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# Canadä

A laser spectroscopic study of the Eu+3 environment and energy transfer in  $\beta$ "-alumina

by

Monique Marie Laberge

A Thesis Submitted to the Faculty of Graduate Studies and Research in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

> McGill University Department of Chemistry Montréal, Québec, Canada © July 1992

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Short title:

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Study of the  $Eu^{3}$  ion environment and energy transfer in  $\beta$ "-alumina

"Spectral changes, What are they ? Mechanistic Overlay. When it sticks, You've got a lot. But can you name The path it shot ?" - E. Castro

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#### ABSTRACT

Site-selective laser excitation and emission spectra were obtained with a 20% Eu<sup>+3</sup> exchanged sodium  $\beta$ "-alumina crystal at 77 and 6.4 K. Excitation into the <sup>5</sup>D<sub>0</sub> level (568-579 nm) shows that the trivalent europium ion occupies at least two types of site distributions. The first distribution occurs at the higher energy of the tuning range and has site symmetry C<sub>3V</sub> or C<sub>3</sub>. It corresponds to the crystallographic Beevers-Ross position. The other site distribution is observed at lower energy and is associated with the mid-oxygen crystallographic position (site symmetry: C<sub>2h</sub>). This work shows that the interpretation of the site-selective spectroscopy of Eu<sup>+3</sup> $\beta$ "-alumina must take into account the occurrence of multipole site-to-site energy transfer linked to vibronic coupling phenomena.

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#### RÉSUMÉ

Des spectres d'excitation et d'émission laser ont été obtenus sur un cristal d'aluminate ß" de sodium échangé à 20% par de l'europium trivalent. L'excitation du niveau <sup>5</sup>D, (568-579 nm) révèle que l'ion d'europium occupe au moins deux types de distributions. La première distribution est observée lorsqu'on excite à plus haute énergie et possède une symétrie de site C<sub>3v</sub> ou C<sub>3</sub>. Elle correspond à la position crystallographique Beevers-Ross. L'autre distribution s'observe à énergie moins élevée et peut être associée à la position crystallographique mi-oxygène (symétrie de site: C2h). Ce travail montre que l'interprétation de la spectroscopie sélective de l'aluminate  $\beta$ " dopée à l'Eu<sup>+3</sup> doit prendre en considération des phénomènes multipolaires de transfert d'énergie et de couplage vibronique.

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"The candidate has the option, subject to the approval of their department, of including as part of the thesis the text, or duplicated published text, of an original paper or papers. - Manuscript-style theses must still conform to all other requirements explained in the Guidelines Concerning Thesis Preparation.

- Additional material (procedural and design data as well as descriptions of equipment) must be provided in sufficient detail (e.g. in appendices) to allow clear and precise judgement to be made of the importance and originality of the research reported. - The thesis should be more than a mere collection of manuscripts published or to be published. It must include a general abstract, a full introduction and literature review and a final overall conclusion. Connecting texts which provide logical bridges between different manuscripts are usually desirable in the interest of cohesion. It is acceptable for these to include, as chapters, authentic copies of papers already published, provided these are duplicated clearly and bound as an integral part of the thesis. In fuch instances, connecting texts are mandatory and supplementary explanatory material is always necessary.

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The thesis is organized as follows: the first chapter consists of a general introduction on rare-earth substituted  $\beta$ "-aluminas and previous spectroscopic investigations. Chapter 2 describes the experimental set-

up used in our laboratory. Chapter 3 presents the first evidence obtained for the occurrence of energy transfer [This work was published in *Chem. Phys. Lett.* <u>182</u>(2), 159 (1991)]. Chapter 4 describes the sites available for europium in  $\beta$ "-alumina [This work was published in *J. Chem. Phys.* <u>96</u>(8), 5565 (1992)]. Chapter 5 proposes an explanation for the observed energy transfer [This work was published in *Solid State Commun.* <u>81</u>(10), 873 (1992)] and chapter 6 concludes that tile energy transfer occurs by a multipole mechanism [This work was submitted to *J. Lumin.*].

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INTRODUCTION

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#### 1.1 RE-substituted sodium ß"-aluminas

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The main characteristics of the sodium  $\beta^{"}$ -alumina [Na<sub>1-x</sub>Mg<sub>x</sub>Al<sub>11-x</sub>O<sub>17</sub>, x = 0.67] structure were determined in 1969 by Betman and Peters [1]. The symmetry is rhombohedra<sup>1</sup>, the cell parameters are a = 5.614 Å and c = 33.85 Å. The space group is R3m. Figure 1 shows the unit cell which stacks three spinel-like blocks (11.3 Å) with a 120° rotation with respect to each other. These spinel blocks do not have the ideal spinel structure which contains Al<sup>+3</sup> and Mg<sup>+2</sup> ions in a 1:2 ratio; in  $\beta^{"}$ , they contain only Al<sup>+3</sup> and smaller amounts of Mg<sup>+2</sup> at the interstices. The spinel blocks also contain four closed-packed oxygen layers. Alternating with the spinel blocks are planes (4 Å-thick) of loosely packed oxygen ions and mobile sodium ions free to migrate in the planes which are thus referred to as "conduction planes". There are three conduction planes per unit cell. The spinel blocks are linked by Al-O-Al bonds and the connecting oxygens are referred to as "bridging" or "column" oxygens (O(5) atom).

In recent years, the realisation that lanthanide  $\beta$ "-aluminas represent a class of interesting materials for applications in solid state lasers and opto-electronic devices has stimulated the doping of the  $\beta$ " host with a wide variety of trivalent rare earth ions such as Eu<sup>+3</sup>, Nd<sup>+3</sup>, Gd<sup>+3</sup>, Sm<sup>+3</sup>, Sm<sup>+3</sup>, etc. Lanthanides substitute for sodium ions in the conduction planes. The x-ray



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Figure 1: The unit cell of Na<sup>+</sup>β"-alumina [8]

structure has been determined for Gd<sup>+3</sup>, Eu<sup>+3</sup> and Nd<sup>+3</sup> B"-alumina [2] and the effects of rare earth substitution are as follows: the c parameter becomes smaller (33.134 Å, 33.190 Å, 33.259 Å respectively for Gd^{\*3} , Eu^{\*3} and Nd^{\*3} B"-alumina); the column oxygens (O(5)) are displaced 0.502 Å (Eu+3), 0.420 Å (Nd<sup>+3</sup>) and 0.490 Å (Gd<sup>+3</sup>) towards mid-oxygen. These oxygens are attracted to the cation thus bending the Al-O-Al bond connecting the spinel blocks and distorting the structure. Substitution occurs in two non-equivalent sites: a four-coordinate Beevers-Ross (BR) site (symmetry C<sub>3v</sub>) and an eight-coordinate mid-oxygen (mO) site (symmetry C<sub>2h</sub>). The unit cell ideally contains two BR sites and three mO sites per conduction plane (The reader is referred to figure 1 in chapter 4 and to figure 1 in chapter 6 for illustrations of the substitutional sites and of the conduction plane). However, Farrington et al.[3] rightly point out that assigning the mobile ions to these five possible sites would be an over-simplification, in that site occupancy is a space-time average and that there is a high probability of finding an ion in a displaced position (relative to the x-ray positions), especially in a mobile ion system. According to the x-ray results [2] rare earth substitution occurs preferentially at mO sites but the local ordering need not be the same. Long-range ordering also occurs in the three rare-earth substituted aluminas with a 3a x 3b x 3c superstructure featuring a long-range ordered spinel host containing either distinct regions of rare earth ordering or regions of random rare earth ion arrangements [4]. The Eu<sup>+3</sup> and Nd<sup>+3</sup>β"-

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aluminas display the most extensive regions of short range ordering and the  $Nd^{+3} \beta$ "-alumina the greatest extent of superlattice ordering.

Factors which are known to influence the rare earth ion distribution are the thermal history, the concentration used for ion exchange and the nature of the rare earth-oxygen bonding [3]. Table 1 lists the europium-oxygen bond distances in fully exchanged Eu  $\beta$ "-alumina. These bond lengths are among the least covalent ever reported for Eu<sup>+3</sup>-O bonds (which explains the unusually fast diffusion rate of trivalent europium in  $\beta$ "-alumina).

Site	Symmetry	Atoms	Bond length (Å)
mO	C <sub>2h</sub>	Eu-O <sub>(5)</sub> Eu-O <sub>(4)</sub> Eu-O <sub>(3)</sub>	2.322 2.751 2.772
BR	C <sub>3v</sub>	Eu-O <sub>(5)</sub> Eu-O <sub>(4)</sub> Eu-O <sub>(3)</sub>	2.851 2.490 2.561

Table 1: Bond lengths in Eu<sup>+3</sup>β"-alumina

The Eu<sup>+3</sup> $\beta$ "-alumina samples used during the course of this work were prepared by Leslie Momoda in Professor B. Dunn's laboratory at UCLA. Single crystals of Na<sup>+</sup> $\beta$ "-alumina (Na<sub>1.67</sub>Mg<sub>0.67</sub>Al<sub>10.33</sub>O<sub>17</sub>) were grown by a flux

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evaporation method (1600 to 1700°C) from a melt of Na<sub>2</sub>CO<sub>3</sub>, MgO and Al<sub>2</sub>O<sub>3</sub>. The ion exchange was performed by immersing the crystals in a molten salt bath containing EuCl<sub>3</sub>, thus allowing the Na<sup>+</sup> ions to diffuse out of the conduction plane and be exchanged for Eu<sup>+3</sup> ions. Gravimetric analysis was used to determine the extent of Na<sup>+</sup> ion exchange in the sample. The Eu<sup>+3</sup> concentration was estimated from absorbance measurements.

#### **1.2 Previous spectroscopic investigations**

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A thesis has already been produced on the site-selective spectroscopy of 34%-exchanged Eu<sup>\*3</sup>β<sup>\*</sup>-alumina in this laboratory [6]. The spectroscopy was done using a continuous pumped dye laser to probe the  ${}^{5}D_{0}\rightarrow{}^{7}J_{1-4}$  region and a pulsed dye laser to probe the  ${}^{5}D_{0,1,2}\rightarrow{}^{7}F_{J}$  regions. The major findings were that the europium ion occupies three sites, two of which were assigned as different mO sites (569 nm and 576 nm) and one as a BR site (578 nm). The central assumption of the thesis was that the europium emission at 572 nm was a  ${}^{5}D_{0}\rightarrow{}^{7}F_{1}$  transition and all the site assignments were based on that assumption [7].

