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BETA ALUMINA: A SOLID-ELECTROLYTE AS A SOLID-STATE

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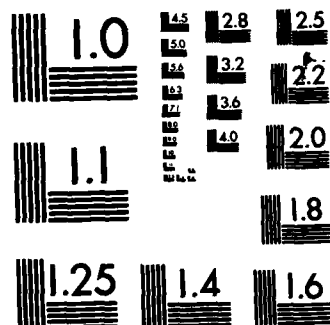
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Task No. NR 627-842

TECHNICAL REPORT NO. 7

Beta'' Alumina: A Solid-Electrolyte as
a Solid-State Laser Host

by

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Prepared for Publication in
Spectral Properties of Solid State Laser Type Materials
B. DiBartolo, ed. (Plenum Press, New York)

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September, 1985

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1. REPORT NUMBER 7	2. GOVT ACCESSION NO. AD-A159 409	3. RECIPIENT CATALOG NUMBER	
4. TITLE (and Subtitle) Beta" Alumina: A Solid-Electrolyte as a Solid-State Laser Host		5. TYPE OF REPORT & PERIOD COVERED Technical Report	
		6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) B. Dunn, J. O. Thomas and G. C. Farrington		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0498	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Materials Science and Engineering University of California, Los Angeles Los Angeles, CA 90024		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Arlington, VA 22217		12. REPORT DATE September 1985	
		13. NUMBER OF PAGES 12	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research Detachment 1030 East Green Street Pasadena, CA 91106		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Nd ³⁺ beta" alumina, X-ray structure, optical properties and laser behavior			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Sodium beta" alumina is a non-stoichiometric sodium aluminate known for its rapid transport of Na ⁺ ions. The unique ability of beta" alumina to exhibit divalent and trivalent cation motion permits optically active ions to be introduced in the structure by low temperature ion ₃ exchange techniques. The synthesis, structure and optical properties of Nd ³⁺ exchanged beta" alumina are reviewed in this paper. The material exhibits interesting optical properties, including laser action in small platelet crystals. The structure of the conduction plane, the presence and motion of Na ⁺ influence optical properties.			

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BETA'' ALUMINA: A SOLID ELECTROLYTE AS A SOLID-STATE LASER HOST

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ABSTRACT

Sodium beta'' alumina is a non-stoichiometric sodium aluminate known for its rapid transport of Na⁺ ions. The unique ability of beta'' alumina to exhibit divalent and trivalent cation motion permits optically active ions to be introduced in the structure by low temperature ion exchange techniques. The synthesis, structure and optical properties of Nd³⁺ exchanged beta'' alumina are reviewed in this paper. The material exhibits interesting optical properties, including laser action in small platelet crystals. The structure of the conduction plane, the presence of Na⁺ and its motion all appear to have a significant influence on optical properties.

INTRODUCTION

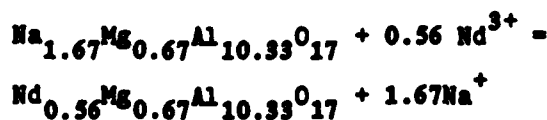
Sodium ^{Beta} alumina is a non-stoichiometric solid electrolyte known for its high conductivity of Na⁺ ions. The structure consists of spinel blocks of closely packed Al³⁺ and O²⁻ separated by loosely packed slabs containing Na⁺ and O²⁻ ions. The open space within these slabs permits rapid Na⁺ migration in two dimensions. The structure is shown schematically in Fig. 1. In a typical composition of Na_{1+x}Mg_xAl_{11-x}O₁₇ in which x = 0.67, Mg substitutes for Al in the spinel block and subsequently stabilizes the beta'' phase.

The Na^+ ions in β'' alumina also exhibit remarkable ion exchange behavior. Both divalent and trivalent ions diffuse in the β'' alumina structure and rapidly exchange with the sodium in β'' alumina. The result is that ion exchange processes have been used to synthesize a wide range of divalent and trivalent β'' aluminas compositions.^{1,2} Transport measurements indicate that β'' aluminas are the first family of solid electrolytes to exhibit high conductivity for divalent and trivalent cations. It should be noted that ion transport in these systems is thermally activated and that rapid divalent and trivalent cation diffusion is generally considered to occur at temperatures above approximately 300°C. Thus, typical conductivities at room temperature are rather low, $10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ and $10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$ for divalent and trivalent cations, respectively.

