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CRYSTALLINE FIELD PARAMETERS OF Cr^{2+} AND Cr^{4+} IN CORUNDUM

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Résumé. — L'objectif principal de cet article est l'évaluation des paramètres de champ cristallin (B , C , Dq , v , v') pour les ions $\text{Cr}^{2+}(3d^4)$ et $\text{Cr}^{4+}(3d^2)$ dans le corindon. L'absence de données expérimentales et les résultats médiocres obtenus avec le modèle de champ cristallin utilisé de façon conventionnelle ont conduit à en effectuer une détermination indirecte. En premier lieu, parmi les résultats optiques publiés qui concernent les ions $3d^n$ dans le réseau cristallin d' $\alpha\text{Al}_2\text{O}_3$ ceux ayant des données optiques connues avec une précision suffisante ont été sélectionnés ou discutés si nécessaire. A partir de ces résultats la variation des paramètres optiques pour des séries d'ions isoélectroniques a été déduite ; les paramètres optiques des ions $\text{Cr}^{4+}(3d^2)$ et $\text{Cr}^{2+}(3d^4)$ dans le même réseau cristallin ont alors été évalués. L'appartenance des bandes additionnelles du rubis irradié est discutée. Il est également montré que les valeurs obtenues des paramètres du champ trigonal des ions V^{3+} et Cr^{4+} expliquent de façon satisfaisante la séparation en énergie de l'état fondamental de ces deux ions.

Abstract. — The main purpose of this paper is to evaluate the crystalline field parameters (B , C , Dq , v , v') of the $\text{Cr}^{2+}(3d^4)$ and $\text{Cr}^{4+}(3d^2)$ ions in corundum. The lack of experimental data and the failure of calculations based on the conventional crystal model led to an indirect determination. The published optical data for the $3d^n$ ions in the $\alpha\text{Al}_2\text{O}_3$ lattice that is known with sufficient accuracy is discussed. From these results the variation of the parameters is obtained as a function of the electronic charge within the electronic series and the optical parameter values of the $\text{Cr}^{4+}(3d^2)$ and $\text{Cr}^{2+}(3d^4)$ in the same lattice are evaluated. The additional absorption bands in irradiated ruby are discussed. The trigonal field parameters of V^{3+} and Cr^{4+} ions are shown to be in good agreement with the ground state splitting of both ions.

1. Introduction. — The $\text{Cr}^{4+}(3d^2)$ and $\text{Cr}^{2+}(3d^4)$ ions have been detected in irradiated ruby respectively by EPR [1, 2] and APR [3] experiments. Using EPR we have recently made an experimental study of the ground state including the hyperfine structure (isotope 53) and the influence of an applied electric field [4]. The knowledge of the different crystalline field parameters of these ions in the $\alpha\text{Al}_2\text{O}_3$ lattice is necessary to analyse the above results. These parameters should be preferably determined from a fit of the optical spectroscopic data. However irradiated ruby shows in its optical spectrum several additional bands with a rather uncertain identification, and this method cannot be used. Consequently to determine the crystalline field parameters of Cr^{4+} and Cr^{2+} we present an indirect approach based on the variation of these parameters in the same lattice as a function

of the electronic charge within the $3d^n$ electronic series. To arrive at the form of this variation of parameters, we were first led to discuss briefly the optical spectra and the parameter values for the $3d^2(\text{V}^{3+})$ and $3d^3(\text{V}^{2+}, \text{Mn}^{4+})$ ions. The energy levels of both ions are calculated and the additional absorption bands in irradiated ruby are discussed. Finally, it is shown that the trigonal field parameters can be used to calculate ground state splitting for V^{3+} and Cr^{4+} , in agreement with experiment.

The analysis of each optical spectrum is made in the strong field scheme. The following parameters are used : B , C for the Coulomb interaction, Dq for the crystalline field of cubic symmetry, v and v' for the trigonal field and ζ for the spin orbit interaction. As previously mentioned the crystal field theory is unable to account for the optical parameter values even in the strong binding ionic crystals, but it becomes a convenient tool when the parameters are fitted to the experimental data. An uncertainty of about 5 % is estimated in the parameter values as the approximate

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TABLE I

Optical fitting parameters of the V^{3+} ion in $\alpha\text{Al}_2\text{O}_3$

Author	Dq cm^{-1}	B cm^{-1}	C cm^{-1}	v cm^{-1}	v' cm^{-1}	B/B_0	C/C_0
—	—	—	—	—	—	—	—
This work	1 812	590	2 800	850	200	0.69	0.73
Macfarlane [7]	1 800	610	2 500	800	200	0.71	0.65
Rahman and Runciman [8]	1 800	605	2 440	830	240	0.705	0.64

model which we used neglects vibronic interactions, configuration mixing, many body and Jahn-Teller effects.

2. V^{3+} in $\alpha\text{Al}_2\text{O}_3$. — 2.1 THE OPTICAL SPECTRUM OF V^{3+} IN $\alpha\text{Al}_2\text{O}_3$. — The optical spectrum of vanadium corundum ($V^{3+} : \alpha\text{Al}_2\text{O}_3$) has been studied experimentally mainly by Pryce and Runciman [5], McClure [6] and discussed by Macfarlane [7], Rahman and Runciman [8].

