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Autor: Ballmer, P. / Blum, H. / Borer, W.J.
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Solid State Reactions and Defects in Verneuil Laser Rubies II

by **P. Ballmer¹⁾, H. Blum, W. J. Borer²⁾, K. Eigenmann and Hs. H. Günthard**

Swiss Federal Institute of Technology, Laboratory of Physical Chemistry,
Universitätsstrasse 22, 8006 Zürich, Switzerland

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Abstract. Results of new computations of crystal field spectra of Cr⁺³ in the interstitial site of the α -Al₂O₃ 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⁺³ at the interstitial site *b* in the α -Al₂O₃ structure [2]. In the meantime extensive crystal field calculations for transition metal ions have been made at this laboratory, based on α -Al₂O₃ 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⁺³ 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 α -Al₂O₃, 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 axes³⁾. In these axes system the structural parameters for α -Al₂O₃ are⁴⁾

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

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

¹⁾ Address: Djévahirdjian S.A., Monthei, Switzerland.

²⁾ Present address: Dept. of Electrical Engineering, University of Rhode Island, Kingston, Rhode Island 02881, USA.

³⁾ Loc. cit. [2], p. 20, c.f. Figure 2.5.3.

⁴⁾ 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 values⁵⁾. In part the discrepancies originate from the new crystallographic data in part from the change in phase of the angle φ 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 φ , 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} ^{a)} ^{b)} ^{c)} imag. part
c	– 0.148, – 0.148, – 0.148	0	0 ^{d)}	-8.628 ± 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 ^{d)}	-0.349 ± 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 ^{d)}	6.878 ± 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

^{a)} 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 $\text{\AA}^{-(l+1)}$.

^{b)} Only those coefficients are given, which are necessary for a certain site symmetry and a certain electron configuration.

^{c)} The lattice sums were carried out over a nearly spherical region of 50 \AA radius.

^{d)} 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 \AA .

3. Crystal Field Energy Levels of 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

⁵⁾ Loc. cit. [1], Table 6.

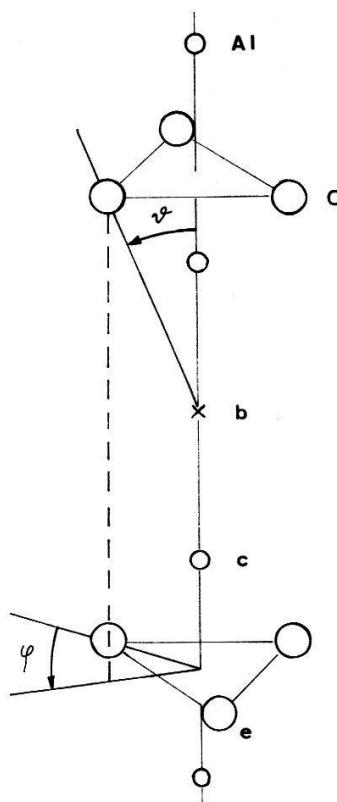


Figure 1
Rhombohedral unit cell of α - Al_2O_3 . The definitions of the spherical coordinates used in this work are given. Notation of sites is as given in Ref. [2].

- (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 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 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 cm^{-1}]

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

^{a)} 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 $\text{Cr}^{+3}(b)$.

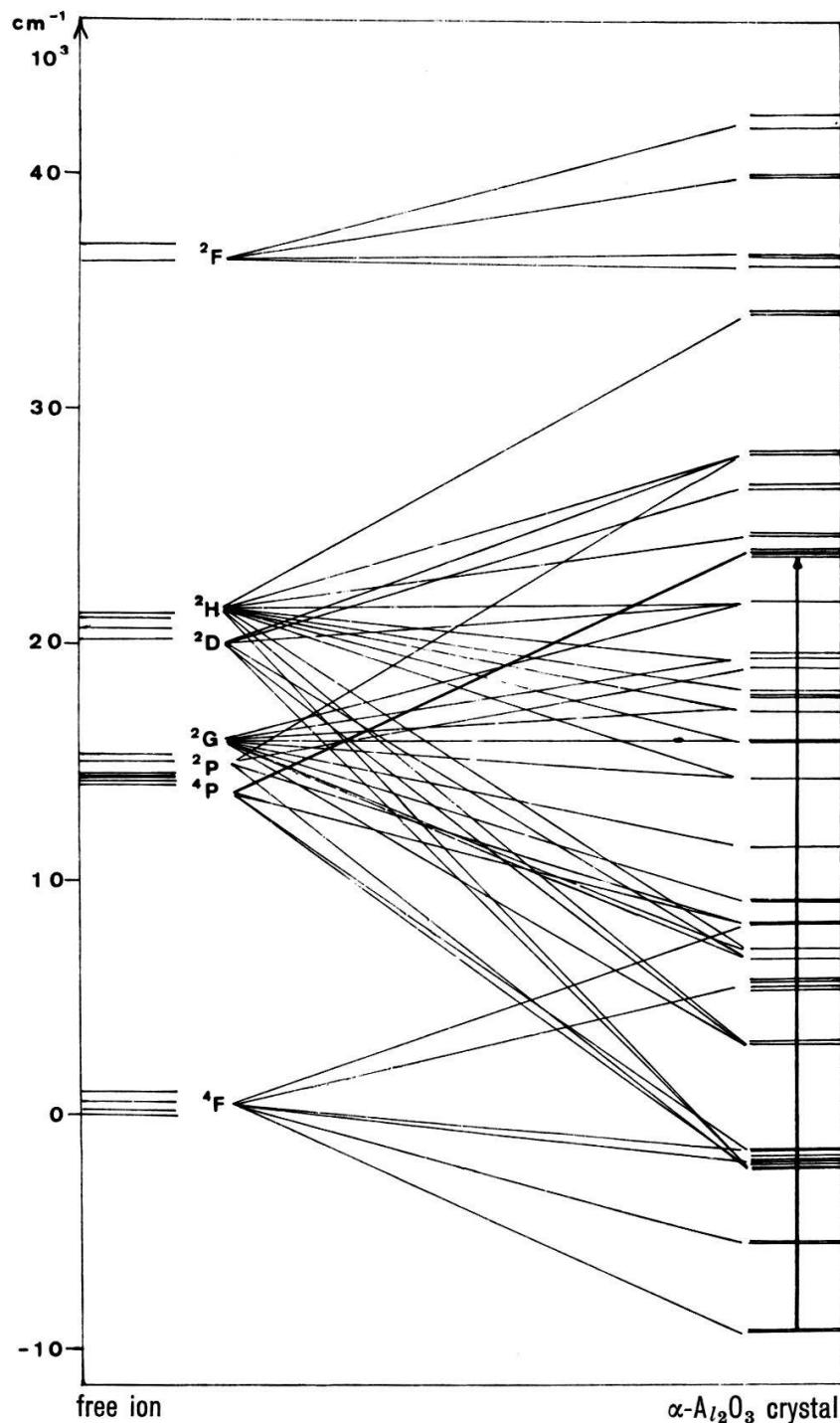


Figure 2
Energy level diagram for interstitial Cr^{+3} ion (at the right). For comparison the levels of free Cr^{+3} ion are given at the left.

Acknowledgment

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