

Structural Determinations of Single-Crystal K β -Alumina and Cobalt-Doped K β -Alumina

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Single-crystal structural refinements of K β -alumina and Co²⁺-doped K β -alumina show that the distribution of potassium ions in the diffusing planes is very similar to that in the isomorphous compound Na β -alumina but quite different from Ag β -alumina. The Co²⁺ ions selectively fill the underbonded, tetrahedrally coordinated, Al(2) sites in the middle of the spinel block portion of the structure. This tends to support the aluminum vacancy mechanism of charge compensation. The positional parameters of the spinel block are well-determined and appear insensitive to the diffusing plane ions and arrangement.

Introduction

Extensive structural determinations of the solid electrolyte sodium β -alumina (1-4) and refinement of its isomorph silver β -alumina (5) have revealed several crucial features. The first is that both compounds contain an "excess" amount of diffusing ion, ≈ 25 -30%, with respect to the idealized formula $M_2Al_{22}O_{34}$ and the second is that considerable disorder occurs among these ions both in site occupancy and positional parameters in the diffusing plane portion of the unit cell. Fourier maps of Na β have shown a smeared-out pattern of electron density about the "ideal" ($\frac{2}{3}, \frac{1}{3}, \frac{1}{4}$), BR (Beever-Ross) site (6) and ($\frac{5}{6}, \frac{4}{6}, \frac{1}{4}$), mO (mid-oxygen) site (6). In this case, the density distribution was approximated by placing sodium ions in threefold equipoints, ($x, 2x, \frac{1}{4}$), about the respective ideal BR and mO sites. Fourier maps of silver β -alumina show a different average site occupancy with the ABR (anti-Beever-Ross) 0, 0, $\frac{1}{4}$, site predominant over the mO site. However, these results from classical crystallographic refinements only show the diffusing ion distribution per "average" unit cell. Further evidence for positional disorder has more recently been demonstrated

by X-ray diffuse scattering experiments done in transmission using the fixed-crystal fixed-film technique (7). In the case of Ag β -alumina it has been proposed that the changes in the diffuse intensity with temperature resembles a transition from a quasi-two-dimensional liquid to microcrystallites with decreasing temperature. As part of a continuing program of research at these laboratories on solid electrolytes, diffuse scattering experiments have been performed on the alkali series of β -aluminas, Li-Rb, which show rather remarkable differences in diffuse X-ray patterns from member to member. (Detailed results and analyses have been reported elsewhere (8).) The diffuse scattering in potassium exchanged β -alumina was in the form of rods parallel to the c -axis which could be indexed on the basis of a $(3a)^{1/2}$ by $(3a)^{1/2}$ superlattice. A similar superlattice but with different relative intensities was observed at low T in Ag β -alumina. These results provided sufficient motivation for performing a classical crystallographic refinement of the K β -alumina structure.

A distinct line of inquiry concerns the "spinel-block" portion of the structure. It has been known for some time that the diffusing ion content may be increased by doping

the spinel block with a divalent element such as magnesium. In fact, if enough aluminum is replaced by Mg, the rhombohedral polymorph β'' -alumina forms with the nominal formula $\text{Na}_2\text{O} \cdot \text{MgO} \cdot 5\text{Al}_2\text{O}_3$. This structure has been refined by Bettman and Peters (9) from single-crystal X-ray diffraction data. It is very similar to β -alumina except that the unit cell contains three spinel blocks separated by diffusing planes rather than two, and the blocks are related by a threefold screw axis. With subsequent neutron diffraction analysis the Mg was found to occupy one of four tetrahedral sites in the spinel block selectively (10), (19). Recently we have successfully grown single crystals of Co^{2+} -doped β and β'' -alumina (11). Many of these ternary β -alumina crystals were subsequently exchanged with other cations including potassium. The diffuse X-ray photographs of both the Na and K ternary β -aluminas were nevertheless practically identical with respect to the binary β -alumina patterns. In addition, it was noted during ion-exchange experiments that the diffusion rate for the β phase material appeared to be enhanced by the cobalt doping relative to the binary β -alumina. Since the scattering power of Co^{2+} is much greater than Al^{3+} , it was decided to carry out a structural refinement of cobalt doped K β -alumina and compare these results directly with that of the K β -alumina refinements.

