

ANALYSIS OF THE ABSORPTION SPECTRUM OF

NEODYMIUM: SODIUM BETA'' ALUMINA

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ABSTRACT

Through an analysis of the absorption spectrum of Nd^{3+} : Na β'' Alumina and derivation of Judd/Ofelt parameters, a model for the nearest neighbor crystal field of the Nd^{3+} ion has been developed. The proposed model indicates that residual sodium in partially exchanged samples is responsible for distorting the symmetric orientation of conduction plane oxygen. This in turn induces a shift in the Nd ion within a sixfold symmetric arrangement of oxygen ions thereby inducing a linear field term in the crystal field parameters. This is responsible for the anomalous absorption strength in Nd^{3+} : Na β'' Alumina.

INTRODUCTION

Recent work has described how optically active trivalent transition metal and rare earth ions can be substituted for monovalent Na^+ in Sodium Beta'' Alumina (SB''A) by using low temperature exchange processes <1,2>. Jansen et.al. <3> used this approach to prepare small platelets of various exchange percentages and observed laser action at 1.06 microns in some of them. In addition, they reported the existence of an anomalously strong absorption line at 5800 angstroms. In the present paper, we provide a more detailed examination of the absorption spectra by performing a so-called Judd/Ofelt analysis <4,5>. Judd/Ofelt parameters are obtained by using the preliminary x-ray diffraction results for the structures of sodium and rare earth beta'' aluminas. Based on this analysis, we propose a model for the nearest neighbor environment of the Nd^{3+} ion.

ABSORPTION SPECTRA AND JUDD/OFELT ANALYSIS

Nd^{3+} ions may be exchanged for Na^+ in a full range of percentages, typically between 20% of all Na^+ exchanged to over 95% Na^+ exchanged. Corresponding Nd^{3+} ion concentrations range from $3.6 \times 10^{20} \text{ cm}^{-3}$ to $1.8 \times 10^{21} \text{ cm}^{-3}$. A typical sample of $5 \times 10^{20} \text{ cm}^{-3}$ concentration yields the absorption spectrum shown in Figure 1, taken on a Cary IR-14 spectrophotometer. There are two major differences between the spectrum of Nd^{3+} in YAG and that for Nd^{3+} in SB''A. The first is that the individual absorption bands in Nd^{3+} : SB''A are heavily broadened in comparison to Nd^{3+} :YAG. This may be attributed to variations in neighbor distances due to doping-induced strain, multiple siting or variations in residual sodium population due to defects. Secondly, one finds that the absorption band at the nominal wavelength of 5800 Å is anomalously large. As has been pointed out by Judd <4>, this

band in Nd^{3+} is strongly influenced by a linear field term in the nearest neighbor crystal field. In the current work, we focus on the origin of this anomalous absorption as it provides both the key to the understanding of the nearest neighbor environment and to efficient optical pumping at 5800 Å.

The Judd/Ofelt analysis begins with the calculation of the oscillator strength P for the transitions between the initial $^4I_{9/2}$ ground state manifold to the final states labelled by RS coupled states that form the major portion of these final states. The oscillator strength for a group of closely spaced transitions is given by

$$P = \chi [8\pi^2 m\nu / 3h(2J+1)] \sum_{i,f} |\langle i | \vec{r} | f \rangle|^2 \quad (1)$$

where

$$\chi = (n^2 + 2)^2 / 9n$$

is the correction for the bulk polarizability for a medium of index of refraction n , $(2J+1)$ accounts for the multiplicity of the ground state, and $\langle i | \vec{r} | f \rangle$ are the matrix elements for the electric dipole operator between initial and final states. Experimentally, the oscillator strengths are derived from the absorption spectra by the expression given by Hoogschagen <6> as

$$P = \frac{1000 \text{ mc}^2}{\pi e^2 N_0} \frac{1}{C\lambda^2} \int_0^\infty k(\lambda) d\lambda \quad (2)$$

where $k(\lambda)$ is the absorption strength measured at a wavelength λ , C is the molar concentration and N_0 is Avogadro's number. Since the spectrophotometer yields absorption plots of $\log(I/I_0)$ versus wavelength through a sample of thickness ℓ , the areas under these curves can be used to find the oscillator strengths for each group of transitions by using the expression

$$P = \frac{1000 \text{ mc}^2}{\pi e^2 N_0} \times \frac{2.3}{\lambda^2 c \ell} \int_0^\infty \log(I/I_0) d\lambda \quad (3)$$

In Table 1 we tabulate the values for oscillator strength for the various transitions for Nd^{3+} in chlorides <4> YAG <7> and SB''A hosts. The transition at 5800 Å is seen to be an order of magnitude stronger in SB''A than in either the chloride or YAG environment.

The group theoretical approach of Judd and Ofelt, based on the work of Racah <8>, has become the popular technique for deriving eigenvectors and transition strengths for f^n electron configurations of the rare earths, particularly for Nd^{3+} in a variety of hosts. In this formulation, the oscillator strength is given by

$$P = \sum_{\lambda} \nu T^{(\lambda)} | \langle i || U^{(\lambda)} || f \rangle |^2 \quad (4)$$

where $\langle i || U^{(\lambda)} || f \rangle$ are the reduced matrix elements for irreducible tensor operators between the initial and final states and the parameters $T^{(\lambda)}$ are given by

$$T^{(\lambda)} = X [8\pi^2 m / 3h(2J+1)] (2+1) \sum_t (2t+1)^{-1} \equiv {}^2(\lambda, t) \sum_p |A_{tp}|^2 \quad (5)$$

The dependence on the crystal field environment enters via the crystal field parameters A_{tp} given by

$$A_{tp} = (-1)^{p+1} \sum_i e q_i r_i^{-t-1} Y_{tp} [4\pi/2t+1]^{1/2} \quad (6)$$

where the r_i are the individual nearest neighbor positions, the Y_{tp} are the spherical harmonics and the summation is over the individual nearest neighbor ions with the Nd^{3+} ion taken at the origin. The variable $\equiv (\lambda, t)$ contains the free ion radial integrals and the various 3-J and 6-J symbols.

