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Magnetic circular dichroism of colour centres in $\text{CaF}_2 : \text{Na}$

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Résumé. — Le dichroïsme circulaire magnétique (D.C.M.) de différents centres colorés dans $\text{CaF}_2 : \text{Na}$ coloré additivement a été mesuré à différentes températures, dans le domaine 1,65-195 K. Les bandes d'absorption 612, 435 et 382-385 nm sont associées à des D.C.M. paramagnétiques importants, ce qui prouve qu'elles proviennent très probablement de centres à nombre impair d'électrons. 612 nm ne peut donc pas être seulement une transition du centre F_{2A} orienté [1, 0, 0] comme on l'admet habituellement. D'autre part, la bande 490 nm ne possède qu'un D.C.M. diamagnétique. Nous discutons quelques identifications possibles pour les principales bandes d'absorption des centres colorés dans $\text{CaF}_2 : \text{Na}$, mais il faut, pour arriver à des conclusions sûres, d'autres travaux utilisant des techniques complémentaires.

Abstract. — The magnetic circular dichroism (M.C.D.) of several centres in additively coloured $\text{CaF}_2 : \text{Na}$ has been measured as a function of temperature in the 1.65-195 K range. The 612, 435 and 382-385 nm bands display significant paramagnetic M.C.D. signals, which proves that they most probably arise from centres with an odd number of electrons. Thus 612 nm cannot be only a transition of the [1, 0, 0] oriented F_{2A} centre, as currently assumed. On the other hand, the 490 nm band only shows a diamagnetic M.C.D. We tentatively discuss some possible assignments for the chief absorption bands of colour centres in $\text{CaF}_2 : \text{Na}$, but further work using complementary techniques is clearly necessary before one comes to a reliable conclusion.

1. Introduction.

Colour centres in pure CaF_2 have been extensively studied, both theoretically and experimentally, particularly at the Clarendon Laboratory [1], and they are now reasonably well understood : several centres have been reliably identified by their absorption and fluorescence bands, by their zero-phonon lines, by their E.P.R. and ENDOR spectra...

As is well known, colour centres in fluorite are very sensitive to impurities. Thus, the optical spectra of coloured pure CaF_2 and of coloured CaF_2 with a few 10^{-4} or 10^{-3} Na doping (of interest as a colour centre laser material [2]) are wholly different. It is therefore quite natural to

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assign the chief transitions observed in $\text{CaF}_2 : \text{Na}$ to F centre aggregates associated with a sodium impurity. Thus, Lisitsyn and Shtanko [3] ascribe the 385 and 435 nm absorption bands to the F_A centre, i.e. an anion vacancy decorated by an electron with a nearest neighbour Ca^{++} replaced by an Na^+ impurity (Fig. 1a). Rauch [4] attributes the conspicuous absorptions at 382 and 612 nm and emission at 755 nm to the F_{2A} centre, which consists of two neighbouring fluorine vacancies, aligned along a $[1, 0, 0]$ direction, decorated with two electrons and close to a Na^+ substitutional impurity [2] (Fig. 1b). Polarization of fluorescence shows the 612 and 755 nm transitions to be orientated along the $[1, 0, 0]$ axis of the defect and the 382 nm band perpendicularly. Rauch [4] also describes two F_{3A}^+ centres (Fig. 1c [5] and 1d) constituted of three fluorine vacancies decorated by only two electrons. One of them is linear along a $[1, 0, 0]$ direction, with absorption at 490 and fluorescence at 554 nm. In the other one, the three vacancies form a right angled isosceles triangle; the absorption is at 450 nm, the emission at 505 nm.

Obviously other, yet unidentified, centres contribute to the observed absorption and emission spectra, with severe problems of overlaps between bands of different origins. Moreover, the above reported assignments rest on much less extensive evidence than those of the bands in pure CaF_2 . We therefore thought worthwhile (as a part of our colour centre research program) to investigate more systematically the identifications of colour centres in $\text{CaF}_2 : \text{Na}$, jointly using several techniques, including excitation spectra, fluorescence polarization, linear dichroism induced by polarized light bleach, study of zero phonon lines, magnetic circular dichroism (M.C.D.). The aim of the present letter is to report some rather unexpected results we have obtained, chiefly by the latter technique. Section 2 will deal with the experimental methods, section 3 with the optical absorption spectra, section 4 with our M.C.D. results and section 5 with the discussion, including tentative assignments of the chief optical bands in $\text{CaF}_2 : \text{Na}$.