The analysis of these data shows that : the observation and assignment of the two broad bands respectively observed at $25\,000\text{ cm}^{-1}$ and $17\,500\text{ cm}^{-1}$ and the sharp line at $21\,025\text{ cm}^{-1}$ are well established. However the observation of the $8\,770\text{ cm}^{-1}$ absorption line reported by Pryce and Runciman [5] is uncertain, since it was not confirmed by McClure [6], Sakatsume and Tsujikawa [9]. In the same way the assignment of the $9\,748\text{ cm}^{-1}$ line within the t_{2g}^3 configuration from selection rules in C_{3v} symmetry is not satisfactory. Moreover the trigonal splitting of the ground state ${}^3T_1(t_{2g}^3)$ in the 10^3 cm^{-1} region a value which would be important to analyse the ground state fine structure has never been measured.

We have performed optical absorption and fluorescence measurements in the visible and infrared region with a very high sensitivity spectrometer and in a wide range of operating conditions (crystal doping, temperature) [10]. Our results are in excellent agreement with the major part of the previously published data but again no absorption is detected near $8\,770\text{ cm}^{-1}$ [11]. This result is confirmed by Runciman⁽¹⁾. In the far infrared region the phonon spectrum of the crystal is responsible for too large an absorption to allow the observation of the ${}^3T_1({}^3\hat{E}) \rightarrow {}^3\hat{A}_2$ ground state trigonal splitting transition.

2.2 DETERMINATION OF THE CRYSTALLINE FIELD PARAMETERS AND DISCUSSION. — We have analyzed the V^{3+} optical spectrum excluding the $8\,770\text{ cm}^{-1}$ line and determined the five crystalline field parameters from a fit of the four detected transitions and the trigonal splitting of the $25\,000\text{ cm}^{-1}$ transition (see Appendix A). The values obtained and the energy levels calculated are listed in table I and figure 1

FIG. 1. — Comparison between experimental and theoretical energy levels of the V^{3+} ion in $\alpha\text{Al}_2\text{O}_3$.

respectively, with those previously given by Macfarlane [7], Rahman and Runciman [8] for comparison. In the Appendix A we give the analytical expressions for the observed transitions valid for small variations of the parameter values from those given in table I.

The fact that the previously reported line at $8\,770\text{ cm}^{-1}$ does not belong to the vanadium corundum spectrum has the following consequences :

The $9\,748\text{ cm}^{-1}$ line must now be identified with the ${}^3\hat{A}_2 \rightarrow {}^1T_2({}^1\hat{E})$ transition.

The Racah parameter C is increased by about 10 % compared to the previous analysis. This allows a better fit of the $({}^3\hat{A}_2 \rightarrow {}^1\hat{A}_1)$ transition while keeping a good agreement for the $({}^3\hat{A}_2 \rightarrow {}^1T_2({}^1\hat{E}))$ transition.

Dq , B , v and v' differ slightly from the previous determinations (within the 5 % estimated error), but simultaneously conserve the energy centre of gravity of the ${}^3T_2 \rightarrow {}^3A_2$ transition and allow a better fit of the $t_{2g}^3 e_g {}^3T_1({}^3\hat{A}_2 - {}^3\hat{E})$ trigonal splitting.

3. V^{2+} and Mn^{4+} in $\alpha\text{Al}_2\text{O}_3$. — The $3d^3$ ions V^{2+} and Mn^{4+} are isoelectronic with Cr^{3+} and some of their optical properties in the visible region have been studied and analyzed by Sturge [12], Geschwind *et al.* [13] and Crozier [14]. The number of transitions detected and measured with enough accuracy for both ions is less than five and does not allow a unique

⁽¹⁾ Runciman, W. A., Private communication.

determination of the five crystalline field parameters as in the more favorable case of the V³⁺ and Cr³⁺ ions. The impurity ions which enter in substitution of Al³⁺ ions are generally of the M³⁺ type in order to maintain the electrical neutrality of the crystal. The formation of M²⁺ and M⁴⁺ ions derived from the M³⁺ may occur through ionizing irradiation (X, γ rays) at a rate of a few per cent of the M³⁺ concentration. Simultaneously, other colour centres are created during the irradiation process but the large M³⁺ spectrum intensity may blur the additional bands. For V²⁺ [12] and Mn⁴⁺ [13, 14] ions the detection of fluorescent lines allows a positive identification of the ionized state and a selective absorption study of the optical spectrum. We have found it necessary to analyse the available data concerning V²⁺ and Mn⁴⁺ ions alongside the more precisely known parameter values for Cr³⁺ [15] and V³⁺, in order to obtain the evolution of *B*, *C*, *Dq*, *v* and *v'* in the isoelectronic series.

3.1 CRYSTALLINE FIELD PARAMETERS OF THE V²⁺ AND Mn⁴⁺ IONS IN αAl₂O₃. — The experimental optical data used to analyse the V²⁺ and Mn⁴⁺ ions and the corresponding values of the crystalline field parameters are listed in figure 2 and table II respectively.

They are determined as follows : *Dq* is obtained in the cubic approximation from the energy transition ⁴A₂(t_{2g}³) → ⁴T₂(t_{2g}²e_g) equal to 10 *Dq*.