The only other spectroscopic work performed on  $Eu^{+3}\beta^{"}$ -alumina [3] used a fluorimeter. Two distinct types of fluorescence spectra excited in the  ${}^{5}D_{2}$  and  ${}^{5}D_{1}$  regions were reported for the  $Eu^{+3}$  ion and associated with BR and mO-type

emission. The work was done at 77 K and the authors concluded that several sites could be contributing to either type of spectrum. The spectrum assigned to the BR site contradicted the assignment made by the previous worker [6].

#### 1.3 Statement of the problem

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This work was undertaken to clarify site assignments and to examine whether energy transfer could be occurring in this system. It was felt that a careful study of the 572 nm-emission was required in order to address the question of conflicting site assignments. Can the 572 nm-emission be solely attributed to  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition ? Could it possibly be a  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  ? If energy transfer is occurring, how does it affect the spectroscopy of the Eu<sup>+3</sup> ion in  $\beta$ "alumina ? Can any conclusions be reached concerning the energy transfer mechanism ?

To avoid erroneous assignments, the spectroscopy was done using a pulsed dye laser to probe the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0-4}$  region, recording both excitation and emission spectra at liquid helium temperatures to minimize inhomogeneous broadening.

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EXPERIMENTAL

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#### 2.1 Experimental Section

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The acquisition of site selective spectra was done using an excimer pumped grazing incidence dye laser.

The excimer laser was a Lumonics Series TE-860-3 laser. These lasers are used as pump sources because they can generate intense pulses of radiation from the vacuum UV to the visible region depending on their gas fill. The Series TE-860-3 operates on the basis of transverse electrical excitation of a lasing gas mixture. This allows the excitation of the gas at relatively high pressure (3 atm) while keeping the voltages within reasonable limits. In our laboratory, the XeCi fill was used. The transitions responsible for lasing are between electronic states of the XeCI molecule. The formation of the molecule only occurs in the excited state which has a very short lifetime (nsec). The formation of the "excimer" gas therefore occurs during the laser discharge. The electrical discharge must have an extremely fast risetime and the lasing pulses produced are typically in the 10 nsec-range. Our excimer was filled with the following proportions of gases: 100 torr of helium, 388 torr of xenon, 41 torr of HCl introduced first followed by helium up to a total of 50 psi. With such a mixture, lasing occured at 308 nm.

The grazing incidence dye laser was built in our laboratory following Littman's design (Ch. 3, ref. 10). Figure 3 presents a schematic view: The



Figure 2: The grazing incidence dye laser

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dye laser is pumped by a fraction of the excimer laser output (ca 10%) reflected off a quartz beamsplitter (BS1). After passing through a pinhole plate (PH1), the beam is directed through a dye cell containing the appropriate dye circulated to avoid heating) - to a cavity mirror (M1). The laser cavity is made of M1, M2 (tuning mirror), the dye cell (oscillator), the grating and M3. Once lasing is achieved, the cavity output is reflected from M3 through another pinhole (PH2) to M4. The laser radiation is then passed through the first amplifier (AMP1). The power is increased by a factor of two by excimer radiation collected off BS2 and directed through a lens (L1). The laser beam is then reflected off M5 to M6 point at which it goes through a second amplifier to be again increased by a factor of two. The oscillator is tuned by means of M2 and the grating. The angle between these two components is calculated using:

$$\sin\phi = \lambda m/x - 1 \tag{1}$$

where  $0 \le \lambda/x \le 2$  and

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where  $x = (No. of grating lines per m)^{-1}$ 

 $\lambda =$ lasing wavelength

 $\phi$  = diffraction angle

m = diffraction order (1)

Thus, for: a 2400 grooves/mm grating,  $x = 4.17 \times 10^{-7} \text{ m}$ 

a 1800 grooves/mm grating,  $x = 5.56 \times 10^{-7} m$ 

a 3600 grooves/mm grating,  $x = 2.78 \times 10^{-7} m$ 

Table 2 lists some of the diffraction angles desired to achieve lasing with the

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Dye	Lasing λ (m)	ф <sub>1800</sub> (°)	ф <sub>2400</sub> (°)	ф <sub>3600</sub> (°)
R560	550E-9	-	18.6	77.9
Coumarin	420E-9	-	0.4	30.7
Coumarin	480E-9	-	8.7	46.6
R590	590E-9	-	24.5	-
Nile blue	690E-9	13.9	40.9	-
R560	560E-9	0.4	20.6	•
R590	570E-9	1.4	21.5	-

# Table 2: Desired angle between tuning mirror and gratingrequired to achieve lasing with the grazingincidence dye laser.

This work was performed at liquid nitrogen and liquid helium temperatures using an Oxford Instruments cryostat, model CF204 (Figure 3), a DTC2 temperature control unit and a GFS300 transfer tube. The CF204 is a continuous flow instrument. The sample is mounted on a sample holder which is inserted from the top of the cryostat. The temperature is continuously variable and easily stabilized. The cryostat is made of aluminium alloy, copper and stainless steel. The sample compartment is surrounded by a gold plated radiation shield and an outer vacuum case. The sample chamber has five windows, including on at the bottom of the cryostat which provides flexible excitation geometries. The coolant flows from a transfer tube down the feed capillary and into the gold plated copper heat exchanger. It leaves the heat exchanger by a stainless steel tube and passes through a second heat exchanger, which cools the radiation shield, before entering the helium return line. After insertion of the sample, the sample chamber is flushed of ambiant air and filled with helium gas at ca 4 psig pressure. The outmost cryostat chamber is pumped to a near vacuum with a diffusion pump and coolant transfer is then initiated.

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Figure 3: The Oxford Instruments Model CF204 cryostat

Evidence for energy transfer between two distinct crystallographic europium sites in Eu<sup>+3</sup> $\beta$ "-alumina and between Eu<sup>+3</sup> and Sm<sup>+3</sup> in co-doped  $\beta$ "-alumina [Chem. Phys. Lett. <u>182</u>(2), 159 (1991)]

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This manuscript presents the first evidence observed which could be linked to energy transfer, namely the occurrence of a risetime when measuring the decay of the Eu<sup>+3</sup> fluorescence in the  ${}^{5}D_{0}\rightarrow{}^{7}F_{2}$  region. At the time, the first lowtemperature selectively excited spectra of Eu<sup>+3</sup> $\beta$ "-alumina and the samariumeuropium co-doped species had just been recorded (at 77 K). Two distinct spectra (Figure 2) were associated Eu<sup>+3</sup> ions in BR and mO sites. The mO-type emission was assigned on the basis of the observed splittings, consistent with group theory. The other type of spectrum having features so distinct from the former, was assigned by deduction to the only other crystallographic possibility, i.e. to Eu<sup>+3</sup> ions occupying the BR sites.

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# STATEMENT OF CONTRIBUTIONS

The work presented in this manuscript was performed under the direction of D. J. Simkin. The sample was provided by B. Dunn. The data were acquired and interpreted by M.Laberge who also wrote the manuscript.

ANTI-STOKES LUMINESCENCE AND ENERGY TRANSFER IN  $\text{Eu}^{*3}\beta^{*-}$  alumina

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Dye-laser excitation into the  ${}^{5}D_{0}$  level of Eu ${}^{2}\beta$ "-alumina results in anti-Stokes luminescence above 35 K. The temperature dependence of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  emission is consistent with the occurrence of phonon-assisted energy transfer between europium ions located in different sites. Our results are also indicative of some unusual competition between upward and downward energy transfer.

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It has recently become clear that the ß"-aluminas have properties that make them especially well-suited as hosts for spectroscopic energy transfer investigations [1]. Na<sup>+</sup> β"-alumina or Na<sub>1+x</sub>Mg<sub>x</sub>Al<sub>11,x</sub>O<sub>17</sub> belongs to centrosymmetric space group R3m and has a structure known to consist of Al<sup>+3</sup> and O<sup>-2</sup> ions arranged in closely packed spinel blocks (11.3 Å-thick) separated by a conduction plane (3.9 Å-thick) containing O<sup>-2</sup> and mobile Na<sup>+</sup> ions . These sodium ions occupy Beevers-Ross (BR) sites which correspond to position 6c in Wyckoff notation [2,3]. In Eu<sup>+3</sup> - exchanged  $\beta$ "-alumina, the conduction plane has two sites available for the rare earth. With space group R3m relaxed to non-centrosymmetric R3m, 96% of the Eu<sup>+3</sup> ions preferentially occupy an octahedral mid-oxygen (mO) site -Wyckoff position 9d -, coordinated to eight oxygen atoms, six of which are located in adjacent spinel blocks with the remaining two in the same conduction plane as the Eu<sup>+3</sup> ions. The rest of the Eu<sup>+3</sup> ions occupy the 6c tetragonal BR site, coordinated to three oxygens in one spinel block and to one oxygen in another [4]. The symmetry of the mO and BR sites respectively belongs to the  $C_{2h}$  and  $C_{3v}$  point groups [5,6]. To date, there are of the Sm<sup>+3</sup> exchanged  $\beta$ "-alumina available. But no x-ray studies single-crystal diffraction studies performed on Gd<sup>+3</sup> and Nd<sup>+3</sup>  $\beta$ <sup>\*</sup>-aluminas

show structures and sodium substitution patterns similar to that of the Eu<sup>+3</sup> species [4]. At UCLA, trivalent rare earth ions are now routinely incorporated in sodium  $\beta$ " alumina using single or double-doping techniques. In the latter case, simultaneous addition of both sensitizer and activator ions has yielded crystals in which energy transfer was seen to occur. The first evidence was observed in Ce+3 - Nd+3 B"-alumina and in the Ce+3 - Tb<sup>+3</sup> and Ce<sup>+3</sup> - Pr<sup>+3</sup> couples as well [1]. The purpose of this work was to investigate possible energy transfer in the europium-samarium co-doped  $\beta$ ". The couple was selected because of the close proximity of the samarium  ${}^{4}G_{5/2}$  and the europium  ${}^{5}D_{0}$  levels ( $\Delta E = 600 \text{ cm}^{-1}$ ) (Figure 1) and because spectroscopic data were available on Eu<sup>+3</sup> ß"-aluminna [7]. Recent broadband [5] and resonance fluorescence [8] results also confirm that the Eu<sup>+3</sup> ion occupies sites consistent with crystallographic mO and BR positions. ln.  $Sm^{+3}$   $\beta$ "-alumina, the emissions of interest, that is from the lowest Stark component of the <sup>4</sup>G<sub>5/2</sub> level to the three levels of the <sup>6</sup>H<sub>5/2</sub> ground state and to the four levels of the <sup>6</sup>H<sub>7/2</sub> level occur between 555 and 580 nm and between 595 and 620 nm respectively. In this work, we wished to address the question as to whether energy transfer could be observed in the Sm-Eu co-doped  $\beta$ " from the  ${}^{4}G_{5r2}$  samarium level to europium's  ${}^{5}D_{0}$  level. Further, could one or more of europium's sites be identified as a preferred acceptor site ?

