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X-ray-scattering study of the fast-ion conductor β''-alumina

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The ion-ion correlations and a new crystal-structure determination of β''_{Na}- and β''_{K}-alumina reveal that the conducting ions are distributed between two independent sites instead of one given by previous work: Beevers-Ross–anti-Beevers-Ross and mid-oxygen with an occupation ratio of 60% and 40%, respectively. The two-dimensional short-range order is found to correspond to a theoretical composition of 1.66 ions per unit plane cell. A relation is established between three parameters: the coherence length of the SRO model (ξ), the thickness of the conduction slab (E), and the resistivities (ρ). It is shown that $(\xi,E,\rho)_{\mathrm{Na}} > (\xi,E,\rho)_{\mathrm{K}}$. The gradual change in the activation energies, observed for β''_{Na} and β''_{K} when the temperature is increased, is interpreted in relation with the decrease of both E and ξ in the same temperature range. Finally, β''-alumina, when compared to β-rich alumina with the same compensation mechanism and composition, exhibit higher conductivities due to larger conduction channels.

I. INTRODUCTION

Many structural studies have been performed on superionic conductors from the β-alumina family, including conventional structure determinations by x-rays[1-3] and neutrons,[4] as well as x-ray diffuse scattering studies of the local arrangement of the conducting ions[5-7] and inelastic neutron scattering measurements.[8] This variety of experimental studies has its origin in the problems arising for the determination of the distribution in the unit cell of the conducting ions which is related to the easy two-dimensional diffusion causing the high ionic conductivity and its temperature dependence. Another reason is the number of such aluminates which can be obtained when the usual sodium ions are exchanged and when the composition is varied.

In its ordinary form β-alumina is a nonstoichiometric compound with an excess sodium x ($0.25 < x < 0.30$) corresponding to the formula

$$(\mathrm{Al}_{11}\mathrm{O}_{16})-(\mathrm{O}-\mathrm{Na}_{(1+x)})-\mathrm{O}_{x/2}.$$

Its hexagonal structure contains two such formula units and is composed of spinel blocks (first parentheses) separated by loosely packed layers of sodium and oxygen where the ion diffusion takes place. In each layer the 1.3 conducting sodium ions per unit cell are distributed over three sites widely referred to as Beevers-Ross (BR), anti-Beevers-Ross (aBR) and mid-oxygen (mO) as recalled in Fig. 1(a). The excess $x/2$ oxygens needed for the electrical compensation of the corresponding excess sodium per layer are found in interstitial mid-oxygen positions and associated with an adjacent Frenkel defect in the spinel block.[4]

In recent years it was shown that the basic β-alumina structure can be retained for a large composition range. At one end is the stoichiometric compound ($11\mathrm{Al}_2\mathrm{O}_3$–$\mathrm{Na}_2\mathrm{O}$) which does not belong to the $\mathrm{Na}_2\mathrm{O}$-$\mathrm{Al}_2\mathrm{O}_3$ phase diagram but can be obtained by indirect methods.[9] For other compositions and more particularly for the higher conducting ion concentrations it is an alternate electrical compensation mechanism by the substitution of Al^{3+} ions from the spinel blocks with Li^{+}, Mg^{++}, Co^{++} ions which allows substantial departures from the ordinary 1.3 mobile ions per unit-cell layer. This other compensation mechanism can come in addition to the usual interstitial oxygens, or even completely replace them leading to a formula unit of the type

$$(\mathrm{Al}_{11-y}\mathrm{O}_{16}\mathrm{Mg}_y)-(\mathrm{O}-\mathrm{Na}_{1+x+y})-\mathrm{O}_{x/2},$$

where x refers to the excess conducting ions compensated by interstitial oxygens, and y to those compensated by substitutional Mg^{2+} ions (or Co^{2+}).

For stoichiometric β-alumina $x \simeq y \simeq 0$,[9] and towards the upper limit of "ion-rich" β-alumina $x \simeq 0$; $y \simeq 1.7$.[10] In these two last cases structural studies of the ion-ion correlations as a function of temperature,[11-13] which is one of the important parameters related to the temperature dependence

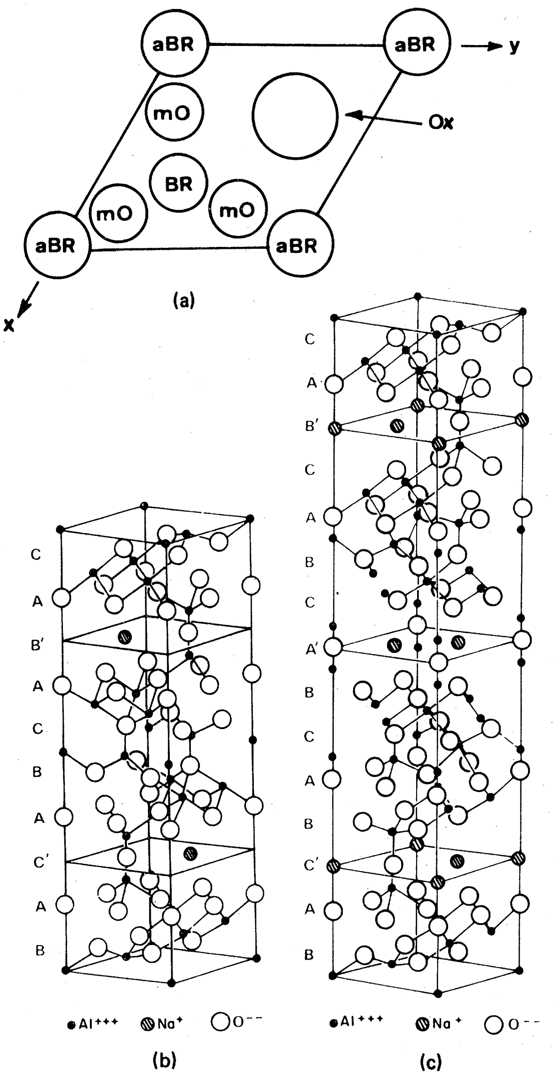


FIG. 1. (a) The different sites in the conducting plane: BR, Beevers-Ross; m O, mid-oxygen; aBR, anti-Beevers-Ross. (b) Structure of stoichiometric β-alumina: *A*, *B*, *C* indicate oxygen layers of the spinel block; *B'*, *C'* show the conducting planes (mirror planes of the space group $P6_3/mmc$). Each conducting plane of the unit cell contains one sodium ion located on the Beevers-Ross site. (c) Structure of β''-alumina (idealized). Each conducting plane of the unit cell contains two sodium ions located on the Beevers-Ross and anti-Beevers-Ross sites which correspond to only one position of the space group $R\bar{3}m$. The "conducting plane" is the projection of a conduction slab on the basal plane.

of the ionic conductivity, is greatly simplified by the absence of interstitial oxygen, the role of which had given rise to controversial descriptions of the type of short-range order in the low-density layer for the ordinary compound.[7,14,15]

The solid electrolyte actually used in the electrochemical systems (Na-S battery) is usally β''-alumina which is a rhombohedral variant of the β-type structure. The general features of the atomic arrangement in β'' were first given from x-ray powder diffraction,[16] since this phase is usually found in syntaxy with β-alumina.[17] Structure determination on single crystals could only be obtained using again the procedure of aluminum substitution by monovalent or divalent ions, which also stabilizes the β'' phase.[17] As was shown in a recent neutron diffraction study,[18] β''- as well as "ion-rich" β-alumina (Ref. 13) seems to correspond to an upper limit of conducting ion concentration with $x \simeq 0$, $y \simeq 1.7$.

