al.* [46]. The model involves all three crystallographically distinct types of mobile cation site, but only two equilibrium configurations of interstitialcy pairs.

An alternative theoretical approach was adopted by de Leeuw and Perram [47] who assumed no *a priori* charge compensation model or diffusion mechanism, but used a molecular dynamics simulation to compute the radial distribution functions and, hence, the motion of  $\text{Na}^+$  ions within the conduction plane. The results of the calculation agreed with experiment in predicting enhanced  $\text{Na}^+$  diffusion for the non-stoichiometric compound.

### Polycrystalline conductivity

The resistivity of polycrystalline  $\beta$ -alumina ceramic of near theoretical density is a function of (1) the relative proportions of  $\beta$  and  $\beta''$  phases present, (2) the composition, and (3) the microstructure and crystallite size. The ionic conductivities of polycrystalline  $\beta$  and  $\beta''$ - $\text{Al}_2\text{O}_3$  at 300 °C are 12 and 5  $\Omega$  cm, respectively [8]. Figure 11 [48] shows that there is an approximately linear relation between the resistivity and the proportion of the two phases present; the scatter of points arises from variations in density, microstructure, etc. From these results it appears that the pure  $\beta''$  phase would be most desirable for use as a solid electrolyte. However, it is more sensitive to moisture than the  $\beta$  phase, resulting in a deterioration of mechanical properties and the need, therefore, to handle under dry box conditions. The presence of water in  $\beta$ - $\text{Al}_2\text{O}_3$  degrades the ionic conductivity by as much as a factor of two [49] but the anhydrous value is regained by heat treatment.

In practice, for use in sodium/sulphur batteries, the ceramic employed is usually a two phase  $\beta + \beta''$  composition with resistivity in the range 5 - 10  $\Omega$  cm at 350 °C. This can be manufactured to have both excellent strength characteristics and resistance to attack by moisture.

The composition of  $\beta$ -alumina is conventionally expressed as weight percentage (wt.%)  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Li}_2\text{O}$ , balance  $\text{Al}_2\text{O}_3$ . Pure  $\beta''$  may be readily prepared using 4 wt.%  $\text{MgO}$ , but an equivalent effect is obtained by as little as 0.7 - 0.8 wt.%  $\text{Li}_2\text{O}$ . The greater effectiveness of  $\text{Li}_2\text{O}$  in stabilizing  $\beta''$  may be explained by the fact that the fully substituted spinel ( $\text{LiAl}_5\text{O}_8$ ) contains only 5.5 wt.%  $\text{Li}_2\text{O}$  compared with 28 wt.%  $\text{MgO}$  in the corresponding magnesium spinel ( $\text{MgAl}_2\text{O}_4$ ).

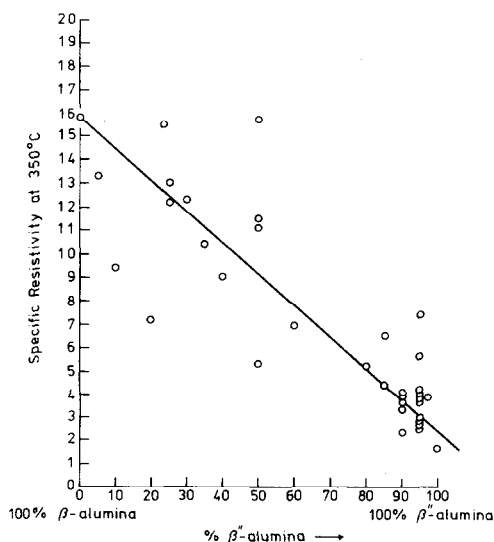


Fig. 11. Resistivity of  $\beta$ -alumina as a function of  $\beta/\beta''$  ratio (after J. L. Sudworth *et al.*, ref. 48).

