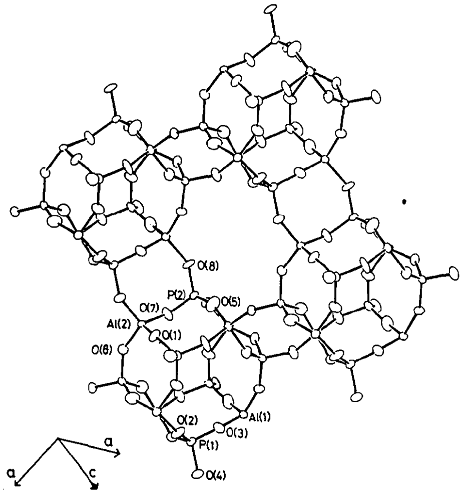

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the four double hexagonal ring units. Thermal ellipsoids are at the 50% probability level. Only the unique atoms have been labeled.

strict 3 symmetry. Si substitution for the P sites results in an excess charge of −1 e per framework Si atom, which may be compensated by protonated water located near the center of the hexagonal ring. The distances between these protonated water O atoms and the O atoms of the hexagonal ring range from 2·75 to 3·10 Å.

The four double hexagonal ring units are interconnected to form circular 12-membered-ring pore openings. There are large ellipsoidal cavities linked by these apertures. These structural features are closely related to the natural zeolite chabazite (Smith, 1962).

Table 3. *Comparison of the pore-size values for ZYT-6 with those of chabazite*

	ZYT-6	Chabazite
Cavity size (Å) (long and short axes)	11·69 (4) 10·63 (5)	11·7 10·6
Diameter of the eight-membered ring (Å)	6·31 (1)	6·34
Diameter of the six-membered ring (Å)	4·15 (1)	4·41

Table 3 compares the pore-size values for ZYT-6 with those of chabazite. The dimensions of the cavity along its long and short axes are 11·69 (4) and 10·63 (5) Å, respectively. The shape of the eight-membered ring is almost circular but non-planar with diameter 6·31 (1) Å. The largest deviations from the best plane of the ring are for O(4) and O(8) at 0·51 (1), 0·53 (1) Å, respectively.

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The Sr^{2+} Distribution in Sr^{2+} β''-Alumina

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Abstract. Idealized formula: $Sr_xMg_{2x-1}Al_{12-2x}O_{17}$, $M_r = 640{\cdot}02$ for $x = \frac{5}{6}$, rhombohedral, $R\bar{3}m$. In hexagonal cell: $a = 5{\cdot}610\,(1)$, $c = 33{\cdot}720\,(5)$ Å, $V = 919{\cdot}1\,(5)$ Å^3, $Z = 3$, $D_x = 3{\cdot}469\,(2)$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}96$ mm^{-1}, $F(000) = 930$, $T = 295$ K, final $R = 0{\cdot}073$, $R(F^2) = 0{\cdot}130$, $wR(F^2) = 0{\cdot}178$ for refinement on 1874 F^2. The Sr^{2+} ions ($r = 1{\cdot}18$ Å) lie distributed along edge-linked hexagonal

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pathways with maxima at sites 6(*c*) and 9(*d*) ($R\bar{3}m$ notation). Best least-squares fit for Sr^{2+} ions following noncentrosymmetric space group $R3m$; occupations of successive 6(*c*), 9(*d*), 6(*c*), ... sites in approximate ratios 1:1:0·65, respectively. Sr^{2+} distribution at 6(*c*) sites is fitted to a vibrational model involving third-rank cumulants (γ_{ijk}'s). Column oxygen O(5) occupies a 3(*b*) site. The refined *x* value in the structural formula is 0·87 (2), indicating a 37% substitution of Al(2) by Mg. The centrosymmetric spinel-block framework is retained from Na^+ β''-alumina.