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 $\beta$ "- alumina crystals were exchanged as previously described [1, 9] with concentration of 7.9 x 10<sup>20</sup> Sm<sup>+3</sup> ions/cc., with samarium in the europium in the same concentration and with both europium and samarium in a 1 Sm: 4 Eu ratio. The samples were heat-treated at 300 °C for some 6 to 24 hours before experiments. Within this range, differences in the amount of time the samples were subjected to heat did not affect results. Broad band emission spectra of the crystals were obtained using a Lumonics TE-861M-3 excimer laser with XeCI fill (308 nm). Resonance fluorescence measurements were made using a pulsed dye laser designed according to Littman [10] and pumped by the excimer laser. Exciton rhodamine 590 was used in the 565 to 590 nm-range. The emission spectra were obtained with a Spex 1702 3/4 m monochromator using a 1200 grooves/mm grating in first order. With 100-mm-slits, the spectral bandpass was 3.5 cm<sup>-1</sup> at 575 The detector was a Hamamatsu R928 photomultiplier tube and the nm. data were collected with a EG&G PAR boxcar averager, model 4400. Resonant, continuous wave spectra were obtained on a Spectra Physics 375 dye laser pumped by a Spectra Physics 164 argon ion laser. Exciton rhodamine 560 was used in the 545 to 565 nm-range. The dye laser output was less than 2 cm<sup>-1</sup> at 560 nm. The emission spectra were recorded with a Ramanor U-1000 (ISA) double monochromator with a 1800

grooves/mm grating. The signal was detected by a cooled RCA C31034-02 photomultiplier tube in photon counting mode and processed through the ISA Model 980028 data acquisition and microcomputer interface system. The low temperature work was performed with liquid nitrogen (77K) using an Oxford Instruments continuous flow cryostat (CF204).

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#### 3. RESULTS AND DISCUSSION

#### 3.1 Site-to-site energy transfer in Eu - $\beta$ "- alumina

We have presented elsewhere [8] the site distributions observed in Eu<sup>+3</sup> exchanged B" which were found to be in agreement with the x-ray structural data [4] and previous broadband fluorescence work [5]. Relevant to this discussion are the three spectra shown in Figure 2. The splittings observed in the spectrum resonantly excited at 577 nm (bottom), i.e. 1,3,5 for J = 0, 1, 2 are consistent with  $C_{2h}$  symmetry and it has been assigned to europium ions inan mO site [5,8]. The spectrum resonantly excited at 569 nm (middle) is representative of europium ions in a BR site. The top of the figure shows the excimer-excited broadband spectrum of Eu<sup>+3</sup>  $\beta$ ". We observe that the broadband spectrum has a shoulder at 608 nm which is too pronounced to be accounted for by the sum of the sites. We suspected that this increased emission at 608.1 nm could be dueto energy transfer between the BR and mO sites. The possibility of recording  ${}^{5}D_{1} \rightarrow {}^{1}F_{1}$  emission in the broadband spectrum was dealt with by introducing a 50 µsec-delay in the acquisition which corresponds to the lifetime of the <sup>5</sup>D, state [7,8]. To verify our assumption, we accordingly performed lifetime measurements at both 608.1 nm (BR site <sup>7</sup>F<sub>2</sub>) and 610.8 nm (mO

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site <sup>7</sup>F<sub>2</sub>). At 77 K, the measurements both yielded similar decay times (Table I), i.e 1.10 and 1.18 ms respectively. At 300 K however, the BR site <sup>7</sup>F<sub>2</sub> lifetime (1.50 ms) was longer than that of the mO site  ${}^{7}F_{2}$  (1.14 ms) and we could also observe a risetime (ca. 100 ms) which was not seen at the mO site (Figure 3). That the decay times are faster at 300 K than at 77 K is not unprecedented: In their study of europium energy migration in EuMgAl<sub>11</sub>O<sub>19</sub>, a compound whose magnetoplumbite structure is closely related to that of β"-alumina, Blasse et al. [11] showed that rise times such as observed here were due to energy transfer between europium ions located in different sites. Moreover, they showed that energy transfer could occur between Eu<sup>+3</sup> ions in the same plane as well as between Eu<sup>+3</sup> ions in different planes with the first process being faster than the second. As temperature is increased, the lifetimes would also increase over the region where energy transfer between different planes predominates. In β"-alumina, this would imply a transfer distance between planes of 11.3 Å which compares well with the 12 Å-interplane distance in EuMgAl<sub>11</sub>O<sub>19</sub>.

3.2 Sm<sup>+3</sup> to Eu<sup>+3</sup> energy transfer in co-doped Sm<sup>+3</sup>:Eu<sup>+3</sup> β<sup>n</sup>

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Figure 4 shows the broadband spectra of all three  $\beta$ " samples studied. In the co-exchanged  $\beta$ "-alumina, the quenching of the  ${}^{6}H_{5/2,7/2} \leftarrow {}^{4}G_{5/2}$ 

samarium emission coupled to the increased europium  ${}^{7}F_{2}$  emission at 608.1 nm shows that highly efficient energy transfer is occurring from samarium to europium ions in BR sites. At 77 K, decay times measured in co-doped species (cf Table I) compare well with the measurements the recorded for  $Eu^{+3}-\beta$ " with the exception that a rise time is also observed at 608.1 nm. Table I also shows that, at 300 K, the presence of samarium along with europium in  $\beta$ " does not significantly affect the europium BR site capacity to accept energy. But at 77 K, in the presence of samarium, the europium BR site becomes an acceptor as indicated by the rise time observed at 608.1 nm. We could not distinguish whether samarium directly transfers <sup>4</sup>G<sub>5/2</sub> energy to europium's <sup>5</sup>D<sub>0</sub> level or whether its incorporation into the  $\beta$ " matrix somehow induces europium mO-to- BR site transfer of the type observed at 300 K in the Eu<sup>+3</sup> crystal. To address this question, we excited resonantly into the samarium <sup>4</sup>G<sub>5/2</sub> level. The results (Figure 5) show that whenever quenching of samarium emission (595 nm) occurs, europium BR-site <sup>7</sup>F<sub>2</sub> (608 nm) emission occurs. The 560.9-excited spectrum shows no samarium quenching and the europium <sup>7</sup>F<sub>2</sub> emission is more of the mO-site type, i.e not blue-shifted. All the data are consistent with the occurence of energy transfer with a BR-site europium as acceptor. The continuous wave results point to the samarium  ${}^{4}G_{52}$  level as a possible donor. But, in the absence of site-selective data for samarium, caution must be

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exercised. This ion is not a good candidate for site-selective studies because its ground and first excited states are both degenerate. But the fact that its 595 nm-emission is not quenched upon 560.9 nm-excitation while being quenched at other excitations suggests that samarium, like its rare earth counterparts [4], also has different sites, some of which could be donors and others not. More work is required to fully address the dynamic and mechanistic questions. Lifetime measurements as well as selectively acquired spectra recording the ground state emission, should provide answers concerning the presence of different sites for samarium.

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TABLE	l:	Lifet	limes	s reco	orded i	n th	e	<sup>5</sup> D <sub>0</sub> →	<sup>7</sup> F <sub>2</sub>	regior	n for
	Eu	+ <sup>3</sup> β"	and	Sm <sup>+3</sup>	:Eu+³-f	" wi	ith	excin	ner	excita	tion.
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	Eu⁺³β"	Sn		
	610.8 nm	608.1 nm	610.8 nm	608.1 nm
300 K:	1.14 ms	1.50 ms *	0.85 ms	1.44 ms *
77 K:	1.18 ms	1.10 ms	1.10 ms	1.10 ms *

# ACKNOWLEDGEMENTS

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FIGURE CAPTIONS:

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- FIGURE 1: The free ion energy levels of Eu<sup>+3</sup> and Sm<sup>+3</sup> in Sm<sup>+3</sup> β", the emission from the lowest Stark component of the  ${}^{4}G_{5/2}$  level to the  ${}^{6}H_{5/2}$ ground state occurs at 560, 564 and 576 nm; the emission to the  ${}^{6}H_{7/2}$  level occurs at 589, 597, 600 and 605 nm. In Eu<sup>+3</sup>β", the  ${}^{7}F_{0}\leftarrow {}^{5}D_{0}$ ,  ${}^{7}F_{1}\leftarrow {}^{5}D_{0}$ ,  ${}^{7}F_{2}\leftarrow {}^{5}D_{0}$  emissions occur between 565 and 580 nm, 580 and 604 nm and 605 and 623 nm, respectively.
- FIGURE 2: Emission spectra of Eu<sup>+3</sup>β"-alumina recorded at 77 K. Top: excited at 308 nm; middle: resonance fluorescence excited at 569 nm; bottom: resonance fluorescence excited at 577 nm.
- FIGURE 3: Emission decay of  $Eu^{+3}\beta^{*}$  recorded at 608.1 nm, 77K. Insert: rise time.
- FIGURE 4: Emission spectra of the β<sup>\*</sup>-aluminas excited at 308 nm and recorded at 77 K. Top: Sm<sup>+3</sup> - exchanged; middle: Eu<sup>+3</sup> - exchanged; bottom: Eu<sup>+3</sup>:Sm<sup>+3</sup> - exchanged
- FIGURE 5: Resonant emission spectra of Eu<sup>+3</sup>:Sm<sup>+3</sup> exchanged β"-alumina recorded at room temperature. Excitation wavelenghts are shown on each spectrum.



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**FIGURE 2** 

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Site-selective resonance fluorescence of Eu\*3

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exchanged sodium  $\beta$ "-alumina

[J. Chem. Phys. <u>96(8)</u>, 5565 (1992)]

In this manuscript, the question of conflicting site assignments was addressed (cf Introduction, p. 6). The selectively excited spectroscopy was done at liquid helium temperatures and focused on the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0-4}$  resonant emission. The 6.8 K resonant  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  emission in particular, not done by previous workers, was felt to be absolutely required for proper assignments. Hard evidence was also lacking for the assignement - arrived at by deduction - of the higher energy emission to Eu<sup>+3</sup> ions located in a BR site.

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# STATEMENT OF CONTRIEUTIONS

The work presented in this manuscript was performed under the direction of D. J. Simkin. The sample was provided by B. Dunn. The data was acquired and interpreted by M. Laberge who also wrote the manuscript.

