Cr3+ CENTERS IN THE LaMgAl11O19 LASER HOST : THEORETICAL STUDY THROUGH A MOLECULAR ORBITAL MODEL
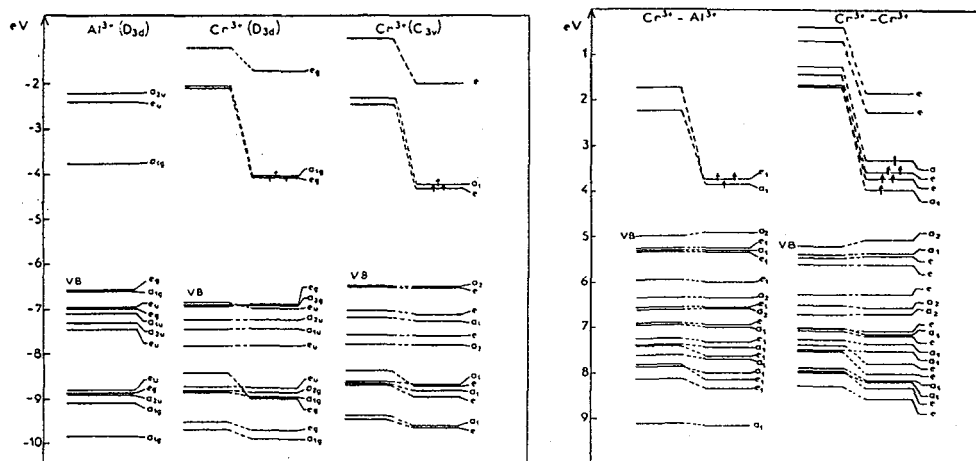
F. Michel-Calendini, K. Bellafrouh, V. Poncon, G. Boulon

Cr^{3+} CENTERS IN THE $LaMgAl_{11}O_{19}$ LASER HOST : THEORETICAL STUDY THROUGH A MOLECULAR ORBITAL MODEL

F. MICHEL-CALENDINI, K. BELLAFROUH, V. PONÇON and G. BOULON

Laboratoire de Physico-Chimie des Matériaux Luminescents, CNRS UA-442 et Greco Celphyra, Université Claude Bernard, Lyon I, F-69622 Villeurbanne Cedex, France

The fluorescence and absorption spectra of $LaMgAl_{11}O_{19}$ crystal doped with Cr^{3+} and EPR investigations gives evidence for the presence of Cr^{3+} multisites [1] : Cr ions are trapped at the 2a, 4f and 12k Al octaedral sites and Cr-Cr pair centers at 4f sites are also assumed. The electronic structures of these different centers are determined through a molecular orbital model using the spin polarized option of the SCF $X\alpha$ method. The computational framework is similar to the one described for Cr^{3+} in perovskite oxydes [2]. The only difference consist in the choice of a local spin density approximation [3] which improves agreement between experimental and calculated term splittings for states with large spin polarizations as Cr^{3+}.

Eigenvalue diagrams are obtained for the $^4A_2$ ground term as shown in figures 1 and 2. AlO_6^{9-} (D_{3d}) and CrO_6^{9-} (D_{3d}) represent the undoped and doped 2a site while CrO_6^{9-} (C_{3v}) is associated to the 4f site. $AlCrO_9^{12-}$ and $Cr_2O_9^{12-}$ picture two adjacent 4f sites doped with one or two Cr^{3+} ions respectively. Atomic distances used in the cluster geometries are taken from Khan et al [4]. These diagrams show the $d\varepsilon\uparrow$ ($d\varepsilon\downarrow$) splittings into a_1 and e levels increase slightly from 2a to 4f sites while the two groups of $d\varepsilon$ levels associated to Cr-Cr pair are spreaded on more than 0.2 ev ; an important covalency of Cr-Cr and Cr-O bonds is noticed in the latter. The energies of excited terms relatively to $^4A_2$ have been evaluated from suitable transition state computations between $d\varepsilon\uparrow^3$, $d\varepsilon\uparrow^2 d\varepsilon\downarrow$ and $d\varepsilon\uparrow^2 d\gamma\uparrow$ configurations. It is possible to deduce the B and C Racach parameters and the Dq crystal field strength from the transitions associated to the 2a site. Assuming C/B = 4.5, we obtain B = 774cm^{-1} and 10 Dq = 15910cm^{-1}. The electrostatic interactions provide the term energy diagram of figure 3a. On the other hand, the fluorescence emission line at 689nm, associated to $^2E \rightarrow ^4A_2$ emission (2a site) and the absorption peak at 565nm, attributed to $^4A_2 \rightarrow ^4T_2$ are used to obtain B_{exp} = 695nm, 10Dq = 17700cm^{-1} and the relevant term energy diagram of figure 3b. Both theoretical and experimental term positions are compared to the absorption spectrum in this figure and allow the assignations of all the experimental structures. Nevertheless, it may be noticed

