Vibronic levels and zero-phonon lines of Cr$^{3+}$ - doped yttrium aluminium garnet (Y$_3$Al$_5$O$_{12}$)

W. Nie, G. Boulon, A. Monteil

To cite this version:

W. Nie, G. Boulon, A. Monteil. Vibronic levels and zero-phonon lines of Cr$^{3+}$ - doped yttrium aluminium garnet (Y$_3$Al$_5$O$_{12}$). Journal de Physique, 1989, 50 (22), pp.3309-3315. 10.1051/jphys:0198900500220330900. jpa-00211144

HAL Id: jpa-00211144
https://hal.archives-ouvertes.fr/jpa-00211144
Submitted on 1 Jan 1989

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
**Short Communication**

**Vibronic levels and zero-phonon lines of Cr$^{3+}$ - doped yttrium aluminium garnet ($Y_3Al_5O_{12}$)**

W. Nie, G. Boulon and A. Monteil

Physico-Chimie des Matériaux Luminescents, UA 442 du CNRS, Université Lyon I, 69622 Villeurbanne, France

*(Reçu le 18 septembre 1989, accepté le 20 septembre 1989)*

**Résumé.** — Les niveaux vibrationnels des deux états excités du doublet $^2E$ et les raies à O-phonon non seulement de $^4A_2 \rightarrow ^2E$ mais surtout des transitions $^4A_2 \rightarrow ^2T_1$ et $^4A_2 \rightarrow ^4T_2$ de l’ion Cr$^{3+}$ inséré comme dopant dans la matrice cristalline de $Y_3Al_5O_{12}$ (appelé plus couramment YAG) ont été observés par application à 4.2 K de la technique de spectroscopie-laser, mettant en œuvre les spectres d’excitation au moyen des lasers à colorants accordables en longueur d’onde et de haute résolution.

**Abstract.** — Vibronic levels of $^2E$ doublets and zero-phonon lines not only of $^4A_2 \rightarrow ^2E$ but mainly of both $^4A_2 \rightarrow ^2T_1$ and $^4A_2 \rightarrow ^4T_2$ transitions of Cr$^{3+}$-doped $Y_3Al_5O_{12}$ (so-called YAG) have been observed by high resolution dye-laser excitation spectra at liquid helium temperature.

**Introduction.**

Progress in the study of solid-state laser materials stimulate spectroscopic research, such as the knowledge of the O-phonon lines, the phonon frequencies of both ground and excited states. The phonon frequency of the ground state can be obtained by Raman or fluorescence techniques, whereas that of excited states must be analyzed with the aid of absorption spectrum. Unfortunately problems occur both with bad spectral resolution and weak intensity signals of usual broad band spectrophotometers. Moreover in many cases depending on the crystal field strength, absorption and emission spectra are shifted, and unstructured vibronic broad bands are observed. On the other hand, another cause of problems is the quality of inorganic luminescent materials: in addition to the unperturbed main site spectrum perturbed sites can be detected the spectra of which overlap with the principal one. Consequently the interpretations of spectroscopic data are compli-
cated and large inhomogeneous broadening can be seen. Among all fluorescent metal transitions, Cr$^{3+}$ ion is of special interest for solid-state laser materials in ruby, emerald, alexandrite, garnets. It may be used either as a lasing ion itself or a sensitizer ion for the Cr$^{3+}$$-$Nd$^{3+}$ and Cr$^{3+}$$-$Tm$^{3+}$ energy transfer mechanisms [1-3]. Only on the solid state laser materials with excellent optical quality accurate spectroscopic research can be performed. In this work, the main goal is to show how new high resolution dye laser excitation spectra allow us to get new and accurate data in this research field. First of all we have chosen one of the most famous laser host: yttrium aluminium garnet Y$_3$Al$_5$O$_{12}$ (also called YAG). In the present paper, we focus on the electron-phonon coupling and the zero-phonon $^4A_2$ $\rightarrow$ $^2T_1$ and $^4A_2$ $\rightarrow$ $^4T_2$ transitions at Cr$^{3+}$ ions in YAG.

The Cr$^{3+}$ ($d^3$) ion spectroscopy is usually analysed in the octahedral coordination case where two kinds of transitions may occur: either $t_{2g}^3$ intraconfigurational transitions or $t_{2g}^3e_g^1$ interconfigurational ones. The former gives rise to $^4A_2$ $\rightarrow$ $^2E$, $^2T_1$, $^2T_2$ transitions with a weak coupling (low Huang-Rhys parameter) and the latter gives rise to $^4A_2$ $\rightarrow$ $^4T_2$, $^4T_1$ transitions with a stronger coupling (higher Huang-Rhys parameter).