Therefore, in this paper, we report the complete structural determination of two potassium exchanged β -alumina crystals with nominal formulas $\text{K}_{2.5}\text{Al}_{21.83}\text{O}_{34}$ and $\text{K}_{2.5}\text{Al}_{21.7}\text{Co}_{0.2}\text{O}_{34}$. In addition, we attempt to resolve the problem of distribution and form of compensating defects such as interstitial oxygen or aluminum vacancies. Single-crystal X-ray refinements were carried out such that common habit, orientation, diffraction technique, refinement procedure, and final set of observed structure factors were maintained.

Experimental

Crystals of sodium β -alumina and cobalt-doped sodium β -alumina were grown by the flux method at 1300°C (11). The sodium ions

were exchanged for potassium in the molten halide as previously described in the literature (12). From the weight change upon ion exchange the potassium content exceeded that of the stoichiometric composition, $\text{K}_2\text{Al}_{22}\text{O}_{34}$, by $26 \pm 5\%$. The nominal aluminum/cobalt ratio for the doped sodium β -alumina crystals was $\text{Al}_{21.8}\text{Co}_{0.2}$. This relatively low cobalt concentration was selected because no extra phase β'' crystals were detected in this batch in contrast to higher nominal concentrations. It was also clear from the variation in the depth of blue color as well as morphological variations at higher cobalt concentrations, that the cobalt distribution coefficient exceeded unity by a considerable margin.

Clear crystals of binary and ternary K β -alumina with sharply defined hexagonal plate habit were chosen for all subsequent diffraction experiments. The dimensions of the crystals were 0.50 (per average hexagonal edge) $\times 0.12$ mm and 0.90×0.25 mm, respectively. Debye-Scherrer diffraction patterns were obtained for lattice parameter determinations using $\text{CrK}\alpha$ radiation. The lattice parameters obtained from least-squares refinements were as follows: $a = 5.591(2)$, $c = 22.711(3)$ and $a = 5.605(1)$, $c = 22.722(2)$ Å for the K β and Co-doped K β -alumina crystals, respectively. Zero layer precession and transmission fixed-crystal fixed-film photographs taken with monochromatic Mo radiation revealed that the symmetry was indeed hexagonal. From the systematic absences, for which hhl , $l = 2n + 1$, it was assumed that the space group was $P6_3/mmc$, as per previous investigators.

X-ray intensity data were collected in an identical fashion for each crystal. The crystal orientations were the same with the $[110]$ direction parallel with the ϕ axis of the goniostat. The integrated intensities were collected on a paper tape controlled General Electric XRD-5 diffractometer with Mo radiation and Zr-Y balanced filters (13). The $0-2\theta$ integrated scan technique was used with a take-off angle of 2° . The scanning rate was $2^\circ/\text{min}$ with 10-sec stationary background counts $\pm 1^\circ 40'$ from the peak maxima. Data were collected in a wedge-shaped section of reciprocal space where all $h \geq 0$, $k \geq 0$, and $l \geq 0$ and $2\theta \leq 80^\circ$.

A standard reflection was measured after every 30 reflections to monitor possible intensity drift during the experiments. Sample orientation was checked and adjusted manually at regular intervals. The total number of reflections measured was 1490, and the total number of independent reflections was 794 including those of essentially zero intensity. After making Lorentz, polarization, and absorption corrections with the program ACAC (14) for plane-faced crystals, each set of reflections was reduced by the elimination of all $|F_{\text{obs}}| \approx 0$ and those cases where the difference between symmetry related hkl 's exceeded 20%. In addition, very weak reflections were discarded where only one of a set of symmetry equivalent hkl 's was observed. Finally, after a few initial cycles of refinement, those reflections whose intensity was seriously effected by secondary extinction were eliminated leaving a common set of 553 reflections for the two crystals.

Refinement Procedure

Starting positional parameters for the K β -alumina refinements were those of Peters *et al.* (4) and the form factors for neutral K, Al, and O atoms from Cromer and Waber (15). The least-squares program ORFLS (16) was used. With occupancy factors of K fixed at the Na β -alumina values and the bridging