By obtaining values for the oscillator strengths from the absorption spectrum, a least squares fit enables determination of the T parameters. Again, in Table 2, we compare the values obtained for Nd^{3+} in the three previously mentioned crystal hosts. Additionally, we note that Krupke <9> has found it convenient to use a parameter $\Omega_{(\lambda)}$ to characterize many of the glass hosts used at Lawrence Livermore Labs. The conversion between $T^{(\lambda)}$ and $\Omega_{(\lambda)}$ is given by

$$T^{(\lambda)} = \chi [8\pi^2 m / 3h(2J+1)] \Omega_{(\lambda)} \quad (7)$$

ORIGIN OF THE T PARAMETERS

Conceivably, given accurate data on the positions of the nearest neighbor ions and accurate calculations of the radial integrals for the Nd^{3+} ion, the T parameters and therefore, the oscillator strengths should be calculable from first principles. Both Judd <4> and Krupke <9> have performed such a calculation on Nd^{3+} in a variety of environments and have had encouraging but not complete success. The inability to attain better than an approximate match between experimental and theoretical calculations is usually blamed on an inaccurate knowledge of the radial integrals, usually known only for the free ion. In the current work, we take a slightly different approach to the problem. Preliminary x-ray data <10> on totally exchanged samples indicates that rare earth ions may substitute into the $\text{SB}''\text{A}$ system in sites of inversion symmetry. This implies that electric dipole transitions are forbidden from parity arguments alone. However, all of the samples studied in the current work have some percentage of sodium remaining in the conduction plane. Further, this x-ray work has indicated that near neighbor ions to the dopant can be distorted from their rest position under the influence of the trivalent dopant.

Based on the fact that such near neighbor distortions are expected in the conduction plane, we have developed a model that treats conduction plane ions as parameters that can be adjusted to yield a best fit to the experimentally observed T parameters. Indeed, because of the matching difficulty found in previous work, it would probably be best to match ratios of the T parameters rather than their absolute values.

One should always be skeptical of such an approach since, with enough parameters, a good theoretical/experimental fit can be obtained with a possibly nonsensical group of parameter values. However, in the current work, we are aided by the abnormally high value of T_2 and further, by the fact that the linear A_{1p} crystal field terms appear only in T_2 . It will be shown that, to achieve a close fit to the experimentally determined T parameters, it will only be necessary to assume that the neodymium ion and nearest neighbor oxygen ion are slightly displaced from their x-ray determined positions in completely exchanged and unexchanged samples respectively. We propose that these displacements are simply the response to the mutual electrostatic interaction felt between remaining sodium and near neighbor oxygen.

STRUCTURE REVIEW AND CALCULATION OF T PARAMETERS

We first review the structure of the SB''A system. As shown in Figure 2, the structure consists of spinel blocks of closely packed Al and O separated by loosely packed slabs containing Na^+ and O^{2-} . The open space in these slabs permits rapid Na^+ migration in two dimensions. Figure 3 shows the results of projecting the conduction slab ions onto the mid-plane, or so-called conduction plane. In a typical composition of $Na_{1.67} Mg_{.67} Al_{10.33} O_{17}$, where Mg substitutes for Al in the spinel block to stabilize the beta'' phase, sodium ions

occupy 5/6 of two crystallographically equivalent sites (the Beevers-Ross and anti-Beevers-Ross sites), these positions being alternately shifted slightly up and down from the mid-plane. A third crystallographic position (mid-oxygen site) is unoccupied. Trivalent rare earths may be substituted for the conduction plane sodium by immersion of the crystal in rare earth molten salts <2>, leaving the spinel blocks unchanged. Recent work <10> has shown that, when gadolinium is totally exchanged for sodium, gadolinium preferentially occupies mid-oxygen sites as shown in Figure 4. A small percentage of cells are found to contain gadolinium at the Beevers-Ross sites. Unpublished preliminary work <11> indicates that neodymium also occupies the same sites as gadolinium with a possibly slightly higher percentage occupation of the Beevers-Ross sites.

As will be shown, variations in the positions of conduction plane O^{2-} and Nd^{3+} are crucial to the Judd/Ofelt analysis. Fourier synthesis maps indicate that not only are the mid-plane O^{2-} distorted towards the mid-oxygen position by 0.5 Å but the Gd^{3+} position is found to vary in an elliptical fashion over several tenths of angstroms <10>.

Consider first the occupation of Nd^{3+} at the mid-oxygen site, along with the nearest neighbor oxygen ions in the spinel blocks above and below the conduction plane (see Figure 5). It can be seen that the Nd^{3+} occupies a site of inversion symmetry, which must be discounted as spectroscopically inconsistent. However, the situation changes slightly in the presence of sodium. As the exchange process is begun, replacing three sodium ions with each neodymium ion, sodium ions are not expected to remain as nearest neighbors to neodymium. However, as the exchange process continues, a situation

is quickly reached in which oxygen in the conduction plane sees an unbalanced distribution of sodium or other neodymium. As a result, conduction plane oxygen is expected to shift to an asymmetrical arrangement about the neodymium ion. This asymmetry leads to a high value for the linear field term at the neodymium ion and a correspondingly large value for T_2 . However, this effect alone cannot account for the values of the observed T parameters; a shift of the Nd^{3+} ion must also be included. As the exchange process is continued and sodium is totally exchanged, distortions in the conduction plane oxygen sites are now caused by adjacent neodymium, but will not be as severe as under the presence of sodium. Therefore, one expects the oscillator strength (average absorption cross section per Nd^{3+} ion) to start out at low values for weak exchange, to rise to a peak at some optimum exchange percentage and to decrease again to low values as total exchange is approached. As shown in Figure 6, this is exactly the effect observed. Indeed, preliminary work indicates that mobil sodium is responsible for a reduction of the oscillator strength at increased temperature. Samples that are nearly totally exchanged show little temperature dependence of oscillator strength. However, the residual oscillator strength at virtually 100% sodium exchange indicates that sodium alone cannot be responsible for the loss of inversion symmetry, and may possibly be caused by adjacent neodymium distorting oxygen positions in the conduction plane. In our parameter fitting procedure, we will not attempt to model the site positions at high exchange percentage, but only the oxygen and neodymium positions required to yield a good fit with the observed T parameters at moderate sodium exchange percentages.

