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Polarized luminescence of an aggregate defect centre in Al$_2$O$_3$

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Abstract. — The dichroic nature of the optical absorption and luminescence bands of a defect centre in fast neutron and proton irradiated $\alpha$-Al$_2$O$_3$ have been studied at 4 K. The investigation centred on an absorption band at 358 nm and a mirror image emission band at 379 nm. These bands show resolved vibronic structure with a zero-phonon line at 368.4 nm and are due to allowed electric dipole transitions. Plane polarized light experiments show that the transition dipole moment is set at 40° to the c-axis of the crystal and we suggest that it originates at a defect centre which consists of two adjacent oxygen ion vacancies which have trapped one or more electrons.

1. Introduction. — Exposure of crystalline $\alpha$-Al$_2$O$_3$ to fast particle or ionizing radiation effects marked changes in the optical properties of the material. The numerous optical absorption bands which may be induced in $\alpha$-Al$_2$O$_3$ by neutron, proton or electron irradiation, or ion-implantation, have been reported in previous papers [1-8]. Three of the higher energy absorption bands have been allocated to specific defect centres, the 205 nm (6 eV) band to the $F$ centre and the 227 nm (5.4 eV) and 256 nm (4.8 eV) bands to the $F'$ centre.

The anisotropic nature of the optical absorption properties of $\alpha$-Al$_2$O$_3$ has been reported by Mitchell et al. [5]. The present paper describes the results of plane polarized light experiments on the 358 nm (3.46 eV) absorption band and its associated mirror image luminescence band at 379 nm (3.27 eV). The theoretical and experimental results are discussed and a defect centre based on two adjacent oxygen ion vacancies assigned to the 358 nm absorption band.

2. Experimental details. — 2.1 Crystals. — Single crystals of $\alpha$-Al$_2$O$_3$, grown using the Verneuil technique, were obtained from Imperial College, London, and Salford Electrical Instruments Ltd. The optical absorption and luminescence properties of all the as-grown crystals were essentially the same. Analysis showed that only Si (200 ppm) and Ca (16 ppm (Salford) and 52 ppm (Imperial College)) were present at levels exceeding 20 ppm.

Suitably sized samples were diamond cut to within 1.5° of the desired planes after first orienting the crystals using a Laue back reflection technique. The samples were then polished to 1 µm and annealed at 1100 °C overnight in vacuum. A sample of dimensions $3.5 \times 3.5 \times 5$ mm was cut along the (0001) and (1010) planes and irradiated with fast neutrons at 60 °C in the Herald reactor at AWRE Aldermaston to a dose of $10^{18}$ neutrons cm$^{-2}$. Samples cut to dimensions $1.5 \times 6 \times 7$ mm were proton irradiated at 50 °C in the 6 MeV Van de Graaff accelerator at Harwell to doses up to $3 \times 10^{18}$ protons cm$^{-2}$. The proton energy was increased from 1 MeV to 3 MeV in equal dose steps of 0.1 MeV to avoid a build-up of hydrogen in one layer of the material. The $6 \times 7$ mm face of the proton irradiated samples was parallel to the (1010) plane.

2.2 Optical studies. — For all studies reported here the samples were held at a temperature of 4 K in an Oxford Instruments CF 104 continuous gas flow cryostat. Absorption measurements were made using a Cary 14 spectrophotometer.

To obtain photoluminescence emission spectra an excitation wavelength was selected by a 365 nm Oriel thin film interference filter tilted at an angle of 20° to the collimated beam of a WOTAN high pressure mercury lamp Type HBO W/2. The emission from the sample was taken off at right angles to the excitation direction, and processed by a Hilger Monospek 1000 monochromator in combination with a cooled EMI 9659 QB extended S20 photomultiplier and
Harwell 2000 series photon counting system. The emission spectrum was displayed on an Oxford Instruments 3000 series chart recorder.

Polarization of the incident and emitted light was achieved by the insertion of Polaroid HNP'B polarizers (for incident wavelengths above 280 nm) and Polacoat 105 UV polarizers (for wavelengths below 280 nm) into the appropriate light path.