Introduction. In the present study, single crystals of Sr^{2+} β''-alumina have been prepared by ion exchange from Na^+ β''-alumina crystals. The ionic conductivity of Sr^{2+} β''-alumina has been reported by Dunn & Farrington (1980). It was found to resemble closely the conductivity behaviour of Ba^{2+}, Ca^{2+} and Cd^{2+} β''-aluminas. The mean ionic distributions and short-range order are found to be significantly different, for example, in Ba^{2+} β''-alumina (Thomas, Aldén, McIntyre & Farrington, 1984) and Ca^{2+} β''-alumina (Aldén, Thomas & Farrington, 1984). The purpose here is to determine the detailed distribution of Sr^{2+} ions in the conduction plane of Sr^{2+} β''-alumina, as part of a project aimed at understanding the ionic-conductivity mechanism for divalent ions in β''-alumina. The Sr^{2+}-ion radius (1·18 Å) is intermediate between that for Ca^{2+} (1·00 Å) and Ba^{2+} (1·35 Å) (Shannon, 1976).

Experimental. Single crystals of Sr^{2+} β''-alumina were prepared by ion exchange from Na^+ β''-alumina crystals grown at 1963–1998 K. The exchange was performed in a $\mathrm{Sr(NO_3)_2{:}SrCl_2}$ melt (mol ratio 47:53) at 823 K for 24 h. The remaining Na^+ content was shown to be <0·1%, using a $^{22}\mathrm{Na}$ radioactive isotopic form of Na^+ β''-alumina to monitor the exchange (Farrington & Dunn, 1982).

Intensity measurements made on a triangular platelet with well defined faces (max./min. dimensions: 0·130/0·048 mm respectively). Intensity data recorded using a Nonius CAD-4 automatic diffractometer, controlled by a PDP8/A computer. Integrated intensities of $-h+k+l = 3n$ reflections measured using an ω–2θ step-scan technique, 50 steps. Total of 2392 reflections of type $\pm h,k,l$ measured out to $\sin\theta/\lambda = 0{\cdot}950$ Å^{-1}. Instrumental stability and crystal setting checked by monitoring the intensities of three test reflections: no significant variation throughout the data collection. The crystal could be confirmed through its systematic absences ($-h+k+l \neq 3n$ in the hexagonal cell) to retain the $R\bar{3}m$ space-group symmetry of Na^+ β''-alumina. Cell parameters determined from a least-squares fit of 25 θ angles in the range 0–20° measured on the diffractometer for the same crystal as was used for the data collection. Intensity data corrected for background, Lp and absorption effects (assuming composition $\mathrm{Sr}_x\mathrm{Mg}_{2x-1}\mathrm{Al}_{12-2x}\mathrm{O}_{17}$, $x = \frac{5}{6}$); calculated transmission range: 0·69–0·83. Internal agreement factor between expected symmetry-equivalent reflections $R_{\mathrm{int}} = 0{\cdot}07$ after absorption correction; corresponding value for the standard reflections 0·014. Full-matrix least-squares refinement with *UPALS*. Function minimized: $\sum w(|F_o|^2 - |F_c|^2)^2$ where $w^{-1} = \sigma_c^2(F_o^2) + (k|F_o^2|)^2$; σ_c based on Poisson counting statistics, *k* an empirical constant (here $k = 0{\cdot}04$). Reflections with $F_o^2 < 2\sigma(F_o^2)$ removed, leaving 1874 for the refinements. A crude picture of the Sr^{2+} distribution in the conduction plane was obtained following a refinement of the scale factor, using the positions of the Al(Mg) and O atoms taken from the Na^+ β''-alumina structure (Bettman & Peters, 1969) as start values. $\Delta\rho$ maps calculated in and near the $z = \frac{1}{6}$ plane showed Sr^{2+} ions to lie at both 6(*c*) and 9(*d*) sites. As for the cases of Ba^{2+} β''-alumina and Ca^{2+} β''-alumina, the space-group constraint on the Sr^{2+} ion was relaxed to $R3m$, while the spinel block still retained its $R\bar{3}m$ symmetry; significant improvement was seen in the refinements. Subsequent refinements were made in which the Sr^{2+} occupations of the two non-equivalent 6(*c*) sites and the 9(*d*) sites ($R\bar{3}m$ notation) were refined along with appropriate positional and anisotropic thermal parameters for all atoms. A vibrational model involving third-rank cumulants was used for the Sr^{2+} ions at the 6(*c*) sites. No evidence was found of extinction effects in the data. Large correlations (up to 80%) were obtained in the refinement of certain of the thermal parameters. It can be seen from the relatively high final agreement factors that much scope remains for improvements to the model; in particular, a model which can better take account of short-range order should be seen as a more long-term goal in this work. A model using the space group $R1$ for the effective Sr^{2+} distribution was refined successfully but gave parameters insignificantly different from those for $R3m$. Final $R = 0{\cdot}073$, $R(F^2) = 0{\cdot}130$, $wR(F^2) = 0{\cdot}178$. Max. Δ/σ in final refinement 0·3 [on the β_{ij}'s of O(5)]. Atomic form factors for Sr^{2+} and neutron Al and O atoms taken from *International Tables for X-ray Crystallography* (1974). No distinction was made between the X-ray scattering power of Al^{3+} and Mg^{2+} ions. All calculations made on NORD 100 and VAX 11/780 computers. The programs used have been described by Lundgren (1982).