With this introductory framework in place, we now present the theoretically calculated T parameters for the proposed model. We use the technique described

by Judd <4> and Krupke <9> and include the contributions due to 5g configurations. As noted above, the undistorted nearest neighbor environment shows inversion symmetry, therefore T parameters will be calculated for various plausible distortions from inversion symmetry. In Figure 7, we plot theoretically calculated T parameters for the introduction of monovalent sodium at a given distance from the Nd^{3+} ion in an otherwise symmetric arrangement of O^{2-} . Figure 8 displays calculated T parameters for an arrangement in which one of the conduction plane O^{2-} ions is moved a given distance from a position of inversion symmetry and finally, Figure 9 displays T parameters for the Nd^{3+} ion initially in a position of inversion symmetry, after which it is displaced in the conduction plane along a line connecting the conduction plane oxygen. From an examination of Figure 7, it is seen that a single sodium ion cannot be solely responsible for the experimentally observed T parameters. Table 3 shows the experimentally determined T parameters for the same sample shown in Figure 1. The second set of T parameters in Table 3 is for a single sodium ion at a distance of 4.29 angstroms from the Nd ion, the nearest site expected to be occupied by sodium after exchanging a single Nd into the conduction plane. As seen from the table, both the absolute values of the T parameters and their ratios are not at all a good match to the experimental values. By allowing both an asymmetrical shift in conduction plane oxygen (Figure 8) and a shift in the neodymium position (Figure 9), a good match can be achieved as shown in the last column of Table 3 and in Figure 10. We stress that the distortions described in Figure 10 are certainly not uniquely determined by the T parameters, rather we consider the orientation of ions in Figure 10 to be an "average" of many possible positions. However, we do suggest that the asymmetric arrangement of conduction plane oxygen and shift of the neodymium ion are the type of distortion that must exist to account for the observed T parameters.

We finally consider the possible contribution due to Nd^{3+} at Beevers-Ross sites, shown by x-ray data to be occupied a small percentage of the time. Table 4 shows the T parameters calculated for this situation with no oxygen or neodymium distortion. When the T parameters are calculated for this site, they must be multiplied by the fractional occupation of this site to properly account for their effect on the absorption spectrum. When this is done, the additional contribution to the T parameters for occupation of the Beevers-Ross site can probably be ignored.

It must be emphasized that the success of the fitting procedure depends on the ability to "tweak" the Na^+ ion positions and that the values of the T parameters are rather sensitive to these positions. Such an artificial luxury could not be enjoyed by Judd or Krupke since their work attempted to calculate T parameters for presumably well-known ion positions. However, we contend that the close fit between experimental and theoretical T parameter ratios is strong support for the technique employed in this work.

CONCLUSION

By analyzing the absorption spectrum of $\text{Nd}^{3+} : \text{SB}''\text{A}$, we have derived the Judd/Ofelt parameters that characterize the local crystal field environment for the Nd^{3+} ion. We have proposed a model for the local crystal field that includes the effect of residual sodium in the conduction plane. We have shown that the experimentally determined T parameters can be accounted for by a slight displacement of the Nd^{3+} ion away from its usual mid-oxygen site and by a slight displacement of the conduction plane oxygen away from a symmetric arrangement around the neodymium ion.

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TABLE 1: Oscillator Strengths ($\times 10^{-6}$)

$\lambda(\text{\AA})$	Nd: YAG	NdCl ₃	Nd:SB ⁺⁺ A($n = 5 \times 10^{20} \text{ cm}^{-3}$)
4200	.032	.08	
4300	.34	.38	.7
4600	.84	2.31	
4750	.93		.48
5300	5.6	6.58	8.3
5800	7.1	10.5	61.
6250	.16	.39	
6800	.76	.83	
7500	8.0	8.88	5.8
7900	8.4	9.22	5.5
8800	1.5	3.02	1.6

TABLE 2: T PARAMETERS - From Least Squares Fit.
(units of 10^{-20} sec.)

	Nd:YAG	NdCl ₃ :6H ₂ O	Nd:SB' 'A
T ₂	.125	.87	8.1
T ₄	1.69	1.73	2.2
T ₆	3.13	3.53	1.4

TABLE 3. T PARAMETERS - Experimental vs. Theoretical
(units of 10^{-20} sec.)

	Nd:SB'A	Single Na ⁺ @ 4.3 A	O ²⁻ and Nd ³⁺ Distortion
T ₂	8.1	1.9	8.2
T ₄	2.2	.002	2.4
T ₆	1.4	.00005	1.8

TABLE 4. T PARAMETERS - Neodymium at Beevers-Ross Site
 Calculations Corrected For Site Occupation Probability.
 (units of 10^{-20} sec.)

T_2	3.2
T_4	.071
T_6	.041

LIST OF FIGURES AND CAPTIONS

Figure 1. Typical absorption spectrum for $\text{Nd}^{3+}:\text{SB}'\text{'A}$, $5 \times 10^{20} / \text{cm}^3$ concentration, .26 mm thickness.

Figure 2. Unit cell for unexchanged $\text{SB}'\text{'A}$.

Figure 3. Conduction plane for unexchanged $\text{SB}'\text{'A}$, indicating one of six possible sodium ion vacancies.

Figure 4. Conduction plane for $\text{Gd}^{3+}:\text{SB}'\text{'A}$, indicating occupation of mid-oxygen site and shifted oxygen ion position. Site labels are from Reference 10.

Figure 5. Nearest neighbor environment for $\text{Gd}^{3+}:\text{SB}'\text{'A}$ following the x-ray analysis presented in Reference 10.