3. Results. — 3.1 Optical Absorption Studies. —
The optical absorption spectra of the neutron irradiated sample are shown in figure 1. The background spectrum of the crystal before irradiation is included. The light beam was incident normal to the [1010] direction and plane polarized with the E vector either parallel (curve B (π)) or perpendicular (curve C (σ)) to the [0001] c-axis of the crystal. There are absorption bands at 358 nm (3.46 eV) and 450 nm (2.75 eV) in spectra C and B and a 302 nm (4.1 eV) band in spectrum B. Bands at shorter wavelengths are not recorded due to the high optical densities which also prevent observation of the 302 nm band in spectrum C. The 358 nm band has strong dichroic properties and also a sharp, strong zero-phonon line at 368.4 ± 0.1 nm with a halfwidth of 0.2 ± 0.05 nm.

Figure 2 shows the polarized absorption spectra of the proton irradiated sample held in the same orientation as the neutron irradiated crystal of figure 1. Again the background spectrum is included. The lower optical densities allow a larger number of bands to be recorded compared with the neutron irradiated sample. The more prominent absorption bands are the 256 nm (4.8 eV), 302 nm, 332 nm (3.7 eV) and 358 nm bands. The dichroic nature of the optical absorption properties has been reported by Mitchell et al. [5]. Unlike figure 1 the zero-phonon line of the proton irradiated sample is too broad and weak to be seen in figure 2. We suggest that the broadening has occurred because of internal stresses created in the crystal by the proton irradiated layers.

The vibronic frequency \( \nu_0 \) derived from the separation of the zero-phonon line and the phonon-assisted sidebands of the 358 nm band is 260 ± 30 cm\(^{-1}\). Using this value the Huang-Rhys factor \( S \) derived from the energy separation \( S_{\nu_0} \) between the band centroid and the zero-phonon line is found to be 3.7 ± 0.6. This value agrees with that derived from the fractional intensity in the zero-phonon line, which should be \( e^{-S} \).

3.2 Photoluminescence Studies. — Excitation of neutron or proton irradiated samples by light in the 358 nm absorption band region results in photoluminescence at 379 nm and 468 nm. We shall limit our discussion to the 379 nm emission band.

![Fig. 1. Absorption spectra at 4 K of an α-Al2O3 crystal neutron irradiated to a dose of 10\(^{18}\) neutrons cm\(^{-2}\). Curve A is the background absorption spectrum of the crystal before irradiation. Curve B (π): absorption spectrum for E//[0001] and \perp [1010]. Curve C (σ): absorption spectrum for E\perp [0001] and \perp [1010].](image1)

![Fig. 2. Absorption spectra at 4 K of an α-Al2O3 crystal proton irradiated to a dose of 3 \times 10\(^{18}\) protons cm\(^{-2}\). Curve A is the background absorption of the crystal before irradiation. Curves B (π) and C (σ) refer to the same polarizations as in figure 1.](image2)

![Fig. 3. Emission spectra of α-Al2O3 measured at 4 K: a) neutron irradiated crystal, dose 10\(^{18}\) n.cm\(^{-2}\), b) proton irradiated crystal, dose 3 \times 10\(^{18}\) protons cm\(^{-2}\). Note reversal of wavelength scale with respect to figures 1 and 2.](image3)
Figure 3a shows the unpolarized 379 nm band from the neutron irradiated sample. The band possesses strong vibronic structure and is the mirror image of the 358 nm absorption band. Its zero phonon line peaks at 368.4 ± 0.1 nm and has a halfwidth of about 0.15 nm. The vibronic frequency is 237 ± 25 cm⁻¹ and the Huang-Rhys factor 3.9 ± 0.6. These agree well with values measured from the absorption band (§3.1).

The unpolarized 379 nm emission band of the proton irradiated sample (Fig. 3b) has a split zero phonon line due to stresses produced by the proton damaged layers. The vibronic frequency is estimated as 230 ± 20 cm⁻¹ and the Huang-Rhys factor as 3.9 ± 0.6. Both values agree well with those deduced from the neutron irradiated sample.

Polarized luminescence experiments have been undertaken to understand the nature of the defect responsible for the emission band. The neutron irradiated sample was oriented so that the excitation path was parallel to the [1010] direction and the emission path to the [0001] direction (Fig. 4a). In the case of the proton irradiated sample the excitation path is also parallel to the [1010] direction but the emission path is parallel to the [1210] direction (Fig. 4b). The polarizers were placed in the excitation and emission paths and could be oriented to produce four configurations for each sample as defined in figures 4a and b. Table I lists the configurations used and the corresponding theoretical and experimental results. There are large differences in the intensity of the 379 nm emission band as the polarization conditions are changed and a discussion of the results is given in section 4.