Discussion. The distribution of Sr^{2+} ions is shown in the final ρ maps in Figs. 1 and 2. Positional parameters and occupations are given in Table 1.*

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* Lists of structure factors, anisotropic thermal parameters, crystal dimensions and orientation matrix have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42429 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

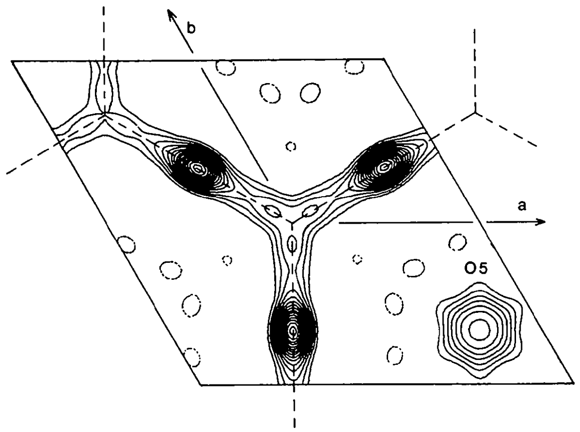

Fig. 1. ρ map in the conduction plane in Sr^{2+} β''-alumina at $z = \frac{1}{6}$. Contour interval: 2·0 e Å^{-3}.

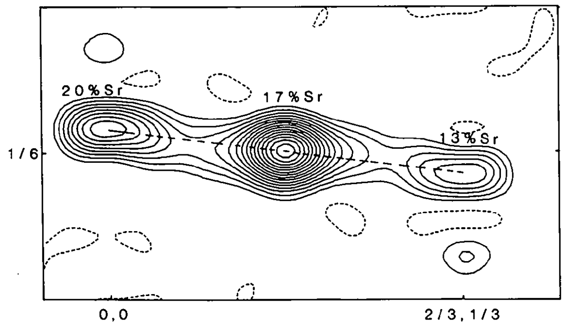

Fig. 2. ρ map in the vertical (2*x*, *x*, *z*) plane through the conduction path in Sr^{2+} β''-alumina. Contour interval: 2·0 e Å^{-3}.