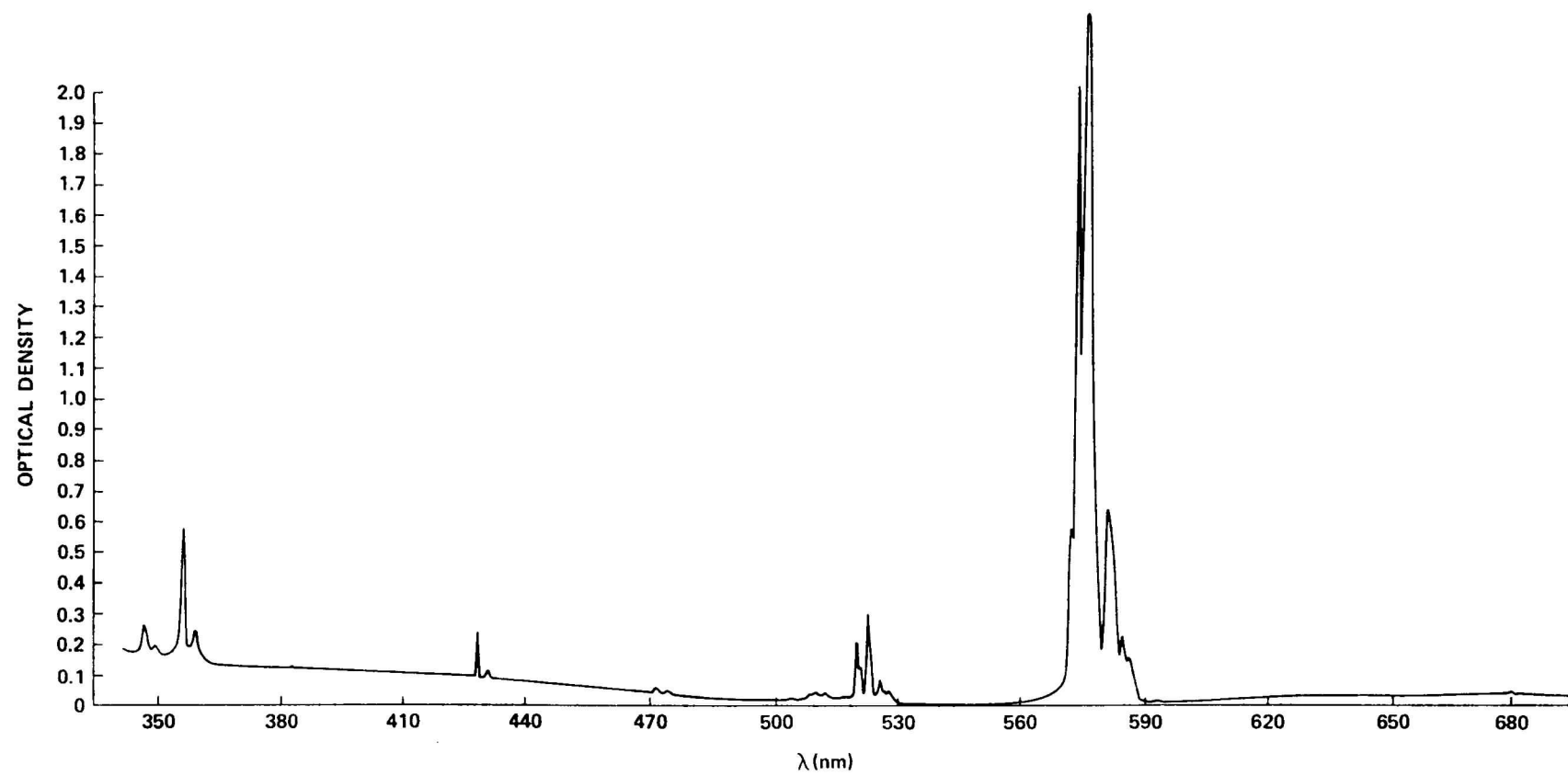
Figure 6. Experimental variation of T parameters versus Nd^{3+} ion concentration.

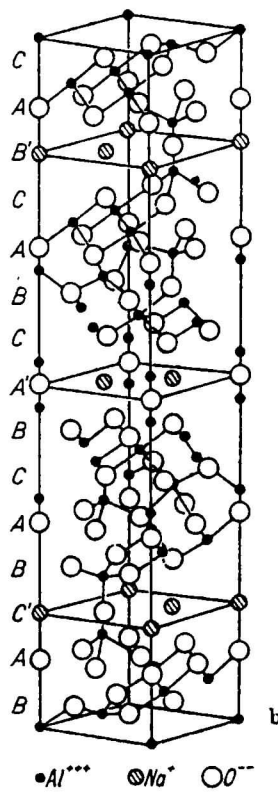
Figure 7. Variation of T parameters for Nd^{3+} versus monovalent ion position for an otherwise symmetric crystal field.

Figure 8. Variation of T parameters versus O^{2-} position with opposite O held at 2.55 Å from mid-oxygen site.

Figure 9. Variation of T parameters versus Nd^{3+} shift from a position of inversion symmetry.