The hexagonal unit cell of β'' is again composed of spinel blocks separated by loosely packed layers, but contains three formula units instead of the two for β-alumina [Figs. 1(b) and 1(c)]. The sodium ions (and generally the conducting ions) are localized on sites which correspond to the BR and aBR positions in β-alumina, but in β'' these sites are crystallographically equivalent. Another important difference between β''- and β-alumina is that the loosely packed layers in the β'' structure are not strictly planar and the mobile ions therefore rather move through a conduction slab. Below when referring to the conducting plane of β'', we mean the projection of this slab on the basal plane.

The purpose of the present paper is to report the results of an x-ray study of β''-Na and β''-K as a function of temperature, in which both conventional structure-determination procedures and diffuse scattering measurements have been used in a complementary way. Concerning the distribution of the mobile ions, this has allowed us to show the existence of an additional site, close to a mid-oxygen position, which could not be revealed in the previous structure determinations. We have further observed a close relation between three parameters:

(i) the coherence length ($\xi_{\parallel}$) obtained from x-ray diffuse scattering, which measures the extensions of the ion-ion correlation in the "conducting plane,"

(ii) the thickness of the conduction slab, determinated by x-ray diffraction, and

(iii) the conducting ion mobility deduced from conductivity measurement.[19]

The relations explain the unexpected easy diffusion of the K^+ ions in the β'' structure and shed light on the behavior of the ionic conductivity observed between 300 and 600 K for β''-Na and between 300 and 500 K for β''-K.[19] The case of β''_{Ag}-alumina which reveals different structural features will be reported separately.[20]

II. EXPERIMENTAL

A. Preparation of samples

Crystals of β''_{NA^+}-alumina are obtained by a self-crucible-heating method with the following components; Al_2O_3 (75 wt.%)–MgO (5 wt.%)–Na_2O (20 wt.%). The excess of sodium ions is needed to favor the presence of the β''-alumina phase and it also contributes to the formation of $NaAlO_2$ acting as a flux for the crystal growth.

The starting composition is melted by high frequency at 1800 °C and cooled down for several hours. The block obtained is constituted of rhomboedral agglomerates which contain alternated layers of sodium aluminate ($NaAlO_2$) and β- or β''-alumina. "Ion-rich" β- and β''-alumina platelets are separated from $NaAlO_2$ by dissolution of this last reagent in boiling HCl. The dimensions of the single-crystal platelets vary from 1 mm^2 to 1 cm^2 for the area from 0.1 to 0.5 mm for the thickness. β'' single crystals with a rhomboedral symmetry can be easily distinguished from ion-rich β-alumina (Ref. 13) with a hexagonal symmetry by Laüe x-ray patterns. The crystals used for the x-ray structural studies were all carefully checked in order to avoid the presence of the β-alumina phase which can coexist by syntaxy with the β'' phase.

During the disaggregation of the block, some H^+ (H_2O) ions can be substituted for Na^+ ions in the β'' structure, requiring a ionic exchange in a molten sodium nitrate at 320 °C. The composition, as determined by neutron activation analysis, shows a number of cations of 1.7 ± 0.1 per unit cell in each conducting plane. In fact, there is a gradient of temperature within the melted bulk and we generally get crystals with various compositions. The Al to Na ratio value, deduced from neutron activation analysis, further clearly confirms that the substitution of Mg^{2+} ions for Al^{3+} ions is the predominant electrical compensation mechanism of the sodium excess, as already shown by other methods.[18]

β''_K is prepared by ionic exchange of β''_{Na} alumina in molten potassium nitrate at 400 °C. The determination of the remaining sodium content is made by neutron activation and clearly shows that the exchange is higher than 99%.

B. X-ray diffuse scattering (local structure)

The x-ray diffuse scattering (Mo $K\alpha$) is recorded on photographic film with the technique often improperly described as "the monochromatic Laüe method."[6] The intensity of each pattern is measured with a Joyce microdensitometer.

C. X-ray diffraction (average structure)

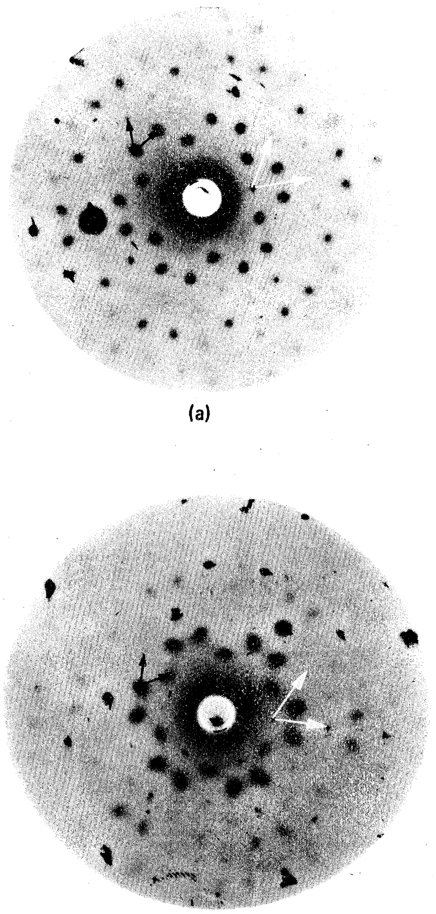
On Weissenberg films of single crystals used for structural studies, one can only observe reflections with $-h+k+1=3n$, in agreement with the space group $R\bar{3}m$ assigned in the previous studies.[18,21] The lattice constants were $a = 5.61$ Å, $c = 33.54$ Å for β''_{Na} and $a = 5.63$ Å, $c = 34.01$ Å for β''_K.