The ability to easily incorporate numerous transition metal and lanthanide ions within the β'' alumina structure has led to the investigation of the optical properties of ion exchanged β'' aluminas. Most of these studies are at their inception primarily because the previous research was largely concerned with the behavior of the β'' aluminas as solid electrolytes. The one composition investigated in some detail, Nd^{3+} exchanged β'' alumina, has been found to exhibit several interesting optical effects, including laser action. At least some of these properties may be attributed to the novel structural environment available within the conduction plane of β'' alumina. In this paper we present recent work concerning the structure and optical properties of the Nd^{3+} exchanged compositions. The results suggest that the β'' aluminas represent an extensive family of compositions which may possess interesting optical behavior.

MATERIAL SYNTHESIS

The techniques used to synthesize Nd^{3+} exchanged β'' alumina were described previously.^{1,2} Single crystals of Na^+ β'' alumina grown by the flux evaporation process (composition: $\text{Na}_{1.67}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17}$) are the starting materials. Ion exchange is accomplished by immersing these crystals in either NdCl_3 or NdBr_3 melts. By varying the length of immersion time (5 min to 24 hrs) and melt temperature (650 C to 800 C) samples containing varying amounts of Nd^{3+} are produced ($\sim 5 \times 10^{19} \text{ cm}^{-3}$ to $\sim 1.8 \times 10^{21} \text{ cm}^{-3}$). The extent of ion exchange is determined radiochemically using ^{22}Na and/or from the weight change associated with the exchange reaction



In addition to monitoring the amount of exchange, the radiochemical method enables one to measure the diffusion coefficient of Na^+ as a function of Nd^{3+} concentration. This approach was used to study the interdiffusion process in $\text{Na}^+/\text{Nd}^{3+}$ β'' alumina.³

Upon exchange, the crystals remain in good physical condition with no evidence of cracking or degradation of optical quality. The X-ray diffraction study presented below verifies that the β'' alumina structure is retained in the exchanged material. Recent work indicates that Nd^{3+} β'' alumina has good thermal stability and begins to transform to other phases only at temperatures above 900°C.⁴

STRUCTURE OF Nd^{3+} BETA'' ALUMINA

The room temperature structures of several rare earth β'' aluminas have been studied by single crystal X-ray diffraction. The structure of Gd^{3+} beta'' alumina was previously reported.⁵ The structure of the material of interest as a laser host, Nd^{3+} β'' alumina, is very similar and is presented here.

Intensity data were collected at 296K on a Nonius CAD 4-F automatic four cycle diffractometer using a small fragment removed from a large single crystal of Nd^{3+} β'' alumina. The synthesis conditions were described in the previous section. Some of the experimental parameters used in the diffraction experiment included the radiation: Mo $K\alpha$ ($\lambda = 0.710688\text{\AA}$); the crystal volume: $1.2 \times 10^{-3} \text{ cm}^3$; and the transmission range: 68-78%. Corrections to the data for background L_p -factor, absorption and extinction were performed in the usual fashion.⁵

Crystal cell parameters were obtained from careful measurements on the diffractometer of Friedel pairs of reflections using the same crystal. Space group: $R\bar{3}m$; $a = 5.628(1)\text{\AA}$, $c = 33.258(2)\text{\AA}$, $V = 912.4(1)\text{\AA}^3$.

The essential features of the structure can be summarized as follows:

- a. The spinel block arrangement is essentially the same as in other β'' alumina structures (Fig. 1). Aluminum ions are octahedrally and tetrahedrally coordinated by oxygen in a spinel-like structure $\sim 11\text{\AA}$ thick. Adjacent blocks are rotated by 120° about the unique c -axis. An Al-O-Al bridge separates the blocks. This oxygen ion (conventionally labelled O5 and termed the column oxygen) is the only other ion located in the so-called conduction plane ($z = \frac{1}{2}$ and $\pm \frac{1}{6}$) besides the mobile cations in the structure (i.e. Na^+ ions in $\text{Na}\beta''$ alumina or Nd^{3+} in $\text{Nd}\beta''$ alumina).
- b. The Nd^{3+} ions occupy primarily the 9d (mid-oxygen) sites between the 6c end-sites within the conduction plane. In contrast, Na^+ ions are located only in 6c sites in $\text{Na}\beta''$ alumina (i.e. the precursor material). The mean Nd^{3+} ion distribution in the vertical and horizontal plane through the conduction pathway is shown in Fig. 2.
- c. A small number of Nd^{3+} ions are found at the 6c end-sites, and there is a slight asymmetry in the mean end-site occupation (Fig. 2a). This asymmetry may also be prevalent in partially exchanged