O(5) atoms fixed at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ (see Fig. 1) complete convergence was attained with isotropic temperature factors after two cycles of refinement yielding an R factor of 0.079. In subsequent refinements many variations in the K(1), K(2), and O(5) occupancy and positional parameters were tried. For example, the K(1) ions were placed exactly on the BR site $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ and R increased to 0.093; K(2) ions exactly on mO $(\frac{5}{6}, \frac{2}{3}, \frac{1}{4})$ sites with $R = 0.138$; three potassium sites with Ag β -alumina distribution gave an $R = 0.185$; and $\approx \frac{1}{2}$ K atom at the origin with two K in $(x, 2x, \frac{1}{4})$ near BR gave an $R = 0.175$. Other variations were performed with O(5) in the $6h$ equipoints $(x, 2x, \frac{1}{4})$ and K(1) and K(2) in the Na β starting positions. This refined to an R factor of 0.077 after two cycles. Finally, all diffusing plane ion occupancy factors were allowed to vary as well as their x coordinates. Complete convergence was attained after three cycles and the final isotropic R factor decreased to 0.069. Releasing the occupancy factors for the aluminum sites yielded nearly the same R factor with all multipliers within $\pm\sigma$ of their stoichiometric values. Although not statistically significant, there was a slight tendency for the Al(1) and Al(3) sites to appear under-occupied with respect to the Al(2) and Al(4) sites.

To test for interstitial oxygen 0.2 atoms were placed exactly on the mO or BR sites while the

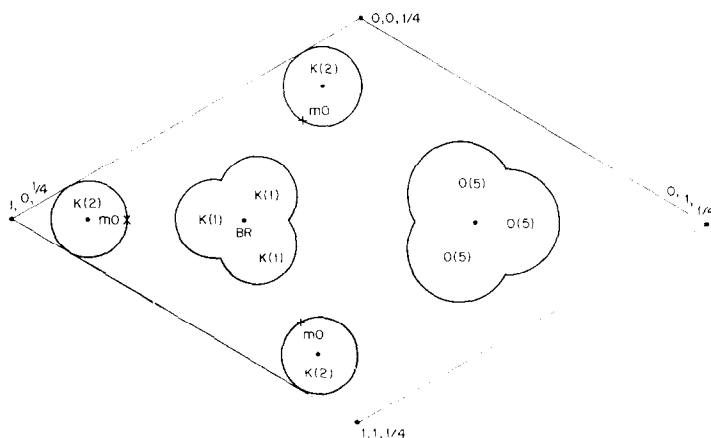


FIG. 1. The diffusing ion plane, $(x, y, \frac{1}{4})$, is shown where the "average" positions of K(1), K(2), and O(5) in equipoints $6h$, $(x, 2x, \frac{1}{4})$, are schematically depicted. The mid-oxygen, mO, and Beevers-Ross, BR, sites are indicated by the cross and dot symbols respectively.

potassium in the corresponding sites was reduced appropriately (19). The possibility of excess oxygen in the BR site was eliminated since the R factor increased substantially to 0.091 but the mO interstitial possibility was somewhat ambiguous since the R factor did not change appreciably and the amount of interstitial oxygen, if present, was chosen arbitrarily. Finally, anisotropic temperature factors were introduced which unfortunately tended to correlate severely with the multipliers of the diffusing plane ions. Hence, these latter factors were fixed at their final isotropic values and the anisotropic refinements converged quickly to yield an R factor of 0.056 and a wR of 0.083.

Three-dimensional Fourier and difference Fourier maps were generated with 0.02 incremental sections from $z = 0$ to $z = 0.25$. For the spinel block portion of the structure no unusual density variations were observed which would suggest "extra" scattering sites or deficient aluminum sites. The potassium and bridging oxygen density distributions were quite similar to those reported for Na β alumina, but the contours were much more tightly packed about the K(1) BR sites. No significant amount of scattering was detected near or on the ABR sites.

The starting positional parameters and occupancy factors for the least-squares isotropic refinements of Co^{2+} -doped K β -alumina were taken from the final cycles of the pure K β -alumina refinements. All spinel block aluminum sites were initially given pure aluminum form factors. However, after a few cycles the isotropic temperature factor for Al(2), the tetrahedrally coordinated ion in the middle of the spinel block (see Fig. 2) dropped anomalously to 0.06 as compared to 0.40–0.50 for the other B_{Al} values. This immediately suggested that more scattering power was required in this site and that cobalt was most likely filling these sites almost exclusively. In subsequent refinements, weighted average form factors for various Co/Al(2) mole fractions were applied with a normal initial temperature factor of $B_{\text{Co/Al(2)}} = 0.45$. Occupancy factors were maintained at their ideal stoichiometric values in the spinel block but allowed to vary in the diffusing plane. Figure 3 shows the results of these trials where R is plotted against x , the Co/Al mole fraction. The minimum in R is obviously well defined where the only hypothesis tested is the Co/Al ratio, i.e., the zero cycle R factor. It is less well defined but nevertheless significant with all parameters free, i.e., after one