Intensities were collected on a $P2_1$ syntex four-circle diffractometer, between $2\theta = 0°$ to 65°, using Mo $K\alpha$ radiation with a graphite monochromator. Three sets of equivalent reflections were measured and, after absorption correction calculations, equivalent reflections were averaged to produce final data of 419 independent reflections for β''_{Na} and 433 for β''_K. The refinements were carried out following the previously described procedure.[3]

III. THE STRUCTURAL PROPERTIES AT ROOM TEMPERATURE

A. Description of the x-ray diffuse scattering patterns

Figure 2 shows x-ray diffuse scattering patterns from sodium and potassium β''-alumina for an


(a)

(b)

FIG. 2. X-ray-scattering patterns at 300 K for β''-alumina (Mo $K\alpha$ incident beam parallel to c axis). (a) β''_{Na} exposure time: 48 h; (b) β''_K exposure time: 30 h. [Note the presence of superlattice diffuse spots (black arrows).] White arrows indicate the main lattice of β''-alumina.

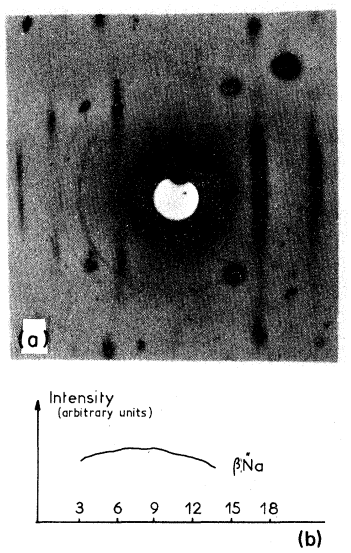


FIG. 3. X-ray-scattering patterns at 300 K for β''-alumina (Mo $K\alpha$ incident beam perpendicular to c axis). (a) $\beta''_{\rm Na}$ exposure time: 60 h. Note diffuse rods with very small intensity modulation along c^* (black arrows), for adequate reflection conditions. (b) Intensity along diffuse rod for $\beta''_{\rm Na}$ as registered by microdensitometer reading of x-ray pattern. The reading corresponds to the rod $\frac{2}{3}$, $\frac{2}{3}$, η [shown by arrow on pattern (a)].

incident x-ray beam parallel to the c axis. In addition to some strong Bragg reflections from the main lattice, the photographs of Fig. 2 reveal a similar and regular pattern of diffuse spots which results from the intersection of the Ewald sphere with intensity distributed along reciprocal rods parallel to the c axis.

The pattern of Fig. 3(a), corresponding to an incident x-ray beam perpendicular to the vertical c axis of a β''-Na crystal, shows further that the intensity along the diffuse rods is uniform; it does not display the relatively sharp intensity modulations of standard β-alumina, nor the weaker variations observed for potassium β''-alumina stabilized by Co^{2+} substitution, both reported in Ref. 7. This experimental fact is confirmed by microdensitometer readings along a diffuse rod shown in Fig. 3(b). In the Discussion (Sec. V) we shall come back to this apparent disagreement with the observations made by McWhan *et al*,[7] which can be here easily traced back to well-characterized sample differences. These results clearly show that the diffuse scattering described above for sodium and potassium β''-alumina stabilized by Mg^{2+} substitutions arises from purely two-dimensional short-range order (or correlations) between the conducting ions in the low-density layers.

From the localization of the diffuse rods which are the type $(h+\frac{1}{3}, k+\frac{1}{3}, \eta)$ and $(h+\frac{2}{3}, k+\frac{2}{3}, \eta)$ referring to the main lattice, one can deduce the existence of a local order (LO) corresponding to a two-dimensional hexagonal superlattice with a lattice constant of $a_{\rm LO}=a\sqrt{3}$ and oriented at 30° from the average cell of β''-alumina. This type of local superstructure is similar to that first observed in silver β-alumina.[5]

From the full width at half maximum of a section of the diffuse rods, or of the diffuse spots as observed on patterns of Fig. 1, one can deduce the coherence length of the order in the conducting planes. The Scherrer formula[22] yields the following values at room temperature:

$$\xi_{\parallel}=70\ \text{Å}\ \text{ for } \beta''\text{-Na},$$

$$\xi_{\parallel}=35\ \text{Å}\ \text{ for } \beta''\text{-K}.$$

From the intensity of the different diffuse rods relative to each other one can obtain direct information on the type of ion distribution which produces the short-range superstructure.

B. Ion distribution deduced from the diffuse scattering

The observed intensities collected by microdensitometer readings of the diffuse spots observed on the patterns shown Fig. 2 can be compared to model calculations using the Laüe formula:

$$I_{\rm diffuse} \propto |F_{\rm loc} - \langle F\rangle|^2,$$

where $F_{\rm loc}$ and $\langle F\rangle$ are, respectively, the local structure factor in the two-dimensional superlattice cell to be determined and the average structure factor corresponding to the ion distribution deduced from conventional structure analysis but taken over the same superlattice cell.

For both $\beta''_{\rm Na}$ and $\beta''_{\rm K}$ it is possible to suggest a schematic ion distribution producing the hexagonal superlattice short-range order which respects the previous x-ray and neutron diffraction studies of the average main structure of $\beta''_{\rm Na}$ (Refs. 18 and 21), i.e.,

(i) The conducting ions are only localized on one independent position of the $R\bar{3}m$ space group ($6c$ or $18h$ if ions are slightly in plane off-center from the theoretical position of $0,0,z$). This gives a maximum of two ions per unit cell in the conducting plane.

(ii) The average composition, obtained by neutron activation analysis or deduced from the neutron diffraction study,[18] is close to 1.7 ions per unit cell. It follows that vacant sites exist in the conducting plane. Figure 4 shows a model where the vacant sites are ordered, leading to a superstructure $(a/\sqrt{3}\times a\sqrt{3})$. The ideal composition of

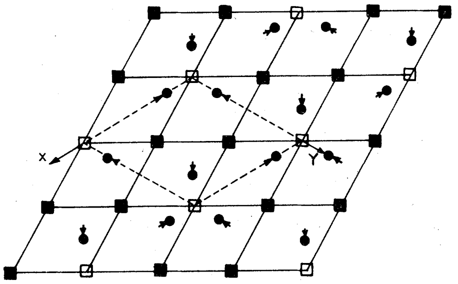


FIG. 4. Ordering of the vacant sites in the "conducting plane" of $\beta''_{\rm Na}$- and $\beta''_{\rm K}$-alumina; — Average unit cell, --- superstructure unit cell. Arrows show the displacements of three conducting ions which make a cluster around a vacant site, as determined in the final refinement of the local structure. ■ occupied Na or K aBR site, □ vacant Na or K aBR site, ● occupied Na or K BR site.

this model is 1.66 per unit main plane cell of β''-alumina, that is to say not very far from the average composition. The vacant sites are localized on the superstructure network (i.e., on BR or aBR equivalent sites).

TABLE I. Local structure in $\beta''_{\rm Na}$-alumina.