B and *C* are obtained simultaneously from a fit of the fluorescence transition ²E(t_{2g}³) → ⁴A₂(t_{2g}³) observed with both ions and the *C/B* ratio.

This ratio is deduced from the free ion value and the *C/B* values for Cr³⁺ and V³⁺ in the same lattice.

The trigonal field parameters *v* and *v'* are obtained by fitting the 2 *D* and *Δ* splittings arising respectively from the ⁴A₂(t_{2g}³) and ²E(t_{2g}³) states which are known with great accuracy for both ions.

For V²⁺ we use also the trigonal splitting of the ⁴T₂ excited state which is approximately equal to *v*/2, and for Mn⁴⁺ we choose the ζ/ζ₀ value about half way between the 0.66 Cr³⁺ value and the 0.5 extreme value in the case of electronic delocalization.

The 2 *D* and *Δ* splittings are calculated with the *Dq*, *B*, *C* values previously determined, using Macfarlane's formalism [16]. The analytical expressions as a function of *v* and *v'* are given in Appendix B. We have

FIG. 2. — Experimental energy levels of the V²⁺, Cr³⁺ and Mn⁴⁺ ions in αAl₂O₃.

checked that in our range of *Dq/B* values their validity is good compared to an exact diagonalization.

3.2 DISCUSSION. — The experimental data for the V²⁺ and Mn⁴⁺ ions do not allow a determination of the optical fitting parameters in a self consistent way. For the Racah parameters *B* and *C* we have found it convenient to take into account the Cr³⁺ and V³⁺ values known with a good accuracy. The trigonal field parameters are determined using Macfarlane's work. When the crystal field calculations are carried out using many perturbation loops they can account quite accurately for the ground state splitting as well as for the splitting of the ²E excited state.

The optical parameters determined in this way explain properly the known optical transitions for

TABLE II
Optical fitting parameters of the V²⁺, Cr³⁺ and Mn⁴⁺ ions in αAl₂O₃

	<i>Dq</i> (cm ⁻¹)	<i>B</i> (cm ⁻¹)	<i>C</i> (cm ⁻¹)	<i>v</i> (cm ⁻¹)	<i>v'</i> (cm ⁻¹)	ζ/ζ ₀	<i>B/B</i> ₀	<i>C/C</i> ₀	<i>C/B</i>	<i>C</i> ₀ / <i>B</i> ₀	<i>Dq</i>	<i>B</i>	<i>C</i>	<i>v</i>	<i>v'</i>
V ²⁺	1 520	540	2 500	460	830	0.77	0.73	0.76	4.65	4.32	1 500	550	2 475	420	1 100
Cr ³⁺	1 810	650	3 120	850	680	0.66	0.70	0.74	4.8	4.5	1 800	650	3 120	830	840
Mn ⁴⁺	2 150	660	3 240	1 500	400	0.61	0.63	0.66	4.9	4.7	2 100	700	3 150	2 100	570

Previous determinations [12, 13, 17].

both ions and the A splitting but underestimate slightly the zero field splitting $2D$ of the ground state. In table II are listed for comparison the values previously given by Feher and Sturge [17].

These values are given by the authors as rough estimates to explain stress effects on the trigonal splitting. Their calculations were carried out using a reduced number of perturbation loops and an overestimated covalency reduction factor of the spin orbit coupling for Mn^{4+} ($\zeta/\zeta_0 = 0.50$) which lead respectively to v' values 30 % less and v value of Mn^{4+} 40 % greater than ours.

4. Cr^{4+} and Cr^{2+} in $\alpha\text{Al}_2\text{O}_3$. — The Cr^{4+} ($3d^2$) and Cr^{2+} ($3d^4$) were first detected in irradiated ruby by Hoskins and Soffer [1] using EPR technique and by Guermeur *et al.* [3] using APR technique. However very little is known about their optical properties. We have performed optical spectra measurements at low temperatures (77 K) with X irradiation *in situ* in order to stabilize the created colour centres. Other measurements were made at helium temperatures after room temperature γ irradiation at a rate varying between 10^4 and 10^6 R. Our purpose was to ionize and stabilize ionic centres without creating new defects inside the lattice. The experimental results are found in good agreement with previously published data and show essentially several broad bands the identification of which is rather uncertain [18, 19, 20].

From a comparison between the additional bands observed in irradiated pure corundum [21] and in irradiated ruby, it can only be stated that the additional bands peaking at $21\,000\text{ cm}^{-1}$ and $26\,000\text{ cm}^{-1}$ are due to centres derived from a Cr^{3+} ion or associated with the mechanism of charge compensation when Cr^{3+} ionization occurs. Under these conditions the optical fitting parameters of the Cr^{2+} and Cr^{4+} ions cannot be directly determined. We have used an indirect approach based on the progression of these parameters for the $3d^3$ series as a function of electronic charge and the known results for the Ti^{3+} ($3d^1$) [22, 23], V^{3+} and Mn^{3+} [6] in the same lattice. With these values the energy levels of both ions are calculated in the cubic approximation and the identification of the two additional bands ($21\,000\text{ cm}^{-1}$, $26\,000\text{ cm}^{-1}$) is discussed.