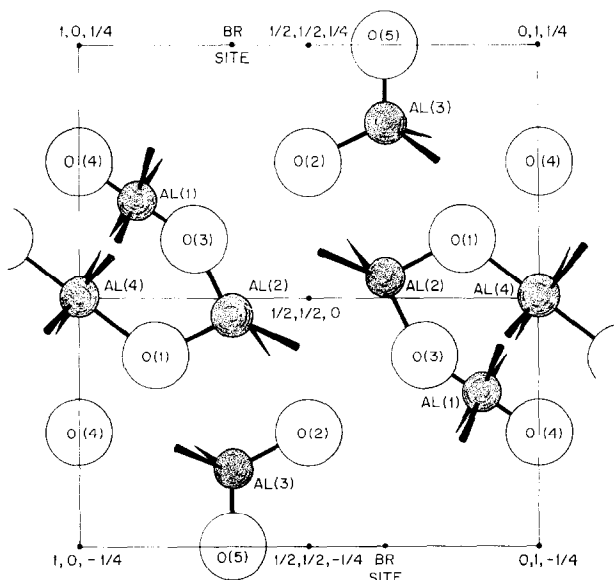


FIG. 2. A vertical section of the spinel block portion of the β -alumina structure is shown and the first nearest neighbor Al-O vectors are indicated. The tetrahedrally coordinated Al(2) sites are selectively occupied by Co^{2+} .

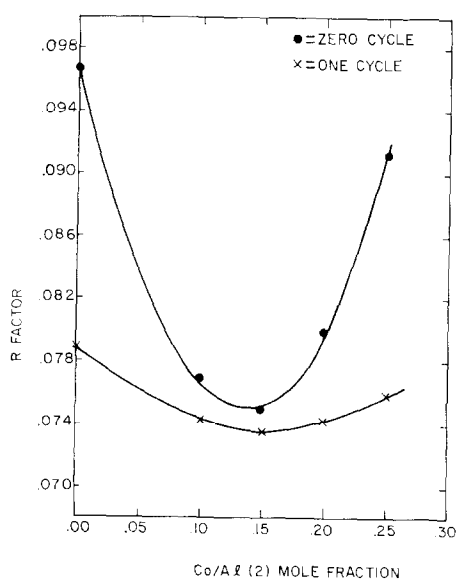


FIG. 3. The statistical residual R factor of Co^{2+} -doped K β -alumina is plotted against the mole fraction of cobalt in the spinel block tetrahedral aluminum site.

cycle. The difference in positions of the minima provides some indication of uncertainty in cobalt content but it would appear that $15 \pm 2\%$ is not an unreasonable value. The discrepancy between the nominal ratio, $\text{Al}_{21.8}\text{Co}_{0.2}$, and this X-ray determined ratio, $\text{Al}_{21.4}\text{Co}_{0.6}$, may be explained by the fact that the cobalt distribution coefficient is considerably greater than unity in β alumina. In all subsequent trials this X-ray determined ratio was fixed. Variation of aluminum occupancy factors gave nearly identical results as the pure K β -alumina refinements. A search for other cobalt sites proved fruitless since the standard deviations and R factors all increased with these attempts. Finally, anisotropic temperature factors were introduced with the same restrictions as for the pure K β case and after three cycles R decreased to 0.061 and wR to 0.093.

Results

Tables of observed and calculated structure factors from the final cycles of refinement for both compounds are available upon request. In Table I are listed the positional parameters,