(a) Diffuse superstructure reflections used in the refinement $R = 10\%$

H	K	$\lvert F_{\rm obs}\rvert$	$\lvert F_{\rm calc}\rvert$
0	2	21.8	23.0
0	4	22.1	22.4
0	5	3.8	3.9
0	7	3.3	3.3
1	2	25.2	23.3
1	3	9.7	7.9
1	5	13.9	12.4
1	6	17.2	20.0
2	3	25.2	21.2
2	4	14.7	14.8
2	6	14.9	17.8
3	4	3.3	3.4
3	5	6.1	8.0

(b) Structural parameters

Two-dimensional positions		Occupation factor	x	y
Na(1)	1(a)	0	0	0
	2(b)	1	$\frac{1}{3}$	$\frac{2}{3}$
Na(2)	3(c)	1	0.24	0
	6(d)	0	0.48	0.15
O	3(c)	1	0.68	0

TABLE II. Local structure in $\beta''_{\rm K}$-alumina.

(a) Diffuse superstructure reflections used in the refinement, $R = 9.6\%$

H	K	$\lvert F_{\rm obs}\rvert$	$\lvert F_{\rm calc}\rvert$
0	2	28.5	30.6
0	4	20.2	22.7
0	5	8.1	9.2
1	2	45.0	45.8
1	3	7.0	4.0
1	5	21.6	23.0
1	6	25.5	28.6
2	3	30.8	30.0
2	4	19.8	20.3
2	6	18.0	16.1
3	4	11.4	8.4
3	5	5.7	3.2

(b) Structural parameters

Two-dimensional positions		Occupation factor	x	y
K(1)	1a	0	0	0
	2b	1	$\frac{1}{3}$	$\frac{2}{3}$
K(2)	3c	1	0.24	0
	6d	0	0.48	0.15

Intensities calculated from this model are however in bad agreement with observed intensities from the x-ray patterns:

$$R\,\% = \frac{\sum \lvert F_{\rm obs} - F_{\rm calc}\rvert}{\sum \lvert F_{\rm obs}\rvert} \times 100 \simeq 50\,\% .$$

The agreement is improved if the position parameters are allowed to deviate in the local order from their value obtained from the average structure.

Taking only into account the superstructure diffuse spots (13 reflections) for the agreement index R, we have refined the atomic position parameters of the conducting ions and oxygen ions of the superstructure cell ($P31m$ two-dimensional space group). This reveals that the conducting ions tend to relax towards the unoccupied aBR or BR sites which results in clusters of three conducting ions at the origin of the superlattice cell, similar to the results in ion-rich β-alumina[13] (Fig. 4).

Tables I(a) and II(a) give the observed and calculated intensities for the diffuse superstructure spots, and Tables I(b) and II(b) show the structural parameters which give the best agreement index ($R = 10\%$ for $\beta''_{\rm Na}$ – $R = 9.6\%$ for $\beta''_{\rm K}$).

This local structure determination shows the following.

(a) K^+ and Na^+ ions are localized on two inde-

TABLE III. Sodium β''-alumina: position and thermal parameters ($a = 5.61$ Å, $c = 33.54$ Å).

Position		Number per unit cell	$x \times 10^5$	$z \times 10^5$	$U_{11} \times 10^4$	$U_{22} \times 10^4$	$U_{33} \times 10^4$	$U_{13} \times 10^4$
Al(1)	18*h*	18	16 723(4)	92 898(1)	51(1)	53(2)	100(3)	3(1)
Al(2)	6*c*	6	0	35 021(2)	64(2)	μ_{11}	104(6)	0
Al(3)	6*c*	6	0	44 988(2)	61(2)	μ_{11}	74(6)	0
Al(4)	3*a*	3	0	0	48(3)	μ_{11}	77(6)	0
O(1)	18*h*	18	16 323(10)	23 504(2)	62(3)	67(4)	118(6)	7(2)
O(2)	18*h*	18	15 371(10)	3 450(2)	82(3)	106(4)	110(6)	−12(2)
O(3)	6*c*	6	0	9 726(5)	72(4)	μ_{11}	134(6)	0
O(4)	6*c*	6	0	29 487(5)	56(5)	μ_{11}	147(6)	0
O(5)	3*b*	3	0	50 000	505(14)	μ_{11}	123(17)	0
			(a) Na$^+$ ions located on one position					
	18*h*	5.20(5)	4 338(80)	−17 222(8)	909(30)	2363(115)	325(17)	258(16)
$R = 1.67\%$								
			(b) Na$^+$ ions located on two positions					
Na(1)	6*c*	2.01(6)	0	−17 168(30)	1355(52)	μ_{11}	205(60)	0
Na(2)	18*h*	3.13(6)	5724(83)	−17 241(24)	739(33)	2418(120)	329(50)	386(28)

$R = 1.61\%$, 1.71(4) Na$^+$ ions by unit cell in the "conducting plane"

μ_{ij} (Å$\times 10^4$) is given by the formula $\exp[-(2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^*)]$.

pendent positions:

(i) a position [Na(1) or K(1) which correspond to Br and aBR sites (2*b* position of the two-dimensional space group $P3_1m$, or 6*c* position of the three-dimensional space group $R\bar{3}m$];

(ii) a position [Na(2) or K(2) not revealed by the previous x-ray-structure determination which is close to a mid-oxygen site (3*c* position of the two-dimensional space group $P31m$ or 18*h* position of the three-dimensional space group $R\bar{3}m$)].

(b) In β''_{Na}, oxygen ions are off-centered from the theoretical position $(00\frac{1}{2})$ and are ordered in the local superstructure.

C. Consequences on the average structure determinations

1. Sodium β''-alumina

The successive cycles of least-squares refinement of 43 variable parameters were carried out to fit 419 observed F (hkl) values, starting from structural parameters proposed by Roth *et al.*[18] The position coordinates, thermal parameters, and occupation factors, corresponding to the best agreement index $R = 1.67\%$, are summarized in Table III(a). Structural parameters are very similar to those proposed by Roth:

Sodium ions are localized on only one position (18*h* Wyckoff positions), off-centered by 0.42 Å from the theoretical position 6*c*.

The z-position coordinate of the sodium ions ($z = -0.1722$) differs from the theoretical one ($z = -0.1666$), which would correspond to a planar distribution of the ions. The sodium ions are located in a conduction slab with a thickness of 0.39 Å.

As described above [item (a) in Sec. III B], the local structure determination has shown, however, that the conducting ions are shared between two positions of the $R\bar{3}m$ space group (6*c* and 18*h*) and not only one. Therefore a second refinement of the average structure was attempted with sodium ions on two positions (6*c* and 18*h*).

With this model, 47 variable parameters were refined to determine the average distribution of sodium ions in the unit cell. This revealed strong correlations between structural parameters of the Na(1) and Na(2) atoms, requiring a refinement by successive steps with a limitation of the variation amplitude of the parameters. The Hamiltonian statistical test (Table IV) shows that the improvement of the agreement index (1.67 → 1.61), arising from the introduction of the second sodium site is significant. The structural parameters for Na(1) 6*c* and Na(2) 18*h* atoms are summarized in Table III(b).