Figures 1 and 2 : O2p, Cr3d and Al3s, Al3p eigenvalues in various cluster representative of undoped and doped 2a, 4f and coupled 4f sites in $LaMgAl_{11}O_{19}$.

that the $^4A_2 \longrightarrow {}^4T_2$ energy is overestimated since the peak maximum lies at shorter wavelength than the zero-phonon line, unresolved in the spectrum, but expected around 650nm [5] ; this would imply Dq $\sim$ 1540 cm^{-1}, much more in agreement with the theoretical data.

For the 4f site, the $^2E \rightarrow {}^4A_2$ emission line is calculated to be 0.075eV lower than in the 2a case. This follows the experimental trends where the wavelength of this line varies from 689 to 695 nm compared to the 623 to 647 nm calculations in the 2a and 4f sites respectively. Simultaneously, $^4A_2 \rightarrow {}^4T_2$ would be spread by the splitting of $^4T_2$ into $^4A_1$ and ^4E terms (estimated around 0.08 ev) and a decrease of its mean energy is predicted. This correlates the experimental observations.

The overall splitting of d$\epsilon\uparrow$, d$\epsilon\downarrow$ and d$\gamma\uparrow$ levels in the pair center creates broad $^2E \rightarrow {}^4A_2$ and $^4A_2 \rightarrow {}^4T_2$ bands, which overlap each other. The minimum energy of $^4A_2 \rightarrow {}^4T_2$ transitions decreases again relatively to the cubic and pseudocubic cases.

The evolution of the calculated ^2E and $^4T_2$ energies show that 2a, 4f and pair centers behave as more and more low-field chromium complexes in the region Dq/B $\sim$ 2 in the Tanabe and Sugano d^3 diagram.

REFERENCES

1. B. Viana, A.M. Lejus, D. Vivien, V. Ponçon and G. Boulon
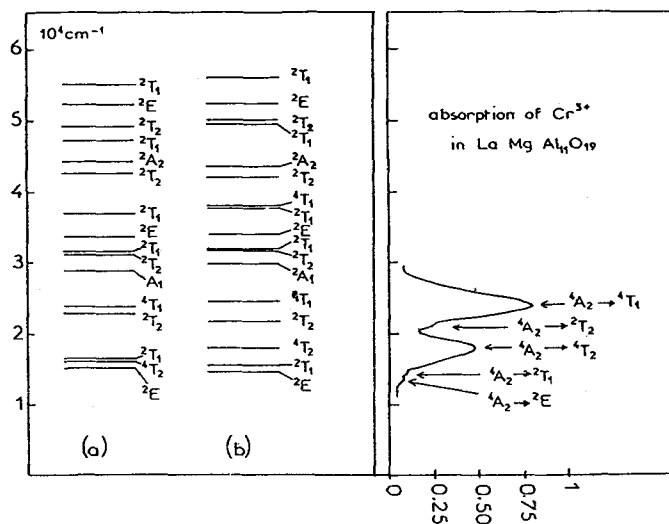   J. of Sol. State Chem. 60 (1987).

Figure 3 - Theoretical and experimental term diagrams of Cr^{3+} in octaedral symmetry compared to absorption spectrum of $LaMgAl_{11}O_{19}$: Cr.

2. P. Moretti and F.M. Michel-Calendini, Phys. Rev. B34, 8538 (1986).

3. S.H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. 58, L1200 (1980).

4. A. Khàn, A.M. Lejus, M. Madsae, J. Thery, D. Vivien and J.C. Bernier, J. Appl. Phys. 52, 6864 (1984).

5. G. Boulon in Disordered solids : structures and processes, Ed di Bartolo, Plenum Press - New-York (1988).