TABLE I
POSITIONAL AND THERMAL PARAMETERS

| | | K- $\beta\text{Al}_2\text{O}_3$ | K- $\beta\text{Al}_2\text{O}_3$ + Co |
|--------------|--------------|---------------------------------|--------------------------------------|
| Al(1) | x | 0.83203(6) | 0.83223(6) |
| | y | 0.66406 | 0.66446 |
| | z | 0.10489(3) | 0.10505(5) |
| | β_{11} | 0.0056(2) | 0.0050(2) |
| | β_{22} | 0.0049(3) | 0.0043(3) |
| | β_{33} | 0.00020(1) | 0.00024(2) |
| Al(2)/Co | x | 0.00002(3) | -0.00003(3) |
| | x | 0.3333 | 0.3333 |
| | y | 0.6666 | 0.6666 |
| | z | 0.02455(5) | 0.02446(5) |
| | β_{22} | 0.0030(4) | 0.0055(4) |
| | β_{33} | 0.00009(1) | 0.00023(2) |
| Al(3) | x | 0.3333 | 0.3333 |
| | y | 0.6666 | 0.6666 |
| | z | 0.17484(5) | 0.17465(6) |
| | β_{22} | 0.0069(5) | 0.0066(5) |
| | β_{33} | 0.00012(2) | 0.0007(2) |
| | Al(4) | x | 0.0000 |
| y | | 0.0000 | 0.0000 |
| z | | 0.0000 | 0.0000 |
| β_{22} | | 0.0041(5) | 0.0050(5) |
| β_{33} | | 0.00010(2) | 0.00019(3) |
| O(1) | | x | 0.1570(1) |
| | y | 0.3140 | 0.3128 |
| | z | 0.04944(7) | 0.04970(9) |
| | β_{11} | 0.0063(4) | 0.0057(4) |
| | β_{22} | 0.0035(4) | 0.0035(5) |
| | β_{33} | 0.00020(2) | 0.00027(4) |
| O(2) | β_{23} | 0.00001(7) | -0.00026(7) |
| | x | 0.5029(1) | 0.5030(1) |
| | y | 0.0058 | 0.0060 |
| | z | 0.14602(6) | 0.14591(9) |
| | β_{11} | 0.0045(3) | 0.0045(4) |
| | β_{22} | 0.0055(5) | 0.0050(5) |
| O(3) | β_{33} | 0.00026(2) | 0.00031(3) |
| | β_{23} | 0.00010(6) | -0.00007(7) |
| | x | 0.6666 | 0.6666 |
| | y | 0.3333 | 0.3333 |
| | z | 0.0551(1) | 0.0554(1) |
| | β_{22} | 0.0047(8) | 0.0045(8) |
| O(4) | β_{33} | 0.00015(3) | 0.00027(4) |
| | x | 0.0000 | 0.0000 |
| | y | 0.0000 | 0.0000 |
| O(4) | z | 0.1416(1) | 0.1414(1) |
| | β_{22} | 0.0038(7) | 0.0030(8) |
| | β_{33} | 0.00017(3) | 0.00029(5) |

TABLE I (continued)

| | | K- β Al ₂ O ₃ | K- β Al ₂ O ₃ + Co |
|-----------|--------------|---|--|
| O(5) | Atoms/cell | 1.91(9) | 1.8(1) |
| | <i>x</i> | 0.3108(8) | 0.3128(8) |
| | <i>y</i> | 0.6216 | 0.6526 |
| | <i>z</i> | 0.2500 | 0.2500 |
| | β_{11} | 0.015(2) | 0.004(1) |
| | β_{22} | 0.015(5) | 0.001(3) |
| | β_{33} | 0.00013(6) | 0.00002(7) |
| K(1) | Atoms/cell | 1.42(2) | 1.46(6) |
| | <i>x</i> | 0.6883(3) | 0.6883(3) |
| | <i>y</i> | 0.3766 | 0.3766 |
| | <i>z</i> | 0.2500 | 0.2500 |
| | β_{11} | 0.0111(6) | 0.0127(6) |
| | β_{22} | 0.015(2) | 0.017(2) |
| | β_{33} | 0.00025(3) | 0.00023(4) |
| K(2) | Atoms/cell | 1.22(2) | 1.22(4) |
| | <i>x</i> | 0.8852(6) | 0.8850(6) |
| | <i>y</i> | 0.7704 | 0.7700 |
| | <i>z</i> | 0.2500 | 0.2500 |
| | β_{11} | 0.017(1) | 0.016(1) |
| | β_{22} | 0.031(2) | 0.033(2) |
| | β_{33} | 0.00039(4) | 0.00028(5) |
| <i>R</i> | | 0.056 | 0.061 |
| <i>wR</i> | | 0.083 | 0.093 |
| <i>S</i> | | 0.814 | 0.954 |

anisotropic temperature coefficients, and diffusing plane unit cell content for both crystals. A comparative list of interatomic distances is presented in Table II, while the root-mean-square principal axes of thermal displacement and orientations are given in Table III. Finally, a bond length comparative analysis is reported in Table IV for both types of spinel block tetrahedra for Na, Ag, K, and Co²⁺-doped K β -alumina.