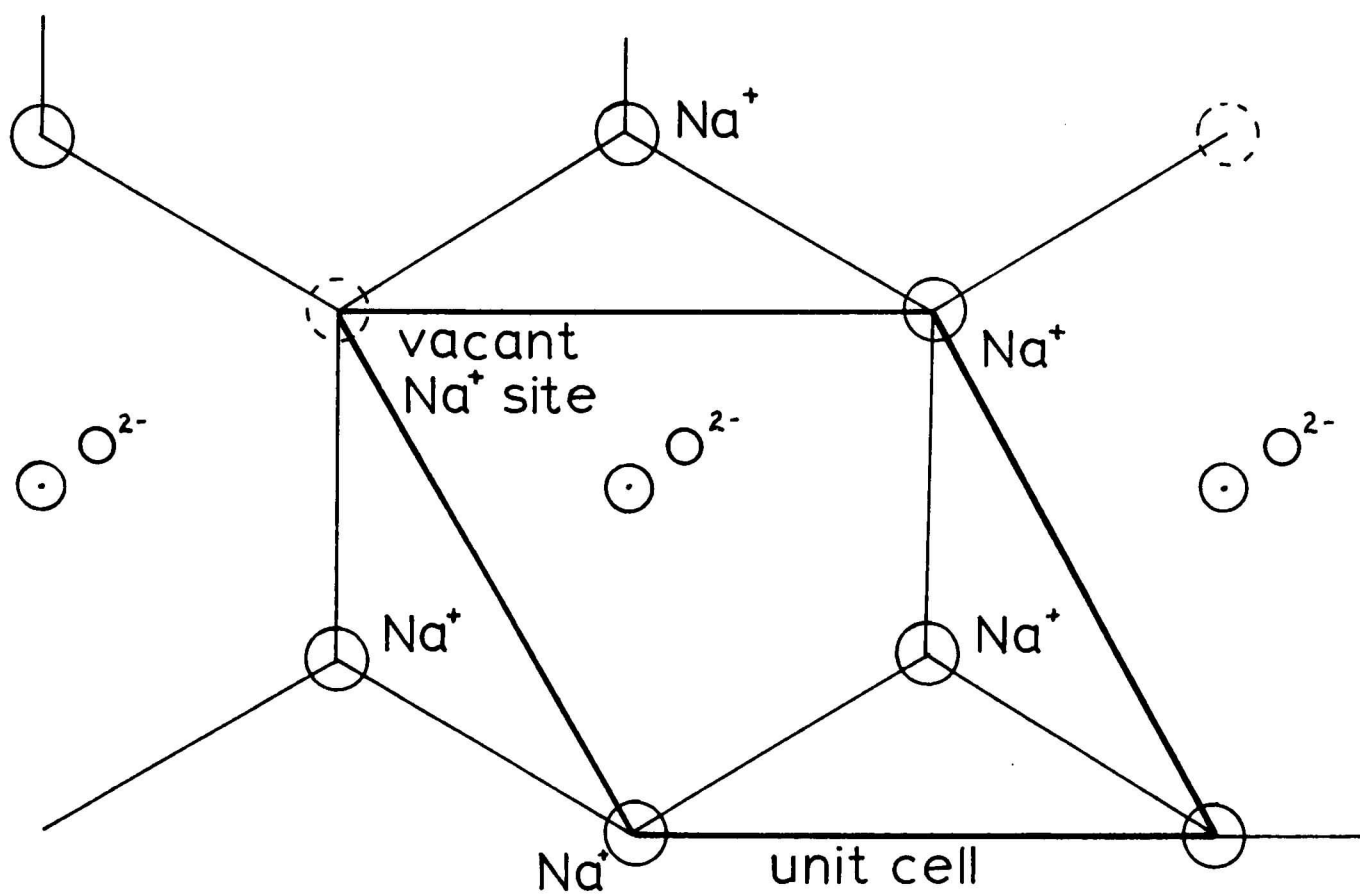
Figure 10. Possible site distortion for $\text{Nd}^{3+}:\text{SB}'\text{'A}$. The distortion is a composite of the shifts described in Figures 8 and 9.