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Site selective Resonance Fluorescence of  $\text{Eu}^{\ast 3}$  - exchanged sodium  $\beta^{\ast} alumina$ 

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## Abstract

Site selective excitation of Eu<sup>+3</sup> β<sup>n</sup>-alumina into the <sup>5</sup>D<sub>0</sub> level (568 to 579 nm) shows that the europium ion occupies at least two types of site distributions. The first distribution occurs at the higher energy of the tuning range and has site symmetry C<sub>3v</sub> or C<sub>3</sub>. It corresponds to the crystallographic Beevers-Ross (BR) position. The other site distribution is observed at lower energy and is associated with the mid-oxygen (mO) crystallographic position (site symmetry: C<sub>2h</sub>). We also show that interpretation of the site-selective spectroscopy of Eu<sup>+3</sup> β<sup>n</sup>-alumina must take into account the occurrence of site-to-site energy transfer linked to vibronic coupling phenomena.

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The ability of sodium  $\beta$ "-alumina (Na<sub>1+x</sub>Mg<sub>x</sub>Al<sub>11-x</sub>O<sub>17</sub>; x = 0.67) to substitute by ion-exchange a wide variety of mono-, di- and trivalent cations has stimulated considerable interest in the optical properties of this and related materials. The crystal structure of sodium B"-alumina belongs to the centrosymmetric space group R3m<sup>1</sup>. It consists of closely packed spinel layers 11.3 Å-thick alternating with conduction planes (3.9 Å) loosely packed with O and mobile Na<sup>+</sup> ions. The idealized structure has two sites available for cation substitution in the conduction plane. They are referred to as mid-oxygen (mO) and Beevers-Ross (BR) sites (Figure 1), corresponding to 9d (mO) and 6c (BR) positions in Wyckoff notation, with site symmetry C<sub>2h</sub> (C<sub>2</sub> axis  $\perp$  c) and  $C_{3v}$  ( $C_3$  axis || c) respectively<sup>2,3</sup>. In Eu<sup>+3</sup>  $\beta$ "-alumina, 96% of the europium ions, substituting for sodium, occupy the mO sites coordinated to three oxygen atoms located in the spinel layer above and to three oxygen atoms located in the spinel layer below as well as to two other oxygens in the same conduction plane. The other europium ions (4%) occupy BR sites, coordinated to three oxygen atoms in one spinel layer and to one oxygen in another<sup>4</sup>. Table 1 shows the site symmetry selection rules. Under C<sub>2h</sub> symmetry, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  emission of europium in an unperturbed mO site should show splittings of 1, 3, 5, 7, 9 for J = 0, 1, 2, 3 and 4. Likewise, the

emission of europium in a BR site  $(C_{3v})$  should have the following splittings for J = 0, 1,2, 3 and 4: 1,2, 3, 5 and 6. Previous Eu<sup>+3</sup>  $\beta$ " spectroscopic investigations<sup>5,6</sup> failed to discuss such splittings when attempting to clarify the site occupancy of the europium ion. In one publication<sup>5</sup>, the Eu<sup>+3</sup> fluorescence from the  ${}^{5}D_{2}$  and  ${}^{5}D_{1}$  levels was interpreted in terms of unusual bonding and coordination characteristics as well as showing the existence of different types of mO and BR sites. In this laboratory, Brown and Simkin<sup>6</sup> three specific sites to europium ions in 34% exchangedassigned Na<sup>+</sup>β<sup>\*</sup>-alumina on the basis of continuous wave emission spectra covering the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1,2}$  region. More recently, Laberge and Simkin<sup>7</sup> reported evidence for the occurence of europium-to-europium energy transfer in 20% exchanged Na<sup>+</sup> $\beta$ "-alumina. The present study was undertaken to clarify site assignments in the light of energy transfer processes. Since a J=0 transition can not be split by the crystal field, we felt that site assignments - complex in the presence of energy transfer - would be facilitated by also recording the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  emission upon resonant excitation.

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### II. EXPERIMENTAL

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The sample of Eu<sup>+3</sup><sup>β</sup>"-alumina used in this work was grown and ion-exchanged by methods described previously<sup>8</sup>. The europium concentration in the crystal was 7.9 x 10<sup>20</sup> ions/cc (20% of Na<sup>+</sup> ions exchanged for Eu<sup>+3</sup>). The sample was heat-treated at 300° C for 6 to 24 hours before experiments. Differences in heat-treatment times did not affect the results within this range. Resonance fluorescence measurements were performed using a pulsed dye laser based on the design of Littman and Metcalf<sup>9</sup> and pumped with an excimer laser (Lumonics TE-861M-3) using a XeCI gas fill (308 nm). Exciton rhodamine 590 was used in these experiments. The emission spectra were obtained with a Spex 1702 3/4 m monochromator using a 1200 grooves/mm grating in first order. With 100-µ slits, the spectral bandbpass was 3.5 cm<sup>-1</sup> at 575 nm. A mechanical chopper was used to block the monochromator slits from the exciting laser pulse. A 500 µs-delay ensured that the resonance fluorescence could be recorded in the absence of stray laser light. The detector was a Hamamatsu R928 photomultiplier tube and the data were collected with a EG&G PAR boxcar averager, model 4400 and digital signal processor. The low temperature work was performed with liquid helium using an Oxford Instruments continuous flow cryostat (CF204). Polarized emission spectra were recorded with the incident radiation

along the crystallographic c-axis of the crystal ( $E_{incident} \perp c$ ) and the detection perpendicular to the incident laser. A sheet polarizer was followed by a quarter-wave plate with its axis at 45° to that of the polarize. The light entering the monochromator slits was thus circularly - and not linearly polarized. In this geometry, the site-selective emission spectra were recorded either with  $E \parallel c$  ( $\sigma$ ) or with  $E \perp c$  ( $\pi$ ).

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## **III. RESULTS AND DISCUSSION**

Figure 2 shows the inhomogeneously broadened emission spectrum of Eu<sup>+3</sup>  $\beta$ "-alumina, excited in the charge transfer region at 308 nm. The emission of interest (  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  ) is found between 565 and 579 nm. In Figures 3 and 4, we present the resonance fluorescence spectra which result from tuning excitation through this region, recording the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0,1,2}$  emission at 77 and 6.8 K respectively. At 77 K, two types of emission spectra can be recognized: first, in the spectra obtained with higher energy excitation (Fig. 3, bottom), we observe several relatively intense features in the  ${}^{7}F_{0}$  region and two broad emissions in the  ${}^{7}F_{2}$  region; in the lower energy spectra, we observe a single emission in the  ${}^{7}F_{0}$  region and several relatively intense peaks in the  ${}^{7}F_{2}$  region. We correlate the observed spectra with the site symmetries expected from the x-ray results<sup>2,3</sup> as follows:

# A. The mid-oxygen site distribution

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We assign the spectra obtained upon 576.1 and 577.2 nm-excitation to the mO (Wyckoff 9d) site as they show the expected  $C_{2h}$  splittings, i.e. 1, 3, 5, 7, 9 for J = 0, 1, 2, 3 and 4 (cf Fig.4, two top spectra and Fig.5,

top). We note that the peaks are not totally symmetrical, which is suggestive of an mO site distribution rather than a single, specific site. We also note that the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  emission is very intense. This transition is known to be electric dipole in character. As such, it is thus forbidden for europium ions located in a centrosymmetric site<sup>10,11</sup>. In this spectrum, it clearly predominates over the magnetic dipole - allowed transition ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ observed between 580.5 and 600 nm). Niewpoort, Blasse and Bril<sup>12</sup> have shown convincingly that forbidden electric dipole transitions can become allowed through the mixing of orbitals of opposite parity which can occur if the inversion center is slightly distorted at the site<sup>11</sup>. It should be noted that europium is substituting in a mobile ion system (conduction plane) and that idealized site symmetry is therefore not expected to occur. Loss of inversion symmetry has also been proposed in the case of Nd<sup>+3</sup>  $\beta$ "-alumina<sup>13</sup>, whose x-ray structure is very similar to that of the europium species.<sup>4</sup> Excitation at both 577.2 and 578.6 nm yield similar mO-type spectra, for which we performed crystal field calculations. Assuming C<sub>2h</sub> symmetry, we estimated crystal field parameters using the observed splittings and parameters calculated from the x-ray atomic positions<sup>4</sup> which yield coordinates for Eu<sup>+3</sup> located in an mO site. The B<sub>ko</sub> parameters obtained point charge calculations over a 100 Å - exploration sphere were from used as starting parameters for the crystal field calculations. Table 2

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compares the observed and calculated peak positions for the spectrum excited at 577 nm using these  $C_{2h}$  crystal field parameters and including the effects of J mixing following the method described in reference 14. The fit is reasonable and supports further the  $C_{2h}$  character of the emissions observed at 576.7 and 577.2 nm.

### B. The BR site distribution

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Inspection of the spectra obtained when exciting between 567.0 and 573.3 nm does not show a spectrum with the splittings expected for the other crystallographic site (BR) of  $C_{3v}$  symmetry, i.e. 1, 2, 3 for J = 0, 1 and 2 : we never observed a single peak for J = 0. If we divide the tuning range into regions of related spectra, we note that the spectra excited at 77 K between 567 and 572.2 nm show similar spectral features characterized by: a) extra structure in the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  region, b) a  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  emission distinct from that of the  $C_{2n}$ -type of spectra and c) the presence of anti-Stokes luminescence at ca. 100 cm<sup>-1</sup> from the resonance line (cf.Figure 3).

