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Short-Range-Ordering in the Ba²⁺ Ion Distribution in Ba²⁺ β"-Alumina at 295 K

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Abstract

The Ba²⁺ ionic distribution in Ba²⁺ β"-alumina has been studied at 295 K by conventional single-crystal X-ray diffraction techniques (Mo Kα radiation: λ = 0.710 688 Å). The structure [idealized formula Ba_xMg_{2x-1}Al_{12-2x}O₁₇ (x = 5/6), M_r = 681.5, F(000) = 972] comprises a rhombohedral framework of spinel-type slabs separating the two-dimensional conduction planes with a spacing of ~11 Å. All atoms in the spinel skeleton appear to satisfy the centrosymmetric space group *R* $\bar{3}m$, with hexagonal cell dimensions: *a* = 5.619 (1), *c* = 34.084 (20) Å, *V* = 932.0 (7) Å³, *Z* = 3, *D_x* = 3.643 (3) Mg m⁻³, μ_{calc} = 3.61 mm⁻¹. The arrangement of Ba²⁺ ions is found to be non-centrosymmetric at short-range, as evidenced by a

distinct preference by the complete unit cell for the space group *R* $\bar{3}m$. The Ba²⁺ ions occupy predominantly the 6(*c*) sites (*R* $\bar{3}m$ notation) with a mean ratio of ~3.5:1 between the refined occupations of adjacent sites. Significant Ba²⁺ density also lies on the conduction pathways between adjacent 6(*c*) sites. The column oxygen O(5) shows no significant displacement from the 3(*b*) site. The best fit to the data is obtained with third-rank cumulants (γ_{ijk}'s) describing the vibration of the Ba²⁺ ions. The effective formula is Ba_{0.82}Mg_{0.63}Al_{10.37}O₁₇, assuming charge neutrality and charge compensation through Mg²⁺ substitution. The implications of the crystallographic result are discussed, particularly in connection with possible ionic conduction mechanisms.

Introduction

Since the discovery sixteen years ago of superionic conducting behaviour in Na^+ β'' -alumina (Yao & Kummer, 1967), interest in the β - and β'' -aluminas has been intense. The field has long been dominated by monovalent cation conductors, particularly solid electrolytes for Na^+ , Li^+ , Ag^+ and H^+ . Recently, however, it was shown that the β'' -alumina structure can also support high ionic conductivity for divalent cations: e.g. Ba^{2+} , Sr^{2+} , Ca^{2+} (Dunn & Farrington, 1980). Conductivities are around $10^{-6} \Omega^{-1} \text{cm}^{-1}$ at 313 K, and rise to around $10^{-1} \Omega^{-1} \text{cm}^{-1}$ at 673–773 K. The value for Pb^{2+} β'' -alumina is exceptionally high, about $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 313 K (Seevers, De Nuzio, Farrington & Dunn, 1983); almost as high as the conductivity of Na^+ β'' -alumina at the same temperature. The structures and particularly the ion distributions have now been studied in many of these: the results are given here for the largest of these ions, namely Ba^{2+} (radius: 1.35 Å). It is possible that, by virtue of its size, Ba^{2+} represents one of the extremes in the ionic conduction mechanisms in divalent ions. A preliminary report has already appeared (Aldén, Thomas & Farrington, 1981). See also Farrington & Dunn (1982) for a more general review of the divalent β'' -aluminas, and Thomas, Aldén & Farrington (1983) for a structure-oriented discussion.

Experimental

Crystal preparation

Single crystals of Ba^{2+} β'' -alumina were prepared by ion exchange from Na^+ β'' -alumina, grown at 1963–1998 K (Farrington & Briant, 1978). The exchange was performed in a 62% $\text{Ba}(\text{NO}_3)_2/38\%$ BaCl_2 melt at 823 K for 20 h. A radiochemical marking technique using the ^{22}Na isotope (developed for subsequent divalent exchanges) was not used for the crystal studied here. The exchange temperature and time used were later shown to result in complete exchange in crystals of comparable size.