material. In general, such an asymmetry is indicative of the existence of short-range order in the ion arrangement.⁶ Additional evidence for the existence of a superlattice for Nd^{3+} ions has recently been found from high resolution transmission electron microscopy.⁷

- d. The O5 column oxygen is displaced from the higher symmetry 3b site by $\sim 0.43\text{\AA}$ in the directions of the almost vacant 6c sites producing an elbow like distortion in the Al-O5-Al bridge.
- e. A given Nd^{3+} ion occupying a 9d site will have a local octahedral coordination consisting of the following pairs of bonds: Nd - O5 = $2.452\text{\AA}$ (closest approach) Nd - O3 = $2.781\text{\AA}$, Nd - O4 = $2.758\text{\AA}$. The local site symmetry of the Nd^{3+} ion is effectively C_{2v} , assuming the simultaneous approach of nearest O5 atoms.

From the X-ray data, the refined total Nd^{3+} content gives a formula unit $\text{Nd}_{0.54} \text{Mg}_{0.63} \text{Al}_{10.37} \text{O}_{17}$. This formula assumes charge neutrality in the structure and no significant concentration of oxygen, magnesium or aluminum vacancies; the composition closely resembles the ideal formula for lanthanide β'' aluminas: $\text{R}_2 \text{Mg}_2 \text{Al}_{10} \text{O}_{17}$, where R is a lanthanide ion with +3 charge. In $\text{Nd}^{3+} \beta''$ alumina, the most probable separation between adjacent Nd^{3+} will be the crystallographic a-(b-) axis, $5.628\text{\AA}$, which corresponds to Nd^{3+} ions at the next-nearest 9d sites. The likelihood of $\text{Nd}^{3+}(9d)-\text{Nd}^{3+}(9d)$ or $\text{Nd}^{3+}(9d)-\text{Nd}^{3+}(6c)$ pairs in the structure at shorter distances is small.

OPTICAL PROPERTIES OF $\text{Na}^+-\text{Nd}^{3+}$ BETA'' ALUMINAS

Jansen et al.⁸ used the ion exchange approach to prepare small single crystal platelets with varying concentrations of Nd^{3+} (from $5 \times 10^{19} \text{ cm}^{-3}$ to $1.5 \times 10^{21} \text{ cm}^{-3}$). They observed laser action in these crystals despite their relatively poor optical quality, short optical path and lack of mirrors on the crystal faces. In addition, they found that $\text{Na}^+/\text{Nd}^{3+} \beta''$ alumina exhibited some rather novel optical effects; an anomalously strong absorption line at $5800\text{\AA}$ and a fluorescence lifetime in excess of $350\mu\text{sec}$, with no evidence of quenching at high concentrations. Recently, Alfrey et al.^{9,10} examined some of these effects and obtained several parameters related to the laser operation of this material. Their results are reviewed in this paper.

The oscillator strengths for the various transitions for Nd^{3+} in YAG and β'' alumina are compared in Table 1.⁹ The transition at $5800\text{\AA}$ is nearly an order of magnitude stronger for the β'' alumina environment while the other transitions are of comparable intensity. The Nd^{3+} concentration for this data is $5 \times 10^{20} \text{ cm}^{-3}$, and it is significant to note that the oscillator strength at $5800\text{\AA}$ depends non-linearly upon the Nd^{3+} concentration. Alfrey et al. performed a Judd-Ofelt analysis on the absorption spectrum. By considering the nearest neighbor environment,