At 6.8 K (Figure 4), the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  extra structure becomes well-resolved into lines separated by ca. 30 cm<sup>-1</sup> with particularly intense emission from the line located at ca 100 cm<sup>-1</sup> from the resonance line. We also note the

absence of anti-Stokes. luminescence and that the  ${}^5D_0{\rightarrow}{}^7F_2$  emission is different from that observed at 77 K for the spectra excited between 570.5 and 573.3 nm. We assign these spectra to europium ions located in BR sites on the basis of their strong  ${}^{5}D_{0} \rightarrow {}^{7}\overline{F_{0}}$  emission  ${}^{15,16}$  (electric dipole allowed under C<sub>av</sub>), the documented correlations associating a large energy separation between the  $\,^5\text{D}_{0}\,$  and  $\,^7\text{F}_{0}\,$  levels with large europium-to-ligand distances and the observed splittings of the  ${}^{7}F_{3}$  and  ${}^{7}F_{4}$  regions (Fig. 5, bottom) in which the required 5 and 6 peaks can be recognized, as expected for  $C_{3v}$  symmetry. The presence of extra structure in the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ region in excess of the one peak predicted by group theory for Cav symmetry suggests that we are observing several  ${}^5D_0{\rightarrow}{}^7F_0$  emissions, each belonging to europium ions located in BR sites having a slightly different local environment. The extra structure, however, is always observed to the energy side of excitation. This behavior led us to invoke the low occurrence of vibronic sidebands. IR<sup>18</sup> and Raman<sup>19,20</sup> results show a rich vibrational structure for Na<sup>+</sup> β<sup>\*</sup>-alumina. The low-frequency infrared spectrum is very complex and not well-resolved but the interpretation associates the observed bands to sodium-oxygen vibrations without specifying if the oxygens are located in the spinel or conduction layers. The Raman results are much better resolved. At 15 K, they feature a sharp band at ca. 111 cm<sup>-1</sup>, assigned to a phonon of the spinel block. As such,

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it is a characteristic of all  $\beta$ <sup>\*</sup>-aluminas, since rare earth substitution occurs in the conduction plane and not in the spinel layers. Of particular interest is the frequency of a band located at ca. 33 cm<sup>-1</sup>, which is interpreted as the "attempt" frequency mode for sodium conduction. To verify our assumption, we plotted the spectra so as to display them with respect to excitation set at zero (Figs 6 & 7). It is clear that there is structure which does not shift with excitation, especially the peak found in Fig. 6 at from excitation (corresponding to the emission observed at ca 725 cm<sup>-1</sup> 591-593 nm in Figs 3 & 4). We accordingly label this emission vibrational. We also note that the strong emission at ca. 100 cm<sup>-1</sup> does shift with respect to excitation. At 570.6 nm-excitation (the excitation at which the anti-Stokes luminescence begins to occur at 77K) we observe the emergence of another, smaller peak from beneath this one. We believe that this is indicative of the coincidence at about 572 nm of both the  ${}^{7}F_{1}$  of one site and either a vibronic sideband or the  ${}^{7}F_{a}$  of another site. We were unable to perform crystal field calculations on these spectra because we could not identify the <sup>7</sup>F<sub>0.1,2</sub> components, as required for the fitting procedure to be meaningful.

To characterize this region further, we acquired polarized emission spectra. As mentioned above, The BR site should have  $C_{3v}$  symmetry in the idealized crystal. Previous workers<sup>4</sup> have argued for a reduction in symmetry

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to  $C_3$  as a result of the superlattice structure. The polarized emission is consistent with either symmetry provided that the main C<sub>3</sub> symmetry axis is parallel to the crystallographicc-axis, which is the case. The polarization therefore does not depend on the orientation of the ab crystal plane with respect to the direction of observation. Figure 8 shows the polarized emission spectrum obtained upon 569 nm-excitation. The peak at ca 592 nm, assigned as vibrational above, need not be discussed further. Table 3 shows that the spectrum is in agreement with the polarization expected either under  $C_{3v}$  or  $C_3$ . Both symmetries should yield a  $\sigma$ -polarized  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  emission, which is the polarization observed for that transition. For a C<sub>3v</sub> site symmetry, we need to assign the second peak ( $\sigma$ ) to a second  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  emission, distinct from the first, observed at 569 nm ( $\sigma$ ). The emission at 583 nm ( $\pi$ ) would be the E component of the  ${}^{7}F_{1}$  emission with the A<sub>2</sub> component too weak to be observed (magnetic dipole) or contained within the broad envelope of the 583-nm peak. This would spread the <sup>7</sup>F, manifold over some 120 cm<sup>-1</sup> as expected for  $Eu^{+3}$  in a site of  $C_{3v}$  symmetry where this manifold is usually observed to range between 70 and 220 cm<sup>-1 21,22</sup>. In the C<sub>3</sub> case, the second peak ( $\sigma$ ) would be assigned as the electric dipole-allowed A component of the <sup>7</sup>F<sub>1</sub> manifold, the emission at 583 nm remaining assigned as the E component. The <sup>7</sup>F<sub>1</sub> region would then extend over some 330 cm<sup>-1</sup>, a value which is not surprising in view of the complexity of

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these spectra. The behavior of the anti-Stokes emission is consistent with this interpretation since it shifts with excitation as the 572-nm emission. Site-selecting on the high energy side of the site distribution could then lead to the simultaneaous selection of lower energy sites (differing by the amount of energy of a phonon) as well as the selected site. BR sites thus coupled would transfer energy along with the creation of one or more phonons of the appropriate frequency (ca. 30 cm<sup>-1</sup> in this case). Alternatively, there are phonons available to promote electron-phonon coupling of the type proposed by Caro<sup>23</sup> and observed by Buijs and Elasse<sup>24</sup> in the EuMgB<sub>\*</sub>O<sub>10</sub> system. These authors identified three sub-sites for europium, referred separations of ca. 24 cm<sup>-1</sup> "regular", trap 1 and trap 2 at to as (regular-trap 1) and 19 cm<sup>-1</sup> (trap 1-trap 2) with both upwards and downwards energy transfer possible. Comparison of the spectra obtained at 6.8 and 77 K (Figs 3 & 4) shows an intermediate region in the tuning range between the BR and mO site distributions (i.e the spectra excited between 570 and 573 nm) which differ at both temperatures in their  ${}^5D_0 {\rightarrow} {}^7F_2$  emission. At 6.8 K, where downward energy transfer is expected to predominate, we observe mainly a mO-type of  ${}^{7}F_{2}$  region. At 77 K, the  ${}^{7}F_{2}$  emission assumes BR character with the occurrence of  ${}^{7}F_{0}$  anti-Stokes emission, showing that upward energy transfer is now favored. We explain elsewhere25 how upward transfer could predominate over the favored downward process.

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This work shows that the  $Eu^{+3}$  ion occupies at least two site 20%-exchanged sodium ß"-alumina. Site-selective distributions in excitation in the higher energy range of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  region yields composite spectra, the result of 1) BR-multisite emission 2) spectral features belonging to the mO-type of emission (weak but recognizable) due to downwards energy transfer and 3) vibronic structure. In spite of their complexity, these spectra are consistent with  $C_{a\nu}$  or  $C_{a}$  symmetry. Excitation at lower energy yields spectra which correspond to the slightly distorted crystallographic mO position of C<sub>2h</sub> symmetry. The details of the energy transfer dynamics, obtained from lifetime measurements and site-selective excitation spectra as well as the further elucidation of the mechanism will be the object of a future publication. Preliminary results, however, confirm that the mO and BR site distributions are further characterized by different lifetimes.

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This work was supported by the Natural Sciences and Engineering Research Council of Canada. One of the authors (ML) gratefully acknowledges the same agency for their support in the form of a graduate scholarship. The U. S. Office of Naval Research is also gratefully acknowledged for their support of this work at UCLA. We also thank Dr. T. F. Belliveau for his assistance with the crystal field calculations. Į

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- FIGURE 1: Top: The Beevers-Ross site in Eu<sup>+3</sup> β"-alumina.
  A' is the conduction plane. We show four column oxygens (corners) and two sodium ions per plane (Wyckoff 6c). The plane is located between spinel layers. The crystallographic c-axis is perpendicular to the A' plane.Dark circles are oxygens; open circles are nearest oxygen neighbors. Bottom: The mid-oxygen site (After ref. 26)
- FIGURE 2: Broadband emission spectrum of Eu<sup>+3</sup> β<sup>\*</sup>-alumina (20% exchanged) recorded at 77 K.
- FIGURE 3: Resonance fluorescence spectra of Eu<sup>+3</sup>  $\beta$ "-alumina recorded at 77 K, tuning the excitation through the  ${}^{5}D_{0} \leftarrow {}^{7}F_{0}$  region. The excitation wavelength is shown on the left.
- FIGURE 4: Resonance fluorescence spectra of Eu<sup>+3</sup>  $\beta$ "-alumina recorded at 6.8 K, tuning the excitation through the  ${}^{5}D_{0} \leftarrow {}^{7}F_{0}$  region. The excitation wavelength is shown on the left.
- FIGURE 5: Resonance fluorescence spectra of the  ${}^{7}F_{3}$  and  ${}^{7}F_{4}$ regions of Eu<sup>+3</sup>  $\beta$ "alumina recorded at 6.8 K. The excitation wavelength is shown on the left.
- FIGURE 6: Expansion of the  ${}^5D_0 \rightarrow {}^7F_0$  region of the 6.8 K Eu ${}^{*3}$   $\beta$ " spectra plotted as shift from excitation  $\lambda$ .

FIGURE 7: Expansion of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0,1}$  region of the 77 K Eu\*<sup>3</sup>  $\beta$ " spectra plotted as shift from excitation  $\lambda$ .

FIGURE 8: Polarized emission spectra of Eu<sup>+3</sup>  $\beta$ "-alumina recorded at 6.8 K.  $\lambda_{ex}$ : 569 nm. [  $\sigma = E \parallel c$ ;  $\pi = E \perp c$ ]

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FIGURE 1 (TOP)

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🔳 mid Oxygen site



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FIGURE 2

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FIGURE 3



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FIGURE 4



FIGURE 5

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FIGURE 6

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FIGURE 7

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FIGURE 8

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ladie II site symmetry selection	Ruies
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Transition	Сзч	Czh	
<sup>5</sup> D <sub>o</sub> → <sup>7</sup> F <sub>o</sub>	Aı (ED;z)	Ag (MD;z)	
<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub>	Az (MD;z)	Ag (MD;z)	
0	E (ED;x,y)	28g (MD; 7)	
<sup>5</sup> D → <sup>7</sup> F	AL (ED;z)	3Ag (MD;z)	
0 2	2E (ED;x,y)	28g (MD;x,y)	
<sup>5</sup> D <sub>2</sub> → <sup>7</sup> F	AL (ED;z)	3Ag (MD;z)	
•	2A2 (MD;z)	4Bg (MD;x,y)	
	2E (ED;x,y)		
<sup>5</sup> D_→ <sup>7</sup> F	2A1 (ED;z)	5Ag (MD;z)	
0 4	Az (MD;z)	4Bg (MD;x,y)	
	3E (ED;x,y)		

TABLE 2: Observed and calculated peak positions of the mD

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site excited at 577. 2 nm and of Czh symmetry.

Crystal field parameters (cm<sup>-1</sup>):  $B_0^2 = -1083.50$ ;  $B_1^2 = 345.37$  (r), -106.07 (i);  $B_0^2 = 945.29$ ;  $B_2^2 = 50.68$  (r), -91.41 (i);  $B_{41}^4 = 500.12$  (r), 3.60 (i);  $B_0^2 = 1299.0$ ;  $B_2^2 = 0.18$  (r), 658.39 (i)  $B_4^2 = 39.49$  (r), -54.65 (i).