The data collection

Single-crystal X-ray diffraction data were collected using a Nonius CAD-4 automatic X-ray diffractometer (Mo $K\alpha$ radiation: graphite-monochromatized). The crystal used was cracked from a larger exchanged crystal: it had a maximum dimension of 0.138 mm. The crystal dimensions and orientation matrix have been deposited.* Data were collected for the hexagonal cell. A preliminary data set containing all hkl combinations was first collected out to $\theta = 10^\circ$, from which it was established that only reflections for which $-h + k + l = 3n$ had intensities significantly

different from background. The subsequent complete data collection measured only such reflections (of type $\pm h, k, l$) using an ω - 2θ scan mode.

In all, 2212 such reflections were measured out to $\sin \theta/\lambda = 0.926 \text{ \AA}^{-1}$; no averaging was made of symmetry equivalents. A set of four standard reflections was monitored at regular intervals during the data collection and found to remain constant in intensity.

Cell parameters were determined from a least-squares fit of 21 2θ angles in the range $10^\circ < 2\theta < 52^\circ$ observed on the diffractometer prior to data collection.

The reflection profiles were corrected for background using the Lehmann & Larsen (1974) method modified to allow for the X-ray $K\alpha$ doublet (Blessing, Coppens & Becker, 1974). Lp corrections and corrections for absorption ($\mu_{\text{calc}} = 3.61 \text{ mm}^{-1}$, assuming a composition $\text{Ba}_x\text{Mg}_{2x-1}\text{Al}_{12-2x}\text{O}_{17}$, $x = 5/6$) were also made; the latter taking account of the explicit shape, size and orientation of the crystal. (No suitable crystal was available for an experimental determination of μ .) Calculated transmissions fell in the range 0.70–0.89.

The refinements

The tentative assumption was made initially that the structure of the spinel skeleton is essentially that of Na^+ β'' -alumina (Bettman & Peters, 1969). It was therefore reasonable to assume that the spatial distribution of Ba^{2+} ions is crudely represented by the contents of a difference Fourier synthesis calculated for an F_c model comprising this spinel block structure (see Fig. 1). It is seen that the Ba^{2+} ion distribution (when forced to follow the $R\bar{3}m$ space group) is concentrated at 6(c) sites (0, 0, z) and is significantly trigonally distorted in the direction of adjacent equivalent 6(c) sites. Very little density is evident in the intermediate 9(d) sites. A centrosymmetric distribution of Ba^{2+} ions was thus included at 6(c) sites and their occupations were refined.

All refinements were made using the full-matrix least-squares refinement program UPALS (Lundgren, 1982). The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$, where $w^{-1} = \sigma_c^2(F_o^2) + (kF_o^2)^2$; σ_c is based on Poisson counting statistics and k was given the value 0.04. Reflections for which F_o^2 was less than $2\sigma(F_o^2)$ were removed from the refinement; this left 1879 for use in the final refinement.

The trigonal distortion apparent in the difference Fourier maps was first modelled by shifting the Ba^{2+} scattering centres out to 18(h) sites (at $2x, x, z$) in combination with anisotropic temperature factors (β_{ij} 's). An alternative approach was to place the Ba^{2+} at (0, 0, z) and refine both second- and third-order cumulants (β_{ij} 's and γ_{ijk} 's) (see, for example, *International Tables for X-ray Crystallography*, 1974). The agreement indices obtained from these refinements

* See deposition footnote.

are summarized in Table 1. It is seen that the R values remained extremely high.

A dramatic improvement came, however, on realizing that the repulsion effect between two large, juxtaposed, doubly charged Ba^{2+} ions, in combination with the greater proportion of vacant sites (compared, for example, with Na^+ β'' -alumina) could give rise to a short-range-ordering effect consistent with the effective loss of a local symmetry centre for the Ba^{2+} ions. This model was achieved by defining the structure formally as noncentrosymmetric $R\bar{3}m$, but then allowing the atoms of the spinel block to generate their centrosymmetric counterparts; this symmetry was also retained in the refinement. The two atoms occurring at centres of symmetry [Al(1) and O(5)] were therefore still held fixed. The dramatic improvement accompanying the introduction of this new degree of freedom for the Ba^{2+} distribution (while still retaining the centre of symmetry for the spinel block) is reflected in Table 1. The model that has thus