The formulations chosen for a practical, two-phase electrolyte have evolved around 8 wt.% Na<sub>2</sub>O, 2 wt.% MgO for Mg<sup>2+</sup> doping [50] and 8.9 wt.% Na<sub>2</sub>O, 0.7 wt.% Li<sub>2</sub>O for Li<sup>+</sup> doping [51]. Mixed compositions, for instance, 8.9 wt.% Na<sub>2</sub>O, 2 wt.% MgO, 0.5 wt.% Li<sub>2</sub>O [51], are also employed to give a ceramic of high conductivity. Studies of specimen resistivity as a function of soda content, at various levels of MgO doping in the range 1 - 4 wt.%, have revealed the basic principle involved [52]. The resistivity passes through a minimum when the soda content corresponds to that in the undoped  $\beta$ -alumina *plus* that which corresponds to the doping level. Thus 2 wt.% MgO is equivalent to 0.59 mole Mg<sup>2+</sup> per mole of  $\beta$ -alumina and this should stabilize an additional 0.59 mole of interstitial Na<sup>+</sup> ion (equivalent to 1.5 wt.% Na<sub>2</sub>O); if the undoped  $\beta$ -Al<sub>2</sub>O<sub>3</sub> contained 6.1 wt.% Na<sub>2</sub>O, then the material doped with 2 wt.% MgO will show a minimum resistivity at 6.1 + 1.5 = 7.6 wt.% Na<sub>2</sub>O. The experimental results confirmed these predictions. Samples containing larger amounts of soda than the optimum value showed an increased resistivity. This is in line with the measurements of conductivity of sodium-rich single crystals [12].

Two remaining factors holding the potential to influence the practical conductivity of  $\beta$ -alumina ceramics are the presence of impurities and the development of pronounced texture (preferred orientation of grains). Two of the more likely contaminants of ceramic electrolytes are calcium and silicon and the effects of both on microstructure and resistivity have been investigated. The presence of calcium at concentrations greater than 400 ppm appears to promote abnormal grain growth and to allow the formation of inter-granular calcium aluminate phases which are likely to impede the passage of mobile ions [37]. The measured resistivity at 300 °C increases exponentially with calcium content and is particularly sensitive to sintering conditions.  $\beta$ -Al<sub>2</sub>O<sub>3</sub> doped with a few weight per cent. of SiO<sub>2</sub> also exhibits increased resistivity [53], with intergranular glassy phases discernible in the t.e.m.

The detailed influence of grain boundary structure on ionic conduction has also been considered [54]. Correlations between structure and resistivity have been advanced and illustrated by examples taken from t.e.m. studies. It appears that a key factor determining the effect of grain boundaries is whether or not screw dislocations with  $b = 1$  spinel block can accommodate the orientational mismatch. This type of dislocation has, indeed, been observed for a number of grain boundaries.

The huge anisotropy in conductivity of  $\beta$ -alumina crystals (around 10<sup>15</sup> at 300 °C [6]) might be expected to manifest itself in the electrical properties of the polycrystalline material. Statistical calculations [55] indicate that, provided the resistance of the grain boundaries is small, the effect of tortuosity (the factor by which the conduction path is lengthened by the random orientation of individual grains) will also be small. The effect of preferred orientation of the grains constituting the ceramic is potentially quite damaging, since the fabrication procedures used for  $\beta$ -alumina would be expected to cause any texture arising to be in an unfavourable sense —



*i.e.*, with the blocking  $c$  axis oriented in a radial direction of the electrolyte tube. In fact, it has been found that although such unfavourable texture is produced during the manufacture of both  $\beta$  [56] and  $\beta''$  [57] artefacts they are small in extent and the resulting degradation of electrolyte conductivity is not prohibitive.

## Conclusions

Recent experimental studies of sodium beta alumina have led to a much better understanding of its structure, the means whereby variable stoichiometry is accommodated, and the influence of non-stoichiometry and impurity dopants on its electrical conductivity. The transmission electron microscope and theoretical studies of diffusion processes in the conduction plane have each played an important role in elucidating and explaining the high cation conductivity observed in the non-stoichiometric material. A sound fundamental understanding of sodium beta alumina now exists which may be utilised in predicting the optimum composition and preparative conditions for the fabrication of  $\beta$ -alumina ceramic electrolyte.

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