4.1 CRYSTALLINE FIELD PARAMETERS OF THE Cr^{2+} AND Cr^{4+} IONS. — Figure 3 shows that for the $3d^3$ ions (Cr^{3+} , V^{2+} , Mn^{4+}) in $\alpha\text{Al}_2\text{O}_3$ lattice Dq increases with the nominal charge of the impurity ion by approximately 20 % when going from a divalent to a trivalent ion (V^{2+} , Cr^{3+}) or from a trivalent to a tetravalent ion (Cr^{3+} , Mn^{4+}). We also note that for the following trivalent ions Ti^{3+} , V^{3+} , Cr^{3+} and Mn^{3+} , Dq has values very close to $1\,850\text{ cm}^{-1}$ within the margin of experimental error. The Racah parameters B , C are estimated from the free ions values B_0 , C_0 and with the condition $C_0/B_0 < C/B$ as occurs for

the neighbouring $3d^n$ ions [10]. The trigonal field parameters v , v' are estimated from the $3d^3$ (V^{2+} , Cr^{3+} , Mn^{4+}) and $3d^2$ (V^{3+}) values previously given, with the hypothesis of a similar progression within an isoelectronic series. The values obtained in this way are listed in table III.

FIG. 3. — Variation of the crystalline field parameters as a function of electric charge.

TABLE III
Optical fitting parameters of the Cr^{2+}
and Cr^{4+} ions in $\alpha\text{Al}_2\text{O}_3$

	Dq (cm^{-1})	B (cm^{-1})	C (cm^{-1})	v (cm^{-1})	v' (cm^{-1})
Cr^{4+}	2 150	660	3 200	1 500	100
Cr^{2+}	1 500	570	2 700		

4.2 DISCUSSION OF THE ADDITIONAL BANDS IN IRRADIATED RUBY. — Using the cubic field approximation we have represented in figures 4 and 5 the Cr^{2+} and Cr^{4+} energy levels dependence in reduced units of B as a function of the dimensionless parameter Dq/B . $Dq/B = 2.67$ is the strong field limit for the Cr^{2+} ion above which the 5E ground state no longer obeys Hund's rules and becomes $^3T_1(t_{2g}^4)$. The vertical dotted lines correspond to the Dq/B values listed in the table III for both ions and give the theoretical energy transitions. The identification of the $21\,000\text{ cm}^{-1}$ and $26\,000\text{ cm}^{-1}$ additional bands can

FIG. 4. — Theoretical energy levels of Cr^{4+} in $\alpha\text{Al}_2\text{O}_3$. FIG. 5. — Theoretical energy levels of Cr^{2+} in $\alpha\text{Al}_2\text{O}_3$.

be made easier by comparison with the experimental results of the isoelectronic ions $\text{Mn}^{3+}(3d^4)$ and $\text{V}^{3+}(3d^2)$. As the only observed Mn^{3+} transition between the ${}^5\text{E}(t_{2g}^3 e_g) \rightarrow {}^5\text{T}_2(t_{2g}^2 e_g^2)$ is centred at $20\,000\text{ cm}^{-1}$, one would expect to observe the corresponding absorption band for the Cr^{2+} ion near $16\,000\text{ cm}^{-1}$ since this energy transition is linearly dependent of Dq and the ratio

$$\frac{Dq(\text{Cr}^{2+})}{Dq(\text{Mn}^{3+})} \simeq 0.8.$$

We are led to conclude that the two additional bands cannot belong to the Cr^{2+} spectrum.

On the other hand V^{3+} has two strong absorption bands peaking at $17\,500\text{ cm}^{-1}$ and $25\,000\text{ cm}^{-1}$. The corresponding Cr^{4+} transitions are expected near $20\,000\text{ cm}^{-1}$ and $30\,000\text{ cm}^{-1}$ with the Dq and B values listed in table III. It would be tempting to assign the additional band peaking at $21\,000\text{ cm}^{-1}$ to the ${}^3\text{T}_1(t_{2g}^2) \rightarrow {}^3\text{T}_2(t_{2g} e_g)$ transition of the Cr^{4+} ion. Unfortunately the following points must be emphasized : (i) If the $21\,000\text{ cm}^{-1}$ band is assigned to the ${}^3\text{T}_1(t_{2g}^2) \rightarrow {}^3\text{T}_2(t_{2g} e_g)$ Cr^{4+} spectrum, the other ${}^3\text{T}_1(t_{2g}^2) \rightarrow {}^3\text{T}_1(t_{2g} e_g)$ band should be observed with about the same intensity (as for V^{3+}) near $30\,000\text{ cm}^{-1}$.

