

constants, indicating partial collapse *via* the tilt mechanism, exhibited greater values. For higher degrees of partial collapse the behaviour became quite complex. Obviously, the contribution of the tilt mechanism to the thermal expansion is significant. For the fully expanded SAM no tilt mechanism is active. Furthermore, the (static) shearing mechanism is absent in the cubic phase, and can be supposed to be saturated in the region where a_c and c , change linearly. The value of about $8.5 \times 10^{-6} \text{ K}^{-1}$ for the linear thermal-expansion coefficient α should therefore be regarded as essentially reflecting the contribution from the normal bond-length expansion.

Concluding remarks

The present work was undertaken in order to shed some light on the phase transition behaviour of aluminate sodalites in general, and of the fully expanded SAM in particular. Special emphasis was given to the discussion of a special type of symmetry-breaking framework distortion, termed 'shearing', which is responsible for a volume reduction of the unit cell. The peculiarities of the phase transition of SAM at 571 K, *i.e.* the quasi-one-dimensional volume contraction of the unit cell, were explained by the proposed superposition of two strain components – associated with the shearing and a ferroelastic distortion of the unit cell, respectively – such that both components add up for the tetragonal (pseudocubic) c lattice parameter, but cancel out for a . Power-law behaviour is observed for the coefficient of the spontaneous strain and for the excess volume, with exponents which indicate the nearly tricritical character of the transition. Deviations from the classical values are probably related to defects.

Financial support granted by the Deutsche Forschungsgemeinschaft (DE412/1-1 and DE412/1-2) is gratefully acknowledged. Thanks are due to T. Wroblewski, HASYLAB/DESY, and H. Arnold, RWTH Aachen, for help during the data collection, to HASYLAB/Hamburg for the beam time, and to an anonymous referee for constructive criticism.

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Acta Cryst. (1993). **B49**, 491–496

Ionic Distribution in the Solid-State Laser Material $\text{Na}^+/\text{Nd}^{3+}$ β'' -Alumina

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(Received 8 October 1992; accepted 25 January 1993)

Abstract

The crystal structure and ionic distribution in the conduction planes in neodymium-doped Na^+ β'' -alumina [refined composition: $\text{Na}_{0.58(2)}\text{Nd}_{0.36(1)}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17}$, $M_r = 632.2$] has been investigated

at room temperature by single-crystal X-ray diffraction (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The layered structure of this solid laser-like material comprises spinel-type blocks of Al^{3+} , Mg^{2+} and O^{2-} ions which interleave two-dimensional conduction planes containing the Nd^{3+} and Na^+ ions. The spinel

blocks are held together by Al—O(5)—Al bonds, where the so-called column oxygen ion, O(5), is located in the conduction planes at $z = \frac{1}{6}, \frac{1}{2}$ and $\frac{5}{6}$. The space group of the crystalline framework is trigonal, $R\bar{3}m$, $a = 5.627(3)$, $c = 33.39(1)$ Å, $V = 915.5$ Å³, $Z = 3$, $D_x = 3.43$ Mg m⁻³, $\mu_o = 2.3$ mm⁻¹, $\mu_c = 2.4$ mm⁻¹. The Nd³⁺ ions are disordered, occupying two different sites in the 'conduction pathways': ~65% at eight-coordinated 9(*d*) sites, and the remaining ~35% at seven-coordinated 6(*c*) sites. The Na⁺ ions also occupy the 6(*c*) sites. Final $R(F) = 0.0294$, $R(F^2) = 0.0474$ and $wR(F^2) = 0.0538$ for refinement on 1880 reflections.

Introduction

Sodium β''-alumina is a unique solid electrolyte in that the sodium ions can be exchanged for a wide variety of mono-, di- and trivalent cations. This is a direct result of the unusual β''-alumina structure (Dunn, Farrington & Thomas, 1989). It consists of close-packed blocks (so called spinel blocks) of Al, Mg and O ions separated by more open, 'liquid-like' regions (referred to as conduction planes) containing the mobile cations and a single supporting oxygen ion [column oxygen or O(5)] which links together the spinel blocks by means of Al—O—Al bonds. Fig. 1(*a*) is a schematic illustration of the whole structure, while Fig. 1(*b*) shows the conduction plane. The honeycomb-shaped conduction pathways are indicated along with the two possible sites for the mobile cations: the seven-coordinated Beavers–Ross (BR) 6(*c*) site (C_{3v} symmetry) and the eight-coordinated mid-oxygen (mO) 9(*d*) site (C_{2h} symmetry). In Na⁺ β''-alumina, sodium ions occupy, on average, five out of six BR sites. Note, however, that the point symmetry for a site in the conduction plane (BR or mO) is determined by the ions of the crystalline framework (spinel-block atoms and column oxygen ions). This is not necessarily the effective local symmetry of an occupied site because of the disorder in the conduction planes. This complicates the interpretation of diffraction results where the crystallographic picture only constitutes a time and space average of the ionic arrangement.