Fig. 1. — Configuration of various colour centres in $\text{CaF}_2 : \text{Na}$. $\bullet = \text{F}^-$; $\square = \text{F}^-$ vacancy; $+$ = Ca^{++} ; $\Delta = \text{Na}^+$. 1a : F_A centre (if the vacancy is decorated with one electron). 1b : F_{2A} or F_{2A}^+ centre depending on whether the vacancies are decorated with two or one electron(s). 1c : Linear F_{3A}^+ centre (the vacancies are decorated with two electrons). 1d : Angular F_{3A}^+ centre (the vacancies are decorated with two electrons).

2. Experimental methods.

The work was performed partly in Orsay (crystal growth by a Bridgman method, spectroscopic study of colour centres in X-rayed samples), partly in Caen (spectroscopic study of additively coloured samples and M.C.D. experiments).

Absorption spectra were measured at Orsay with a Cary 14 R in the whole 250-750 nm range, whereas the home-made Caen absorption and M.C.D. apparatus had an U.V. cut off at ~ 360 nm. The main part of this latter equipment has already been described [6]; the chief recent improvement is the on-line use of a Tandy TRS 80 microcomputer which controls the monochromator through a stepping motor, registers the optical absorption or M.C.D. data and performs part of their analysis.

Fig. 2. — 2a : Absorption spectrum (left scale) at 1.65 K of an additively coloured sample (200 ppm of Na) in its « blue » state (see text). 2b : M.C.D. (right scale) of the same sample in the same state, in a 0.89 T field, at 1.65 K (· · ·) and 110 K (- - -).

We used samples from 3 different crystals with sodium contents, respectively 200, 290 and 770 p.p.m. as determined by COGEMA through emission spectroscopy. X-ray coloration was performed either at 77 K or room temperature by a tube with a tungsten anticathode and a beryllium window, operated under 50 kV voltage. For additive coloration, the samples were heated at $\sim 700^\circ\text{C}$ in a calcium atmosphere, inside sealed silica bulbs, and then quenched by dropping the bulbs into liquid nitrogen.

3. Absorption spectra.

3.1 ADDITIVELY COLOURED SAMPLES. — After the latter described treatment, the absorption spectrum consists of several poorly resolved bands, but it does not contain the 612 nm band of chief interest to us. As recommended by [5], we therefore irradiated the samples for several hours at room temperature with near U.V. light (Osram 1.2 A Hg lamp, Schott UG 11 filter). We thus obtained a « blue » sample, with the low temperature absorption spectrum of figure 2a⁽¹⁾.

Fig. 3. — Same as figure 2, but with the sample in its « violet » state.

⁽¹⁾ Throughout this text, we refer to the 385 and 435 nm bands, like reference [3], and to the 382, 490 and 612 nm bands, like reference [4], although there are some slight differences between these wavelengths and the positions of absorption maxima in our own spectra. The discrepancies may arise from experimental errors on either part; from variations of the absorption wavelengths with the temperature; from some bands being unresolved absorptions of different centres, the proportion of which may vary from sample to sample.

This spectrum may be altered in several ways among which we shall only need below the following ones :

a) Spontaneously, at room temperature in a few days and at 100 °C in less than one hour, the crystal turns to « violet », i.e. its low temperature absorption spectrum becomes the one of figure 3a [5], with an increase of the 490 nm band at the expense of the 612 and 382 nm bands. The reverse transformation (spectrum 3a → spectrum 2a) is obtained by room temperature irradiation with near U.V. light during one or two hours.

b) At liquid nitrogen temperature, the samples are indefinitely stable in the dark, but they may be made « yellow » by irradiation with near U.V. light. The 612 nm band bleaches first, then the 490 nm band. Simultaneously, the 435 nm band grows and the near U.V. spectrum is

