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To cite this version:
F. Michel-Calendini, K. Bellafrouch, V. Poncon, G. Boulon. Cr$^{3+}$ CENTERS IN THE LaMgAl$_{11}$O$_{19}$ LASER HOST: THEORETICAL STUDY THROUGH A MOLECULAR ORBITAL MODEL. Journal de Physique Colloques, 1987, 48 (C7), pp.C7-497-C7-499. <10.1051/jphyscol:19877118>. <jpa-00226935>

HAL Id: jpa-00226935
https://hal.archives-ouvertes.fr/jpa-00226935
Submitted on 1 Jan 1987

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

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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 Xa method. The computational framework is similar to the one described for Cr$^{3+}$ in perovskite oxides $^2$. 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$^{2-}$ ($D_{3d}$) and CrO$^{2-}$ ($D_{3d}$) represent the undoped and doped 2a site while CrO$^{2-}$ ($C_{3v}$) is associated to the 4f site. AlCrO$_9^{12-}$ and Cr$_2$O$_9^{12-}$ 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 $d_{e^1}$ ($d_{e^2}$) splittings into $a_g$ and $e$ levels increase slightly from 2a to 4f sites while the two groups of $d_{e}$ 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 $d_{e^1}$, $d_{e^2}$,$d_{e^4}$ and $d_{e^2}$$d_{e^4}$ configurations. It is possible to deduce the B and C Racah parameters and the $D_q$ crystal field strength from the transitions associated to the 2a site. Assuming $C/B = 4.5$, we obtain $B = 774$ cm$^{-1}$ and $10D_q = 15910$ cm$^{-1}$. 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 $B_{exp} = 695$ nm, $10D_q = 17700$ cm$^{-1}$ 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: 02p, Cr3d and Al3s, Al3p eigenvalues in various cluster representative of undoped and doped 2a, 4f and coupled 4f sites in LaMgAl11O19.

that the $4_{A_2} \rightarrow 4_{T_2}$ 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 $Dq \approx 1540$ cm$^{-1}$, much more in agreement with the theoretical data.

For the 4f site, the $2^E \rightarrow 4_{A_2}$ 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, $4_{A_2} \rightarrow 4_{T_2}$ would be spread by the splitting of $4_{T_2}$ into $4_{A_1}$ and $4^E$ terms (estimated around 0.08 eV) and a decrease of its mean energy is predicted. This correlates the experimental observations.

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

The evolution of the calculated $2^E$ and $4_{T_2}$ 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
Figure 3 - Theoretical and experimental term diagrams of $\text{Cr}^{3+}$ in octaedral symmetry compared to absorption spectrum of $\text{LaMgAl}_{11}O_{19}$.