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New optical transitions of colour centres in $\text{CaF}_2 : \text{Na}^+$

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Résumé. — Nous mettons en évidence de nouveaux centres colorés dans $\text{CaF}_2 : \text{Na}^+$ par leurs spectres optiques d'absorption, d'émission et d'excitation. Le centre que nous appelons f est responsable d'une bande de fluorescence qui culmine à 573 nm, d'une bande d'excitation à 510 nm et d'une raie à zéro-phonon à 541,8 nm. Le centre que nous appelons g a des bandes d'émission et d'excitation respectivement centrées à 681 et à environ 562 nm. De nombreuses raies fines apparaissent dans les spectres d'absorption et de fluorescence; les unes sont des raies à zéro-phonon de centres connus, ou leurs satellites vibrationnels, tandis que les autres ne sont pas encore attribuées.

Abstract. — New colour centres are detected in $\text{CaF}_2 : \text{Na}^+$ by their absorption, emission and excitation optical spectra. The so-called f centre accounts for a fluorescence band peaking at 573 nm, an excitation band at 510 nm and a zero-phonon line at 541.8 nm. The so-called g centre has emission and excitation bands respectively centred at 681 and approximately 562 nm. A number of sharp lines appears in the absorption and fluorescence spectra, some of which are zero-phonon lines of known centres, or their vibrational satellites, while others are still unidentified.

1. Introduction.

Colour centres (C.C.'s) in pure CaF_2 have been extensively studied and are now reasonably well understood [1]. However, as little as a few 10^{-4} doping with sodium entirely changes the optical spectra of coloured fluorite, which suggests that C.C.'s are formed in the immediate vicinity of sodium impurities, rather than in the perfect parts of the lattice. Fairly little is known about these C.C.'s in $\text{CaF}_2 : \text{Na}^+$ which are of interest, in particular, owing to their

possible use as active material for C.C. lasers [2]. Several authors have described C.C.'s in $\text{CaF}_2 : \text{Na}^+$; F_A centres [3], F_{2A} centres [2, 4], F_2 centres weakly disturbed by a fairly distant Na^+ [4, 5] and two different varieties of F_{3A}^+ centres [4, 6] (see Table I). However, the assumed microscopic models of these C.C.'s do not seem to be firmly established, as we have shown recently [7] from a study of their magnetic circular dichroism.

We have recently discovered in $\text{CaF}_2 : \text{Na}^+$ several other C.C.'s which, to the best of our knowledge,

Table I. — Colour centres in $\text{CaF}_2 : \text{Na}^+$. With the exception of « a F_{3A}^+ » centres, listed wavelengths are our measured values at helium temperatures. They may differ by a few nanometers from the corresponding values quoted in the literature, either because of the thermal shift of band maxima, or because some bands are unresolved blends of transitions from different centres, the proportions of which may vary from sample to sample.

Centre	Absorption or excitation band(s) (nm)	Emission band (nm)	Zero-phonon line (nm)	Reference
« F_{2A} »	387; 620	757	684.6	[2], [4]
g	562 ± 3	681		this work
b	360; 532	611	571.8 ?; 577.4 ?	[4], [5]
f	510	573	541.8	this work
« F_{3A}^+ »	490	548	521.6	[4], [6]
« a F_{3A}^+ »	450	505		[4], [6]
F_A	390; 435	—		[3]

have not been previously reported. The principal aim of the present paper is to describe two of these new centres which we have studied in greater detail. We are presently unable to suggest microscopic models for these C.C.'s, so that we shall call them simply f and g centres, without any specific meaning underlying the letters f or g. We shall use, for the previously described centres, the names « F_{2A} », « F_{3A}^+ », « aF_{3A}^+ » of references [2, 4, 6], the quotation marks suggesting our doubts concerning the validity of the microscopic models, and the letter a being an abbreviation for « angular ». As for the « F_2 centre weakly disturbed by Na^+ » of references [4, 5], we shall call it below b centre for brevity.