In β''-alumina, the compensation mechanism is exclusively due to Mg^{2+} substitution in the spinel blocks, which is supported by neutron activation analysis and undetectable Frenkel defects. As a consequence the formula can be written:

$$(\mathrm{Al}_{11-y}\mathrm{O}_{16}\mathrm{Mg}_y)(\mathrm{O{-}Na}_{(1+y)}) \text{ with } y = 0.71(4) \ (Z = 3).$$

TABLE IV. Hamilton statistical test.

	Sodium ions located on:	
	(a) one position	(b) two positions
Number of variable parameters	$m_a = 43$	$m_b = 47$
Number of independent reflections	$n = 419$	$n = 419$
R factor	$R_a = 1.67\%$	$R_b = 1.61\%$
Ratio of weighted R factor	$R = 1.037$	
R factor ratio for 0.005 level of significance	$R_{m_b - m_a, n, 0.005} = 1.023$	

$(39 \pm 1)\%$ of sodium ions are located on the Na(1) position and $(61 \pm 1)\%$ on the Na(2) position, in agreement with the repartition deduced from the local structure determination [40% on Na(1), 60% on Na(2)].

The x-position coordinate of the Na(2) atom ($x = 0.057$) differs from the one obtained from the refinement of the local structure ($x = 0.09$). This can result from the strong correlation of this parameter with the occupation and thermal factors of the same atom.

Moreover, the vibration amplitude of sodium atoms is large (up to 0.4–0.5 Å) and anisotropic, showing an in-plane overlap of the thermal ellipsoids of these atoms, which are only 0.55 Å distant one from another. It is possible, that taking into account the anharmonic contribution by including third- and fourth-order terms in the refinement could individualize more clearly these two positions.

The off-centering of the O(5) atom from the theoretical position $(00\frac{1}{2})$ does not improve the agreement factor index R, but its high vibrational amplitude (0.22 Å) is consistent with the small in-plane off-centering observed in the local structure determination (0.20 Å).

The Al-O average interatomic distances in the spinel block are similar to those observed in ion-rich β_{Na} (Table V). In both compounds, compensating Mg^{2+} ions are mainly located on the Al(2) position, involving Al(2)-O distances which are slightly larger than Al(3)-O ones.

TABLE V. Interatomic distances.

Sodium β''-alumina		Average	Rich β_{Na}-alumina
Al(1) octahedron	O(1) 2×1.844	1.909	1.913
	O(2) 2×1.986		
	O(3) 1.848		
	O(4) 1.947		
Al(4) octahedron	O(2) 6×1.889	1.889	1.891
Al(2) tetrahedron	O(2) 3×1.842	1.845	1.838
	O(4) 1.856		
Al(3) tetrahedron	O(1) 3×1.763	1.742	1.738
	1.681		
Na(1) oxygen of blocks	O(1) 3×2.647	2.611	
	O(3) 2.502		
oxygen of planes	O(5) 3×3.244		
Na(2) oxygen of blocks	O(1) 2×2.523	2.657	
	3.003		
	O(3) 2.578		
oxygen of planes	O(5) 3×3.005		

TABLE VI. Potassim β''-alumina: position and thermal parameters; $a = 5.63$ Å, $c = 34.01$ Å.

Position		Number per unit cell	$x \times 10^5$	$z \times 10^5$	$U_{11} \times 10^4$	$U_{22} \times 10^4$	$U_{33} \times 10^4$	$U_{13} \times 10^4$
Al(1)	18*h*	18	16 712(5)	92 980(1)	68(1)	67(1)	63(6)	−1(1)
Al(2)	6*c*	6	0	34 988(3)	83(3)	μ_{11}	75(6)	0
Al(3)	6*c*	6	0	44 935(3)	76(3)	μ_{11}	41(4)	0
Al(4)	3*a*	3	0	0	67(4)	μ_{11}	50(6)	0
O(1)	18*h*	18	16 419(13)	23 615(3)	87(4)	91(5)	95(6)	2(1)
O(2)	18*h*	18	15 396(13)	3 384(3)	102(4)	122(6)	86(6)	−10(2)
O(3)	6*c*	6	0	9 512(6)	86(6)	μ_{11}	71(8)	0
O(4)	6*c*	6	0	29 520(6)	93(6)	μ_{11}	108(9)	0
O(5)	3*b*	3	0	50 000	217(11)	μ_{11}	57(14)	
			(a) K^+ ions located on one position					
K(1)	18*h*	4.79(4)	4 480(96)	−16 949(9)	1124(35)	4340(145)	130(12)	271(19)
$R = 3.31\%$								
			(b) K^+ ions located on two positions					
K(1)	6*c*	1.84(2)	0	−17 086(12)	520(16)	μ_{11}	114(17)	0
K(2)	18*h*	2.95(3)	8 717(73)	−16 784(13)	921(40)	3396(170)	139(17)	285(18)

$R = 2.26\%$, 1.60(2) K^+ ions by unit cell in the "conducting plane"

μ_{ij}(Å$\times 10^4$) is given by the formula $\exp[-(2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^*)]$.

2. Potassium β''-alumina

Starting from the structural parameters proposed by Roth *et al.*,[18] the average structure determination of β''_K-alumina leads to results similar to those obtained by these authors for the β''_{Na} compound [Table VI(a)].

K^+ ions, located on only one position, are off-centered by 0.43 Å from the theoretical position (6*c*) (to be compared with 0.42 Å for the sodium ions).

In comparison with the β''_{Na}-alumina compound, the improvement of the agreement index R (3.31% → 2.26%), arising from the introduction of a second potassium site, is very important in the average structure determination of β''_K-alumina. This can be explained by the higher scattering factor of the conducting ions and a less important anharmonic contribution. Structural parameters, corresponding to the best agreement index ($R = 2.26\%$) are summarized in the Table VI.

Assuming that the compensation mechanism is exclusively due to Mg^{2+} substitution in the spinel block, the formula can be written

$$(Al_{11-y}O_{16}Mg_y)(O{-}K_{(1+y)}) \text{ with } y = 0.60(2)\ (Z = 3).$$

(38.4 ± 0.4)% of potassium ions are located on the K(1) position and (61.6 ± 0.6)% on the K(2) position, in agreement with the repartition found in the local superstructure model [40% on K(1), 60% on K(2)].

The thickness of the conduction slab is only 0.28 Å (to be compared with 0.39 Å for β''_{Na}-alumina).

The x-position coordinate of the K(2) atom ($x = 0.087$) is similar to that obtained from the refinement of the local structure (0.093). The amplitudes of vibration of the conducting ions are large (up to 0.58 Å) and anisotropic, but the distance (0.84 Å) between K(1) and K(2) positions is sufficient to avoid an in-plane overlap of the thermal ellipsoids.