(ii) As the Cr^{4+} concentration deduced from EPR measurements is less than 5 % of the nominal Cr^{3+} concentration and considering the absorption intensity observed with the V^{3+} isoelectronic ion as a function of impurity concentration, we should observe a Cr^{4+} additional band intensity about two orders of magnitude less than really observed if the V^{3+} and Cr^{3+} oscillator strengths are similar. (iii) The peak value of the $21\,000\text{ cm}^{-1}$ absorption band seems to be correlated with the number of defects and other impurities present into the lattice [24]. These considerations lead us to rule out the assignment of the $21\,000\text{ cm}^{-1}$ band to Cr^{4+} and to correlate the two observed additional bands to colour centres associated with charge compensation mechanisms when Cr^{3+} ions are ionized. This conclusion suggested previously by Stickley *et al.* [24] and Hoskins and Soffer [1] is now based on converging observations both from experimental EPR and optical results and from the estimated optical spectra. Due to its low intensity the $21\,000\text{ cm}^{-1}$ estimated

transition of Cr^{4+} is then hidden in the $21\,000\text{ cm}^{-1}$ colour centre band. At 4 K the ionizing centres are thermally quenched and recombination is prevented

leading to a situation more favourable to an optical detection of Cr^{2+} and Cr^{4+} .

4.3 TRIGONAL FIELD PARAMETERS AND GROUND STATE SPLITTING OF V^{3+} AND Cr^{4+} . — Under the combined action of the trigonal field and the spin orbit-coupling on the ground state triplet of the $3d^2$ ions we have by increasing order of energy a spin singlet and a spin doublet with a splitting D which is known with great accuracy for both ions [4]. A large part of this splitting ($\approx 70\%$) arises from a second order perturbation loop between ${}^3\text{T}_1({}^3\hat{\text{A}}_2)$ and ${}^3\text{T}_1({}^3\hat{\text{E}})$ states interacting via the spin-orbit coupling. This approximation which gives a $(\zeta^2/4 \Delta({}^3\hat{\text{A}}_2 - {}^3\hat{\text{E}}))$ dependence must be improved considerably to interpret the evolution of the D splitting of the V^{3+} and Cr^{4+} ions which differ only by 10% . A more precise analysis of the D splitting can be performed in the following way.

The application of the Wigner-Eckart theorem allows one to treat the ${}^3\text{T}_1$ mixed ground state as a ${}^3\text{T}_1(t_{2g}^2)$ pure state [25]. The hamiltonian of the trigonal and spin orbit interactions acting on this ${}^3\text{T}_1(t_{2g}^2)$ state is as follows :

$$\mathcal{H}({}^3\text{T}_1) = \alpha_T U_z(T_2) + \alpha_{so} V_{so}. \quad (1)$$

The multiplying factors α_i are given by the ratio of the corresponding operator values between mixed and pure $|{}^3\text{T}_1\rangle$ wave functions :

$$\alpha_i = \langle {}^3\text{T}_1 | O_i | {}^3\text{T}_1 \rangle / \langle {}^3\text{T}_1(t_{2g}^2) | O_i | {}^3\text{T}_1(t_{2g}^2) \rangle.$$

From the wave function of the ${}^3\text{T}_1$ mixed state we obtain :

$$\alpha_T = \cos^2 \beta + 3 \sqrt{2} \sin \beta \cos \beta v'/v + \sin^2 \beta/2$$

with

$$\text{tg } 2\beta = 12B + 2\sqrt{2}v'/9B + 10Dq + v/3$$

$$\alpha_{so} = \cos^2 \gamma + 2 \sin \gamma \cos \gamma - \sin^2 \beta/2$$

with

$$\text{tg } 2\gamma = 12B - \sqrt{2}v'/9B + 10Dq - v/6.$$

After diagonalization of the hamiltonian (1) the splitting of the two lowest energy levels gives the following analytical D value :

$$D = \frac{-\alpha_{so}\zeta}{4} + \frac{1}{2} \times \sqrt{\left(\alpha_T v + \frac{\alpha_{so}\zeta}{2}\right)^2 + 2\alpha_{so}^2 \zeta^2 - \frac{1}{2}\sqrt{\alpha_T^2 v^2 + \alpha_{so}^2 \zeta^2}}.$$

In table IV are listed the experimental and calculated D values with the crystalline field parameters previously given. The fit is satisfactory with the trigonal parameters determined above for V^{3+} and Cr^{4+} and ζ/ζ_0 values in good agreement with the

increase of covalency as a function of the impurity ionic charge.

A more detailed analysis including the fit of Landé g factors and a discussion of the action of the Jahn-Teller effect on the ground state will be given in a forthcoming paper.

TABLE IV

Comparison between experimental and theoretical ground state splitting D of the V^{3+} and Cr^{4+} ions in $\alpha\text{Al}_2\text{O}_3$.

ion	V^{3+}	Cr^{4+}
D (cm^{-1})		
experimental	8.29 ± 0.02	7.55 ± 0.02
D (cm^{-1})		
theoretical	8.35	7.85
ζ/ζ_0	0.78	0.60

4.4 CONCLUSION. — The crystalline field parameters of Cr^{4+} in $\alpha\text{Al}_2\text{O}_3$ evaluated indirectly are given with enough accuracy to analyse the ground state structure of Cr^{4+} . The progression of the D splitting for the two $3d^2$ known ions (V^{3+} , Cr^{4+}) is explained in a satisfactory way. The optical spectra of Cr^{2+} and Cr^{4+} deduced from the estimated parameters confirm that the two additional bands of irradiated ruby peaking at $21\,000\text{ cm}^{-1}$ and $26\,000\text{ cm}^{-1}$ probably do not belong to the Cr^{4+} or Cr^{2+} ions. Comparison with the V^{3+} and Mn^{3+} spectra suggests that they arise from colour centres caused by compensating electric charges when Cr^{3+} centres are ionized, contrary to some previous interpretations. A successful optical study would probably require a simultaneous detection of the EPR and optical spectra under X irradiation *in situ* at helium temperatures. Our analysis gives a good indication of the Cr^{2+} and Cr^{4+} transition energies for their experimental investigation.