Several transition-metal and lanthanide ions have been exchanged into the β''-alumina conduction plane, and some of the resulting materials have shown interesting optical properties. This, in combination with possibilities to control and modify the chemical composition, leads to a variety of potential applications for β''-aluminas in the areas of lasers, phosphors and other optical components. Of the rare-earth (RE) doped β''-aluminas studied so far, most interest has been focused on those involving trivalent neodymium. The absorption spectra from differently doped Na⁺/Nd³⁺ β''-alumina shows that

the oscillator strength of the so-called hypersensitive transition, $^4I_{9/2} \rightarrow ^4G_{5/2}$, is up to ten times larger than in the Nd:YAG system (Alfrey, Stafsudd, Dunn & Yang, 1988; Dai & Stafsudd, 1991). A characteristic feature of absorption spectra for different RE³⁺:host systems is that the energy levels vary only very slightly (within a few 100 cm⁻¹). This is because of the partial shielding of the 4*f* electrons

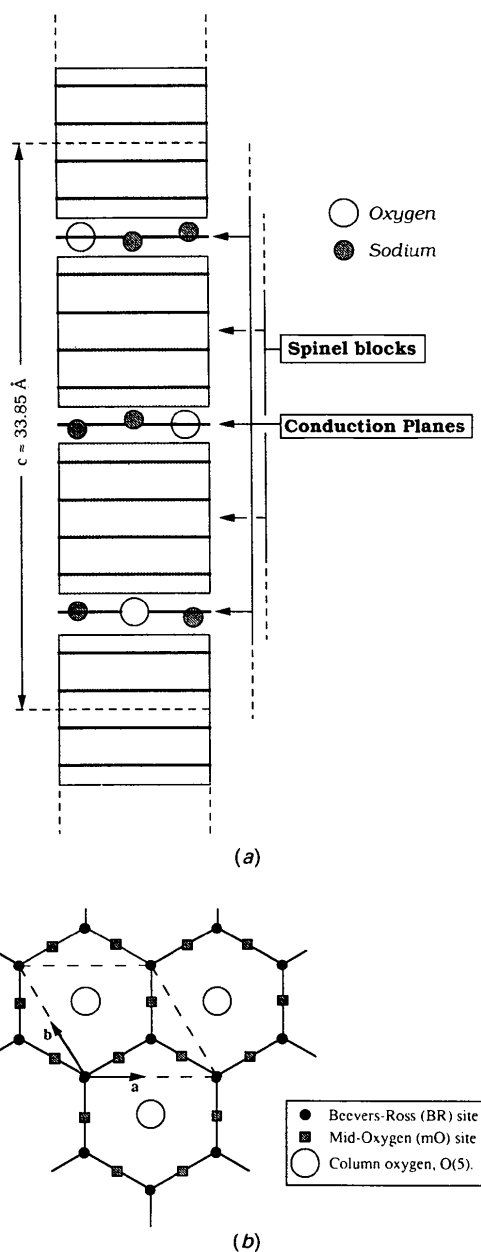


Fig. 1. The Na⁺ β''-alumina structure (schematic) showing (*a*) the overall block structure, and (*b*) the conduction plane, showing the unit-cell (dashed), the conduction pathways (solid), and two possible sites for the cations (BR and mO).