The vibronic levels of the ground state $^4A_2$ have already been obtained from emission spectra at low temperatures but those of the first excited state $^2E$ doublets cannot be studied by fluorescence spectra neither at low temperatures since the emission occurs only from the lowest vibronic level of the lowest excited state $^2E$ (2Å) nor at high temperatures because they overlap with those of the ground state.

In addition, the O-phonon $^4A_2$ $\rightarrow$ $^4T_2$ and $^4A_2$ $\rightarrow$ $^2T_1$ transitions have never been precisely assigned even some traces were observed in a excitation spectrum using a lamp [4]. For lack of these accurate experimental data, the crystal field calculations cannot be carried out. Here, we give new result only on the dominant R site (C$_{3v}$ symmetry with a slight trigonal distortion characterized by a strong crystal field strength at 4.2 K). The other data concerning multisites we have found in YAG [2] will be published later in a forthcoming paper.

Experimental.

The crystals were prepared by Monocrystaly Turnov, Research Institute for Single Crystals, Leninova 175, 51119 Turnov, Czechoslovakia. The measurement was carried out on the sample containing 2% Cr in weight concentration.

The absorption spectrum was obtained on a VARIAN 2300 spectrophotometer in association with a liquid He cryostat. The excitation spectra were made using a Quantel Nd : YAG pulsed laser with a tunable dye laser (repetition rate : 10 Hz, time constant 15 ns, spectral width of the dye laser 0.1 cm$^{-1}$) to scan the required wavelength and a photon counting system (ORTEC) to accumulate the signals with different delays and different gatewidths. In order to avoid the laser beams, the signals were accumulated between laser pulses (delay : 1 μs; gate : 80 ms) for figure 1a. The excitation spectra shown in figure 1 were obtained with the mixture of the rhodamin 640 and oxazine 720, and that shown in figure 2a was got with the dye DCM.

Results.

Figure 1a shows the excitation spectrum of YAG : Cr$^{3+}$ at 4.2 K by monitoring the lowest component of $^2E$ $\rightarrow$ $^4A_2$ transition so called R$_1$ emission line. The phonon lines are resolved. A spread part is shown in figure 1b. Figure 1a is less precise than figure 1b since it is recorded in a larger wavelength interval between the recording points. We found that the energy difference between i and i' lines is the same (about 19 cm$^{-1}$). This is equivalent to that between the R$_1$ and R$_2$ lines, i.e., the splitting of $^2E$ levels [2]. These pair lines with $\Delta$ ($^2E$) difference in energy must correspond to the absorption of vibronic levels of each of the two $^2E$ excited states ($^2E$ (E) and $^2E$ (2Å)).
Fig. 1.— a) Excitation spectra of YAG : Cr at 4.2 K. Monitored wavelength : 687.3 nm (R₁ line), b) a spreaded part, c) schematical principle.
Figure 2a shows the excitation spectrum between 634-666 nm. Four absorption lines at the edge of the $^4A_2 \rightarrow ^4T_2$ broad band are observed. These lines coincide with that in the absorption spectrum at 10 K (Fig. 2b). The first line situated just on the tail of the $^4A_2 \rightarrow ^4T_2$ broad band can be attributed to the zero-phonon $^4A_2 \rightarrow ^4T_2$ transition. The other three lines should correspond to $^4A_2 \rightarrow ^2T_1\left(^2A_2\right)$, $^4A_2 \rightarrow ^2T_1\left(^2E\left(E\right)\right)$ and $^4A_2 \rightarrow ^2T_1\left(^2E\left(2A\right)\right)$ transitions. All the spectral data is summarized in table I.

Table I.— Zero-phonon transitions of the Cr$^{3+}$ R site in YAG at 4.2 K.