Table 1. Agreement factors at various stages in the refinement

Refinement No.	Model refined	No. of parameters refined	$R(F)$	$R(F^2)$	$R_w(F^2)$
(1)	Centrosymmetric $R\bar{3}m$. Ba(1) at 6(c) (β_{ij} 's)	40	0.1308	0.1594	0.3519
(2)	As (1), but Ba(1) at 18(h)	43	0.1184	0.1527	0.3305
(3)	As (1), but β_{ij} 's and γ_{ijk} 's on Ba(1)	43	0.1200	0.1528	0.3339
(4)	As (3), but occupations of Ba(1) and Ba(1') different [at 6(c) and 6(c')], z(O(5)) refined.	45	0.0627	0.0967	0.1678
(5)	As (4), +Ba(2) at 9(d) (mid-oxygen). Isotropic thermal description.*	47	0.0605	0.0888	0.1622
(6)	As (5), but Ba(1) and Ba(1') completely independent ($R\bar{3}m$: different z, occupation, β_{ij} 's and γ_{ijk} 's).	53	0.0568	0.0826	0.1520

* Mid-oxygen occupation refined to zero in refinements (1)–(3).

far given the best agreement involves partial occupation of the two 6(c) sites by Ba^{2+} atoms with independent occupation factors [in the ratio 3.5(2):1], z coordinates and thermal tensors up to third-order, and partial occupation of the 9(d) (mid-oxygen) sites by an isotropic Ba^{2+} ion (Tables 2 and 3).

The final observed and difference Fourier syntheses (using calculated phases) of the average spatial occupation of the Ba^{2+} ions parallel to the conduction plane and in the $(2x, x, z)$ plane are shown in Figs. 2 and 3, respectively. Clearly, inadequacies do still remain in the description of the extended form of the Ba^{2+} distribution. Attempts to include further partial Ba^{2+} scattering power at sites corresponding to the peaks in the difference map met with only limited success. That inclusion of partial Ba^{2+} ions at the 9(d) sites led to a significant decrease in the R factor should not be taken as conclusive proof that Ba^{2+} ions are actually localized at these sites, but only that their inclusion improves the description of the extended Ba^{2+} distribution.

An isotropic extinction parameter (g) was refined to the value 4200 (1200) in the final refinement. The atomic form factors for Ba^{2+} , Al and O were taken from *International Tables for X-ray Crystallography* (1974), as were their appropriate anomalous-dispersion contributions. No distinction was made between the scattering power of Al^{3+} and Mg^{2+} [found predominantly at Al(2) by neutron diffraction studies]. Both were described formally as neutral Al, while O^{2-} was described as neutral O.*

Calculations were made on the departmental NORD 100 computer and on the IBM 370/155 computer of the Uppsala Computer Center. All programs used have been described by Lundgren (1982).

* Lists of structure factors and the crystal dimensions and orientation matrix have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39095 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