(where the optical transitions occur) by the filled $5s^25p^6$ shells. The main difference between the various hosts is, in general, the oscillator strengths for the individual transitions. In principle, the oscillator strengths can be calculated theoretically using the Judd–Ofelt (JO) Theory (Judd, 1962; Ofelt, 1962) if the environment of the rare-earth ion is known or, more specifically, if the crystal field created by the surrounding ions can be calculated at the RE site. The crystal field is introduced into the theoretical treatment as a first-order perturbation, which is such that the odd-parity crystal-field parameters are responsible for the admixing of opposite-parity wavefunctions into the $4f$ functions, thereby making it possible for the otherwise parity-forbidden electric dipole transitions to occur. A minimal requirement for such a calculation is a knowledge of the positions of the surrounding ions. A conventional diffraction study of the β'' -aluminas cannot give a complete picture of the local order around a rare-earth ion because of the disorder in the conduction planes. It can, however, give some indication as to the true local situation, and the average occupations can further be used to arrive at start configurations for a molecular dynamics simulation (MD) which, in principle, makes it possible to study the histories of individual ions and their environments (Zendejas & Thomas, 1990). More recently, MD has been used in combination with JO theory in taking account of dynamical motion in a simple crystalline solid (Edvardsson, Wolf & Thomas, 1992).

The structural study presented here is a single-crystal X-ray diffraction experiment of an $\text{Na}^+/\text{Nd}^{3+}$ β'' -alumina where $\sim 64\%$ (refined value) of the original sodium content has been exchanged for Nd^{3+} ions [refined composition: $\text{Na}_{0.58(2)}\text{Nd}_{0.36(1)}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17}$]. The motivation for the study is that absorption intensity enhancement was most pronounced for partially doped $\text{Na}^+/\text{Nd}^{3+}$ β'' -alumina (Alfrey *et al.*, 1988). Additional spectroscopic studies (ESR and optical absorption spectroscopy) showed further that the Nd^{3+} ions behave quite differently in samples containing high and low Nd concentrations. In fully exchanged samples, Nd^{3+} ions were found both as isolated ions and as discrete pairs; in a low Nd-concentration sample ($\sim 18\%$ exchange), Nd ions were observed as isolated species only (Dunn, Yang & Vivien, 1988). A structural study is essential, therefore, to achieve greater insight into the relationship between structure and optical properties in these materials.

Experimental

Single crystals of $\text{Na}^+/\text{Nd}^{3+}$ β'' -alumina were obtained by an ion-exchange technique (Sattar *et al.*,

1986). The starting material was crystals of Na^+ β'' -alumina, grown by a flux evaporation technique (Briant & Farrington, 1980). The ion exchange was then achieved by immersion of the crystals in a NdCl_3 – NaCl flux at 973 K for typically 1 h; the molar ratio between the salts determines the Nd concentration in the final samples. The crystals were then cooled to room temperature under a nitrogen atmosphere for 2 h. The degree of exchange was determined from weight-change measurements. These crystals had a typical size of $2.5 \times 2.5 \times 0.2$ mm.

The crystal used for the diffraction study was cracked from a larger crystal (58% exchanged from gravimetric analysis), and had maximum/minimum dimensions of 0.18/0.08 mm. Intensity data were collected on a Stoe four-circle diffractometer using graphite-monochromized $\text{Mo } K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and an $\omega/2\theta$ step scan. A preliminary data collection was made in the range $15 < 2\theta < 30^\circ$. Absence of reflections of the type $-h + k + l \neq 3n$ confirmed the correctness of the trigonal space-group assignment. Reflections of this type were then eliminated from the data collection, which proceeded for reflections of type $-h, -k, \pm l$ out to $\sin\theta/\lambda = 1.08 \text{ \AA}^{-1}$. Five standard reflections were chosen to monitor the stability of the diffractometer and the crystal. No systematic variation was observed.

The measured intensity profiles were corrected: for background using the Lehmann–Larsen method (Lehmann & Larsen, 1974); for absorption using an experimentally determined linear absorption coefficient; and for Lp effects. The experimental parameters are summarized in Table 1, along with details of the refinements.

Refinement

The refinements were performed using the full-matrix least-squares program *DUPALS* (Lundgren, 1982). The function $\sum w(|F_o|^2 - |F_c|^2)$ was minimized for the unmerged data set [$w^{-1} = \sigma^2(F_o^2)$; $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (kF_o^2)^2$; $\sigma_c(F_o^2)$ assumes Poisson counting statistics; k is an empirical constant, here set to 0.015]. The coherent-scattering amplitudes and the anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The progress in the refinements is described below and summarized in Table 2.

(i) The initial model consisted of the β'' -alumina framework, *i.e.* spinel blocks and column oxygen ions. Start parameters were taken from Bettman & Peters (1969). Anisotropic temperature factors were used for all ions. A difference Fourier synthesis map, in the ab plane at $z = \frac{1}{6}$ using this model, gives a crude picture of the electron density associated with the cations in the conduction plane (Fig. 2).

