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Bernard Champagnon, E. Duval. Emission spectrum of $V^{3+}-\alpha Al_2O_3$. Journal de Physique Lettres, 1977, 38 (14), pp.299-301. 10.1051/jphyslet:019770038014029900 . jpa-00231381

HAL Id: jpa-00231381

<https://hal.science/jpa-00231381>

Submitted on 1 Jan 1977

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Classification
 Physics Abstracts
 78.60

EMISSION SPECTRUM OF V^{3+} - α - Al_2O_3

B. CHAMPAGNON and E. DUVAL

Laboratoire de Spectroscopie et de Luminescence
 Université Claude-Bernard, Lyon I, 69621 Villeurbanne, France

(Reçu le 11 mai 1977, accepté le 13 juin 1977)

Résumé. — Deux raies d'émission de V^{3+} - α - Al_2O_3 ont été mises en évidence dans le proche infra-rouge ($9\,740\text{ cm}^{-1}$) à 2 K, 10 K et 77 K. Leur temps de vie et leur comportement sous l'effet d'une contrainte ont été analysés et une interprétation est proposée.

Abstract. — Two emission lines of V^{3+} - α - Al_2O_3 have been obtained in the near infrared region ($9\,740\text{ cm}^{-1}$) at 2 K, 10 K and 77 K. Lifetimes of these lines and their behaviour under stress have been analyzed and an interpretation is suggested.

Although absorption spectra of V^{3+} in corundum (α - Al_2O_3) has been extensively studied [1, 2, 3], no emission spectrum has been reported until now. Two absorption lines were known I_1 ($9\,740.0\text{ cm}^{-1}$) and I_2 ($9\,748.3\text{ cm}^{-1}$) at 4.2 K in the near infrared region [4]. By exciting with a laser we have been able to obtain an emission in the region of these I lines.

Experiments have been performed with an argon laser (Ar^+ C.R. 3) exciting a V^{3+} - α - Al_2O_3 monocrystal. The best choice was found to be the $5\,145\text{ Å}$ line of Ar^+ which excites the edge of the $^3A_2 \rightarrow ^3T_2$ absorption band. The emission light is collected in the direction perpendicular to the excitation, polarized and analyzed by a grating spectrometer (Jobin-Yvon HRS dispersion 12 Å/mm) blazed at $7\,500\text{ Å}$. A cooled photomultiplier (S 1 photocathode) collects the signal which is displayed on a chart recorder. Experiments have been made at 2 K, 10 K and 77 K.

The emission spectrum is shown in figure 1. In agreement with the results of absorption [4], the lowest energy I'_1 line is much more intense than the I'_2 line. The splitting between these two lines corresponds to the splitting (8.3 cm^{-1}) of the fundamental 3A_2 level ($M_s = 0$; $M_s = \pm 1$). These two lines are more intense in the σ polarization perpendicular to the C_3 -axis. The axial spectrum coincides with the σ -spectrum : that shows that the transition is electric dipole [5].

Stress spectra of these emission lines has been recorded for pressures varying between 0 and 90 kp.mm^{-2} at 10 K. For the highest pressure, I'_1 and I'_2 shift towards lower energy and I'_1 begins to be split (this splitting is too small to be measured with accuracy).

Lifetimes have also been determined. The method has been described by Engström and Mollenauer [6]. The excitation signal is chopped at 50 kHz or 100 kHz. The phase difference φ between the excitation signal (measured on the second order of the laser $5\,145\text{ Å}$ line) and the emission signal is proportional to the lifetime and to the frequency of the signal N .

$$\text{tg } \varphi = 2\pi N\tau.$$

With that technique we found lifetimes

$$\tau = 2.5 \pm 0.4 \times 10^{-6}\text{ s} \quad \text{for } T < \lambda \text{ point of He}$$

$$\tau = 1.6 \pm 0.4 \times 10^{-6}\text{ s} \quad \text{for } T = 77\text{ K}.$$

In absence of any other competing process the integrated absorption coefficient μ_{mK} is related to the pure electronic lifetime of the level τ' [7]. We compared the absorption of the I_1 and I_2 lines of V^{3+} - α - Al_2O_3 with those of the R-lines of ruby. Detailed balance in ruby has been verified by Nelson and Sturge [8], and the emission lifetime of the R-lines is $4 \times 10^{-3}\text{ s}$ at 77 K. From this we can deduce the order of magnitude of what would be the electronic lifetime τ' of I lines for V^{3+} - α - Al_2O_3 if the detailed balance conditions were satisfied $\tau' \simeq 10^{-2}\text{ s}$. The ratio $\tau'/\tau = 10^4$ shows that the non-radiative process is strongly predominant.

In C_3 symmetry three energy levels have a calculated position corresponding to the upper state of the emitting transition (Fig. 2). A uniaxial stress produces an enlargement of the lines which tends to give a splitting. We can then assign the emission to one of the twofold degenerate states : one of them originates from the $^1T_1(t^2)$ state split by the trigonal crystal field

FIG. 1. — Emission spectrum of $V^{3+}-\alpha Al_2O_3$.

and the other one is a ${}^1E(t^2)$ state level which is a 1E level even in cubic symmetry. Both of these can be coupled by spin-orbit coupling [9] to the ${}^3E(t^2)$ state originating from the ${}^3T_1(t^2)$ ground state. Previous results on the ${}^3A_2 \rightarrow {}^1A_1$ transition have shown that the Jahn-Teller effect in the ground state is small

compared with the effect in the ${}^3T_2(te)$ level, and the V^{3+} ion is known to interact with modes which are mainly trigonal [10]. The sharpness of the emission lines shows that the emitting level is not submitted to a Jahn-Teller effect : such an effect would displace (in the configuration coordinate diagram) the state, in order to give a broad band. Trigonal modes have no effect on a 1E cubic state although they act on a ${}^1E({}^1T_1)$ state. So we can believe that the state responsible of the emission is the ${}^1E(t^2)$ state coming from the cubic 1E state.

FIG. 2. — Energy levels of $V^{3+}-\alpha Al_2O_3$ from ref. [3].

The transition ${}^1E(t^2) \rightarrow {}^3A_2(t^2)$ is spin-forbidden and measurements of the fluorescent lifetime compared to the absorption shows that the non-radiative transitions have a great importance. Both phenomena can be explained by the spin-orbit coupling of the 1E level with the ${}^3E(t^2)$ lower state. The ${}^1E(t^2)$ vibronic relaxed state is mixed with the vibronic levels of the 3E state and borrows a triplet-spin character which partially enables the radiative transition ${}^1E \rightarrow {}^3A_2$. At the same time excitation is transferred from the 1E to the 3E state and gives a non-radiative decay. This transfer occurs predominantly between the relaxed vibronic level of the 1E state and the high vibronic levels of the 3E which are nearly degenerate. The vibrations of the lattice and spin-orbit coupling must together intervene to allow this mechanism. Radiative and non-radiative processes are competitive because the more the levels are mixed the more the radiative transition is allowed, but at the same time the more the non-radiative transition takes place. This explains the weak intensity of the emission and the importance of the non-radiative decay.

The intensity of the I'_1 line is five times stronger than the intensity of the I'_2 line. This is in agreement with previous absorption spectra at 20 K [4]. The ratio is the same in π or σ polarization and needs to be explained for a better knowledge of the excited state.

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