Table 1. *Atomic positional parameters* (×10^5) *and equivalent isotropic thermal parameters* (*expressed as average r.m.s. amplitudes*) *in* Sr^{2+} *β''-alumina*

	Site*	*x*	*y*	*z*	$\bar{U}$(Å)
Sr(1)	6(*c*) [occupation: 20·5 (6)%]	0	0	17025 (21)	0·241
[Sr(1′)	6(*c*) [occupation: 13·2 (6)%]	0	0	−17025 (21)	0·241]
Sr(2)	9(*d*) [occupation: 17·0 (3)%]	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{6}$	0·185
Al(1)	3(*a*)	0	0	0	0·056
Al(2)	6(*c*)	0	0	35004 (3)	0·065
Al(3)	18(*h*)	33485 (11)	*x*/2	7072 (2)	0·066
Al(4)	6(*c*)	0	0	44996 (3)	0·065
O(1)	18(*h*)	15438 (14)	2*x*	3413 (4)	0·077
O(2)	6 (*c*)	0	0	29539 (8)	0·065
O(3)	6(*c*)	0	0	9695 (8)	0·078
O(4)	18(*h*)	16355 (12)	2*x*	23530 (4)	0·067
O(5)	3(*b*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{6}$	0·218

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

Table 2. *Some interatomic distances* (Å) *in* Sr^{2+} *β''-alumina*

Contact	Distance	Mean	Mean in Ca^{2+} β''-alumina	Mean in Ba^{2+} β''-alumina
Sr(1)–O(3)	2·472 (10) (×1)	2·650	2·516	2·697
Sr(1)–O(4)	2·709 (8) (×3)			
Sr(2)–O(3)	2·855 (6) (×2)	2·829	2·766	—
Sr(2)–O(4)	2·816 (5) (×4)			
Sr(2)–O(5)	2·805 (1) (×2)	2·805	—	—
Al(1)–O(1)	1·891 (2) (×6)	1·891	1·891	1·890
Al(2)–O(1)	1·835 (2) (×3)	1·838	1·847	1·849
Al(2)–O(2)	1·843 (6) (×1)			
Al(3)–O(1)	1·995 (2) (×2)	1·915	1·913	1·916
Al(3)–O(4)	1·847 (2) (×2)			
Al(3)–O(3)	1·852 (2) (×1)			
Al(3)–O(2)	1·955 (2) (×1)			
Al(4)–O(4)	1·765 (1) (×3)	1·746	1·751	1·754
Al(4)–O(5)	1·687 (5) (×1)			

Description of the structure

The spinel-block structure of Na^+ β''-alumina (Bettman & Peters, 1969) is retained in Sr^{2+} β''-alumina. Al atoms are octahedrally and tetrahedrally coordinated by O atoms to form layers of spinel structure separated in the **c** direction by Al(4)—O(5)—Al(4) bridging bonds (Table 2). The planes containing the column-oxygen O(5) (at $z = \frac{1}{6}, \frac{1}{2}$ and $\frac{5}{6}$) are otherwise occupied only by Sr^{2+} ions – the conduction 'planes' in the structure. The Sr^{2+} ions can move in the hexagonal toroid-like regions around the O(5) supporting O atom. The O(5) atom itself occupies a 3(*b*) site as in K^+ β''-alumina (Brown, Schwinn, Bates & Brundage, 1981) and in Ba^{2+} β''-alumina (Thomas, Aldén, McIntyre & Farrington, 1984). The apparent absence of O(5) disorder of the type observed in Ca^{2+} β''-alumina (Aldén, Thomas & Farrington, 1984) can be related to the larger Sr^{2+}-ion radius (1·18 Å); it is presumably large enough to result in a stretched Al(4)—O(5)—Al(4) bond. The smaller polarization of O(5) oxygen atoms by the relatively larger Sr^{2+} ions may also be an important factor.

On the assumption that charge compensation in the structure is achieved solely through Mg^{2+} substitution of the Al(2) sites, the Sr^{2+} occupations would imply a 37% substitution of Al(2) by Mg, and an effective structural formula: $Sr_xMg_{2x-1}Al_{12-2x}O_{17}$, $x = 0{\cdot}87$ (2).

It may be noted from Table 2 that the *increase* in mean Al—O distance on Mg substitution [as given by comparing the situations for the two tetrahedrally coordinated Al atoms Al(2) and Al(4)] is extremely similar in the three cases studied: 5·3, 5·5 and 5·4% in Sr^{2+}, Ca^{2+} and Ba^{2+} β''-aluminas, respectively.