Table 1. Summary of the experimental parameters

Diffractometer	Stoe four-circle
Radiation	Mo Kα (λ = 0.71073 Å)
Temperature (K)	295
Scan type	ω/2θ
F(000)	918.6
Cell parameters, a, c (Å)	5.627 (3), 33.38 (2)
No. of reflections for cell determination (2θ interval)	18 (15–30°)
Cell volume (Å ³)	915.5
D _c (Mg m ⁻³)	3.43
Crystal dimensions (mm)	0.18 × 0.18 × 0.08
μ _{av} , μ _c (mm ⁻¹)	2.30, 2.37
Transmission factors	0.714–0.835
(sin θ/λ) _{max} (Å ⁻¹)	1.08
h, k, l range	-10 ≤ h ≤ 0, -10 ≤ k ≤ 0, -72 ≤ l ≤ 72
No. of standards	5
No. of observed reflections	2551
No. of unique reflections	1273
No. of reflections excluding zero weight [I ≤ 2σ(I)]	1880
R _{int} = Σ I _o - I _c /ΣI _o	0.0339
Max./min. in final difference map (e Å ⁻³)	0.39/-0.57
No. of parameters refined	67
R(F _o)	0.0294
R(F _o ²)	0.0474
wR(F _o ²)	0.0538
S	1.20
Δ/σ	0.02

Table 2. Summary of progress in the refinement (R values in %)

Refinement No.	Model/change from previous refinement	R(F)	R(F ²)	wR(F ²)
1	The β''-alumina framework	(23.0)	(38.0)	(39.4)
2	Nd ³⁺ in mO; Na ⁺ in BR	3.77	5.73	6.36
3	Nd ³⁺ in BR	3.14	4.98	5.62
4	γ _{jkl} temperature factors on BR ions δ _{jklm} temperature factors on mO ions	3.08	4.90	5.53
5	O(5) relaxed from 6(c) to an 18(h) site	2.94	4.74	5.38

(ii) Nd³⁺ and Na⁺ ions were included at mO and BR sites, respectively, to describe the features in the difference density observed in Fig. 2.

(iii) The optical absorption spectra of partially doped compounds indicated two distinctly different sites for the neodymium ions (Dai & Stafsudd, 1991; Dunn *et al.*, 1988). Some Nd³⁺ ion occupation was thus also introduced at the BR site. The cation occupations were constrained to give charge neutrality ($q = +\frac{5}{2}$ in the conduction planes) as well as to correspond to the degree of exchange obtained from the gravimetric measurement.

(iv) The complexity of the thermal motion of the ions in the conduction planes has previously justified the inclusion of higher order displacement tensors to provide for an anharmonic contribution to the temperature factors. Third- (γ_{jkl}) and fourth-rank (δ_{jklm}) polar tensors were therefore included for the ions at the BR and mO sites, respectively. No constraints were applied in the refinements.

(v) The local distribution of cations in the conduction plane influences the position of the column oxygen ions. This is observed as a displacement of O(5) from its mean 3(b) site (Fig. 2). Refinement of the same model as used to represent O(5) in fully exchanged Nd³⁺ β''-alumina (Carrillo-Cabrera, Thomas & Farrington, 1988), *i.e.* a displacement

towards the neighbouring BR sites [3(b)→18(h)], also resulted in improved agreement factors. This displacement brings about a contraction of the *c* axis as a result of the bending of the Al—O(5)—Al bonds. Here the *c* axis is ~0.5 Å shorter than in Na⁺ β''-alumina, and O(5) is displaced 0.45 Å from its mean position.

It can be noted that Mg²⁺ ions were never introduced explicitly into the refinements. The X-ray form factors for Mg²⁺ are insignificantly different from those of Al³⁺ for which it substitutes at the Al(2) site close to the centre of the spinel block ($z \approx 0$). Moreover, the short-range aspect of the disorder is unclear.

An isotropic extinction correction factor was subsequently refined, resulting in a final *g* value of 1.24 (5) × 10⁴ (Becker & Coppens, 1974). The final positional parameters, fractional occupancies and thermal parameters are given in Table 3,* the final observed (*F_o*) synthesis perpendicular to the conduction plane is plotted in Fig. 3. The Nd—O distances for the two different Nd sites are given in Table 4, along with distances in the fully exchanged system from Carrillo-Cabrera *et al.* (1988). The two Nd environments are illustrated schematically in Fig. 4.