they were able to identify the origin of both the anomalous absorption at 5800Å and its concentration dependence.⁹ Specifically, they demonstrated that the experimentally determined T parameters could be obtained by a slight displacement of the Nd^{3+} and an asymmetric shift of the column oxygen from their respective equilibrium positions within the conduction plane. These subtle distortions are shown in Fig. 3. It is important to recognize that the displacements involved here are well within the variation in the position parameters as determined by X-ray diffraction analysis. The composition dependence of the oscillator strength is explained by considering the influence of conduction plane sodium on the oxygen distortion. At intermediate compositions, there is likely to be an unbalanced site distribution of Na^+ and Nd^{3+} (i.e. Na^+ on one side of the unit cell, Nd^{3+} on the other) because Na^+ will not remain as nearest neighbors to Nd^{3+} . This charge separation will cause the O5 to shift asymmetrically which, in turn, produces a high value for the linear field term at the neodymium ion and a correspondingly large oscillator strength. As sodium becomes completely replaced (i.e. high Nd^{3+} concentration), the asymmetric distortions will not be as severe. Thus one expects the oscillator strength to start at low values at low Nd^{3+} concentrations (very little distortion), rise to a maximum at some optimum exchange and then decrease as complete Nd^{3+} exchange is achieved. The existence of a maximum in the oscillator strength vs. Nd^{3+} concentration is exactly what is observed.⁹

Alfrey et al. have also reported other optical properties of $\text{Na}^+/\text{Nd}^{3+}$ β'' alumina.¹⁰ They found the emission spectrum at 1.06 μ to be nearly as inhomogeneously broadened as Nd^{3+} glass, with an effective linewidth of some 250 cm^{-1} . The stimulated emission cross section, both calculated and measured, was in the range of $2 \times 10^{-20} \text{ cm}^2$ and is also comparable to that for glass hosts. Finally, single pass gain measurements indicated that Nd^{3+} in β'' alumina can exhibit rather high values (4/cm). These values agree well with the earlier work on platelet lasers.⁸

One final topic of interest is the issue of how Na^+ motion influences the optical properties of Nd^{3+} exchanged β'' alumina. The absorption spectra and the Judd/Ofelt analysis clearly indicate that the presence of Na^+ has a profound effect on the oscillator strength. As the temperature increases and sodium ions become more mobile, the oscillator strength begins to decrease substantially.¹⁰ This behavior is expected because the Na^+ ions would tend to randomize their site occupations as temperature is raised.¹¹ In contrast, samples with low Na^+ concentrations (i.e. nearly complete Nd^{3+} exchange) display very little temperature dependence. There is also evidence which implies that Na^+ motion is involved in non-radiative processes. Fluorescence measurements indicate that the rate of non-radiative recombination increases exponentially with temperature.¹⁰ The activation energy for this process, 0.5eV, is in excellent agreement with the activation energy for Na^+

motion as obtained from dielectric relaxation measurements of comparable compositions.¹² These results suggest that the motion of Na^+ within the conduction plane influences non-radiative processes in $\text{Na}^+/\text{Nd}^{3+}\beta''$ alumina, although the precise coupling mechanism is presently unknown.

CONCLUSIONS

Beta'' alumina is the first of a new generation of fast ion conducting solid electrolytes to display interesting optical behavior. The extraordinary ion transport properties of this material are applied in the ion exchange processes used to introduce the optically active ions. A large number of transition metal and rare earth ions have been incorporated in β'' alumina by this technique, and it is apparent that the ion exchange approach permits one to control the nature of the ion, its concentration and its distribution within the host material. Another significant feature associated with β'' alumina is its structure. The dopant ions are not located in close-packed surroundings, but rather they are distributed within a 2-dimensional layer containing numerous vacancies. In this sense β'' alumina represents a unique host material which is not only convenient for readily incorporating a large variety of different optically active ions, but also a material which produces novel ion environments for spectroscopy studies.

The one composition to be investigated in some detail, Nd^{3+} exchanged β'' alumina, exhibits several interesting optical effects, including laser action. A Judd/Ofelt analysis of its absorption spectrum suggests that subtle distortions of oxygen and neodymium within the conduction plane can produce the anomalously strong absorption at 5800Å. In contrast, the reasons for long fluorescent lifetime at high Nd^{3+} concentrations have yet to be explained, despite the obvious importance of this factor for producing laser action and the large gain values observed. Other optical properties indicate that $\text{Na}^+/\text{Nd}^{3+}\beta''$ alumina possesses certain characteristics which resemble a glass host rather than a crystalline solid. It is evident that although the prior solid electrolyte studies are quite helpful, there is still much to be learned about Nd^{3+} and the other ion exchanged β'' aluminas. The unique chemistry of these materials and the interesting optical properties discovered to date warrant the continued investigation of this family of compositions.