Discussion

On balance, the similarities between Na β -alumina and K β -alumina are quite strong even with respect to the relative amount of alkali in the BR and mO sites. Significant differences in positional and thermal parameters however, are most notable. The *x* coordinate for K(1) is closer to the ideal BR value of $\frac{2}{3}$ while that of K(2) is further away

TABLE II
INTERATOMIC DISTANCES^a

| | K- β Al ₂ O ₃ (Å) | K- β Al ₂ O ₃ + Co(Å) |
|--------------------------------|---|---|
| Al(1) octahedron | | |
| -O(1) × 2 | 2.020 | 2.018 |
| -O(2) × 2 | 1.849 | 1.848 |
| -O(3) × 1 | 1.962 | 1.964 |
| -O(4) × 1 | 1.830 | 1.827 |
| Average | 1.922 | 1.920 |
| Al(2) tetrahedron-spinel block | | |
| -O(1) × 3 | 1.801 | 1.811 |
| -O(3) × 1 | 1.809 | 1.814 |
| Average | 1.803 | 1.812 |
| Al(3) tetrahedron-bridging | | |
| -O(2) × 3 | 1.769 | 1.772 |
| -O(5) × 1 | 1.722 | 1.723 |
| Average | 1.757 | 1.759 |
| Al(4) octahedron | | |
| -O(1) × 6 | 1.891 | 1.892 |
| K(1) Polyhedron-9 coordinated | | |
| -O(5) ₁ × 1 | 3.169 | 3.139 |
| -O(5) ₂ × 1 | 3.170 | 3.139 |
| -O(5) ₃ × 1 | 3.479 | 3.449 |
| -O(2) ₁ × 2 | 2.968 | 2.972 |
| -O(2) ₂ × 2 | 2.795 | 2.798 |
| -O(2) ₃ × 2 | 2.795 | 2.798 |
| Average | 2.993 | 2.985 |
| K(2) Polyhedron-8 coordinated | | |
| -O(5) × 2 | 2.863 | 2.851 |
| (Average of three) | | |
| -O(4) × 2 | 2.702 | 2.707 |
| -O(2) × 4 | 3.037 | 3.040 |
| Average | 2.910 | 2.910 |

^a All distances have standard deviations of less than ± 0.001 Å except K-O vectors, which are less than ± 0.003 Å.

from the mO value of $\frac{5}{6}$. Back ion scattering experiments on K β using helium as a probe are consistent with the deviations from the ideal BR and mO positions determined from the X-ray refinements (17). Also the distribution of cations about an "average" equilibrium position is considerably sharper in the case of K β alumina since the standard deviations on the basal plane coordinates are 7 to 10 times