Discussion

The structural results can be viewed from two distinct aspects: the spinel block and the conduction

* Lists of harmonic and anharmonic atomic displacement parameters, interatomic distances and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55916 (53 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0294]

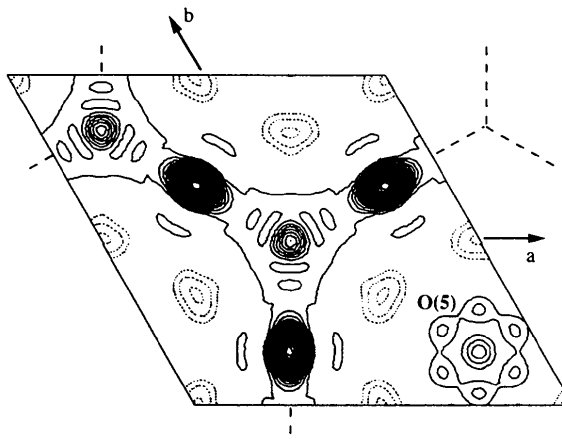


Fig. 2. Difference Fourier synthesis at $z = \frac{1}{4}$ calculated from a model comprising the spinel block and the column O atom, O(5). Contour interval: 1.0 e Å⁻³.

Table 3. Atomic positional parameters, occupancies (expressed as fractional site occupancy and as number of atoms per formula unit) and isotropic displacement parameters (expressed as mean-square amplitudes)

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	Site	x	y	z	Atoms per formula unit	Site occupancy	$U_{\text{eq}} \times 10^{-3}$ (\AA^2)
Nd(mO)	9(d)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.223 (2)	0.074 (1)	18.0
Nd(BR)	6(c)	0	0	0.1759 (1)	0.123 (3)	0.061 (2)	8.7
Na(BR)	6(c)	0	0	0.1711 (3)	0.58 (2)	0.29 (1)	117
Al(1)	3(a)	0	0	0	1.0	1.0	4.6
Al(2)	6(c)	0	0	0.35015 (1)	2.0	1.0	5.9
Al(3)	18(h)	0.33411 (4)	$x/2$	0.07182 (1)	6.0	1.0	5.8
Al(4)	6(c)	0	0	0.45021 (1)	2.0	1.0	5.3
O(1)	18(h)	0.15372 (5)	$2x$	0.03481 (1)	6.0	1.0	7.7
O(2)	6(c)	0	0	0.29449 (3)	2.0	1.0	7.5
O(3)	6(c)	0	0	0.09831 (3)	2.0	1.0	7.3
O(4)	18(h)	0.16300 (5)	$2x$	0.23407 (1)	6.0	1.0	7.1
O(5)	18(h)	0.2872 (5)	$2x$	$\frac{1}{2}$	1.0	$\frac{1}{2}$	25.5

Table 4. Selected Nd—O distances (\AA) in partially and fully Nd^{3+} -exchanged Na^+ β'' -alumina

The values for the fully exchanged system are from Carrillo-Cabrera *et al.* (1988).

Nd—O	64% exchanged	100% exchanged
Nd(mO)—O(5) ($\times 2$)	2.434 (4)	2.460 (1)
Nd(mO)—O(4) ($\times 4$)	2.764 (1)	2.758 (1)
Nd(mO)—O(3) ($\times 2$)	2.800 (1)	2.781 (1)
Nd(BR)—O(5) ($\times 3$)	2.816 (5)	—
Nd(BR)—O(4) ($\times 3$)	2.507 (4)	—
Nd(BR)—O(3) ($\times 1$)	2.591 (5)	—

plane. The structure of the spinel block is here essentially the same as in other β'' -alumina structures studied and will therefore not be discussed in any further detail (see Dunn *et al.*, 1989; and references therein). The more interesting aspect is the ionic distribution in the conduction plane. The presence of neodymium ions in the conduction plane restricts the mobility of the sodium ions and, as a consequence, their distribution becomes more localized at the BR site. This makes it possible to describe their otherwise complex distribution in terms of conventional anisotropic temperature factors (β_{ij} 's); as a further consequence, the refined overall charge in the conduction plane, $+1.65(3)$, agrees well with the ideal $+\frac{5}{3}$. The types of problem experienced in modelling the structure in the disordered conduction plane can be exemplified by the fact that both Na^+ and Nd^{3+} ions occupy the BR site (Table 3). The different character of the two ions makes it possible, however, to resolve them in a model. The heavier Nd^{3+} ion has almost the same radius as the Na^+ ion (0.98 and 1.02 \AA , respectively) but its $+3$ charge brings it closer to the oxygen ions in the spinel blocks: *cf.* $z(\text{Na}) = 0.171$; $z(\text{Nd}) = 0.176$. The mass difference is reflected in the values of the displacement parameters (Table 3).