ACKNOWLEDGEMENTS

The discussions and insights of Professor O. M. Stafsudd and Dr. A. J. Alfrey are greatly appreciated. The research was supported by the U.S. Office of Naval Research, and the Swedish National Science Research Council (NFR).

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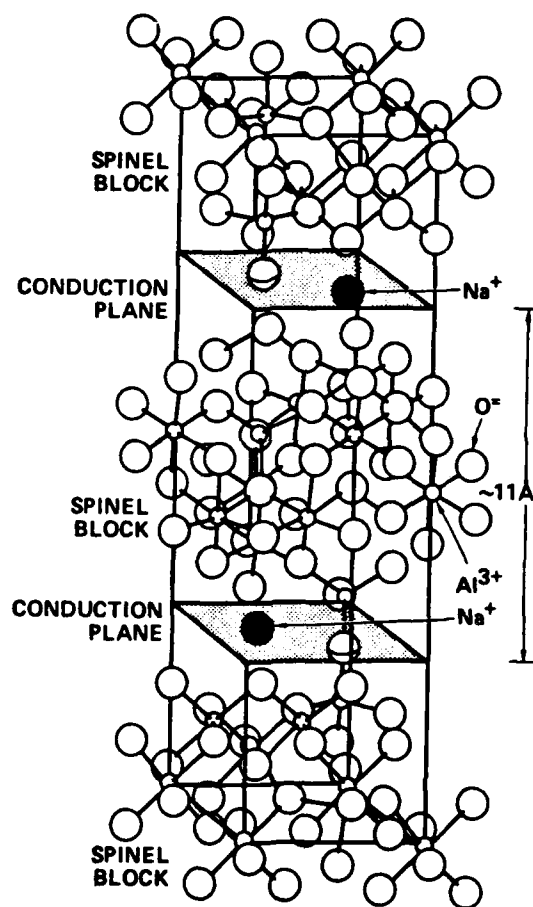
TABLE 1. Oscillator Strengths ($\times 10^{-6}$) for Nd^{3+} in YAG and β'' Alumina.⁹

$\lambda(\text{\AA})$	Nd:YAG	Nd: β'' alumina ($5 \times 10^{20} \text{ cm}^{-3}$)
4200	.032	
4300	.34	.7
4600	.84	
4750	.93	.48
5300	5.6	8.3
5800	7.1	61
7500	8.0	5.8
7900	8.4	5.5
8800	1.5	1.6

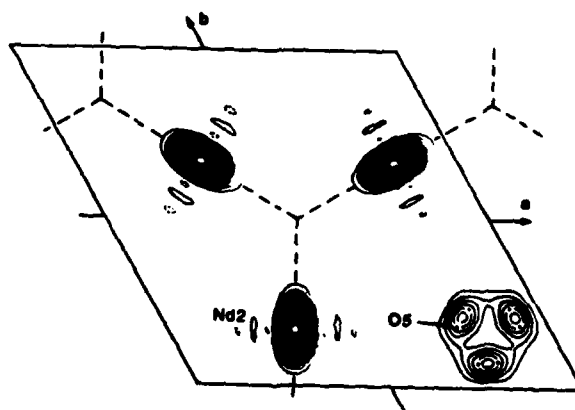
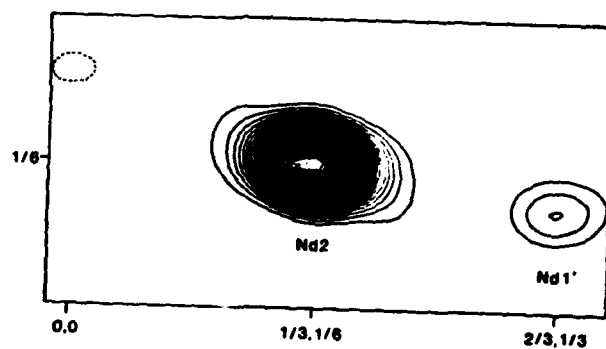
Figure 1. Schematic of the Na^+ β'' alumina structure.