Fig. 4. — Same as figure 2, but with the sample in its « yellow » state. The M.C.D. scale differs from the one of figures 2b and 3b by a factor 2.5.

slightly modified (the absorption band broadens somewhat and its top shifts by approximately 6 nm towards longer wavelengths). Figure 4a shows the 1.65 K absorption spectrum of the sample after a nearly thorough bleach at 77 K by near U.V. light. The reverse transformation (spectrum 4a $\rightarrow$ spectrum 2a) is obtained by merely raising the sample temperature up to ~ 195 K (or above).

It should be stressed that the three spectra of figures 2a, 3a and 4a (as well as intermediate ones) may be obtained in turn with the same sample any number of times without any noticeable loss of coloration, which is quite natural for an additively coloured crystal. We have quoted here these results about the bleaching properties of colour centres in $\text{CaF}_2 : \text{Na}$ because they are useful for the understanding of our M.C.D. experiments; we postpone to another publication the full report of our work in this domain.

3.2 X-RAYED SAMPLES. — After X-ray irradiation at 77 K, the absorption spectrum is of the « yellow » type, without the remainders of 612 and 490 nm bands of figure 4a, but with some additional features arising from V_K or V_H centres.

Annealing at 295 K this low temperature irradiated sample, one obtains, upon cooling back to low temperatures, a « blue » spectrum (see Fig. 5), purer than the one of figure 2a (no 490 nm band). One observes, besides the 382 and 612 nm peaks, a third maximum, further in the U.V. at 326 nm (which may also exist in the case of Fig. 2a, but which is out of the spectral domain of the Caen apparatus). A spectrum similar to the one of figure 5 may also be obtained by X-ray irradiation at room temperature.

Finally, a « violet » spectrum may be obtained by a 95 °C annealing of a room temperature X-irradiated sample. It presents some differences with the « violet » spectrum of figure 3a, but we shall not discuss them here any further as they have no incidence on the main topic of the present letter.

Fig. 5. — Absorption at liquid nitrogen temperature of a sample (770 p.p.m. of Na) which has been X-irradiated at 77 K, then annealed for 10 min. at room temperature.

4. Magnetic circular dichroism.

Let l be the sample thickness, k^+ and k^- its absorption coefficients for σ^+ and σ^- light respectively. We have measured the M.C.D. $l(k^+ - k^-)$ at 1.65, 110 and 195 K in a 0.89 T magnetic field. It is plotted in figures 2b, 3b and 4b for states of the sample corresponding to the absorption spectra of figures 2a, 3a and 4a respectively ⁽²⁾. The following observations may be made :

⁽²⁾ 195 K data are not shown on the figures for the sake of clarity. Similar results were also obtained with other sodium contents in the sample, as well as with an X-rayed crystal.

4.1 The 612 nm band has nearly the same shape in the optical absorption and in the M.C.D. spectra (the M.C.D. band however has a somewhat more extended blue wing). We define the « relative dichroism » :

$$\rho = \frac{k^+ - k^-}{k^+ + k^-}. \quad (1)$$

The observed values of ρ are listed in table I along with the estimated accuracy ; the chief error arises from the complexity of the spectrum and partial overlap of bands from different centres. Within this accuracy, the observed relative dichroism does not depend on the magnitude of the optical absorption : for instance, it is the same in figures 2 and 3.

When one suddenly modifies the value of the magnetic field H_0 , the M.C.D. of the sample at 1.65 K does not « follow » immediately. It varies exponentially with a time constant T_1 of 170 ± 20 seconds ⁽³⁾. This behaviour, together with the temperature variation of the M.C.D. (see Table I), demonstrates that a paramagnetic specie is responsible for at least a significant part of the 612 nm absorption band, T_1 being the spin-lattice relaxation time of the degenerate ground level of this species.