Appendix A. — V^{3+} optical fitting parameters. — The fine structure of V^{3+} in $\alpha\text{Al}_2\text{O}_3$ resulting from spin orbit interaction is not resolved experimentally in the two broad bands and the energy levels of the sharp lines are shifted only by a few cm^{-1} by the spin orbit interaction (second-order perturbation). Consequently the computations are limited to the trigonal field approximation.

— In a crude analysis v' is neglected ($\ll v$). The central positions of band I ($25\,000\text{ cm}^{-1}$) and II ($17\,500\text{ cm}^{-1}$), the trigonal splitting of band I ($\approx v/2$) and the sharp line III ($21\,025\text{ cm}^{-1}$) are fitted with the following first-order values :

$$\begin{aligned} Dq &= 1\,823\text{ cm}^{-1} & B &= 570\text{ cm}^{-1} \\ C &= 2\,600\text{ cm}^{-1} & v &= 760\text{ cm}^{-1}. \end{aligned}$$

— In a second step the wave functions of the ${}^3\text{T}_1(\text{t}_{2g} e_g)$ state are calculated with the above values in a trigonal basis :

$$|{}^3\hat{\text{A}}_2\rangle = \cos \alpha |t_{2g} e_g {}^3\text{T}_1({}^3\hat{\text{A}}_2)\rangle + \sin \alpha |t_{2g} {}^3\text{T}_1({}^3\hat{\text{A}}_2)\rangle$$

$$\text{with } \text{tg } 2\alpha = \frac{12B + 2\sqrt{2}v'}{10Dq + 9B + v/3}$$

$$|{}^3\hat{\text{E}}\rangle = \cos \alpha' |t_{2g} e_g {}^3\text{T}_1({}^3\hat{\text{E}})\rangle + \sin \alpha' |t_{2g} {}^3\text{T}_1({}^3\text{E})\rangle$$

$$\text{with } \text{tg } 2\alpha' = \frac{12B - \sqrt{2}v'}{10Dq + 9B - v/6}$$

giving the following analytical expression for the trigonal splitting of the ${}^3\text{T}_1(\text{t}_{2g} e_g)$ state :

$$t_{2g} e_g {}^3\text{T}_1({}^3\hat{\text{E}}) - t_{2g} e_g {}^3\text{T}_1({}^3\hat{\text{A}}_2) = 0.54v - 0.6v'.$$

The 380 cm^{-1} splitting is fitted with $v = 800 \text{ cm}^{-1}$, $v' = 150 \text{ cm}^{-1}$. With this complete set of values, we calculate all the energy levels within the t_{2g}^2 configuration and notice particularly the following values :

$$\text{t}_{2g}^2({}^1\text{E}) - \text{t}_{2g}^2({}^3\text{A}_2) = 9550 \text{ cm}^{-1}$$

$$\text{t}_{2g}^2 {}^1\text{T}_2({}^1\text{E}) - \text{t}_{2g}^2({}^3\text{A}_2) = 10400 \text{ cm}^{-1}.$$

The line IV (9748 cm^{-1}) may then be assigned to the $\text{t}_{2g}^2 {}^1\text{T}_2({}^1\hat{\text{E}}) \rightarrow \text{t}_{2g}^2({}^3\hat{\text{A}})$ transition.

— In the third step we calculate analytical expressions for the energy splittings of the different levels with the ground state. The final values listed in table I give the best fit with the experimental data.

The analytical energy splittings valid for small variations of the parameters listed in table I are as follows :

Band I

$$\begin{aligned} t_{2g} e_g {}^3\text{T}_1({}^3\hat{\text{E}}) - \text{t}_{2g}^2 {}^3\text{T}_1({}^3\hat{\text{A}}_2) &= 9.558 Dq + 12.08 B + 0.879 v + 0.226 v' \\ t_{2g} e_g {}^3\text{T}_1({}^3\hat{\text{A}}_2) - \text{t}_{2g}^2 {}^3\text{T}_1({}^3\hat{\text{A}}_2) &= 9.522 Dq + 12.235 B + 0.317 v + 0.831 v'. \end{aligned}$$

Trigonal splitting

$$t_{2g} e_g {}^3\text{T}_1({}^3\hat{\text{E}}) - t_{2g} e_g {}^3\text{T}_1({}^3\hat{\text{A}}_2) = 0.036 Dq - 0.155 B + 0.562 v - 0.605 v'.$$

Band II

$$\begin{aligned} t_{2g} e_g {}^3\text{T}_2({}^3\hat{\text{E}}) - \text{t}_{2g}^2 {}^3\text{T}_1({}^3\hat{\text{A}}_2) &= 9.753 Dq - 1.346 B + 0.774 v + 0.461 v' \\ t_{2g} e_g {}^3\text{T}_2({}^3\hat{\text{A}}_1) - \text{t}_{2g}^2 {}^3\text{T}_1({}^3\hat{\text{A}}_2) &= 9.757 Dq - 1.379 B + 0.325 v + 0.434 v'. \end{aligned}$$