The vibration amplitude of the O(5) atom (0.15 Å) is less important than that of the same atom in the β''_{Na}-alumina compound (0.22 Å), in agreement with the absence of off-centering in the local structure determination of this β''_K compound.

The Al-O interatomic distances (Table VII) in the spinel block are similar to those observed in ion-rich β_K-alumina (Ref. 13). Mg^{2+} ions are still mainly located on the Al(2) position [d(Al(2)-O) > d(Al(3)-O)].

IV. TEMPERATURE DEPENDENCE OF THE ION-ION CORRELATIONS

X-ray diffuse scattering patterns taken in the temperature range between 20 and 800 K do not reveal drastic qualitative differences in the cases of β''_{Na} and β''_K, contrary to the earlier observation made, for instance, with silver β-alumina[5] or with sodium and silver stoichiometric β-alumina.[11,12] The clear variable parameter is the coherence length ξ of the local superstructure of the con-

TABLE VII. Interatomic distances.

Pottassium β''-alumina		Average	Rich β_K-alumina
Al(1) octahedron	O(1)2×1.855	1.916	1.911
	O(2)2×1.998		
	O(3) 1.837		
	O(4) 1.952		
Al(4) octahedron	O(2)6×1.892	1.892	1.887
Al(2) tetrahedron	O(2)3×1.845	1.848	1.839
	O(4) 1.859		
Al(3) tetrahedron	O(1)3×1.770	1.758	1.746
	O(5) 1.722		
K(1) oxygen of blocks	O(1)3×2.737	2.697	
	O(3) 2.575		
oxygen of planes	O(5)3×3.253		
K(2)	O(1)2×2.705	2.885	
oxygen of planes	2×3.200		
	O(3) 2.614		
	O(5)2×2.920		

ducting ions, as deduced from the width of a section of the diffuse rods. The quasicrystalline nature of the ion-ion correlation is retained in the whole temperature range.

The temperature dependence of the coherence length shown in Fig. 5 further reveals that the variation takes place almost exclusively between 300 and 600 K.

V. DISCUSSION

The first point to clarify is the purely experimental question of the intensity modulations of the diffuse rods reported by McWahn *et al.*[7] As noted in their work, the relatively sharp intensity modulations observed for β-alumina disappear for β''-alumina, that is, when the interstitial-oxygen Frenkel-defect concentration tends to be completely replaced by the substitution compensation mechanism. The smaller intensity modulations observed by these authors along the diffuse rods of K β''-alumina stabilized by Co^{2+} and attributed to correlations between the diffusing ions and the Co^{2+} substituted for Al^{3+} in the spinel blocks would not be observable with the crystals from the present work, in which Mg^{2+} is substituted for Al^{3+} because of the negligible difference between the x-ray scattering factors of Mg^{2+} and Al^{3+}. In other words, the absence of intensity modulations along the diffuse rods reported here is not only consistent with the McWhan *et al.* results, if well-known differences in the samples are taken into account, but even supports the interpretation given in Ref. 7.

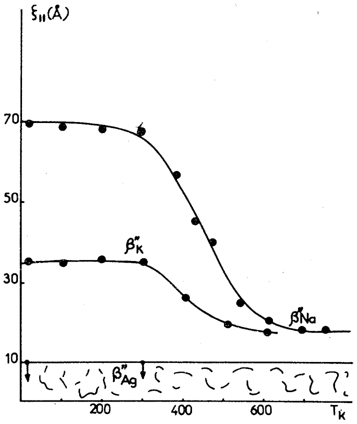


FIG. 5. Temperature dependence of the coherence length ($\xi_{\parallel}$) of the ordered regions in different β''-aluminas.

The absence of intensity modulations along the rods shows that the correlations observed in the present work are clearly two-dimensional. In addition to the absence of interstitial-oxygen Frenkel defects and the nondetectability of the Mg^{2+} ions, this fact greatly simplifies the determination of the distribution of the conducting ions. In this respect the ion-ion correlation model shown in Fig. 4, which is strongly supported by the convergence of the analysis of the diffuse scattering and the Bragg diffraction from the main lattice, differs from the model worked out in Ref. 7 for β-alumina and rather recalls the earlier

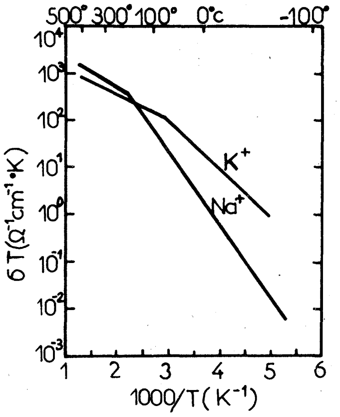


FIG. 6. Temperature dependence of conductivity of various β''-alumina isomorphs (Farrington *et al.*, Ref. 19). Simplified curves. In fact, for β''_{Na} and β''_K, the crossover from the high-activation-energy state to the low-activation-energy state is smoother and takes place on a temperature range of about 100 K.

descriptions.[6,12–15]

For consistency with numbers given in previous papers, we have continued to describe the ion-ion correlation in terms of microdomains rather than the statistical short-range order used by McWhan *et al.*[7] The difference between these two descriptions is for the most part academic; it is clear that for very small correlations the short-range-order description is more adequate while for larger correlations as observed here for K and Na β''-alumina the domain description is more realistic. We shall discuss below the relation of the new structural results of the present study with the ionic conductivity.

A. Effect of the nature of the conducting ions and their concentration

From the preparation method alone, it can be understood that the compositions deduced from the average structure determinations of various single crystals of β''-alumina yield a long spread of concentrations of the conducting ions (from 1.60 to 1.71 ions per unit cell in the conducting plane). In addition, it must be noted that the sodium ion concentration proposed for the β''_{Na} compound (1.71) is probabily higher than the real one, as shown by Reidinger[23]; if anharmonic contributions are taken into account the occupation factor of the sodium site decreases.

Further, x-ray diffuse scattering patterns from several single crystals of β''_{Na}-alumina are similar, showing that slight discrepancies between assigned sodium concentrations (whether real or not) do not involve a significant change in the organization of the conducting ions. From these observations one can conclude that it is the nature of the conducting ions which is a prominent parameter for β''-alumina compounds.

At room temperature, a clear relation can be shown as a function of the conducting ion between the electrical properties and the structural parameters which are characteristic of the cationic disorder as follows.

(i) The magnitude of the in-plane vibration amplitudes, deduced from the average structure study $U_{22}(\mathrm{K}) > U_{22}(\mathrm{Na})$, are in the same sequence as the ionic conductivity determined by G. Farrington *et al.*[19] ($\sigma_{\beta''_K} > \sigma_{\beta''_{Na}}$ at 300 K, Fig. 6).

(ii) In β''_K-alumina the in-plane coherence length ($\xi_{\parallel}$) is smaller than that observed in β''_{Na}-alumina, which is consistent with the higher ionic conductivity of the β''_K compound.