The Sr^{2+} *distribution*

The Sr^{2+} ions occupy the hexagonal toroid-like pathways in the planes between the spinel blocks. These planes are otherwise only occupied by the supporting column oxygen O(5) occupying the 3(*b*) position at ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{6}$). The conduction planes lie at $z = \frac{1}{6}$, $\frac{1}{2}$ and $\frac{5}{6}$ in the unit cell, although the conduction pathways can be described more exactly as undulating from 0·16 Å above the mean plane at a 6(*c*) site (an *up* site), *via* a symmetry centre at a 9(*d*) site, to 0·16 Å below the plane at a 6(*c*) site (a *down* site). We note that all sites are significantly less than fully occupied. The occupations refined within the $R3m$ space group are 20·5, 13·2, and 17·8% in the 6(*c*) (*up*), 9(*d*) and 6(*c*) (*down*) sites, respectively. As in the case of Ba^{2+} β''-alumina and Ca^{2+} β''-alumina, the average Sr^{2+}-ion distribution is better described in the noncentrosymmetric space group $R3m$, suggesting short-range correlation effects. The collection of the complete data set under the absence condition $-h+k+l \neq 3n$ implies that we do not have access to data capable of giving evidence of short-range symmetry lower than rhombohedral. That no significantly observed reflections appeared outside the $-h+k+l = 3n$ condition in the preliminary data set (out to $\theta = 10°$) implies that any divergence at short range from rhombohedral symmetry must be small.

Two general features can be noted in the Sr^{2+} distribution:

(i) The ratio of the refined 6(*c*) (*up*) to 6(*c*) (*down*) occupations (or *vice versa*) is ~1·5:1, compared to ~2·0:1 in Ca^{2+} β''-alumina and ~3·5:1 in Ba^{2+} β''-alumina. On the basis of earlier discussions for the Ca^{2+} and Ba^{2+} cases, the lower ratio would here suggest a shorter correlation length for the short-range ordering of the Sr^{2+} ions.

(ii) The majority of Sr^{2+} ions (61%) occupy the 9(*d*) mid-oxygen (*MO*) site, compared to 47% in Ca^{2+} β''-alumina and only 15% in Ba^{2+} β''-alumina.

In view of the equivalent electronic configurations of the three ion types studied (Ca^{2+}, Sr^{2+} and Ba^{2+}), it is tempting to seek some simple unifying picture to explain the qualitatively different average ionic distributions. A simple argument would be as follows: while Ba^{2+} ions are too large to occupy *MO* sites to any significant extent, both Ca^{2+} and Sr^{2+} ions fit comfortably into both *MO* and 6(*c*) end sites. Since the occupation of an *MO* site will tend to induce a transition from a local region of *up* dominance to an equivalent *down* region, the larger the *MO* occupation, the shorter will be the SRO correlation length, and the closer to 1·0 the 6(*c*) *up* to 6(*c*) *down* occupation ratio. This is indeed what we observe: a larger *MO* occupation for Sr^{2+} can be related to the lower *up*/*down* ratio. It must be stressed, however, that the observed average ionic distribution assumes translational symmetry for the unit-cell content. This is certainly not true for the X^{2+} ions. Arguments of the above type are therefore highly tenuous.

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Multicomponent Polyanions. 38. Structure of $K_5NaMo_6V_2O_{26}.4H_2O$, a Compound Containing a New Configuration of the Hexamolybdodivanadate Anion

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Abstract. Pentapotassium sodium hexamolybdodivanadate tetrahydrate, $M_r = 1384·1$, monoclinic, $C2/m$, $a = 14·765$ (2), $b = 12·859$ (1), $c = 9·062$ (1) Å, $\beta = 127·97$ (1)°, $V = 1356·4$ (3) Å^3, $Z = 2$, $D_m = 3·35$ (3), $D_x = 3·39$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0·71069$ Å, $\mu = 4·156$ mm^{-1}, $F(000) = 1304$, $T = 298$ K, $R = 0·043$

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