<table>
<thead>
<tr>
<th>Transition</th>
<th>nm</th>
<th>cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4A_2 \rightarrow ^4T_2$</td>
<td>641.3</td>
<td>15589</td>
</tr>
<tr>
<td>$^4A_2 \rightarrow ^2T_1\left(^2A_2\right)$</td>
<td>648.1</td>
<td>15425</td>
</tr>
<tr>
<td>$^4A_2 \rightarrow ^2T_1\left(^2E\left(E\right)\right)$</td>
<td>657.1</td>
<td>15214</td>
</tr>
<tr>
<td>$^4A_2 \rightarrow ^2T_1\left(^2E\left(2A\right)\right)$</td>
<td>659.4</td>
<td>15161</td>
</tr>
<tr>
<td>$^4A_2 \rightarrow ^2E\left(E\right)$</td>
<td>686.4</td>
<td>14565</td>
</tr>
<tr>
<td>$^4A_2 \rightarrow ^2E\left(2A\right)$</td>
<td>687.3</td>
<td>14546</td>
</tr>
</tbody>
</table>

Figure 3 shows the detailed absorption spectrum between 640-720 nm. Besides the part shown in figure 2b, the $R_1$, $R_2$ lines and their phonon sideband are observed. Not like dye laser excitation spectra (Fig. 1), the phonon lines are not resolved in the absorption spectrum due to the bad resolution of the spectrophotometer.

Discussion.

The phonon assisted emission lines have been already observed by other authors [4, 6]. At liquid helium temperature, the fluorescence occurs only from the lowest excited state ($^2E\left(2A\right)$),
the vibronic levels of the $^4A_2$ ground state can be calculated by the energy difference between the R1 line and its phonon emission lines. There are extensive difficulties with respect to a detailed interpretation of the electron-phonon coupling at Cr$^{3+}$ impurity ions in YAG. First of all, the $k = 0$ approximation which is well established for single phonon processes, like the IR-absorption or the Raman scattering, can no longer be applied and the whole $k$-space or at least the critical points of the first Brillouin zone which exhibit large phonon densities, should be considered. Second, the phonon solutions of the unperturbed lattice may be modified by the impurity ions and localized modes may contribute to the phonon sidebands. In consequence, there exists a large number of vibrational modes. In addition, there is a possibility of multiphonon modes. The aim of the present work is to show a picture on the vibronic levels of $^2E_4$ excited states and to give definitively attributions of the $^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^2T_2$ transitions.

Vibronic levels of excited states of Cr$^{3+}$ have never been studied. Using a powerful high resolution dye laser, phonon energies coupling to $^2E$ doublets of Cr$^{3+}$ are observed (Fig. 1). The interpretation of these phonon assisted absorption lines is based on the assumption that the phonon energies, due to either different vibrational modes or multiphonon modes, coupling to $^2E$ excited states should not be very different from those coupling to the $^4A_2$ ground state. This seems to be reasonable since both $^2E$ and $^4A_2$ states belong to the same electron configuration $t_{2g}$. Moreover the phonon wavenumbers of $^2E$ ($^E$) should be practically identical with those of $^2E$ ($^2A$) because $^2E$ ($^E$) is only 19 cm$^{-1}$ from $^2E$ ($^2A$). The first intense phonon energies of the $^4A_2$ ground state have been reported to be 124, 142, 162, 184, 196 cm$^{-1}$ [5, 6]. The observed phonon lines in figure 1 are due to the absorption of the vibronic levels of $^2E$ doublets. The detailed interpretation is given in table II. The reproducible 19 cm$^{-1}$ between $i$ and $i'$ lines and 5 cm$^{-1}$ between $i + 1$ and $i'$ lines are indicative. From reference [2], we know that $\Delta (^2E) = 19$ cm$^{-1}$ ($\Delta (^2E)$ is the $^2E$ splitting of the principle R site). So if $i$ corresponds to the $^2E$ ($^2A$) level (R$_1$), $i'$ must correspond to $^2E$ ($^E$). The 5 cm$^{-1}$ between $i + 1$ and $i'$ lines is the energy gap between the No. $i'$ vibronic level of $^2E$ ($^E$) and No. $i + 1$ of $^2E$ ($^2A$). The principle is schematically represented in figure 1c. The line no. 2 in figure 1b corresponds to the second vibronic level of the $^2E$ ($^2A$) level (R$_1$). The trace of the first vibronic level of the $^2E$ ($^2A$) level can be found in figure 1a. Such an attribution consists well with the basic assumption. From table II, we can see that the phonon wavenumbers...
Table II. — Phonon wavenumbers of the split $^{2}E$ excited states of Cr$^{3+}$ in YAG.