4. Discussion. — The polarization data are used to deduce the orientation of the transition dipole moment of the defect centre. The anisotropic absorption ratio $A$ represents the ratio $\mu_{\parallel}/\mu_{\perp}$, where $\mu$ is the optical absorption coefficient. From figures 1 and 2 $A$ was measured. For a defect whose transition dipole moment is at an angle $\theta$ to the $c$-axis, it is easily shown that \[ A = 2 \cot^2 \theta. \] The value of $\theta$ is calculated to be 40.2 ± 2.0° and 39.7 ± 2.0° for the neutron and proton irradiated samples respectively.

In order to apply the results from the polarized luminescence experiments it is essential to study the distorted hexagonal lattice of $\alpha$-Al₂O₃. Projections along the [1210] and [0001] directions are given in figures 5a and b. Aluminium ions are represented by points and oxygen ions by circles. The line joining two next nearest neighbour oxygen ions from adja-

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![Figure 4](image-url)  
Fig. 4. — Geometrical arrangement for polarized luminescence measurements on: a) neutron irradiated $\alpha$-Al₂O₃, b) proton irradiated $\alpha$-Al₂O₃. The arrows and symbols refer to the direction of the electric vectors of the exciting and emitted light.

![Figure 5](image-url)  
Fig. 5. — Projection of the positions of oxygen ions surrounding an Al³⁺ ion in $\alpha$-Al₂O₃ on: a) the (1210) plane, b) the (0001) plane.  
• : Al³⁺ ion, ○ : O²⁻ ion above plane, ○ : O²⁻ ion below plane.

Table I. — Polarization data for the 379 nm emission band.

<table>
<thead>
<tr>
<th>Polarization configuration</th>
<th>379 nm emission band</th>
<th>379 nm emission band</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$\theta = 40.2^\circ$ ± 2.0°</td>
<td>$\theta = 39.7^\circ$ ± 2.0°</td>
</tr>
<tr>
<td>$\pi, \pi$</td>
<td>0.75 sin² $\theta$</td>
<td>2 cos $\theta$</td>
</tr>
<tr>
<td>$\sigma, \sigma$</td>
<td>0.25 sin $\theta$</td>
<td>$\pi, \pi$</td>
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<td>$\sigma, \sigma$</td>
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<td>$\sigma, \sigma$</td>
<td>0.25 sin $\theta$</td>
<td>$\pi, \pi$</td>
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</tbody>
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The values in Table I were deduced from the results of the polarized luminescence experiments.
cent (0001) planes makes an angle of 33° with the c-axis (see Fig. 5a). This is fairly close to the experimental value of ≈ 40° obtained from the absorption data and leads us to suggest that the origin of the 358 nm absorption band is a defect centre of two such next nearest neighbour oxygen vacancies which have trapped one or more electrons. The lines joining the oxygen ions from adjacent (0001) planes which are drawn in figures 5a and b represent all orientations for such a defect, the angle \( \phi \) being defined as in figure 5b. The data obtained from the polarized luminescence measurements are summarized in table I alongside the theoretical predictions for transition dipoles at an angle \( \theta \) to the c-axis in the orientations given in figure 5b.

To calculate the theoretical luminescence intensities the six dipole vectors \( d_n \) (where \( n = 1-6 \)) were resolved into their component vectors in the [1\( \overline{2} \)10] (i), [10\( \overline{1} \)0] (j) and [0001] (k) directions. The theoretical values in table I are calculated from the expression for polarized luminescence intensity

\[
I = \sum_{n=1}^{6} (d_n \cdot e_x)^2 (d_n \cdot e_y)^2
\]

where
- \( e_x \) : unit polarization vector of exciting light,
- \( e_y \) : unit polarization vector of emitted light.

The unit vectors \( e_x \) and \( e_y \) are put equal to \( i \), \( j \) or \( k \) according to the appropriate polarization combination depicted in figure 4.

Note that the angle \( \phi \) cancels out from the theoretical predictions in table I. The good agreement between the theoretical and experimental data in table I shows that our model is consistent with both the absorption and luminescence results. The agreement is better for the neutron irradiated sample. Discrepancies in the proton irradiated data are probably due to the large stresses introduced into the crystal by the stepped irradiation technique which results in platelets of damaged \( \alpha \)-Al\(_2\)O\(_3\) separated by relatively undamaged regions.

5. Conclusions. — We have adopted the simplest model which allows good agreement between the theoretical and experimental results. This model is a defect which has a transition dipole moment at about 40° to the c-axis of the crystal and consists of a pair of next nearest neighbour oxygen vacancies with one or more trapped electrons.

References