TABLE III
RMS PRINCIPAL AXES AND ORIENTATIONS

| Atom | r_j | K- β Al ₂ O ₃ (Å) | K- β Al ₂ O ₃ + Co (D) | Orientation (angle, in degrees, r_j makes with) | | |
|-------|-------|---|--|--|----------|----------|
| | | | | x | y | z |
| Al(1) | 1 | 0.072(2) | 0.080(3) | 90 | 82, 97 | 171, 9 |
| | 2 | 0.076(2) | 0.072(3) | 90 | 31, 149 | 81, 99 |
| | 3 | 0.084(2) | 0.080(2) | 180 | 60 | 90 |
| Al(2) | 1 | 0.048(5) | 0.077(3) | 90 | 90 | 180 |
| | 2 | 0.060(5) | 0.082(4) | 0 | 120 | 90 |
| | 3 | 0.060(5) | 0.082(4) | 60 | 180 | 90 |
| Al(3) | 1 | 0.057(4) | 0.064(4) | 90 | 90 | 110 |
| | 2 | 0.091(4) | 0.089(3) | 120 | 0 | 90 |
| | 3 | 0.091(4) | 0.089(3) | 180 | 60 | 90 |
| Al(4) | 1 | 0.050(6) | 0.069(5) | 90 | 90 | 180 |
| | 2 | 0.070(5) | 0.082(4) | 0 | 120 | 90 |
| | 3 | 0.070(5) | 0.082(4) | 60 | 180 | 90 |
| O(1) | 1 | 0.065(4) | 0.058(4) | 90 | 148, 141 | 88, 116 |
| | 2 | 0.073(4) | 0.088(4) | 90 | 88, 112 | 1.9, 26 |
| | 3 | 0.093(3) | 0.089(3) | 180 | 60 | 90 |
| O(2) | 1 | 0.071(4) | 0.068(4) | 180 | 60 | 90 |
| | 2 | 0.078(4) | 0.078(4) | 90 | 51, 30 | 47, 84 |
| | 3 | 0.085(3) | 0.091(4) | 90 | 54, 85 | 137, 174 |
| O(3) | 1 | 0.062(7) | 0.084(7) | 90 | 90 | 180 |
| | 2 | 0.075(8) | 0.076(8) | 0 | 120 | 90 |
| | 3 | 0.075(8) | 0.076(8) | 60 | 180 | 90 |
| O(4) | 1 | 0.066(6) | 0.088(7) | 90 | 90 | 180 |
| | 2 | 0.067(8) | 0.060(9) | 0 | 120 | 90 |
| | 3 | 0.067(8) | 0.060(9) | 60 | 180 | 90 |
| O(5) | 1 | 0.06(1) | 0.02(5) | 90 | 90 | 180 |
| | 2 | 0.13(2) | 0.06(3) | 90 | 30 | 90 |
| | 3 | 0.14(1) | 0.10(1) | 180 | 60 | 90 |
| K(1) | 1 | 0.081(4) | 0.080(6) | 90 | 90 | 180 |
| | 2 | 0.108(4) | 0.119(4) | 0 | 120 | 90 |
| | 3 | 0.134(9) | 0.151(8) | 90 | 150 | 90 |
| K(2) | 1 | 0.101(6) | 0.088(8) | 90 | 90 | 180 |
| | 2 | 0.120(6) | 0.107(5) | 0 | 120 | 90 |
| | 3 | 0.191(7) | 0.203(6) | 90 | 150 | 90 |

TABLE IV
COMPARISON OF SPINEL BLOCK TETRAHEDRAL DISTANCES (Å)

| | Na β (4) | Ag β (5) | K β | K β + Co |
|-----------------------|----------------|----------------|-----------|----------------|
| Al(3)-O(2) \times 3 | 1.768 | 1.762 | 1.769 | 1.772 |
| Al(3)-O(5) \times 1 | 1.677 | 1.675 | 1.722 | 1.723 |
| Average | 1.745 | 1.740 | 1.757 | 1.759 |
| Al(2)-O(1) \times 3 | 1.801 | 1.806 | 1.801 | 1.811 |
| Al(2)-O(3) \times 1 | 1.809 | 1.800 | 1.809 | 1.814 |
| Average | 1.803 | 1.804 | 1.803 | 1.812 |

smaller than the Na isomorph. The anisotropic temperature coefficients in the basal plane also are very much smaller, 6 to 9 times, as are their respective standard deviations. Although the bridging O(5) atoms were restricted to $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ positions in the Peters *et al.* (4) structural refinements, we found that in the case of K β -alumina the average cell very definitely contained O(5) displacements into the $6h$ positions as in the case of Ag β -alumina (5). Unlike this latter compound, however, essentially no scattering matter was found near $(0, 0, \frac{1}{4})$ and again the standard deviations on the diffusing plane positional parameters as well as the thermal components were smaller.

From these observations it would appear that ionic radius plays a crucial role with respect to any subtle structural differences among these isomorphous materials. For example, from Table II one can see that the shortest K(1)–O(2) vectors would be too short with respect to the sum of the ionic radii if the average potassium x coordinate were further away from the ideal BR value of $\frac{2}{3}$, as is the case in Na β -alumina. Similar bond length arguments may be proposed for the K(2) equilibrium positions with respect to the O(4) and O(5) separations. Of the many permutations of BR and mO–O(5) separations it is also quite clear that some bond lengths are certainly less probable, and hence, it is very likely that definite correlations exist between the $6h$ site diffusing plane ions. For the smaller sodium ion this is not nearly as crucial while for the much larger rubidium ion the O(5) bridging atoms must appear as first nearest neighbors with very highly correlated displacements. In addition, it follows that the thermal vibrations in the basal plane will be smaller for the larger K ion than the smaller Na ion for a nearly fixed nearest neighbor coordination sphere (see Table III).