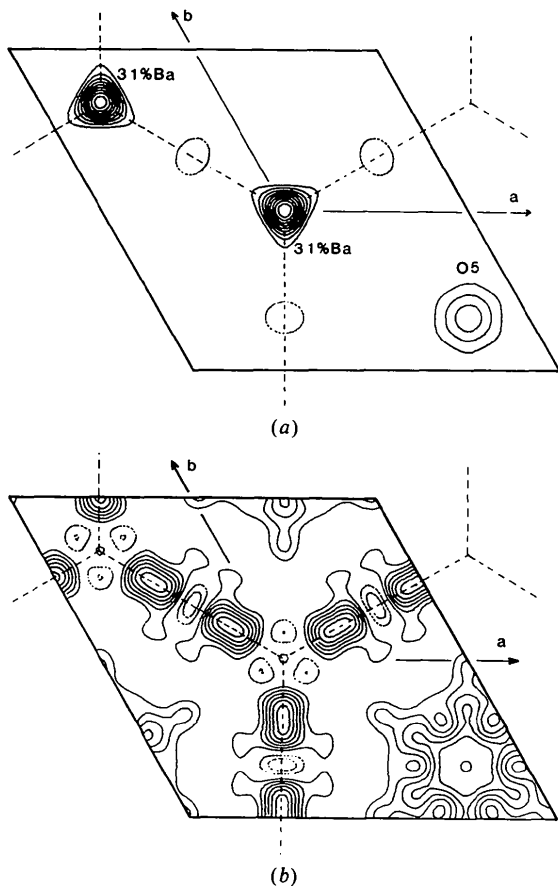


Fig. 1. Difference ($F_o - F_c$) syntheses for $Ba^{2+}\beta''$ -alumina at $z = \frac{1}{2}$ assuming the centrosymmetric space group $R\bar{3}m$ for the Ba^{2+} distribution. (a) F_c calculated for the spinel block only. Contour interval: $6.0 e \text{ \AA}^{-3}$. (b) F_c calculated with Ba^{2+} at 6(c) [refinement (3); Table 1]. Contour interval: $0.6 e \text{ \AA}^{-3}$. Note: The percentages given here and in Figs. 2 and 3 correspond to the refined Ba^{2+} occupations at the sites concerned.

Table 2. Atomic positional parameters ($\times 10^5$) in Ba^{2+} β'' -alumina

	Site*	x	y	z
Ba(1)	6(c) [occupation: 54.0 (4)%]	0	0	16952 (8)
Ba(1')	6(c') [occupation: 15.3 (5)%]	0	0	-17157 (74)
Ba(2)	9(d) [occupation: 4.1 (5)%]	1/3	1/6	1/6
Al(1)	3(a)	0	0	0
Al(2)	6(c)	0	0	34977 (4)
Al(3)	18(h)	33411 (15)	x/2	7019 (2)
Al(4)	6(c)	0	0	44953 (4)
O(1)	18(h)	15397 (19)	2x	3379 (5)
O(2)	6(c)	0	0	29496 (10)
O(3)	6(c)	0	0	9522 (9)
O(4)	18(h)	16418 (17)	2x	23588 (5)
O(5)	18(h)	1/3	2/3	16598 (31)

* $R\bar{3}m$ notation.

Table 3. Anisotropic thermal parameters ($U_{ij} \times 10^4 \text{ \AA}^2$), where $U_{ij} = (2\pi^2 a_i^* a_j^*)^{-1} (h^2 a_i^{*2} + \dots + 2hka_i^* a_j^* + \dots)$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)†	299 (4)	U_{11}	18 (2)	$U_{11}/2$	0	0
Ba(1')	752 (40)	U_{11}	401 (44)	$U_{11}/2$	0	0
Ba(2)	1055 (130)‡	—	—	—	—	—
Al(1)	40 (4)	U_{11}	57 (6)	$U_{11}/2$	0	0
Al(2)	48 (3)	U_{11}	67 (5)	$U_{11}/2$	0	0
Al(3)	41 (3)	39 (2)	70 (3)	$U_{11}/2$	5 (2)	$U_{13}/2$
Al(4)	44 (3)	U_{11}	42 (5)	$U_{11}/2$	0	0
O(1)	63 (4)	93 (6)	73 (6)	$U_{22}/2$	-10 (2)	$2U_{13}$
O(2)	36 (6)	U_{11}	109 (11)	$U_{11}/2$	0	0
O(3)	48 (6)	U_{11}	88 (11)	$U_{11}/2$	0	0
O(4)	48 (4)	39 (5)	86 (6)	$U_{22}/2$	8 (2)	$2U_{13}$
O(5)	459 (27)	U_{11}	22 (22)	$U_{11}/2$	0	0

† Refined values for third-order cumulants (γ_{ijk} in \AA^3) for Ba(1): $\gamma_{111} (= -\gamma_{222} = 2\gamma_{112} = -2\gamma_{122}) = 0.0018$ (1); $\gamma_{333} = -0.000001$ (1); $\gamma_{113} (= \gamma_{223} = 2\gamma_{123}) = -0.00003$ (1); $\gamma_{133} = \gamma_{233} = 0$. For Ba(1'): $\gamma_{111} = -0.0021$ (9); $\gamma_{333} = -0.000005$ (4); $\gamma_{113} = -0.00011$ (10).

‡ Ba(2) isotropic.

Results and interpretation

The structure

No evidence has been obtained to indicate any significant departure from the Na^+ β'' -alumina structure of Bettman & Peters (1969) as far as the spinel block is concerned (see Table 4). Nor is the O(5) column oxygen in the Al(4)-O(5)-Al(4) bridge between the blocks found to be affected by the type

of disordering process noted, for example, in Ca^{2+} β'' -alumina (Aldén, Thomas & Farrington, 1981). No attempt was made here to establish the degree of substitution of Al^{3+} sites by Mg^{2+} ions. Comparison of Al-O distances with those obtained from accurate neutron studies suggests, however, that the Mg^{2+} substitution occurs primarily at the Al(2) site.