Figure 2. Density maps (observed) in Nd^{3+} β'' alumina. (a) in the vertical ($2x, x, z$) plane (b) in the horizontal ($z = 1/6$) plane through the $6c-6c$ conduction pathway (interval = $2.0 \text{ e.}\text{\AA}^{-3}$).

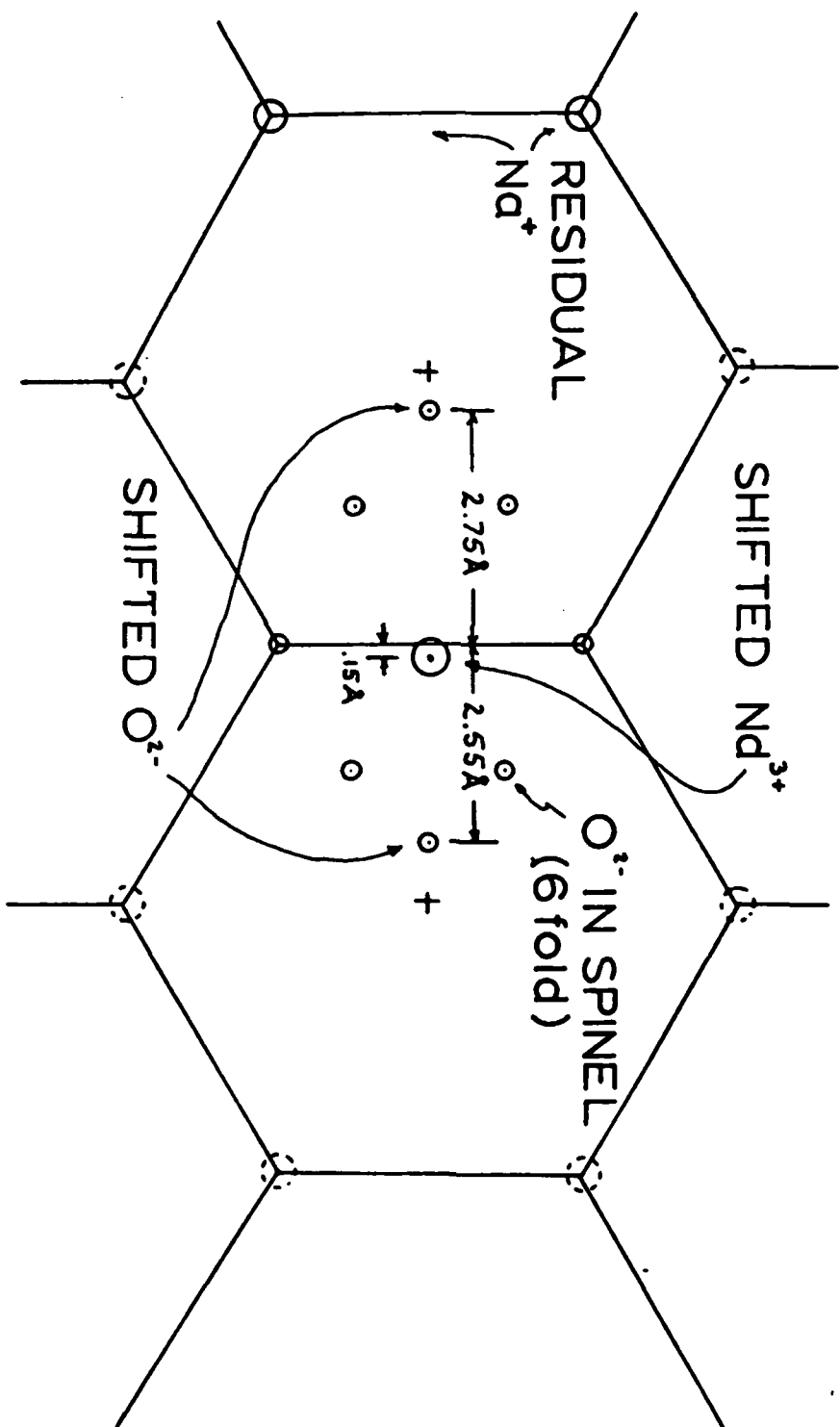
Figure 3. Ion displacements in the conduction plane of $\text{Na}^+/\text{Nd}^{3+}$ β'' alumina as determined from T parameters (after Alfrey et al.⁹).



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