The problem of stoichiometry is a serious and persistent one. Two compensating mechanisms have been proposed by others (4, 5, 19) which consist of aluminum vacancies in the spinel blocks or interstitial oxygen in the diffusing plane with the mO sites as likely positions. Evidence for the latter case is that the number of diffusing ions per unit cell as

determined from weight change on ion exchange is slightly smaller than that determined by X-ray structural refinement. Thus, the X-rays might not discriminate between K in the mO sites and K plus a small amount of oxygen in this same site. As pointed out earlier the interpretation of the X-ray results testing this hypothesis is ambiguous in the case of K β -alumina. Also the aluminum occupancy factors did not vary significantly from their stoichiometric values which tends to support the interstitial mechanism. On the other hand, there is considerable structural evidence supporting the aluminum vacancy mechanism. A bond length comparison between the bridging Al(3) tetrahedron and the Al(2) tetrahedron buried deep in the spinel block is presented for the four structures Ag, Na, K, and Co²⁺-doped K β -alumina in Table IV. One can immediately see that the Al(2)–O average separation is considerably greater than the Al(3)–O bridging tetrahedron. In fact, by comparison with a calculated distance of 1.75 Å, based on the sum of ionic radii, or by a crude length and strength argument (18) it is clear that Al(2) is underbonded in all these compounds. This common structural feature cannot be ignored nor the fact that the spinel block portion of the structure should mimic MgAl₂O₄ so closely despite the absence of any divalent element. Furthermore, when a divalent element is present such as Co²⁺, it selectively occupies this Al(2) tetrahedral site. These results strongly support an aluminum vacancy mechanism. Nevertheless, there is still some ambiguity here since the X-ray determined formula, K_{2.68}Al_{21.4}Co_{0.6}O_{34+x}, suggests that this latter mechanism may not be sufficient nor mutually exclusive.

Another point concerns the magnitude of the statistical residuals or R factors. It would seem that placing the diffusing plane ions in the $6h$ sites $(x, 2x, \frac{1}{4})$ is an approximation which, depending on the scattering power of the ions and relative sharpness of their average positional distribution, may be more appropriate in some cases than others. For example, in order of increasing scattering power of the diffusing ions Na–K–Ag, the final R factors are 0.034–0.056–0.072. In the case of K β -alumina we have determined via

TABLE V
K β -Al₂O₃ ANISOTROPIC REFINEMENTS

| | With diffuse plane <i>hkl</i> 's | Without diffuse plane <i>hkl</i> 's |
|----------------------------|-------------------------------------|--|
| Number of <i>hkl</i> 's | 553 | 374 |
| O(3) <i>z</i> | 0.0551(1) | 0.0552(1) |
| O(4) <i>z</i> | 0.1416(1) | 0.1416(1) |
| Al(2) <i>z</i> | 0.02455(5) | 0.02458(5) |
| Al(3) <i>z</i> | 0.17484(5) | 0.17482(5) |
| O(1) <i>x</i> | 0.1570(2) | 0.1570(1) |
| <i>z</i> | 0.04944(7) | 0.04947(7) |
| O(2) <i>x</i> | 0.5028(1) | 0.5027(1) |
| <i>z</i> | 0.14601(6) | 0.14600(7) |
| Al(1) <i>x</i> | 0.83023(6) | 0.83203(5) |
| <i>z</i> | 0.10489(3) | 0.10491(4) |
| <i>R</i> | 0.056 | 0.039 |
| <i>wR</i> | 0.083 | 0.058 |
| <i>S</i> | 0.814 | 0.568 |

an empirical method just how seriously this approximation effects the spinel block coordinates and overall fit. Diffusing plane sensitive reflections were delineated by giving zero multipliers to the diffusing plane atoms K(1), K(2), and O(5). These sensitive reflections were eliminated from subsequent refinements and the spinel block portion of the structure was rerefined. In Table V, the results of this procedure show that not only does the *R* factor drop to a very reasonable level of 0.039, but the positional parameters of the spinel block atoms are insensitive to the diffusing plane arrangement.

Therefore, one can conclude from these results that the tetrahedrally coordinated Al(2) ions in the spinel blocks are underbonded and Co²⁺ selectively occupies this site. These results strongly favor the aluminum vacancy mechanism. Furthermore, the positional parameters of the spinel block portion of the structure are not only very well determined, but they appear relatively insensitive to the diffusing plane ions and arrangement. Finally, the distribution of potassium among the diffusing plane sites is very similar to that of

Na β -alumina but quite different from Ag β -alumina.

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