Trigonal splitting of band II

$$t_{2g} e_g {}^3\text{T}_2({}^3\hat{\text{E}}) - t_{2g} e_g {}^3\text{T}_2({}^3\hat{\text{A}}_1) = -0.0039 Dq + 0.0324 B + 0.449 v + 0.027 v'.$$

Line I

$$\text{t}_{2g}^2({}^1\text{A}_1) - \text{t}_{2g}^2 {}^3\text{T}_1({}^3\hat{\text{A}}_2) = 1.210 Dq + 13.899 B + 3.649 C + 0.779 v + 0.371 v'.$$

Levels with symmetry ${}^1\text{E}$

$$\begin{aligned} \text{t}_{2g}^2 {}^1\text{E}({}^1\hat{\text{E}}) - \text{t}_{2g}^2 {}^3\text{T}_1({}^3\hat{\text{A}}_2) &= -0.160 Dq + 7.134 B + 1.998 C + 0.987 v + 0.51 v' \\ \text{t}_{2g}^2 {}^1\text{T}_2({}^1\hat{\text{E}}) - \text{t}_{2g}^2 {}^3\text{T}_1({}^3\hat{\text{A}}_2) &= -0.116 Dq + 7.002 B + 1.999 C + 0.003 v + 0.219 v' \\ \text{t}_{2g}^2 {}^1\text{E}({}^1\hat{\text{E}}) - \text{t}_{2g}^2 {}^1\text{T}_2({}^1\hat{\text{E}}) &= -0.044 Dq + 0.132 B - 0.001 C + 0.984 v + 0.291 v'. \end{aligned}$$

Trigonal splitting of the ground state

$$\text{t}_{2g}^2 {}^3\text{T}_1({}^3\hat{\text{E}}) - \text{t}_{2g}^2 {}^3\text{T}_1({}^3\hat{\text{A}}_2) = -0.0392 Dq + 0.119 B + 0.986 v + 0.615 v'.$$

Appendix B. — V^{2+} and Mn^{4+} optical fitting parameters. — The B and C Racah parameters cannot be obtained directly from the optical data.

The ${}^4\text{A}_2(\text{t}_{2g}^3) \rightarrow {}^4\text{T}_1(\text{t}_{2g}^2 e_g)$ absorption band depends only on Dq and B .

However it was not observed for Mn^{4+} and was

only detected in the case of V^{2+} through the excitation spectrum of the ${}^2E \rightarrow {}^4A_2$ fluorescence line and there are indications that the measured value is perturbed by the existence of the very strong absorption band of V^{3+} . Consequently the only other optical result is the fluorescence transition ${}^2E(t_{2g}^3) \rightarrow {}^4A_2(t_{2g}^3)$ situated respectively at $11\,691\text{ cm}^{-1}$ and $14\,781\text{ cm}^{-1}$ for V^{2+} and Mn^{4+} which has an energy depending simultaneously of Dq , B and C . There it is necessary to define the value of the ratio C/B from other data. This was done from a comparison of the ratio C_0/B_0 of the Racah parameters for the free ions and the values for Cr^{3+} and V^{3+} . C_0/B_0 increases with the ion charge within an isoelectronic series and $C/B > C_0/B_0$ for a given ion. Therefore we choose for V^{2+} and Mn^{4+} C/B values equal to 4.65 and 4.9 respectively. Then we diagonalize the 2E levels matrix and draw the normalised curve

$$\Delta E[{}^2E(t_{2g}^3) \rightarrow {}^4A_2(t_{2g}^3)]/B$$

as a function of C/B . With the above C/B values and the experimental energy transitions ΔE we obtain the values of B and C listed in table II. We use the following procedure to evaluate the trigonal field parameters :

— The trigonal splitting of the 4T_2 excited state is approximately equal to $v/2$ and is known experimentally for Cr^{3+} and V^{2+} but not for Mn^{4+} . The trigonal splitting of the 4T_1 excited state which is

$${}^4T_1(t_{2g}^2 e_g) ({}^4\hat{E}-{}^4\hat{A}_2) \simeq v/2 + v'$$

is also known experimentally for Cr^{3+} and V^{2+} . However it has been shown by Rimmer and Johnston [26, 27] that it is not fitted correctly in the optical spectrum and we shall not use this result.