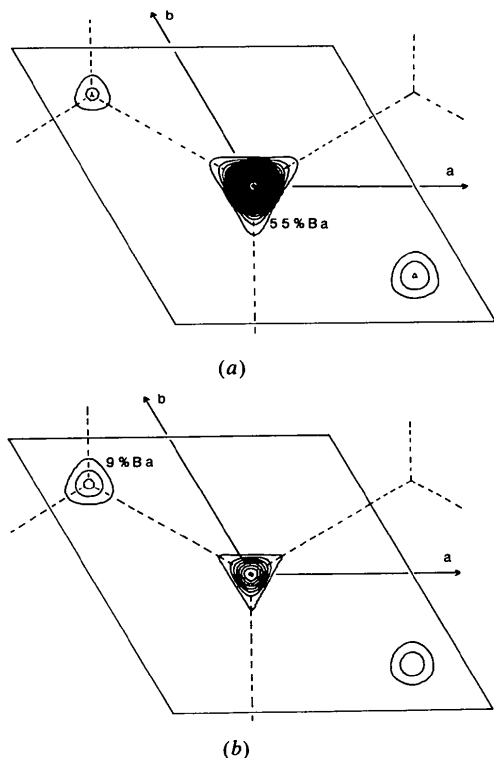


Fig. 2. F_o syntheses for Ba^{2+} β'' -alumina calculated using phases taken from F_c assuming the noncentrosymmetric space group $R\bar{3}m$ for the Ba^{2+} distribution [refinement (6); Table 1]. Contour interval: $6.0 e \text{ \AA}^{-3}$. (a) $z = 0.1695$; (b) $z = 0.1618$.

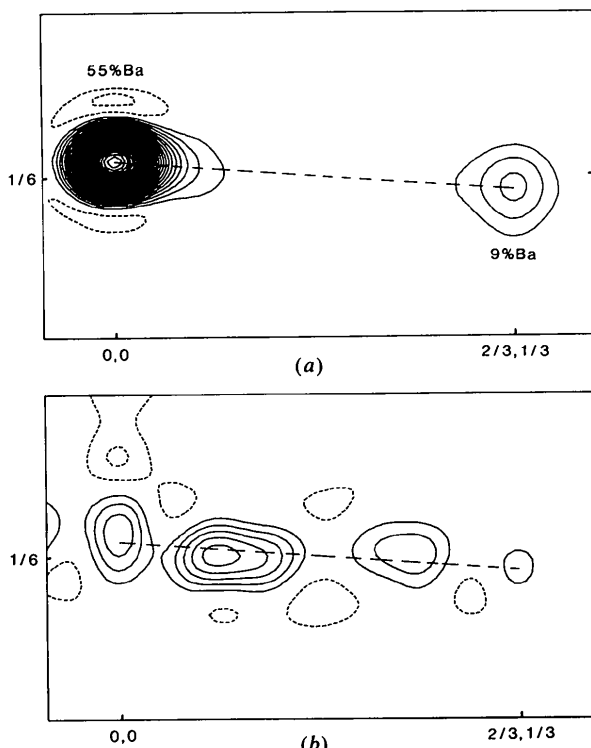


Fig. 3. Fourier syntheses for Ba^{2+} β'' -alumina calculated as in Fig. 2 in the $(2x, x, z)$ plane. (a) F_o synthesis; contour interval: $6.0 e \text{ \AA}^{-3}$. (b) $(F_o - F_c)$ difference synthesis; contour interval: $1.0 e \text{ \AA}^{-3}$.