Table I. — *Magnetic circular dichroism for $H_0 = 0.89$ tesla of the main absorption bands in additively coloured $\text{CaF}_2 : \text{Na}$. Parameters ρ and r are defined by equations (1) and (2) of the text. Calculated values of ρ were obtained from formula*

$$\rho = \left[-\frac{A}{2} \text{th} \left(\frac{g_s \beta H_0}{2 kT} \right) + g \beta H_0 \right] \left(\frac{1}{E_i - E_j} + \frac{1}{E_i - E_{j'}} \right)$$

where β is the Bohr magneton, k the Boltzmann constant, T the temperature, g , the g -factor of the s -like ground state (assumed to be equal to 2.0). E_i is the energy of the excited level of interest, E_j and $E_{j'}$ are the energies of the two other levels arising from the splitting of the p -like excited state. For the F_A centre, we assumed $E_i = 22\,990 \text{ cm}^{-1}$, $E_j = E_{j'} = 25\,970 \text{ cm}^{-1}$ from the absorption spectrum ; $A_1 = -23 \text{ cm}^{-1}$, $g_1 = 0.07$ to fit our M.C.D. data. The « Y » centre has been assumed to be F_{2A}^+ , as tentatively suggested in section 5.3, with the following values of the parameters : E_i , $E_j = 16\,340, 26\,180 \text{ cm}^{-1}$, $E_{j'} = 30\,670 \text{ cm}^{-1}$ from the absorption spectrum ; $A_3 = -23 \text{ cm}^{-1}$, $g_3 = 0.41$ to fit our M.C.D. data.

	$10^5 \rho$ (612 nm band) « Y »	$10^5 \rho$ (435 nm band) F_A	$10^5 \rho$ (382 nm band) « Y »	$r \text{ (cm}^{-1}\text{)}$ (490 nm band) « X »
1.65 K {				
obs	-65 ± 4	-270 ± 70	-62 ± 10	-0.22 ± 0.02
calc	-71	-270	-50	
110 K {				
obs	-4.0 ± 0.5	-6 ± 1.5	-3 ± 1	-0.22 ± 0.02
calc	-4.0	-6.1	-2.8	
195 K {				
obs	-3.3 ± 0.5		-3 ± 1	-0.24 ± 0.02
calc	-3.5	-4.3	-2.5	

⁽³⁾ This value of T_1 corresponds to a field H_0 of 0.89 tesla. T_1 decreases slowly with H_0 and equals 60 s for $H_0 = 0.05$ tesla.

4.2 The 435 nm band has a similar paramagnetic behaviour (see Fig. 4 and Table I). When one modifies the magnetic field at 1.65 K, the 435 nm M.C.D. varies with a time constant T'_1 of 160 ± 20 seconds (in a 0.89 tesla field). The difference between T_1 and T'_1 is not significant.

4.3 In the near ultraviolet, observed M.C.D. phenomena are somewhat more complex. For « blue » samples (Fig. 2), one chiefly observes an absorption shaped M.C.D., the ρ of which are listed in table I. The corresponding time constant at 1.65 K is close to the T_1 of the 612 nm band ; unfortunately an accurate measurement was impossible because of a too poor signal to noise ratio : our light source is not intensive enough in the near ultraviolet.

When the sample is in the « yellow » condition (Fig. 4), we again observe a paramagnetic signal, but with a positive sign and with a maximum noticeably shifted (21 nm) toward shorter wavelengths with respect to the absorption band maximum. The time constant of the low temperature transients at 370 nm is similar to the T'_1 of the 435 nm band but, again, poor signal to noise ratio in the U.V. region prevents a precise comparison.

4.4 The M.C.D. associated with the 490 nm band is quite different from all previous ones : it is clearly dispersion shaped, positive in the short wavelength wing and negative in the long wavelength one (Figs. 3b and 4b). It can therefore be compared with the derivative of the absorption curve with respect to the wavenumber σ . More precisely, we divide both experimental curves by σ , consistently with Henry *et al.*'s [7] theoretical analysis, and we compare $\frac{l(k^+ - k^-)}{\sigma}$ with $l \frac{d}{d\sigma} \left(\frac{k^+ + k^-}{\sigma} \right)$. The agreement is not so good that the one between absorption and dichroism curves in the 612 nm region : the D.C.M. curve is shifted by ~ 6 nm to the blue of the absorption derivative and it is somewhat sharper. We introduce the « best » ratio r by :

$$r = \frac{[(k^+ - k^-)/\sigma]_{\text{peak to peak}}}{\left[\frac{d}{d\sigma} \{ (k^+ + k^-)/\sigma \} \right]_{\text{peak to peak}}} . \quad (2)$$

