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# Solid State Reactions and Defects in Verneuil Laser Rubies II

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(10. VI. 70)

*Abstract.* Results of new computations of crystal field spectra of Cr<sup>+3</sup> in the interstitial site of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> structure are presented. The results are used to support an assignment of the absorption band at 315 nm ascribed to a typical defect in Verneuil grown laser rubies.

## 1. Introduction

In a recent paper, W. Borer et al. [1] reported crystal field analysis results of a defect observed in Verneuil laser rubies. This defect is characterized by an absorption band near 315 nm and has been assigned to transitions between crystal field levels of Cr<sup>+3</sup> at the interstitial site *b* in the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> structure [2]. In the meantime extensive crystal field calculations for transition metal ions have been made at this laboratory, based on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystal structure data given by Newnham [3], whereas earlier calculations were based on data published by Pauling et al. [4]. The use of the newer data led to significant changes of the crystal constants  $c_{lm}$  at sites *b*, *c* and *e*. In this paper we wish to report the corrected values for these constants and the energy levels for Cr<sup>+3</sup> at site *b*.

## 2. Calculation of Crystal Field Constants

Using the same assumptions for the calculation of the crystal field parameters  $c_{lm}$  as in *I*, but basing on Newnham's crystal structure data for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, the results collected in Table I are obtained. With respect to the crystallographic data it should be mentioned, that Newnham's data were first transformed to rhombohedral axes<sup>3)</sup>. In these axes system the structural parameters for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are<sup>4)</sup>

$$a = 5.128 \pm 0.0034 \text{ \AA},$$

$$\alpha = 55^\circ 17' \pm 3' 8''.$$

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<sup>3)</sup> Loc. cit. [2], p. 20, c.f. Figure 2.5.3.

<sup>4)</sup> Error derived from Newnham's data.

The following remarks concerning the crystal field coefficients listed in Table I seem to be in order

- the coefficients  $c_{0,0}$  are uncertain to the limits given owing to the well known convergence difficulties for the unipole terms,
- the coefficients  $c_{+4,-3}$ ,  $c_{4,3}$  of sites  $b$  and  $c$  and  $c_{1,\pm 1}$ ,  $c_{2,\pm 2}$  of site  $e$  show considerable differences to earlier published values<sup>5)</sup>. In part the discrepancies originate from the new crystallographic data in part from the change in phase of the angle  $\varphi$  originating from the new choice of crystallographic axis and in part however from errors in the earlier computations. Since all coefficients  $c_{lm}$ ,  $m \neq 0$ , depend on the choice of phase of the angle  $\varphi$ , the choice adapted for this paper is shown in Figure 1.

Table I  
Lattice potentials at the various sites of the corundum structure.

Site	Rhombohedral coordinates	$l$	$m$	Coefficient real part	$c_{lm}$ <sup>a)</sup> <sup>b)</sup> <sup>c)</sup> imag. part
$c$	– 0.148, – 0.148, – 0.148	0	0 <sup>d)</sup>	$-8.628 \pm 0.009$	0
		2	0	0.06717	0
		4	– 3	+ 0.235078	0.044656
		4	0	0.188189	0
		4	+ 3	– 0.235078	0.044656
		0	0 <sup>d)</sup>	$-0.349 \pm 0.008$	0
$b$	0, 0, 0	2	0	0.91569	0
		4	– 3	– 0.2044556	– 0.05278977
		4	0	0.463771	0
		4	+ 3	0.2044556	– 0.05278977
		0	0 <sup>d)</sup>	<b>6.878</b> $\pm$ 0.009	0
		1	– 1	– 0.07824	0
$e$	0.055998, – 0.555998, 0.250001	1	0	0	0
		1	+ 1	+ 0.07824	0
		2	– 2	+ 0.0759626	0
		2	– 1	0	– 0.475755
		2	0	0.0743679	0
		2	+ 1	0	– 0.475755
		2	+ 2	0.0759626	0

<sup>a)</sup>  $c_{lm}$  are the coefficients of the expansion  $V(r, \vartheta, \varphi) = e_0 \sum_{l,m} c_{lm} r^l Y_l^m(\vartheta, \varphi)$  for the lattice potential. Their dimension is  $\text{\AA}^{-(l+1)}$ .

<sup>b)</sup> Only those coefficients are given, which are necessary for a certain site symmetry and a certain electron configuration.

<sup>c)</sup> The lattice sums were carried out over a nearly spherical region of 50  $\text{\AA}$  radius.

<sup>d)</sup> The confidence interval given in this table for  $c_{00}$  represents the standard deviation of the constant calculated for twenty statistically selected values of  $r$  within 47.5 and 50  $\text{\AA}$ .

### 3. Crystal Field Energy Levels of $\text{Cr}^{+3}$ in the Interstitial Site $b$

Using the same technique for the computation of the crystal field levels as in I the results shown graphically in Figure 2 are obtained. Only few comments should be made

<sup>5)</sup> Loc. cit. [1], Table 6.

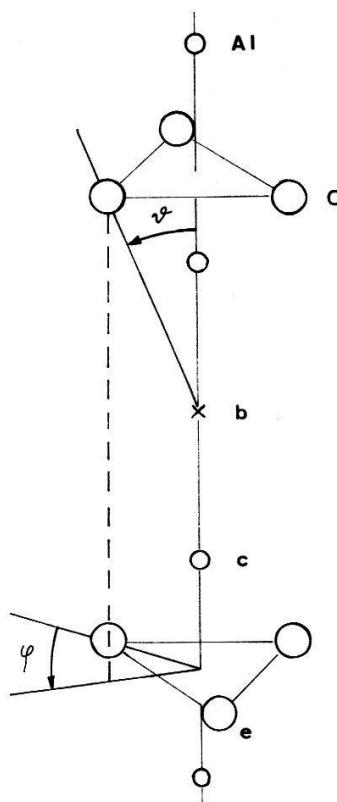


Figure 1  
Rhombohedral unit cell of  $\alpha\text{-Al}_2\text{O}_3$ . The definitions of the spherical coordinates used in this work are given. Notation of sites is as given in Ref. [2].