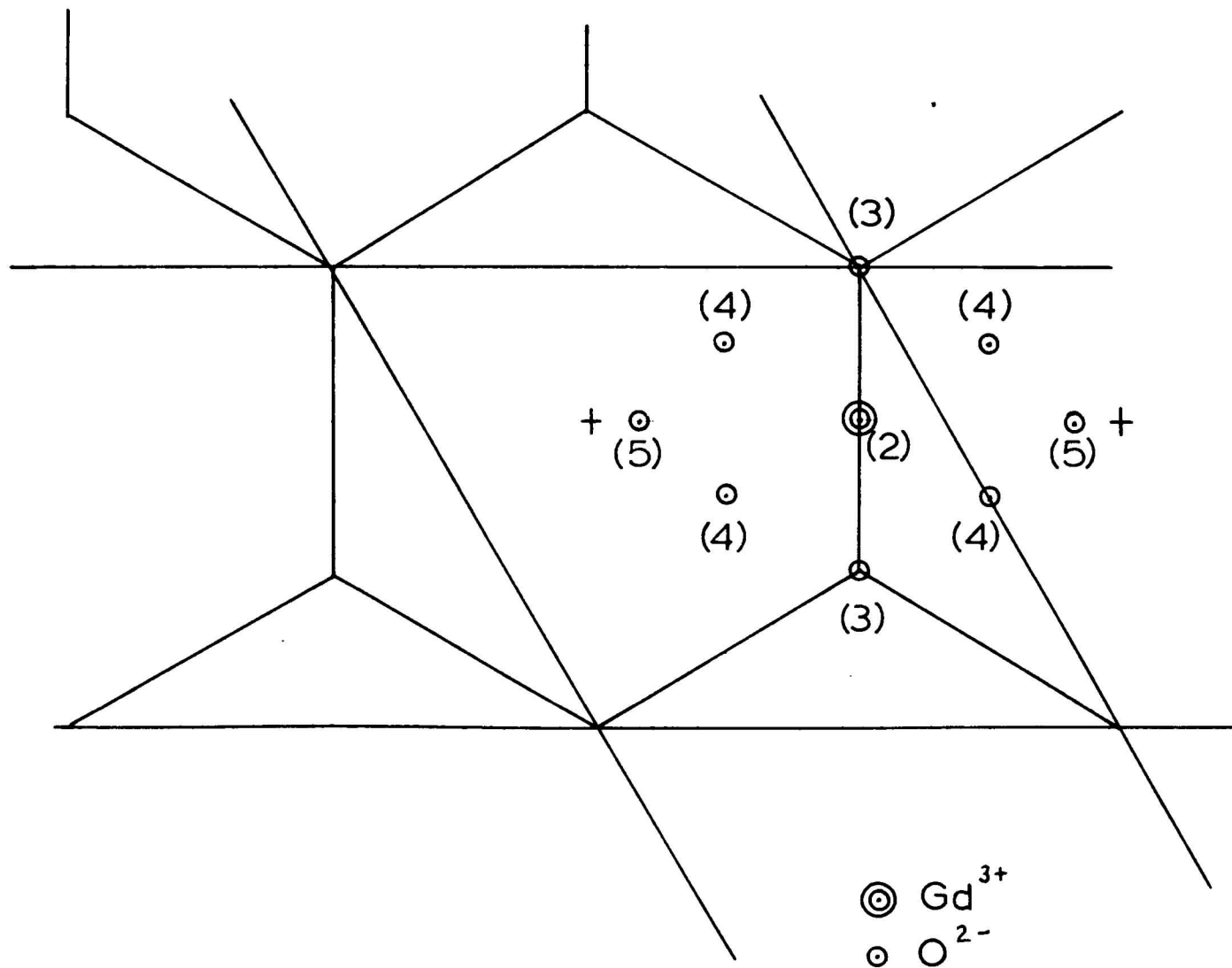
SODIUM β'' ALUMINA

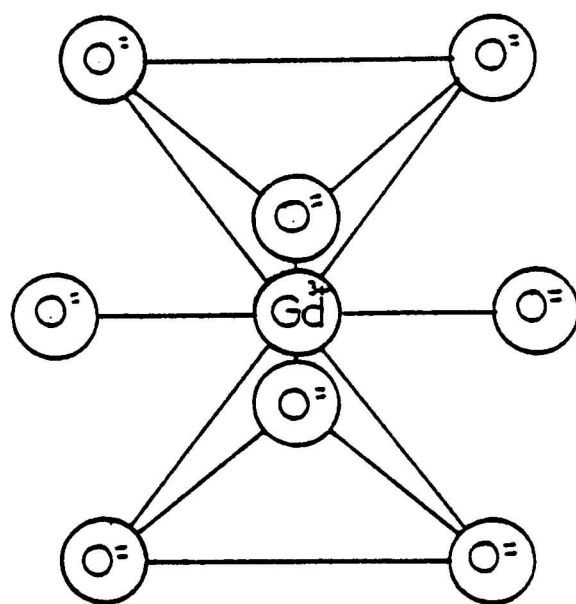
CONDUCTION PLANE
SODIUM β'' ALUMINA - UNEXCH.