From Table 3, we also see that the Nd^{3+} distribution in the conduction planes is different in the partially and fully exchanged Nd^{3+} β'' -alumina, where $\sim 95\%$ of the trivalent ions were found to

occupy the octahedral mO site. The presence of Na^+ ions clearly influences the ordering of the Nd ions: $\sim 35\%$ of the neodymium ions here occupy tetrahedral BR sites. This also agrees with results from the optical absorption spectra of partially doped $\text{Na}^+/\text{Nd}^{3+}$ β'' -alumina, where contributions from Nd^{3+} ions in two different sites were identified (Dunn *et al.*, 1988; Dai & Stafsudd, 1991).

It is clearly futile to speculate on the nature of the local $\text{Na}^+/\text{Nd}^{3+}$ distribution on the basis of the overlapped distribution obtained here. We can, however, reflect on the earlier optical measurements in the light of this present study. Using JO theory, it can be shown that an RE^{3+} ion at a centre of inversion should give rise to a zero oscillator strength for the electric dipole transitions. In the β'' -alumina structure, we can note that the mO site is an inversion centre while the BR site is not. Note, however, that crystallography gives the average picture. Trivalent lanthanide ions at mO sites can, in fact, have non-zero oscillator strengths since the local structure in the disordered conduction planes can be of lower symmetry than the average structure, *i.e.* a local breakage of inversion symmetry can occur. Hence, although it may seem reasonable that RE^{3+} ions at non-centrosymmetric C_{3v} (BR) sites contribute more to the absorption spectrum than ions at C_{2h} (mO) sites, it is important that this is not taken for granted. It is essential that the absorption spectra of disordered non-stoichiometric systems,

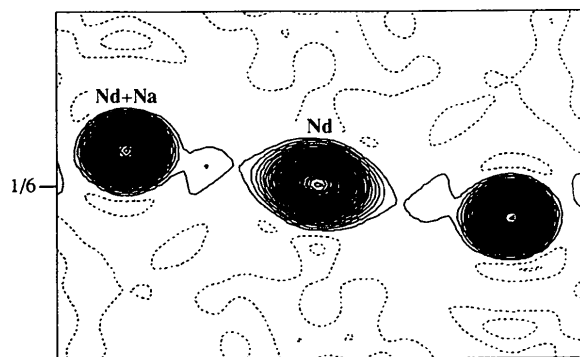


Fig. 3. Observed Fourier synthesis perpendicular to the conduction path. Contour interval: $1.0 e \text{\AA}^{-3}$.

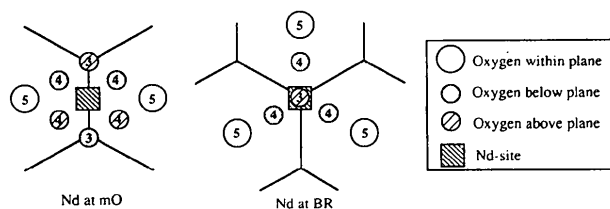


Fig. 4. The oxygen environment at mO and BR sites.

like the β''-alumina, be analysed more rigorously, with the structural situation of each individual ion being treated separately. In the Na⁺/Nd³⁺ β''-alumina systems with high Nd concentration, the situation is complicated further by the possible formation of Nd³⁺—Nd³⁺ pairs (Dunn *et al.*, 1988). These cannot be identified from our present diffraction results, but will clearly influence the absorption spectra, both with regard to energy levels and oscillator strengths. We see, therefore, that it is quite impossible to draw any definitive conclusions as to the structural origin of the optical properties of differently doped Na⁺/Nd³⁺ β''-aluminas on basis on diffraction studies alone. A more sophisticated treatment of the problem (using an MD approach) is currently underway at this laboratory, *cf.* Edvardsson *et al.* (1992).

We are most grateful to our laboratory technician Hilding Karlsson for his skilled assistance. This work has been supported in part by the Swedish Natural Science Research Council (NFR) and in part by a DARPA grant administrated through a contract monitored by The United States Office of Naval Research (ONR).

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