Transition	Peak position		
	Ot	served	Calculated
	(nm) (d	:# * from exc.)	(cm from exc.)
"D"F			
°0 °	577.2	0.00	0.00
<sup>9</sup> D. —→ <sup>7</sup> F.		102.10	104 01
0 1	283.3	187.10	190.86
	341.3	418.80	423.05
	24/1/	394.20	286.74
'D'F_			
0 2	611.0	958.40	947.30
	614.5	1051.60	1042.31
	616.5	1104.40	1111.68
	617.5	1130.70	1128.99
	623.0	1273.65	1287.38
D → <sup>7</sup> F			
0 3	648.0	1892.90	1902.32
	649.0	1916.70	1919.32
	630.0	1940.40	1942.19
	652.0	1987.60	1991.12
	634.3	2046.20	2047.31
	656.0	2001.10	2065.85
	637.0	2104.30	2102.59
D <sub>0</sub> → <sup>7</sup> F <sub>4</sub>	684.0	2705.10	7710.94
- •	688.0	2790.10	2781.68
	693.0	2895.00	2892.0
	695.0	2736.50	2938.19
			2975-61
	697.5	2988.10	2987.94
	703.0	3100.30	309 63
		3120 50	3125.59
	704.0	3120.30	

Point Group Сэч C3 - -<sup>5</sup>D<sub>o</sub>→<sup>7</sup>F<sub>o</sub> A1 (σ) A (0)  ${}^{5}D_{O} \rightarrow {}^{7}F_{1}$ A2 (π) A (0) Ε (π) Ε (π)  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ A1 (0) A (σ) **2E (**π) 2E (π)

Table 3: Polarization of transitions

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[ $\sigma$  refers to  $\vec{E} \parallel c$  and  $\pi$  to  $\vec{E} \perp c$  polarizations]

# Anti-Stokes luminescence and energy transfer

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in Eu<sup>+3</sup>β"-alumina

[Solid State Commun. 81(10), 873 (1992)]

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This manuscript proposes a scheme for the site-to-site energy transfer occurring in Eu<sup>+3</sup>β"-alumina. The anti-Stokes experiment also confirms the conclusions of the previous manuscript with respect to the presence of a  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  emission at 572 nm. Indeed, if this emission was solely a  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  emission, no spectrum would result when exciting at 3.5 K.

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# STATEMENT OF CONTRIBUTIONS

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The work presented in this manuscript was performed under the direction of D. J. Simkin. The sample was provided by B. Dunn. The data were acquired jointly with M. Nafi (same research group). The results were interpreted by M. Laberge who also wrote the manuscript.

# ANTI-STOKESLUMINESCENCE AND ENERGY TRANSFER IN Eu+3B\*-ALUMINA

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Dye-laser excitation into the  ${}^{5}D_{0}$  level of Eu ${}^{+3}\beta^{*}$ -alumina results in anti-Stokes luminescence above 35 K. The temperature-dependence of the  ${}^{5}D_{0} \longrightarrow {}^{7}F_{0}$  emission is consistent with the occurrence of phonon-assisted energy transfer between europium ions located in different sites. Our results are also indicative of some unusual competition between upward and downward energy transfer.

#### **1. INTRODUCTION**

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Sodium B"-alumina has recently been proposed as an interesting matrix for the study of energy transfer interactions between rare earth ions [1]. The structure is known to consist of  $Al^{+3}$  and  $O^{-2}$  ions arranged in spinel blocks separated by a conduction plane in which rare earth ions predominantly substitute for the Na<sup>+</sup> ions occupying mid-oxygen (mO) sites and, to a lesser degree, Na<sup>+</sup> ions found in Beevers-Ross (BR) sites [2]. This conduction plane is not close-packed and provides an environment of flexible symmetry for the rare earth impurities. At UCLA, trivalent rare earth ions are now routinely incorporated in sodium B"-alumina (Na, Mg, Al, O, ) using single or double-doping techniques. Energy transfer in rare-earth substituted B"-alumina was first observed by Momoda et al. [1] in the Ce<sup>+3</sup>-Nd<sup>+3</sup>, Ce<sup>+3</sup>-Tb<sup>+3</sup> and Ce<sup>+3</sup>-Pr<sup>+3</sup> couples with Ce<sup>+3</sup> acting as donor. The transfer mechanisms were not fully characterized but the results were found to be consistent with the occurrence of nonradiative processes. Up-conversion was also observed in the Yb+3-Er+3 couple. More recently, Laberge and Simkin reported some evidence for energy transfer in the Eu<sup>+3</sup>-Sm<sup>+3</sup> couple as well as between europium ions in  $Eu^{+3}\beta^{n}$ -alumina [3]. Energy transfer between rare-earth ions of the same element occupying different sites has also been observed in closely related materials [4,5]. In this work, we examine one of the interesting spectroscopic features of the  ${}^{5}D_{n} \rightarrow {}^{7}F_{n}$  luminescence of Eu ${}^{+3}\beta$ "-alumina: the occurence of anti-Stokes emission at 35 K. This phenomenon is not common in crystals doped with only one rare-earth element [6,7] in the context of energy transfer and in this paper, we present the temperature dependence of this unusual emission under site-selective laser excitation.

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#### 2. EXPERIMENTAL

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The B"-alumina crystal was grown and exchanged as previously described i1] with europium concentration of 7.9 x 10<sup>20</sup> ions/cc (20% of Na<sup>+</sup> ions exchanged). The sample was heat-treated at 300°C for some 6 to 24 hours before experiments. Within this range, differences in the amount of time the samples were subjected to heat did not affect results. Resonance fluorescence measurements were made using a pulsed dye laser designed according to Littman [8] and a mechanical chopper arrangement to block the monochromator slits from the exciting laser source. The dve laser oscillator was pumped with a Lumonics TE-861M-3 excimer laser with a XeCI fill (308 nm-emission), triggered by a pulse derived from the chopper. The delay introduced by the chopper before signal acquisition was 500 µs, which is well within the limit set by the europium lifetime in this matrix ( $\tau$  = 3.0 ms @ 3 K; 2.8 ms @ 77 K). Exciton rhodamine 590 was used. Spectra were recorded using a Spex 1702 3/4 m monochromator fitted with a 1200 grooves/mm grating in first-order. The spectral bandpass was 3.5 cm<sup>-1</sup> at 572 nm with 100 μ-slits. The detector was a Hamamatsu R928 photomultiplier tube and the data were collected with an EG&G boxcar averager, model 4400. The low temperature work was performed with liquid helium, using an Oxford Instruments continuous flow cryostat (CF 204).

### 3. RESULTS AND DISCUSSION

Figure 1 shows the temperature-dependence of the Eu<sup>+3</sup>  $\beta''$ -alumina emission upon site-selective excitation at 569 nm in the  ${}^{5}D_{0}$  level. Two prominent peaks are observed: the resonance at 569 nm and a stronger peak at 572.5 nm. Figure 2 shows the same temperature range for 572 nm excitation. Three temperature regimes can be discerned under 572 nm excitation. From 3.5 k to 25 k, we observe the resonant emission peak as well as a peak ca. 576 nm. At 35 K and 45 K, we still observe the resonant and 576 nm emissions as well as the growth of an anti-Stokes emission at 569 nm. Finally, at 77 K, the Stokes emission has disappeared, leaving only the resonant and anti-Stokes emission bands.

Anti-Stokes emission is only observed ca. 100 cm<sup>-1</sup> from excitation. As such, it clearly does not originate from higher  ${}^{5}D_{J}$  levels. If this were the case, anti-Stokes luminescence corresponding to the  ${}^{5}D_{J} \rightarrow {}^{7}F_{0}$  or the  ${}^{5}D_{2} \rightarrow {}^{7}F_{0}$  manifolds should have also been observed in the 530 or 480 nm regions. Another obvious possibility could be that we are observing an electronic or vibrational Raman effect. Indeed, within the same site, the absorption of a lattice phonon could populate a component of the  ${}^{7}F_{1}$  multiplet or a vibrational sublevel of the  ${}^{7}F_{0}$  state. If that were the case, we would expect the luminescence spectra under 572 and 569 excitation to be identical. Figure 4 shows that this is not the case. We interpret these results as evidence for the occurrence of phonon-assisted energy transfer processes between Eu<sup>+3</sup> ions located in different sites. The diagrams presented in Fig. 3 help to rationalize our observations as well as Fig. 4 which shows the three types of emissions observed from the  ${}^{5}D_{0}$  level in Eu<sup>+3</sup>  $\beta$ "-alumina. They are referred as sites I, II and III for the

purposes of this discussion.

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Selective excitation into the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition of site I (Fig. 3a) followed by the creation of a phonon ( $\alpha$ )-and energy transfer from site I to site II leads to the observation of simultaneous emission from both of these sites. Due to the expected average distance between europium ions, exchange processes are not expected to occur and some form of multipolar coupling must therefore be involved. Under the same excitation conditions, as the temperature increases, the ratio of intensities of the two emissions is expected to remain approximately constant; this is fully consistent with the experimental results presented in Fig. 1.

At the very low temperatures only downward energy transfer from site If to site III is expected to occur (Fig. 3b). Consequently, at temperatures between 3.5 and 25 K, the emission spectra obtained under selective excitation into the  ${}^{5}D_{0} \rightarrow {}^{7}F_{c}$  transition of site II are expected to show the resonance at 572 nm as well as Stokes emission at 576 nm (Fig. 2). As the temperature increases, processes which require the annihilation a phonon start to occur. Fig. 3c illustrates the intermediate Of – temperature regime where such processes are expected to co-exist with the ones that were present at lower temperatures. In a simple model, involving single phonon processes with comparable phonon occupation numbers and equal multipolar coupling strengths between all relevant levels, one expects to see the scheme illustrated in Fig. 3c prevail as thetemperature is increased even further. However, as previously noted, Fig. 2 clearly shows that the growth of the anti-Stokes peak at 569 nm is accompanied by a decrease of the intensity in the Stokes peak at 576 nm (35 K to 45 K). The same figure also shows that at 77 K, the upward process predominates to the

point where emission from the site at 576 nm completely disappears. Examination of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0,1,2}$  spectra (Fig. 4) at both temperatures leads to the same conclusion. Indeed, at 6.8 K the spectrum obtained under 572 nm excitation (site II) is dominated by features that are clearly characterisitic of the emission from site III, while at 77 K it is the features from site I that predominate. These experimental data are inconsistent with the persistence of the scheme described in Fig. 3c at temperatures higher than 45 K and suggest, rather, that the process illustrated in Fig. 3d is taking place.