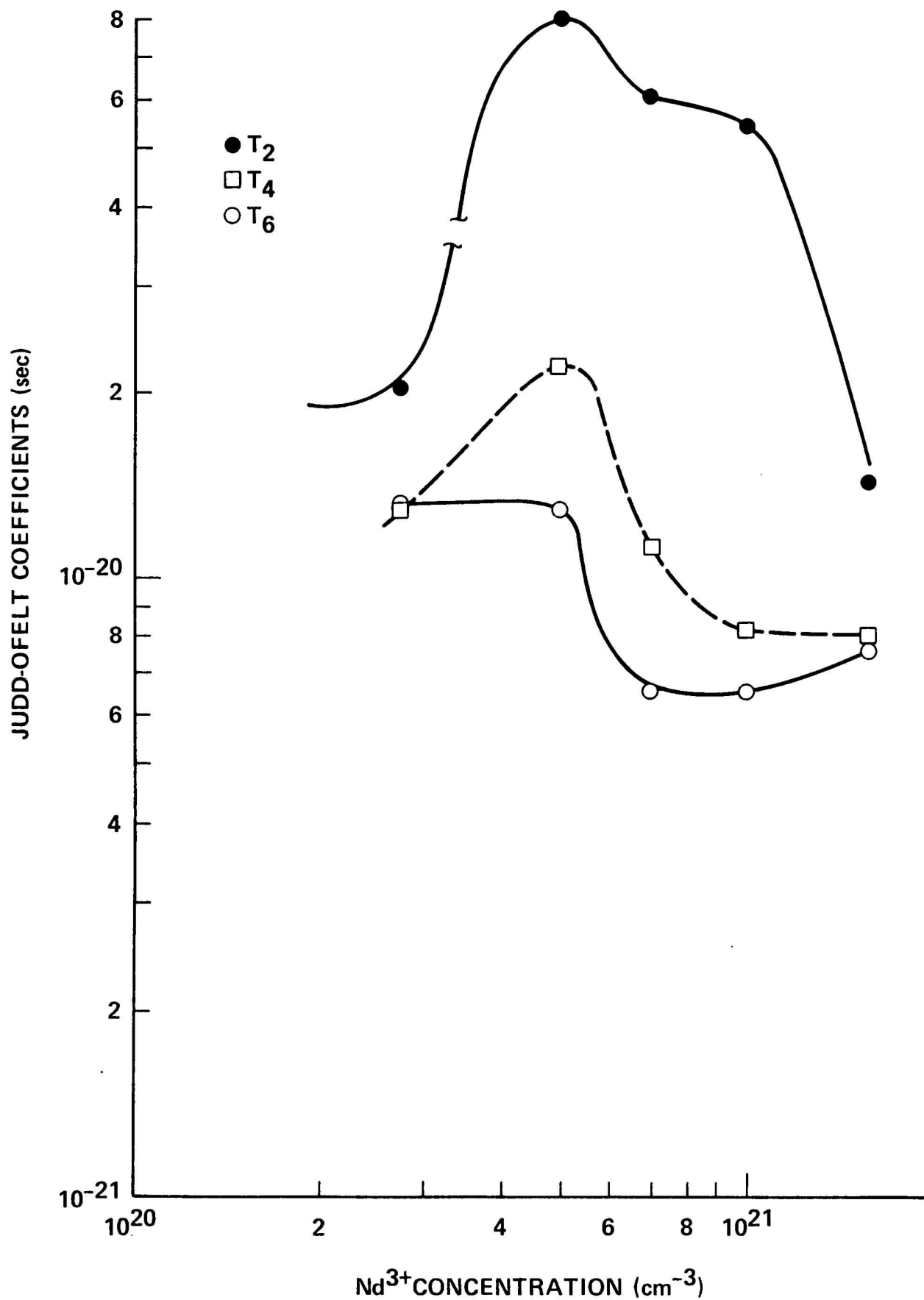


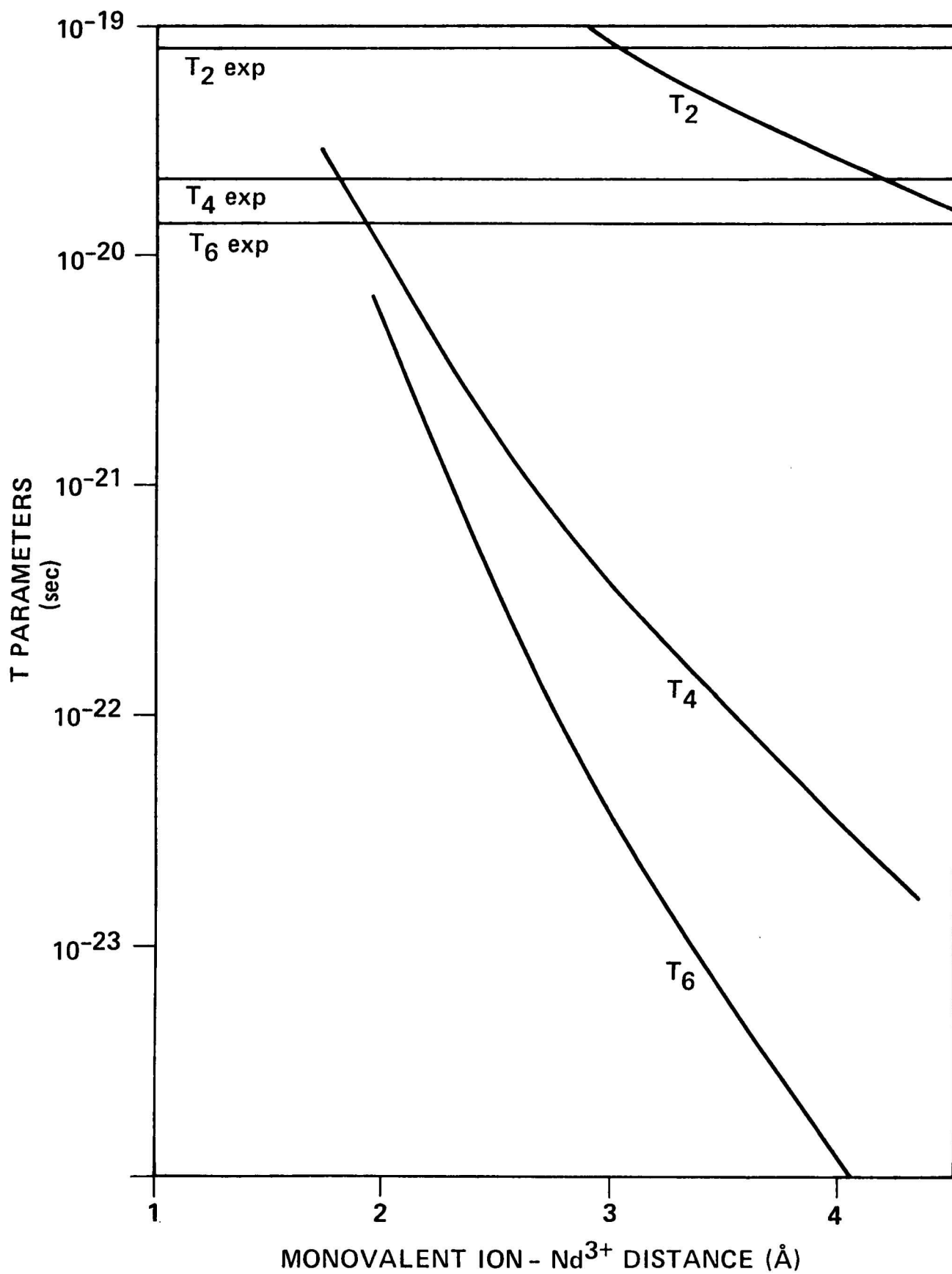
CONDUCTION PLANE

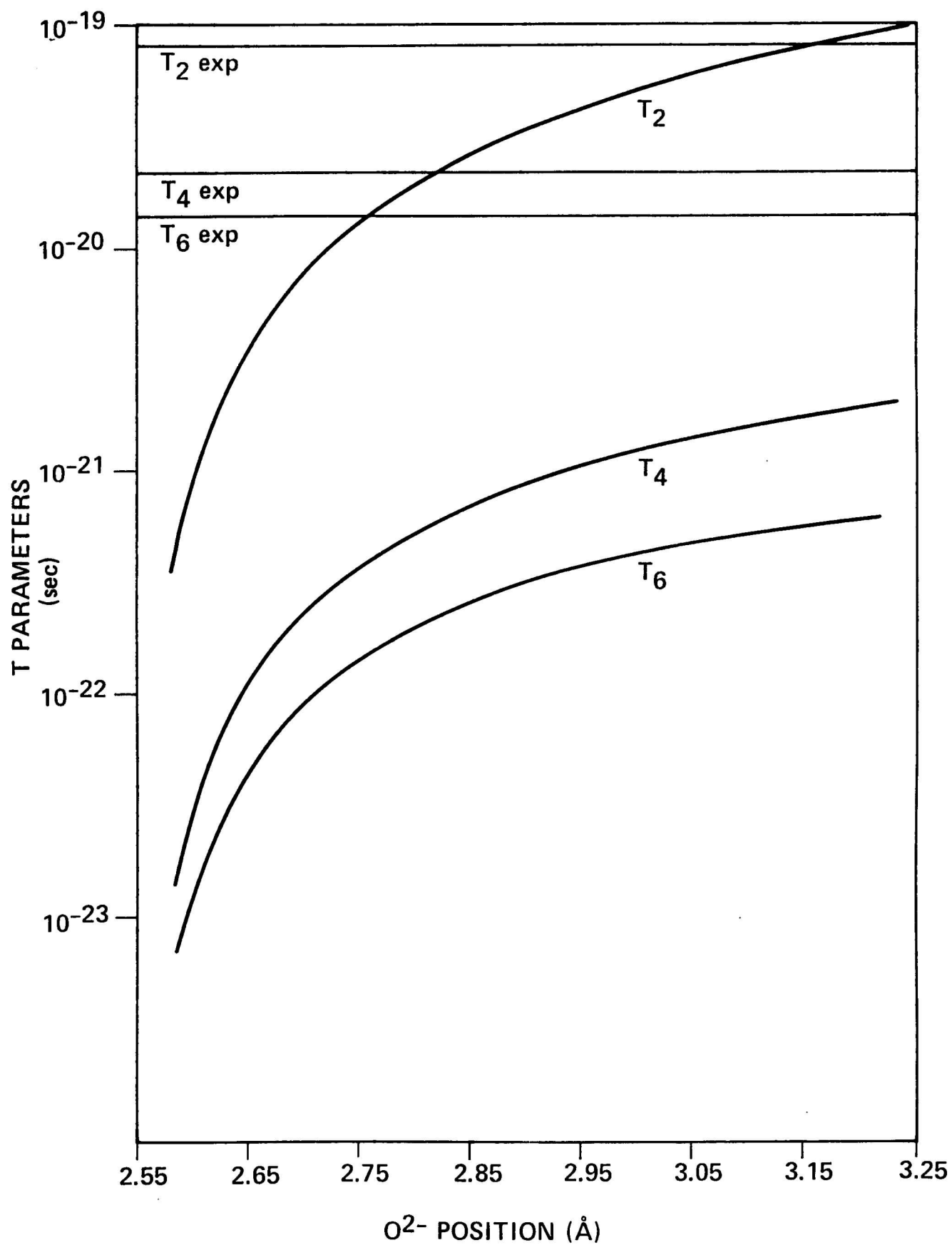