Parameter r is given in the last column of table I for 1.65, 110 and 195 K. One may remark that it is indeed independent of the temperature⁽⁴⁾. Moreover, it does not depend of the « state » of the sample, i.e. on the magnitude of the 490 nm absorption. Finally, when one modifies the value of H_0 , the M.C.D. associated with the 490 nm band changes « immediately », even at pumped helium temperatures (i.e. it is observed to vary with the instrumental time constant of a few seconds). All these observations suggest an M.C.D. of purely diamagnetic origin.

5. Discussion.

5.1 The « yellow » spectra of figure 4 are consistent with Lisitsyn and Shtanko's [3] identification of the F_A centre absorption at 380 and 435 nm. C.H. Henry *et al.* [7, 8] have studied both theoretically and experimentally the M.C.D. of F_A centres in KCl : they found an absorption shaped negative signal at the location of the long wavelength band (polarized parallel to the defect axis) and the superposition of absorption and dispersion shaped signals at the location of the short wavelength band (polarized perpendicular to the defect axis)⁽⁵⁾. This is nearly exactly what

⁽⁴⁾ When temperature increases, the 490 nm absorption band broadens and its maximum decreases. This explains how parameter r may be temperature independent, while $[(k^+ - k^-)/\sigma]_{\text{peak to peak}}$ is smaller at 110 K than at 1.65 K (see Fig. 3b).

⁽⁵⁾ The geometry of F_A centres is not the same in the KCl and in the CaF_2 lattices (C_{4v} symmetry in the former case, C_{3v} in the latter) but it makes no difference in the predicted M.C.D., at least if one uses « isotropic » samples, i.e. without a previous alignment of the F_A centres in a preferential direction.

appears in figure 4b for $\text{CaF}_2 : \text{Na}$ at helium temperature. There is a negative, absorption shaped signal at 435 nm; the positive maximum at 374 nm, shifted towards shorter wavelengths with respect to the absorption maximum may arise from the dispersion shaped component of the M.C.D. in the perpendicularly polarized band. Presumably the negative minimum of the dispersion shape is lost in the wing of the 435 nm centred signal. Henry *et al.*'s [7] theory predicts equal areas for the positive and negative lobes of the F_A centre M.C.D. This is not the case of the data of figure 4b: the positive lobe is too weak (even when one takes into account the change from wavelength to wavenumber abscissa scale and when one divides the observed dichroisms by σ). We do not know the reason for it. Maybe there is in the 380 nm region another band with a negative absorption shaped M.C.D. which shifts all observed M.C.D. data toward the bottom. Numerically, the M.C.D. of the 435 nm peak may be calculated from the formula quoted in the caption of table I. The temperature dependence of this formula allows determination of two parameters of the unrelaxed excited state of the F_A centre: its orbital g -factor $g_1 \simeq 0.07$ and its spin orbit coupling constant $A_1 \simeq -23 \text{ cm}^{-1}$. These parameters are of the same order of magnitude, although somewhat smaller, than the corresponding ones for F centres in pure CaF_2 ($g_{\text{orb}} = 0.29$ and $A = \frac{2}{3} \times (-41.7) = -28 \text{ cm}^{-1}$ according to Roger *et al.* [9]).

5.2 The rather narrow 490 nm absorption band is associated with an obviously diamagnetic dispersion shaped signal (section 4.4). This suggests a centre (we shall call it « X ») with a singlet ground level and a doubly or triply degenerate (or nearly degenerate) excited state. This is only partly consistent with Rauch's [4] assignment of a linear F_{3A}^+ centre: this two electrons defect should be non-paramagnetic (as observed), but its longer wavelength 490 nm transition should have a non degenerate excited state (contrarily to the observed M.C.D. spectrum). Let us add that our polarized bleaching experiments do not support one of Rauch's [4] conclusions based on fluorescence polarization experiments: the 490 nm transition dipole of the « X » centre is not oriented along [1, 0, 0] axes, since no linear dichroism is induced by partial bleach of an X-rayed sample with 490 nm light polarized parallel to one of the [1, 0, 0] directions.