The larger coherence length in β''_{Na} can be explained by a more important thickness of the conduction slab (0.39 Å for β''_{Na}, 0.28 Å for β''_K). The increase of the conduction slab thickness reduces the interionic repulsions by increasing the screening effects due to oxygen atoms and allows the extension of the ordered domains. In contrast with the β-alumina-type structure,[25] the K^+ ion's mobility is higher than that of the Na^+ ion's in the β''-alumina structure, emphasizing the importance of the host lattice.

B. Temperature effects

It must first be noted that the rapid changes of the coherence length in β''_{Na} and β''_K occur in the same temperature range as the rapid changes in the activation energy observed by Farrington *et al.*[19] (Fig. 6).

In β''_{Na}, the sodium ions evolve from a low-temperature state ($T < 300$ K), characterized by a coherence length of 70 Å and by the existence of an ionic motion with an activation energy of 0.35 eV to a high-temperature state ($T > 600$ K), characterized by a coherence length of 20 Å and an ionic motion with an activation energy of 0.10 eV.

The amplitude of the variation of the activation energy and of the coherence length are smaller in β''_K ($\xi = 35$ Å $- E_A = 0.21$ eV at $T < 300$ K; $\xi = 20$ Å $- E_A = 0.10$ eV at $T > 500$ K). They tend to zero for β''_{Ag}, in which the activation energy is 0.19 eV and the coherence length remains lower than 10 Å in the temperature range 20–800 K.[20] Further, the amplitude of the variation of the coherence length and of the activation energy between the high- and the low-temperature state increases, as does the thickness of the conduction slab.

The relations between different physical parameters described above leads to a suggestion concerning the ionic motion in different β''-alumina compounds as a function of temperature. The ionic motion characterized by a low activation energy is only obtained at high temperatures; one may therefore wonder whether the change of regime, with a discontinuous decrease of the activation energy (above 400 K for β''_K and above 450 K for β''_{Na}), is not related to a crossover between a low-temperature slightly three-dimensional conduction (in the slab) and a high-temperature two-dimensional conduction.

Even at high temperature there is a conduction slab in β''_K and β''_{Na}, but one can think that above a certain temperature the thermal fluctuations become more important than the differences in the z coordinates of the conducting ions, allowing a quasi-two-dimensional-type of motion characterized by an activation energy which is much smaller than in the low-temperature quasi-three-dimensional-type of motion. The two-dimensional high-temperature state is further obviously more disordered in agreement with the smaller coherence length of the ion-ion correlation deduced from the diffuse scattering.

C. Host lattice effects

Several studies[24,25] have shown the ionic conductivity of β''-alumina is higher than that of usual β-alumina. In fact, these electrical measurements did not clearly show the influence of the host lattice, because the compositions and the electrical compensation mechanism in β- and β''-alumina samples were very different (1.25 Na^+ per unit cell in the conducting plane and interstitial oxygen atoms in β-alumina compared with 1.7 Na^+ ions and Mg^{2+} substitution in β''-alumina).

The recent synthesis of an "ion-rich" β-alumina[19] with similar composition and electrical compensation mechanism as β''-alumina allows us to discuss now the influence of the host lattice (β or β'') on the organization of the conducting ions and consequently on the electrical properties of compounds with formula

$$(Al_{11-y}O_{16}Mg_y)—(O—B_{(1+y)}) \quad (B^+ = Na^+, K^+)$$

$$(0.6 < y < 0.7)$$

$$(Z = 2 \text{ for } \beta \text{ and } Z = 3 \text{ for } \beta'')$$

(i) In the sodium and potassium compounds, the short-range order observed in the β-alumina structure by x-ray diffuse scattering is replaced by a two-dimensional quasi-long-range order in the ion-rich β-alumina structure; the coherence length in ion-rich β-alumina is larger than the experimental resolution[13] ($\xi > 150$ Å).

(ii) The c lattice constant of the hexagonal unit cell of β-alumina decreases when the conducting ion concentration increases (for β_{Na}, $y = 0$, $c = 22.57$ Å, $y = 0.30$, $c = 22.49$ Å, $y = 0.62$, $c = 22.29$ Å). In other words the increase of the conducting ion concentration induces the compaction of the β alumina structure. The contrary is observed for β'' alumina, with the existence of a conduction slab.

(iii) In the ion-rich β-alumina compounds, the channel along the honeycomb conduction path is narrower than that in the β''-alumina compounds.[13] Indeed, a traveling alkali ion must move through or close to an aBR position where the oxygen atoms from the spinel blocks project more into the conduction plane of the ion-rich β-alumina structure than in the β-alumina structure. ($d_{aBR\text{-}O} = 2.40$ Å for rich β_K-alumina and $d_{aBR\text{-}O} = 2.31$ Å for rich β_{Na}-alumina compared with, respectively, 2.58 Å for β''_K and 2.50 Å for β''_{Na}.)

Consequently, in ion-rich β-alumina, the aBR-O intersite distances are much smaller than the sum of ionic radii. Obviously, if the O-aBR intersite distances are large enough as those in usual β-alumina compounds, one can observe a decrease of the coherence length in the conducting plane [$d_{aBR\text{-}O} = 2.48$ Å and $\xi_{\parallel} = 40$ Å for the β_K compound $(Al_{11}O_{16})-(O-B_{1+x})O_{x/2}$ with $x \simeq 0.3$] and an easy ion diffusion along the conducting path, in spite of the presence of the interstitial oxygens. Altogether the observations made above about the effects of the host lattice allow us to predict lower ionic conductivities for the ion-rich β structure than those for β''-alumina.

VI. CONCLUSION

One of the conclusions which can be made from the present work concerning the methods of investigation of structural properties in complex cases such as the β-alumina family is the great advantage of combining diffuse scattering studies with conventional structure-determination procedures. In the case considered here, it has allowed a more precise structure determination and consequently a better idea of the relation of the structural parameters with the ionic conductivity.

Another conclusion concerns the magnitude in plane ion-ion correlations. It was often said that the ionic conductivity decreases with the increase of the ion-ion coherence length. This is not only true for a given structure when, for instance, the temperature is varied or when the ions are exchanged without further modification, but also for cases in which important parameters such as the compensation mechanism and the ion concentrations are similar as for β''- and ion-rich β-alumina. It does not apply in other cases: In spite of larger coherence lengths, K and Na β''-alumina are better ion conductors than the usual β-alumina.

Note added. The structure factors corresponding to average structure determinations are available from the authors.

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[1] C. R. Peters, M. Bettman, J. W. Moore, and M. D. Glick, Acta Crystallogr. Sec. B 27, 1826 (1971).

[2] J. P. Boilot, Ph. Colomban, G. Collin, and R. Comes, J. Phys. Chem. Solids 41, 47 (1980).