The other available experimental results are the $2D$ and $1A$ splittings of the ${}^4A_2(t_{2g}^3)$ and ${}^2E(t_{2g}^3)$ states. Macfarlane has performed a perturbation calculation of these splittings for $3d^3$ ions in trigonal and tetragonal symmetry using many loops with excited states and obtained analytical expressions. He has also shown that their validity is good compared to an exact diagonalisation for the Dq/B values of the $3d^3$ ions in Al_2O_3 . Using Macfarlane's results, we obtained the following expressions for the $2D$ and $1A$ splittings as function of the trigonal parameters v and v' and the reduced spin orbit parameter ζ/ζ_0 :

Splitting $2D$:

$$\begin{aligned} V^{2+} & 21.08 \times 10^{-9} \zeta^2 v' - 1.29 \times 10^{-9} \zeta^2 v \\ Cr^{3+} & 14.41 \times 10^{-9} \zeta^2 v' - 0.93 \times 10^{-9} \zeta^2 v \\ Mn^{4+} & 11.76 \times 10^{-9} \zeta^2 v' - 0.62 \times 10^{-9} \zeta^2 v. \end{aligned} \quad (1)$$

Splitting $1A$:

$$\begin{aligned} V^{2+} & 25.4 \times 10^{-5} \zeta v - 1.35 \times 10^{-5} \zeta v' \\ Cr^{3+} & 20.9 \times 10^{-5} \zeta v - 1.1 \times 10^{-5} \zeta v' \\ Mn^{4+} & 19.82 \times 10^{-5} \zeta v - 1.1 \times 10^{-5} \zeta v'. \end{aligned} \quad (2)$$

The relations (1) and (2) show distinctly that $2D$ is mostly determined by the trigonal parameter v' and $1A$ by v .

Using for the V^{2+} and Cr^{3+} ions the first order value of v obtained from the 4T_2 band trigonal splitting and the experimental values of $2D$ and $1A$, we obtain a first determination of v' and ζ/ζ_0 . In the case of Mn^{4+} , as we do not know the ${}^4T_2({}^4\hat{E}-{}^4\hat{A}_1)$ splitting, we must choose one of the three unknown parameters. Consequently we fix the value of ζ/ζ_0 for Mn^{4+} to 0.60, about half-way between the 0.66 Cr^{3+} value and 0.5 which may be thought as an extreme value of the spin-orbit reduction factor in the case of strong covalency and obtain v and v' .

References

- [1] HOSKINS, R. H. and SOFFER, B. H., *Phys. Rev.* **133** (1964) 499.
- [2] STANDLEY, K. J. and VAUGHAN, R. A., *Proc. Phys. Soc.* **86** (1965) 861.
- [3] GUERMEUR, R., JOFFRIN, J., LEVELUT, A. and PENNE, J., *Phys. Rev.* **187** (1969) 1153.
- [4] PONTNAU, J. and ADDE, R., *J. Phys. & Chem. Solids* **36** (1975) 1023.
- [5] PRYCE, M. H. L. and RUNCIMAN, W. A., *Discuss. Faraday Soc.* **26** (1958) 34.
- [6] MCCLURE, D. S., *J. Chem. Phys.* **36** (1962) 2757.
- [7] MACFARLANE, R. M., *J. Chem. Phys.* **40** (1964) 373.
- [8] RAHMAN, H. U. and RUNCIMAN, W. A., *J. Phys. C* **4** (1971) 1576.
- [9] SAKATSUME, S. and TSUJIKAWA, I., *J. Phys. Soc. Japan* **19** (1964) 1080.
- [10] PONTNAU, J., Thesis, Orsay (1974) unpublished.
- [11] PONTNAU, J. and ADDE, R., *C.R. Hebd. Séan. Acad. Sci.* **278B** (1974) 943.
- [12] STURGE, M. D., *Phys. Rev.* **130** (1963) 639.
- [13] GESCHWIND, S., KISLIUK, P., KLEIN, M. P., REMEIK, J. P. and WOOD, D. L., *Phys. Rev.* **126** (1962) 1684.
- [14] CROZIER, M. H., *Phys. Lett.* **18** (1965) 219.
- [15] MACFARLANE, R. M., *J. Chem. Phys.* **39** (1965) 3118.
- [16] MACFARLANE, R. M., *Phys. Rev.* **B 1** (1970) 989.
- [17] FEHER, E. and STURGE, M. D., *Phys. Rev.* **172** (1968) 244.
- [18] MARUYAMA, T. and MATSUDA, Y., *J. Phys. Soc. Japan* **19** (1964) 1096.
- [19] LOW, W., *Appl. Phys. Lett.* **5** (1964) 35.
- [20] ARKHANGELSKII, G. E., MORGENSHTERN, Z. L. and NEUSTRUEV, V. B., *Phys. Stat. Sol.* **29** (1968) 831 and **36** (1969) 451.
- [21] GAMBLE, F. T., Ph. D. Thesis (1963) University of Connecticut.
- [22] NELSON, E. D., WONG, J. Y. and SCHAWLOW, A. L., *Phys. Rev.* **156** (1967) 298.
- [23] WONG, J. Y., BERGGREN, M. J. and SCHAWLOW, A. L., *J. Chem. Phys.* **49** (1968) 835.
- [24] STICKLEY, C. M., MILLER, H., HOELL, E. E., GALLAGHER, C. C. and BRADBURY, R. A., *J. Appl. Phys.* **40** (1969) 1792.
- [25] ABRAGAM, A. and BLEANEY, B., *Electron paramagnetic resonance of transition ions* (London : Oxford University Press) 1970.
- [26] RIMMER, D. E. and JOHNSTON, D. F., *Proc. Phys. Soc.* **89** (1966) 943.
- [27] RIMMER, D. E. and JOHNSTON, D. F., *Proc. Phys. Soc.* **89** (1966) 953.