One possible explanation for this seemingly unusual observation is the possible existence of a very large multipolar interaction between site I and site II. Such an interaction could arise from the privileged geometrical relationship between sites I and II. In this perspective, downward energy transfer occurs only when the upward is thermodynamically impossible. The system readily follows the channel of the upward transfer as soon as it becomes physically available because of the special relationship between site I and II. The assumption that these two sites are closely coupled is further supported by the experimental fact that the 569 nm excited spectra (Fig. 1) show nearly exclusive downward energy transfer to site II (572 nm emission). In EuMgAl<sub>11</sub>O<sub>19</sub> [5], Buijs at al. invoked the distinction between intra-planar and inter-planar energy transfer to explain the unusual temperature dependence of the dynamics of the Eu<sup>+3</sup> luminescence. Considering that sodium  $\beta^{n}$ -alumina is a very similar material and that the average distance between Eu<sup>+3</sup> positions within the same plane and in two consecutive planes are

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very comparable in the two systems (5.6 Å and 11.3 Å respectively) we would expect to be able to draw similar conclusions concerning the occurrence of interplanar energy transfer: at a temperature close to 77 K, inter-planar energy transfer starts to occur because the probability of such a process becomes approximately equal to that of radiative decay. On the other hand, because of coulombic repulsions, a Eu<sup>+3</sup> located in a given site is more likely to have its first Eu<sup>+3</sup> neighbour in a different plane rather than within the same plane. Therefore, when inter-planar energy transfer processes start to occur they are likely to predominate over intra-planar processes. We suggest that this could be the explanation for our own observations.

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## ACKNOWLEDGEMENTS

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### FIGURE CAPTIONS

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- Fig. 1: Temperature dependence of the  ${}^{5}D_{0} \longrightarrow {}^{7}F_{0}$  region upon 569 nm dye-laser excitation in Eu<sup>+3</sup> $\beta$ "-alumina.
- Fig.2: Temperature dependence of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  region upon 572 nm dye-laser excitation in Eu ${}^{+3}\beta$ "-alumina.

Fig. 3:Energy transfer scheme: (a) 569 nm excitation,

at any temperature T, (b) 572 nm-excitation,

3.5 K < T < 25 K, (c) 572 nm-excitation,

35 K < T < 45 K, (d) 572 nm-excitation,

- T > 45 K. Vetical arrow indicates excitation processes,
- $(\alpha' i)$  indicates the annihilation of a phonon  $\alpha'$ ,

( $\alpha$ ) indicates the creation of a phonon  $\alpha$  and E.T stands for energy transfer.

Fig. 4:<sup>5</sup>D<sub>0</sub> $\longrightarrow$ <sup>7</sup>F<sub>6,1,2</sub> emission regions under 569 (site I), 572 (site II) and 577 nm- excitation (from bottom to top). (A) T = 6.8 K, (B) T = 77 K. Intensities in each spectrum normalized to the most intense peak.



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FIGURE 1



FIGURE 2

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FIGURE 3 (a & b)



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T > 45 K

FIGURE 3 (c & d)



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FIGURE 4 (A)



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FIGURE 4 (B)

Energy transfer in Eu<sup>+3</sup>β"-alumina

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[Submitted to J. Lumin.]

In this last section, the laser excitation spectra of  $Eu^{*3}\beta$ "-alumina acquired at CNRS Lyon are presented and the decay times are fitted to the Inokuti-Hirayama equation, thus showing that the observed energy transfer has multipole charcter.

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# STATEMENT OF CONTRIBUTIONS

The work presented in this manuscript was performed under the joint direction of D. J. Simkin and G. Boulon. The data were acquired using Professor A. Monteil's equipment with some assistance from P. Nelson. The results were interpreted by M.Laberge who also wrote the manuscript.

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# Site-to-site Energy Transfer in Eu\*3 β"-alumina

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#### Abstract

Laser excitation spectra of Eu<sup>+3</sup> $\beta$ "-alumina and resonance fluorescence decay measurements performed on the  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  emissions confirms the BR and mO multisite character of the Eu<sup>+3</sup> ion in the  $\beta$ "-matrix. The non-exponential decays and the risetimes observed show that energy transfer occurs between sites within the conduction plane by a multipole mechanism.

#### **I INTRODUCTION**

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The structure of Na<sup>+</sup> $\beta$ -alumina contains spinel blocks of closely packed Al<sup>+3</sup> and O<sup>-2</sup> ions alternating with conduction planes consisting of loosely packed Na<sup>+</sup> and O<sup>-2</sup> ions, allowing rapid migration of Na<sup>+</sup> ions. The Na<sup>+</sup> ions occupy two crystallographically equivalent sites, referred to as Beevers-Ross (BR) and anti-Beevers-Ross (aBR) sites (Wyckoff position 6d) as well as a mid-oxygen position (Wyckoff 9d) [1]. Trivalent rare earth ions can be incorporated into the conduction plane where they substitute for the Na<sup>+</sup> ions without disturbing the spinel layers, occupying either BR or mO sites [2]. The main effect of substitution is to modify the c parameter (33.54 Å in Na<sup>+</sup> $\beta$ "-alumina vs 33.190 Å in Eu<sup>+3</sup> $\beta$ "-alumina) and to distort the positions of the conduction plane ions. Figure 1 shows the sites available for substitution in Eu<sup>+3</sup> $\beta$ "-alumina.

Energy transfer between trivalent europium ions has been studied in many different crystalline systems [3-5]. Of particular interest is the work performed on lanthanum magnesium aluminate (LMA) whose structure is closely related to that of  $\beta$ "-alumina [3]. In this system, the europium ions - distributed according to these authors in four different sites - are also located in planes perpendicular to the crystallographic axis. In LMA, the separation between two Eu<sup>+3</sup> ions is 5.6 Å and 12 Å between two Eu<sup>+3</sup> located in different planes. At 4.2 K, energy transfer occurs via dipole-dipole interaction. In  $\beta$ "-alumina, high non-radiative energy transfer efficiencies were measured in crystals co-doped with both activator and sensitizer ions (Ce<sup>+3</sup>-Nd<sup>+3</sup>; Ce<sup>+3</sup>-Tb<sup>+3</sup>; Ce<sup>+3</sup>-Pr<sup>+3</sup>) [6]. In a recent site-selective study of Eu<sup>+3</sup> $\beta$ "-alumina, we assigned spectra to Eu<sup>+3</sup> ions located in two different crystallographic site distributions, namely the BR and mO distributions [7]. We also presented evidence for the occurrence of site-to-site energy transfer in this material [7-9]. This work was undertaken to complement the previous site-selective study and address the energy transfer

processes more fully. Also, previous energy transfer studies were - to our knowledge - always performed by exciting into the  ${}^{5}D_{1,2}$  levels rather than directly into the resonant  ${}^{5}D_{0}$  level. In this sense, these studies had the drawback of not being rigorously site-selective due to the occurrence of numerous accidental degeneracies in the emissions of the different manifolds. The energy transfer schemes usually proposed in these studies are thus derived from complex spectroscopic measurements, i.e a  ${}^{5}D_{2}$  population can transfer energy to another  ${}^{5}D_{2}$  site or to a  ${}^{5}D_{3}$  belonging to the same or to another site, etc. which results in far too many competing processes.

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### **II EXPERIMENTAL**

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The crystal of Eu<sup>+3</sup>B"-alumina used in this work had a concentration of 7.9 x 10<sup>20</sup> ions/cc (20% of Na<sup>+</sup> ions exchanged for Eu<sup>+3</sup> ions). The sample was subjected to heat treatment (300° C) for 8 hours before experiments. Resonance fluorescence experiments were performed using a pulsed dye (Exciton rhodamine 590) laser designed according to Littman [10] and pumped with a Lumonics TE-861M-3 excimer laser filled with XeCI gas (308-nm emission). Spectra were recorded with a Spex 1702 3/4 m monochromator fitted with a 1200 grooves/mm grating in first order. The spectral bandpass was 3.5 cm<sup>-1</sup> at 575 nm with 100-µ slits. A mechanical chopper was used to block the monochromator slits from the exciting laser pulse. The detector was a Hamamatsu R928 photomultiplier tube and the data were collected with an EG&G Parr boxcar averager, model 4400 and digital signal processor. Laser excitation spectra were measured using a nitrogen-pumped dye laser. Decay times were measured using a pulsed dye laser (R590) pumped by a frequencydoubled YAG Quantel laser, model TDL50. The luminescence was analyzed with a Jobin-Yvon monochromator with a 25 Å/mm resolution. The data were collected with a Stanford Research SR430 multichannel scaler. The low temperature work was performed using a closed-cycle refrigerating unit.
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Figure 2 shows the two different emission spectra obtained upon site-selective excitation of the <sup>5</sup>D<sub>0</sub> level of a Eu<sup>+3</sup> β"-alumina crystal and representative of the europium ions located in mO (Fig. 2, B) and BR (Fig. 2 C) sites. Figure 2, A superposes both mO and BR spectra and table I lists the assignments of the observed transitions. We previously discussed [7] the difficulties associated with spectral assignments and now the 569 nm-excited spectrum could be interpreted as consistent with either C<sub>av</sub> or C<sub>a</sub> local site symmetry. The important conclusion however is that the 572 nm-emission is indeed a  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  emission. Exciting at 569 nm always results in exciting one BR subsite which transfers energy to another BR subsite located some 100 cm<sup>-1</sup> away. Under C<sub>3</sub>, the 572 nm-emission is interpreted as the accidental coincidence of the emission of the A component of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  emission of the directly excited subsite and of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  emission of another BR subsite located ca 100 cm<sup>-1</sup> away from the first. Under  $C_{3v}$ , The 572 nm emission is solely assigned to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  emission of the other close site indirectly excited by energy transfer from the directly excited site.

To clarify these assignments we then recorded the laser excitation spectra by monitoring the emission where minimal site overlap was observed (cf Fig. 2 A). Upon monitoring an mO-type emission (such as 591.5, 597.7, 611.5, 614.4 or 617.3 nm) we obtained excitation spectra such as shown in Figure 3, B. Peak positions were the same for all mO excitation spectra. We can recognize three site distributions with maxima at ca 574.3 (17412.5 cm<sup>-1</sup>), 577.2 (17325.0 cm<sup>-1</sup>) and 579.0 nm (17271.2cm<sup>-1</sup>). Figure 3, A shows a spectrum acquired while monitoring a BR-type emission (620.9 nm) which has almost no mO-type overlap. Four site distributions are apparent with maxima at ca 568.9 nm (17577.8 cm<sup>-1</sup>), 574.3 nm (17412.5 cm<sup>-1</sup>), 577.7 (17310.0 cm<sup>-1</sup>) and 579 nm (17271.2 cm<sup>-1</sup>). Figure 3, C shows a region of maximum BR/mO overlap (611.2 nm) with the higher energy emitting center too weak to be observed. Figure 4 shows another BR/mO overlap-type excitation spectrum ( $\lambda_{mon} = 610.1$ nm) and it shows the higher energy site. To verify whether energy was indeed transferred between the high-energy BR subsites, we recorded excitation spectra monitoring in the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  region (Fig. 5). They always show peaks ca 100 cm<sup>-1</sup> before the monitoring wavelength. We then measured the decay time of the 572 nm emission upon 569 nm-excitation. We observed a fast risetime (Figure 6) which confirms the "multisubsite" character of the BR-site distribution and that these sub BR sites do indeed transfer energy amongst themselves.