The values of r listed in table I suggest that the « X » centre, whatever may it be, has an unrelaxed excited state g factor $g_2 = 0.55 \pm 0.05$, again a reasonable order of magnitude for an electron excess colour centre in a fluorite (or fluorite-like) lattice.

5.3 The results of section 4.1 demonstrate that the centre responsible for the 612 nm band has a paramagnetic ground level. More precisely, the 612 nm absorption may be the unresolved superposition of transitions due to several centres, among which one at least (let us call it the « Y » centre) has a paramagnetic ground level. « Y » is not a minor component of the 612 nm absorption, otherwise its observed M.C.D. would be incredibly large (see note ⁽⁹⁾). In fact, « Y » may be the principal component of the 612 nm band as suggested by the following facts: within experimental uncertainty, a partial bleach does not alter the ratio ρ of M.C.D. to optical absorption. Moreover, the shapes of the absorption and M.C.D. signals are nearly the same. Thus, if we assumed, for instance, the 612 nm band to be due with equal weights to a paramagnetic centre « Y » and to a non paramagnetic centre « Z », we should be obliged to suppose that these quite different centres have nearly exactly the same absorption shape and also the same bleaching rate ⁽⁶⁾, which is not impossible but which requires two accidental coincidences.

The 382 nm absorption and M.C.D. signals, most easily observed with a « blue » sample (Fig. 2), may be attributed to the same « Y » centre since they bleach at the same rate than absorption and M.C.D. signals in the 612 nm region. This is consistent with Rauch's [4] assignment of 382 and 612 nm absorptions to the same centre. The absorption spectrum of figure 5 strongly suggests that the 326 nm band also arises from centre « Y ». It is unfortunate that the short wavelength cut-off of our M.C.D. equipment has prevented us from checking this important

⁽⁶⁾ As well with near U.V. light as with intense red light, according to unpublished results of ours.

point by comparing the bleaching rate of absorption and M.C.D. signals in the 612 nm and 326 nm regions.

Now, what may be the microscopic structure of the « Y » centre ? We discuss below several hypotheses, without contending the list to be exhaustive.

5.3.1 If « Y » is the F_{2A} centre of figure 1b as postulated by Rauch [4], we are obliged to suppose its ground state to be the lowest spin triplet (the lowest spin singlet being metastable). This behaviour would be opposite to the customary one of two electrons colour centres which have a ground spin singlet and a metastable triplet [10].

5.3.2 R. C. Alig [11] predicted, on theoretical grounds, a F_A centre lowest transition in the red portion of the spectrum. Thus F_A could have been identified as the paramagnetic « Y » species, but for the wrong orientation of its optical axis : $[1, 1, 1]$ whereas numerous experimental evidence prove the « Y » centre to have a $[1, 0, 0]$ axis.

5.3.3 One may also think of a $[1, 0, 0]$ F_2 centre perturbed by an interstitial neutral sodium atom (see Figure 6b, to be compared with 6a showing the Rauch's [4] model of the F_{2A} centre with a substitutional sodium ion). The defect of figure 6b, with three electrons, should have a paramagnetic ground state, although elaborate calculations would be necessary to predict its energy levels and its M.C.D. Its symmetry (as well as the one of Fig. 6a, Rauch's model) is in agreement with the observed behaviour of the « Y » centre : orthorhombic with principal axes parallel to $[1, 0, 0]$, $[0, 1, 1]$ and $[0, 1, -1]$. However, if « Y » is the centre of figure 6b, it seems difficult to understand the easy conversion of « blue » to « yellow » condition and conversely (section 3.1, Fig. 2a and 4a). (Let us recall that the « yellow » spectrum arises from $[1, 1, 1]$ F_A centres, Fig. 1a).