Table 4. Some distances (Å) in Ba²⁺ β"-alumina

			Mean
Ba(1)–O(3)	2.532 (4)	(×1)}	2.710
Ba(1)–O(4)	2.769 (3)	(×3)}	
Ba(1')–O(3)	2.602 (25)	(×1)}	
Ba(1')–O(4)	2.712 (20)	(×3)}	
Ba(1)–Ba(1')	3.255 (2)	(×3)	2.684
Ba(1)–Ba(2)	1.625 (1)	(×3)	
Ba(1')–Ba(2)	1.631 (3)	(×3)	
Ba(2)–Ba(2')	2.809 (0)	(×4)	
Al(1)–O(1)	1.890 (1)	(×6)	1.890
Al(2)–O(1)	1.843 (2)	(×3)}	1.849
Al(2)–O(2)	1.868 (4)	(×1)}	
Al(3)–O(3)	1.836 (2)	(×1)}	1.916
Al(3)–O(4)	1.857 (1)	(×2)}	
Al(3)–O(2)	1.948 (1)	(×1)}	
Al(3)–O(1)	1.998 (1)	(×2)}	
Al(4)–O(4)	1.766 (1)	(×3)}	1.754
Al(4)–O(5)	1.697 (11)	(×1)}	
Al(4')–O(5)	1.743 (11)	(×1)}	

Apart from the column oxygen O(5), the 'conduction planes' (at $z = \frac{1}{6}, \frac{1}{2}$ and $\frac{5}{6}$) contain only Ba²⁺ ions predominantly at 6(c) sites ($R\bar{3}m$ notation). These sites represent the common corners of the hexagonal 'pathways' available to the ions for their passage through the structure. Adjacent 6(c) sites are actually displaced above and below the $z = \frac{1}{6}$ plane. Hereafter, a 6(c) site *above* the plane will be referred to in the discussion as an *up* site, and a 6(c) site *below* the plane as a *down* site.

We must consider carefully the implications of the Ba²⁺ positions and occupations given in Table 2. While the Fourier map shown in Fig. 1 may portray the average Ba²⁺ distribution over all sites, *i.e.* the crystal as a whole contains a 50%–50% admixture of *up* and *down* Ba²⁺ ions, we actually obtain a ratio of approximately 3.5:1 between the occupations of the adjacent 6(c) sites (in space group $R\bar{3}m$) in the conduction plane (Fig. 3 and Table 2) in the final refinement.

An explanation for the observed noncentrosymmetry in divalent β"-aluminas has been presented in detail elsewhere (McIntyre & Thomas, 1983). The main points of the argument follow.

At short range, the Ba²⁺ ions will tend to arrange themselves such that the local atomic structure is noncentrosymmetric; the occupation of an *up* site will, by virtue of the Ba²⁺ ion radius and +2e charge, tend to exclude the occupation of any of the neighbouring *down* sites (*up*–*down* distance: 3.25 Å). However, the next-nearest sites (also *up* sites) can be occupied. If only next-nearest-neighbour sites were allowed, this noncentrosymmetric character would propagate throughout the whole crystal if it were not that this would result in too much Ba²⁺ in the layers (Ba_{1.0}²⁺ per cell layer). However, another possibility is that, instead of the two next-nearest *up* sites in a given

hexagon being occupied, the centrosymmetrically related *down* site diametrically opposite the occupied *up* site is occupied. Such a situation would seed the development of a new region of local order in the conduction plane, centrosymmetric with respect to the original region (*down* with respect to *up* and *vice versa*) and, moreover, facilitate the necessary reduction of the overall Ba²⁺ content. These regions of local order within the conduction plane are the counterpart in β"-alumina of the domains that van Gool & Bottelberghs (1973) have proposed to explain the high conductivity in β-alumina. They assume that, in one domain, the ions occupy one type of position (in β-alumina the *BR* or *aBR* positions); in an adjacent domain the alternative position is occupied. Since the average energy per additional ion to increase the size of one domain is much smaller than the energy required to move just one ion, van Gool & Bottelberghs (1973) postulate that fast ion transport occurs by the movement of domain walls.

Following the general notion of a range of local order associated with each Ba²⁺ ion, the implication is that the site occupations become statistically decorrelated with respect to a given occupied site on moving away from that site. From symmetry considerations, the site-occupation correlation in the conduction plane is likely (on average) to be radially dependent. The ordering could also be maintained across the 11 Å thick spinel blocks, but the average correlation length in the *c* direction will, in general, be different from that in the conduction plane.