<table>
<thead>
<tr>
<th>$i$ or $i'$</th>
<th>nm</th>
<th>cm$^{-1}$</th>
<th>assignment (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>681.49</td>
<td>14669.7</td>
<td>$124 - R_{1}(2) - ^{2}E(2\AA)$</td>
</tr>
<tr>
<td>1'</td>
<td>681.25</td>
<td>14674.9</td>
<td>$110.1 - R_{2}(1) - ^{2}E(E)$</td>
</tr>
<tr>
<td>2'</td>
<td>680.61</td>
<td>14688.6</td>
<td>$123.8 - R_{2}(2) - ^{2}E(E)$</td>
</tr>
<tr>
<td>3</td>
<td>680.41</td>
<td>14693</td>
<td>$147.3 - R_{1}(3) - ^{2}E(2\AA)$</td>
</tr>
<tr>
<td>4</td>
<td>679.71</td>
<td>14708.1</td>
<td>$162.4 - R_{1}(4) - ^{2}E(A)$</td>
</tr>
<tr>
<td>3'</td>
<td>679.47</td>
<td>14713</td>
<td>$148.5 - R_{2}(3) - ^{2}E(E)$</td>
</tr>
<tr>
<td>4'</td>
<td>678.80</td>
<td>14727.8</td>
<td>$163 - R_{2}(4) - ^{2}E(E)$</td>
</tr>
<tr>
<td>5</td>
<td>678.53</td>
<td>14733.6</td>
<td>$187.9 - R_{1}(5) - ^{2}E(2\AA)$</td>
</tr>
<tr>
<td>6</td>
<td>677.80</td>
<td>14749.5</td>
<td>$203.8 - R_{1}(6) - ^{2}E(2\AA)$</td>
</tr>
<tr>
<td>5'</td>
<td>677.56</td>
<td>14754.8</td>
<td>$190 - R_{2}(5) - ^{2}E(E)$</td>
</tr>
</tbody>
</table>

$R_{1}(^{2}E(2\AA))$, $R_{2}(^{2}E(E))$, $^{4}A_{2}$

of the $^{2}E(E)$ level are practically identical with those of the $^{2}E(2\AA)$ level whereas weakly different from those of the $^{4}A_{2}$ ground state.

The $^{4}A_{2} \rightarrow ^{4}T_{2}$ zero-phonon line position has been estimated to be 1000 cm$^{-1}$ above $^{2}E$ level by temperature dependence of lifetime and $^{2}E$ radiative decay measurements [4]. We found it was 1043 cm$^{-1}$ above $^{2}E(2\AA) - R_{1}$ and 1024 cm$^{-1}$ above $^{2}E(E) - R_{2}$ exactly. The other three lines in figure 2a can easily be attributed to $^{4}A_{2} \rightarrow ^{2}T_{1}$ absorptions. We know that in trigonal crystal field T level will split into A and E levels. On the other hand E will further split due to the additional spin-orbit interaction. From the line shapes, two narrow lines clearly show “E” characteristics. The other one can be assigned to the $^{4}A_{2} \rightarrow ^{2}T_{1}(^{2}A_{2})$ transition.

The crystal field has been calculated with a $D_{q}$ value derived from the mean position of $^{4}A_{2} \rightarrow ^{4}T_{2}$ broad band and a $^{4}A_{2} \rightarrow ^{2}T_{1}$ position approximate [7]. We have got the splitting of the $^{4}A_{2} \rightarrow ^{4}T_{1}$ broad band [5], together with the $D_{q}$ calculated from the $^{4}A_{2} \rightarrow ^{4}T_{2}$ zero-phonon line position and $^{4}A_{2} \rightarrow ^{2}T_{1}$ positions in the present work, the crystal field calculation can more precisely be carried out, and the accurate configuration coordinate curves could be drawn. It is worthwhile to mention that for such precise spectroscopic data one has to take into account the air index for the calculation of the wavenumbers from the wavelengths. Taking directly the reciprocals of the wavelengths, in the measuring spectral domain, it will lead to an increase of wavenumbers of approximately 4.5 cm$^{-1}$.

We think such systematic experiments are promising for solving the difficult problem of O-phonon line positions and phonon frequencies of the Cr$^{3+}$ ion levels in solids.
Summary.

By dye laser excitation spectra at 4.2 K the phonon lines associated with $^2E (2\bar{A})$ and $^2E (\bar{E})$ excited states are observed. The zero-phonon $^4A_2 \rightarrow ^4T_2$, $^4A_2 \rightarrow ^2T_1 (^2A_2)$, $^4A_2 \rightarrow ^2T_1 (^2E (\bar{E}))$, $^4A_2 \rightarrow ^2T_1 (^2E (2\bar{A}))$ absorptions are identified both on excitation and absorption spectra.

Acknowledgement.

We would like to thank Dr. J. Mares who very kindly donated the YAG : Cr crystals.

References