Fig. 6. — Two possible configurations of F_{2A} centres : $[1, 0, 0]$ direction is perpendicular to the figure plane. ● = F^- ion at heights $+a/2$ and $-a/2$; □ = F^- vacancy at heights $+a/2$ and $-a/2$; + = Ca^{++} ion at height 0; △ = Na^+ ion at height 0; ▲ = Na atom at height 0. 6a : Rauch's [4] F_{2A} centre (the same as in Fig. 1b). 6b : F_{2A} centre with an interstitial Na atom. Both 6a and 6b defects are decorated with two electrons.

5.3.4. Our M.C.D. results are consistent with a model in which the « Y » centre would be F_{2A}^+ (i.e. the centre of Fig. 1b with only one electron) and the « X » centre would be F_{2A} with two electrons. In this hypothesis, the room temperature slow conversion of « Y » to « X » centres in the dark would arise from the neutralization of F_{2A}^+ into F_{2A} centres by capture of electrons, slowly released from traps. The room temperature regeneration of « Y » centres under near U.V. irradiation would be merely the ionization of F_{2A} centres and capture of the released electrons by the traps. It is more difficult to explain how the low temperature U.V. irradiation can lead to

$\text{F}_{2\text{A}}^+ \xrightarrow{h\nu} \text{F}_\text{A} + \square$ or $\text{F}_{2\text{A}} \xrightarrow{h\nu} \text{F}_\text{A} + \text{F}$ (⁷). On the other hand, the reverse reactions on raising the temperature to circa 200 K would merely arise from the vacancies becoming mobile at these temperatures.

The $\text{F}_{2\text{A}}^+$ centre has the requisite symmetry properties to be « Y » (point group $\text{C}_{2\text{v}}$). It is expected to have an orbitally non degenerate (s-like) ground state and a p-like excited state, the orbital degeneracy of which is fully lifted by the $\text{C}_{2\text{v}}$ crystal field. We may assume that the [1, 0, 0] component (Fig. 1b) corresponds to energy E_1 (612 nm absorption), the [0, 1, 1] component to energy E_2 (382 nm absorption) and the [0, 1, -1] component to energy E_3 (the 326 nm absorption of Fig. 5) (⁸). With these assignments, the M.C.D. is predicted to be negative (as observed) for both 612 and 382 nm bands and to be positive in the 326 nm region. As may be seen on table I, fair quantitative agreement with experimental data is obtained using the experimental values of E_1 , E_2 , E_3 and assuming, for the unrelaxed excited state of the $\text{F}_{2\text{A}}^+$ centre, a spin orbit coupling constant $A_3 = -23 \text{ cm}^{-1}$ and an orbital g -factor $g_3 = 0.41$. Like in the case of F_A centres (section 5.1), these parameters are of the same order of magnitude than those of the F centre in pure CaF_2 [9], which is quite satisfactory (⁹).

5.4 CONCLUSION. — Our M.C.D. data allow us to discard the current assignments of some of the most conspicuous absorption bands in sodium doped CaF_2 . On the other hand they are clearly unable to provide by themselves reliable new assignments. They must be complemented by results from several different techniques before the colour-centres spectrum in $\text{CaF}_2 : \text{Na}$ may be really said to be understood.

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(⁷) But it is not easier to understand the same experimental fact with « Y » = $\text{F}_{2\text{A}}$ as postulated by Rauch [4].

(⁸) W. C. Collins [12] observes 3 absorption bands at 300, 360 and 545 nm in the analogous case of the F_2^+ centre in pure CaF_2 , even if his discussion refers to 360 and 545 nm bands only. Similar complete splitting of a p-like excited state was also observed for the F_2^+ centre in $\text{SrCl}_2 : \text{Rh}^+$ [13].

(⁹) If one assumes that the $\text{F}_{2\text{A}}^+$ centres are responsible only for a fraction f of the 612 nm absorption, the spin-orbit coefficient A_3 would be $-23/f \text{ cm}^{-1}$. Thus f cannot be chosen too small; otherwise A_3 would be incredibly large for a colour centre in a crystal made up of ions with comparatively small spin orbit couplings.

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