[3] G. Collin, J. P. Boilot, A. Kahn, J. Thery, and R. Comes, J. Solid State Chem. 21, 283 (1977).

[4] W. L. Roth, F. Reidinger, and S. La Placa, in *Superionic Conductors*, edited by G. D. Mahan and W. L. Roth (Plenum, New York, 1976), p. 223.

[5] Y. Le Cars, R. Comes, L. Deschamps, and J. Thery, Acta Crystallogr. Sec. A 30, 305 (1974).

[6] J. P. Boilot, G. Collin, R. Comes, J. Thery, R. Collongues, and A. Guinier, in *Superionic Conductors*, edited by G. D. Mahan and W. L. Roth (Plenum, New York, 1977).

[7] D. B. McWhan, P. D. Dernier, C. Vettier, A. S. Cooper, and J. P. Remeika, Phys. Rev. B 17, 4043 (1978).

[8] See S. M. Shapiro and F. Reidinger, in *Physics of Superionic Conductors*, Topics in Current Physics, edited by M. B. Salamon (Springer, Berlin, 1979), Vol. 15, p. 45.

[9] Ph. Colomban, J. P. Boilot, A. Kahn, and G. Lucazeau, Nouveau Journal de Chimie 2, 21 (1978).

[10] Ph. Colomban, Ph.D. thesis, Université de Paris (1979) (unpublished).

[11] J. P. Boilot, Ph. Colomban, G. Collin, and R. Comes, in *Fast Ion Transport in Solids*, edited by P. Vashishta, J. N. Mundy, and G. K. Shenoy (North-Holland, Amsterdam, 1979), pp. 243 and 303.

[12] J. P. Boilot, Ph. Colomban, R. Collongues, G. Collin, and R. Comes, Phys. Rev. Lett. 42, 785 (1979).

[13] G. Collin, R. Comes, J. P. Boilot, and Ph. Colomban, Solid State Ionics 1, 59 (1980).

[14] J. P. Boilot, J. Thery, R. Collongues, R. Comes, and A. Guinier, Acta Crystallogr. Sec. A 32, 250 (1976).

[15] J. P. Boilot, G. Collin, Ph. Colomban, J. Thery, and R. Comes, J. Phys. (Paris) Colloq. 39, C2-204 (1978).

[16] J. Thery and D. Briancon, C. R. Acad. Sci. 254, 2782 (1962); G. Yama Guchi, and K. Suzuki, Bull. Chem. Soc. Japan 41, 93 (1968).

[17] D. Gratias, Y. Le Cars, J. P. Boilot, and J. Thery, Phys. Status Solidi 38, 595 (1976).

[18] W. L. Roth, W. C. Hamilton, and S. J. Laplaca, Am. Crystallogr. Ass. Abstracts., Ser. 2, 1, 169 (1973).

[19] G. C. Farrington and J. L. Briant, in *Fast Ion Transport in Solids*, edited by P. Vashishta, J. N. Mundy, and G. K. Shenoy (North-Holland, 1979), p. 395; T. Cole, N. Weber, and T. K. Hunt, *ibid.*, p. 277.

[20] J. P. Boilot, G. Collin, R. Comes, and Ph. Colomban (unpublished).

[21] M. Bettman and C. R. Peters, J. Phys. Chem. 73, 1774 (1969).

[22] A. Guinier, *Théorie et technique de la radiocristallographie* (Dunod, Paris, 1956). The Scherrer formula used here corresponds to a microdomain model; if a short-range-order model corresponding to correlations falling off exponentially is used as in Ref. 3, smaller values are obtained: ξ (microdomain) = ξ (SRO) × 2.8.

[23] F. Reidinger, Ph.D. thesis, State University of New York at Albany (1969) (unpublished).

[24] J. T. Kummer, Prog. Solid State Chem. 7, 141 (1972).

[25] J. F. Kennedy, in *Solid Electrolytes*, Topics in Applied Physics, edited by S. Geller (Springer, New York, 1977), Vol. 21, p. 105.

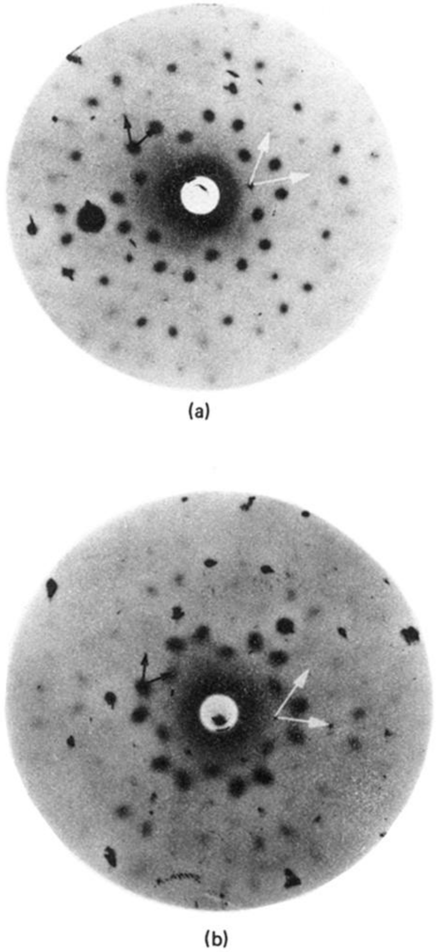

FIG. 2. X-ray-scattering patterns at 300 K for β''-alumina (Mo $K\alpha$ incident beam parallel to c axis). (a) β''_{Na} exposure time: 48 h; (b) β''_{K} exposure time: 30 h. [Note the presence of superlattice diffuse spots (black arrows).] White arrows indicate the main lattice of β''-alumina.

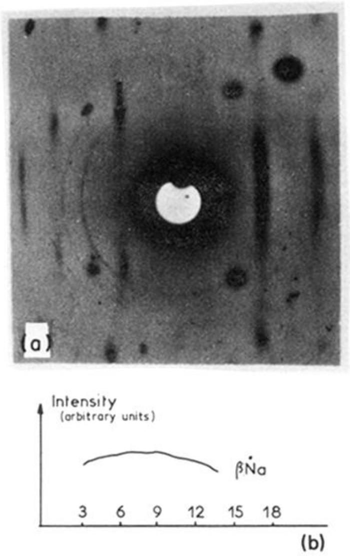

FIG. 3. X-ray-scattering patterns at 300 K for β''-alumina (Mo $K\alpha$ incident beam perpendicular to c axis). (a) β''_{Na} exposure time: 60 h. Note diffuse rods with very small intensity modulation along c^* (black arrows), for adequate reflection conditions. (b) Intensity along diffuse rod for β''_{Na} as registered by microdensitometer reading of x-ray pattern. The reading corresponds to the rod $\frac{2}{3}$, $\frac{2}{3}$, η [shown by arrow on pattern (a)].