- (i) the general pattern of the crystal field levels shows marked differences to that obtained in *I*,
- (ii) the newly obtained levels fulfil the Kramers degeneracy to within better  $0.1\text{ cm}^{-1}$ . In *I* much larger discrepancies were obtained.

#### 4. Assignment of the Defect Absorption Bands

Basing on Figure 2, the absorption band of the defect near 315 nm ( $31750\text{ cm}^{-1}$ ) may be related to the transitions collected in Table 2.

Table 2  
Calculated transitions in the UV/VIS region, which explain the observed 315 nm band [ $31746\text{ cm}^{-1}$ ]

Energy of level [ $\text{cm}^{-1}$ ] <sup>a)</sup>	Assignment to free ion levels
33042.2	$4\text{ F} - 4\text{ P}$
33138.9	$4\text{ F} - 4\text{ P}$
33237.1	$4\text{ F} - 4\text{ P}$
33336.8	$4\text{ F} - 4\text{ P}$

<sup>a)</sup> Every level is doubly degenerate, according to Kramers theorem.

The results may be commented upon as follows:

- (i) the transitions assigned are both symmetry and spin allowed (in the free ion picture),
- (ii) the assignment proposed in *I* is not changed by the newly calculated crystal field levels for  $\text{Cr}^{+3}(b)$ .

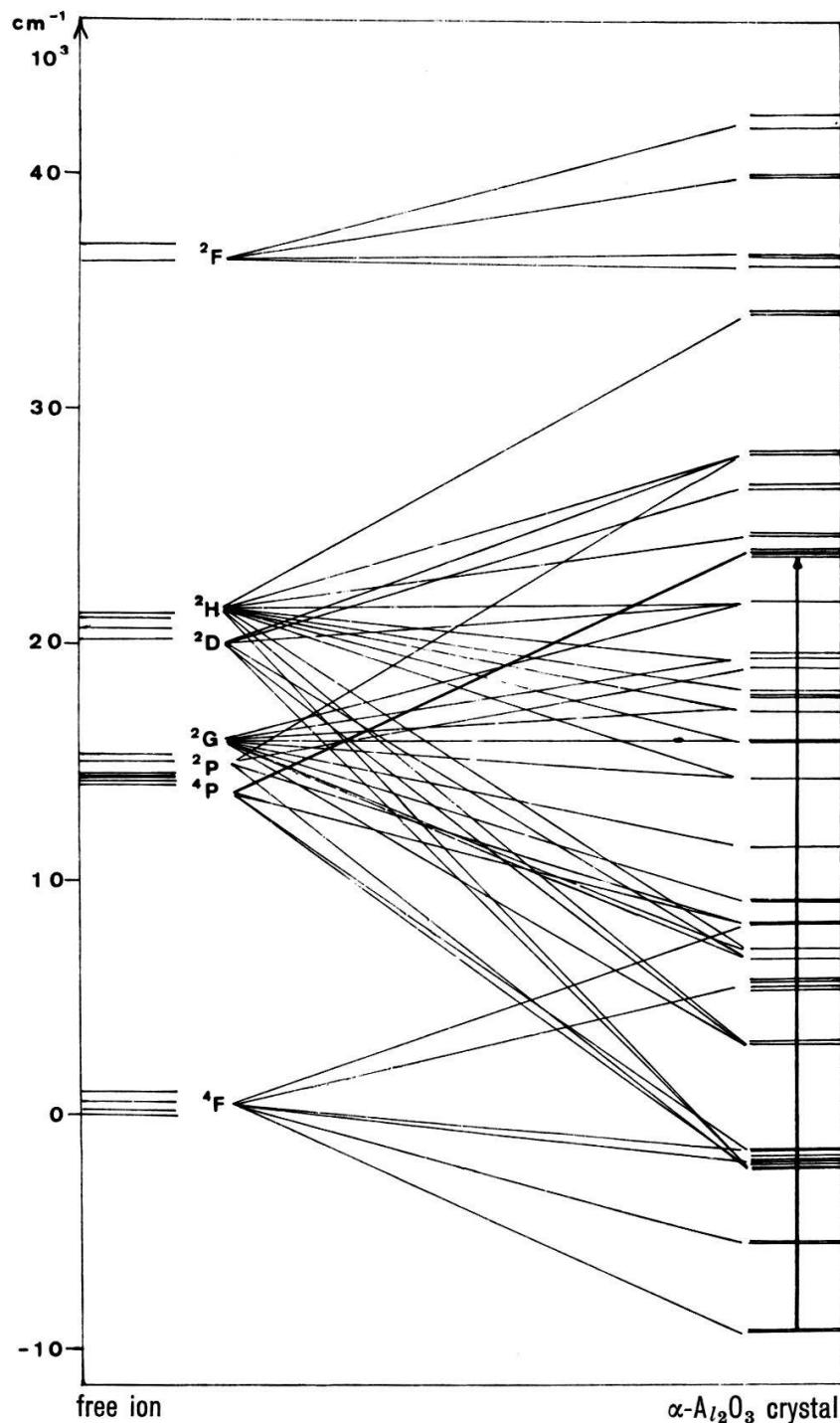


Figure 2  
Energy level diagram for interstitial  $\text{Cr}^{+3}$  ion (at the right). For comparison the levels of free  $\text{Cr}^{+3}$  ion are given at the left.

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