There is, however, an apparent contradiction in the domain model as applied to our observations. Intensities of Bragg reflections are most commonly assumed to be determined by the average of the structure in both time and space; the spatial average being over the whole crystal. An observed difference in the occupation factors for Ba²⁺ on the *up* and *down* sites would then imply that the crystal is polar. This contradicts firstly the observed high conductivity of this compound, and secondly the observation that reversing the polarity of the structure does not alter the refinement despite the strong anomalous-scattering contribution from Ba ($f'' = 2.282$). On the other hand, if ordered domains exist only locally, the average symmetry of $R\bar{3}m$ over the whole crystal would be reflected in equal occupation factors for the *up* and *down* sites.

These apparently conflicting observations can be reconciled by introducing the mosaic block model (Darwin, 1922) in which the crystal is composed of many small perfect-crystal regions or, more generally, the model of a statistically coherent diffraction volume (Kato, 1976*a, b*) characterized by the correlation length of the lattice phase factors. Within this model, each coherent diffraction volume is assumed to diffract independently. The amplitude of the ob-

served structure factor is then determined by the average amplitude of the scattering from all coherent diffraction volumes. In calculating the amplitude for each volume, the phase-delayed scattering only from planes within this volume is included. If the diffraction correlation length is less than or comparable to the correlation length of the short-range order in the site occupations *in all three dimensions*, the Ba^{2+} ions within any coherent diffraction volume will lie predominantly on the *up* sites or predominantly on the *down* sites, and hence an occupation ratio different from 1:1 will be refined even though the true ratio over the entire crystal is 1:1. Note also that the observed ratio is itself dependent on the relation between correlation lengths and is not, in general, simply the ratio of the occupations of adjacent *up* and *down* sites. The value of the ratio observed will be lower for longer diffraction correlation lengths, and for shorter site occupation correlation lengths. The value refined can nevertheless be taken as a lower limit for the ratio of the occupancies of adjacent 6(c) sites.

A neutron diffraction study of Na^+ β'' -alumina at three temperatures (Frase, Thomas & Farrington, 1983) has revealed that the data are much better fitted when the constraint imposed by the centre of symmetry on the occupancies of the Al(2) sites is also released. In fact, the final refined occupations suggest that one of the two Al(2) sites is occupied completely by Mg^{2+} , the other somewhat less than 100% by Al^{3+} . Ordered domains of Mg^{2+} occupancy of one or other of the Al(2) sites could also exist similar to the Ba^{2+} domains proposed here. However, since none of the atoms in Na^+ β'' -alumina are significant anomalous scatterers of neutrons, the neutron study cannot distinguish between ordering of Mg^{2+} through the entire crystal and local ordering.

The ordering of Mg^{2+} in Ba^{2+} β'' -alumina must be the same as that in Na^+ β'' -alumina, since crystals of the former are obtained by slow diffusion of Ba^{2+} into crystals of the latter; the spinel blocks are believed to be unaffected by the ion exchange. Although we do not distinguish in the refinements between Al^{3+} and Mg^{2+} , let us assume for the moment that the Mg^{2+} ordering is local, but certainly permanent. A different Mg/Al arrangement in the different domains could be the main cause of breakdown of diffraction coherence. It could also be that the Ba^{2+} ion arrangement is sensitive to the local Mg/Al order. This could explain why the Ba^{2+} ordering correlation length is observed to be approximately equal to (or greater than) the diffraction correlation length. Maintenance of the ordering across the spinel blocks is most unlikely unless there are structural differences in the host lattice in the regions of different order in the conduction plane.

These ideas are not in conflict with the inherent mobility of the Ba^{2+} ions, since the time-scale of the

X-ray experiment ($\sim 10^{-18}$ s) is much less than the jump frequency of the Ba^{2+} ions. The description of the average statistical short-range order (as given) applies instantaneously for all Ba^{2+} ions in the crystal.

In recent X-ray diffuse scattering studies of other divalent β'' -aluminas, Boilot, Collin, Colomban & Comes (1980) and Boilot, Colomban, Lee, Collin & Comes (1983) have observed short-range ordering of the conduction ions with correlation lengths ranging from 10 Å to several hundred Å, depending on the ion and the temperature. The Bragg reflections observed from our crystal were not significantly broader than instrumental resolution. Therefore, the diffraction correlation length, and hence the short-range-order correlation length, in our Ba^{2+} β'' -alumina crystal must be at least several hundred Å in all directions.

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