We also recorded the decay times at longer times (over 15 to 40 msec). Figure 7 shows the decay of the 569 nm-emission upon 569 nm-excitation, i.e of a pure donor site. We used the Inokuti-Hirayama equation [11] which fits the decay of donor intensity in the absence of backtransfer:

$$I(t) = I_{o} \exp \left[-t/\tau_{o} - \Gamma (1-3/s)c_{a}/c_{o}(t/\tau_{o})^{3/s}\right]$$
(1)

where the donor-acceptor interaction is of multipolar type (s = 6 for dipoledipole; s = 8 for dipole-quadrupole and s = 10 for quadrupole-quadrupole interaction), I<sub>o</sub> is the intensity at t = 0,  $\tau_0$  is the radiative decay time, c<sub>a</sub> the acceptor concentration and c<sub>o</sub> the critical transfer concentration, evaluated using:

$$c_o^{-1} = 4/3\pi R_o^{-3}$$
 (2)

where  $R_o$  is the critical transfer distance for which the rate of energy transfer equals the radiative decay rate. The decay times of the emissions recorded for 569 nm-excitation could all be reasonably well fitted to (1) for s = 8 and 10 and somewhat more poorly for s = 6 (cf Table II). In performing the fitting procedure, we allowed the radiative lifetime to be a free parameter and the dipole-dipole fit yielded radiative lifetimes that were too long for europium. We accordingly conclude that the dipole-dipole mechanism is the least adequate. Futhermore, considering that the distance between two europium ions located in adjacent BR sites is of 5.6 Å [2] we can also conclude that Eu<sup>+3</sup> ions located in BR sites transfer energy amongst themselves by dipole-quadrupole or quadrupolequadrupole interaction. The distances are shortened in the 572 nm-emission fit (Fig. 8) but we must bear in mind that this emission has both acceptor (from the higher energy BR site) and donor (to lower energy sites) character. Finally, it should be noted that a concentration dependence study would surely distinguish

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between the proposed mechanisms.

## CONCLUSIONS

This work, in conjunction with our previous site-selective  $Eu^{*3}\beta$ "-alumina study [7], represents a valiant effort at trying to elucidate in resonance some of the site-to-site energy transfer features of a system characterized by great complexity (multisites, overlap between donors and acceptors, impossibility to directly measure a BR-type or mO-type spectrum not affected by energy transfer or vibronic phenomena). It will provide a basis for investigating the dynamics of energy transfer processes in other  $\beta$ "-alumina co-doped materials.

Our results can be summarized as follows: upon incorporation into the  $\beta$ "-alumina matrix, europium ions occupy either BR or mO site distributions. There are four broad emitting centres (Fig. 3, A & 4). Two are identified as as mO sites (with maxima at ca 577.2 and 579.9 nm). The higher energy site distribution (568 to 573 nm) are a series of BR subsites separated by ca 100 cm<sup>-1</sup> which can be selectively excited and which transfer energy amongst themselves. The distribution centered at ca 574.5 nm can not be assigned to either BR or mO positions. It seems to provide the link between high energy BR sites and lower energy mO sites. That the europium ions exhibit such multisite

spectroscopic behavior is not too surprising considering the intrinsic defect structure of the host crystal.

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TABLE I: Observed emission of the BR and mO sites respectively excited at 569.03 and 577.2 nm at 4.2 K. Assignments made according to ref.7.

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BR Site (C <sub>2</sub> )					
Transition	Observed (nm)	cm <sup>.1</sup> from ex.			
<sup>5</sup> D₀→ <sup>7</sup> F₀	569.03 (A <sub>1</sub> )	0.00			
⁵D₀→ <sup>7</sup> F₁	583.27 (E) 593.06 (A <sub>2</sub> )	430.00 712.00			
⁵D₀→ <sup>7</sup> F₂	608.54 (A <sub>1</sub> ) 610.4 (E) 620.9 (E)	1141.00 1191.00 1468.09			
BR Site (C <sub>3</sub> )					
<sup>5</sup> D <sub>o</sub> → <sup>7</sup> F <sub>o</sub>	569.03 (A)	0.00			
<sup>5</sup> D₀→ <sup>7</sup> F₁	572.56 (A) 583.27 (E) 593.06 vib.	109.02 430.00 712.00			
<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>2</sub>	608.54 (A) 610.40 (E) 620.90 (E)	1141.00 1191.00 1468.09			
mO Site (C <sub>2h</sub> )					
${}^{5}D_{0}\rightarrow {}^{7}F_{0}(A_{p})$	577.2	0.00			
<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub> (A <sub>g</sub> ) (B <sub>g</sub> ) (B <sub>g</sub> )	583.5 591.5 597.7	187.10 418.80 594.20			
	611.0 614.5 616.5 617.5 623.0	958.40 1051.60 1104.40 1130.70 1273.65			

TABLE II: Results of the fits to eqt. (1).

569 nm-emission upon 569 nm-ex. (6 K)				
Interaction	τ,	R。	R	Г
dipole-dipole	12.1 ms	6.8 Å	0.99433	1.77245
dipole-quadrupole	5.0 ms	5.2 Å	0.98274	1.43453
quadrupole-quadrupole	4.5 ms	5.1 Å	0.99393	1.29806
572 nm-emission upon 569 nm-ex. (6 K)				
dipole-dipole	10.0 ms	6.3 Å	0.99143	1.77245
dipole-quadrupole	4.2 ms	3.9 Å	0.99911	1.43453
quadrupole-quadrupole	4.1 ms	4.1 Å	0.99908	1.29806

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#### FIGURE CAPTIONS:

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- FIGURE 1: Conduction plane of sodium β"-alumina. View is looking down on plane. Open circles are oxygens above plane; shaded circles are oxygens below plane; dark circles are oxygens in plane; There are three conduction planes per unit cell and each contains two BR and three mO sites.
- FIGURE 2: A Superposition of mO (dashes) and BR (line)-type spectra.
  - B Emission spectrum of Eu<sup>+3</sup> $\beta$ "-alumina selectively excited at 577.2 nm and acquired at 4.2 K.
  - C Emission spectrum of Eu<sup>+3</sup> $\beta$ "-alumina selectively excited at 569.0 nm and acquired at 4.2 K.
- FIGURE 3: Laser excitation spectra of Eu<sup>+3</sup> $\beta$ "-alumina acquired at 8 K.
  - A Monitoring 620.9 nm (predominantly BR-emission)
  - B Monitoring 614.5 nm (predominantly mO-emission)
  - C Monitoring 611.2 nm (maximum BR/mO overlap)
- FIGURE 4: Laser excitation spectrum of Eu<sup>+3</sup>β<sup>\*</sup>-alumina acquired at 8 K, monitoring 610.1 nm, BR/mO overlap region.
- FIGURE 5: Laser excitation spectrum of Eu<sup>+3</sup> $\beta$ "-alumina acquired at 8 K, monitoring the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  region, namely 572.5, 572.0 and 571.5 nm.

FIGURE 6: Risetime observed at 572 nm upon 569 nm-excitation at 8 K.

- FIGURE 7: Fluorescence decay time measured at 569 nm following pulsed selective excitation (T = 6 K) at 569 nm. The full line is the best fit to eqt. (1) using s = 8.
- FIGURE 8: Fluorescence decay time measured at 572 nm following pulsed selective excitation (T = 6 K) at 569 nm. The full line is the best fit to eqt. (1) using s = 8.

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FIGURE 7



FIGURE 8

CONCLUSIONS

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### CONCLUSIONS

It is with confidence that this thesis proposes the occurrence of site-tosite energy transfer in Eu<sup>+3</sup>β-alumina by a dipole-quadrupole or quadrupolequadrupole mechanism. This finding also explains many features of the Eu<sup>+3</sup> spectral characteristics which were poorly understood before, such as the observed "extra peaks" in the emission spectra. More significantly, the work also proposes to carry out energy transfer studies in resonance, i.e. by exciting the lowest excited level of the ion and monitoring only the emission of that level including the important resonant emission. This is particularly required to also take advantage of the emission characteristics of an ion such as Eu<sup>+3</sup> which has non-degenerate ground and first excited states. Eu<sup>+3</sup> is always described in the literature as a "useful probe" for that reason and yet, published studies are still based on the acquisition of  ${}^{5}D_{1,2}$  excited levels.

## Contributions to knowledge:

The contributions of this work can be summarized as follows:

 The first site-selective resonant study of the site-to-site energy transfer between Eu<sup>+3</sup> ions is presented.

- 2. In the  $\beta$ "-alumina host, the Eu<sup>+3</sup> ion occupies site distributions which have been associated with the crystallographic BR and mO positions.
- 3. Energy transfer occurs between subsites within the BR site distribution by a multipole mechanism and downwards to the mO site distribution.
- 4. The question of conflicting assignments by previous workers is resolved.
- 5. The first site-selective polarization work on this material is presented.
- 6. The first 3.5 K resonant excitation and emission spectra of  $Eu^{+3}\beta^{+}$ -alumina are also presented.

# Suggestions for futher work:

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- 1. A concentration dependence study would further probe the exact nature of the multipole energy transfer interaction.
- 2. A Raman study would allow positive identification of the europium vibrational structure.
- 3. The crystal field  $C_{3v}$  fit could also be performed after the vibrational spectral assignments are made.

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APPENDIX

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This appendix presents the fits to the Inokuti-Hirayama equation obtained for the decay times of  $Eu^{+3}\beta$ -alumina measured at 6 K.

Fits A - C are for the data acquired exciting at 569 nm and monitoring at the same wavelength.

Fits D - F are for the data acquired exciting at 569 nm and monitoring at 572 nm.

Fit A: dipole-dipole, s = 6

Fit B: dipole-quadrupole, s = 8

Fit C: quadrupole-quadrupole, s = 10

Fit D: dipole-dipole, s = 6

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Fit E: dipole-quadrupole, s = 8

Fit F: quadrupole-quadrupole, s = 10

The fits were performed using Prof. Grosser's Kaleidagraph software using the user-defined function menu option.



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