$\text{Gd}^{3+}: \beta''$

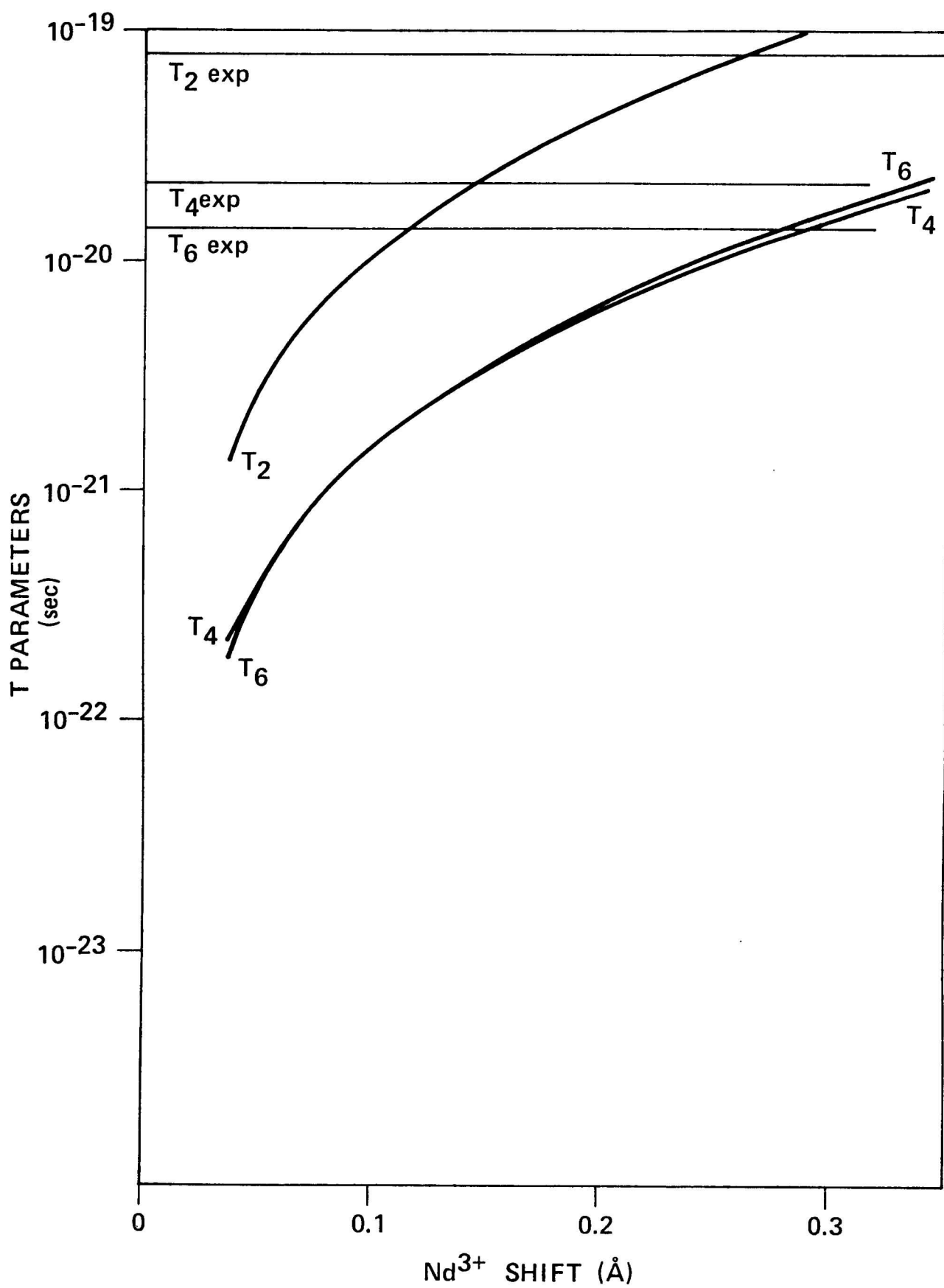












PROPOSED SITE DISTORTION