In section 2, we describe the experimental methods; in sections 3.1 and 3.2, we give our results concerning f and g centres respectively. Finally, section 4 lists the numerous sharp lines observed in $CaF_2 : Na^+$ optical spectra and discusses them briefly.

2. Experimental techniques.

Our samples were cut out of a crystal grown by a Bridgman technique in Laboratoire de Physique Cristalline d'Orsay (Professor J. P. Chapelle). 300 p.p.m. of Na (in the form of NaF) were added to the melt. Optical emission spectroscopy analysis by Cogema yielded 180 and 220 p.p.m. of Na for two different regions of the grown crystal. The samples are sawn in the shape of approximately 2 mm thick platelets; then they are additively coloured by heating at 670 °C in calcium vapour inside a sealed silica bulb. The calcium chips are in a colder part, at ~ 570 °C. After 10 to 20 min, the bulb is rapidly quenched in liquid nitrogen (which, however, does not mean a very rapid cooling of the crystal itself, since the fairly thick walls of the bulb do not break during the quench). The sample faces are then polished with diamond powder on type 410 plates from Lamplan.

Optical measurements are performed at approximately 5 K with the sample clamped on the cold finger of a liquid helium cryostat. For absorption spectra, the sample is illuminated by an iodine tungsten 100 W lamp through a Jobin-Yvon HRS 2 monochromator. Emission spectra are observed with the same monochromator, the crystal being excited, nearly in the observation direction (Fig. 1 α) by one of the lines of a Kr^+ laser (Coherent Radiation CR 750 K). For excitation spectra, the sample is illuminated by the same source as for absorption spectra (iodine tungsten lamp + HRS 2) but with wider monochromator slits; the emission is monitored, nearly collinearly, through a second, home made, Czerny-Turner grating monochromator (Fig. 1 β). Suitable Wratten or Schott filters are used in the emission and excitation measurements in order to increase the rejection of stray light at the excitation wavelength.

Fig. 1. — α : Diagram of the fluorescence experiments. β : Diagram of the excitation experiments (L = laser, I.T.L. = iodine tungsten lamp, C = crystal, M_1 = HRS2 monochromator, M_2 = home-made monochromator). γ : Ideal geometry assumed for calculating the absorption correction.

The chromatic sensitivity of the experimental set-up has been measured by two preliminary experiments. For emission spectra, the crystal of figure 1 α was replaced by a white lamp, the spectral emissivity of which had been previously calibrated in the 350-800 nm range by the Laboratoire National d'Essais; we thus obtained the wavelength sensitivity of the monochromator + photomultiplier system, which allowed us to correct all our fluorescence results. For excitation spectra, the crystal of figure 1 β was replaced by a Hamamatsu R928 photomultiplier which had been calibrated by the manufacturer; we thus obtained the relative variations, *versus* wavelength, of the incident light power; these data were subsequently used to correct the results of our excitation experiments.

Our samples noticeably absorb light : the product kl of absorption coefficient k and thickness l is typically in the 0.5-4. range. Therefore, the emission and excitation spectra are much distorted and a correction is necessary. To perform it, we assume the ideal geometry of figure 1 γ instead of the actual ones of figures 1 α or β . Excitation light of wavelength λ_1 and fluorescence light of wavelength λ_2 both travel perpendicularly to the polished faces of the sample. If k_1 and k_2

are the absorption coefficients at wavelengths λ_1 and λ_2 respectively, the fluorescence signal I_2 is :

$$I_2 = \int_0^l [I_1 \exp(-k_1 x)] [K(\lambda_1, \lambda_2) dx] \times \\ \times [\exp\{-k_2(l-x)\}] \\ = K(\lambda_1, \lambda_2) I_1 [\exp(-k_1 l) - \exp(-k_2 l)] / (k_2 - k_1) \quad (1)$$

where I_1 is the incident intensity and $K(\lambda_1, \lambda_2)$ the parameter of interest. If λ_1 is kept fixed, $K(\lambda_1, \lambda_2)$ versus λ_2 is the fluorescence spectrum; if λ_2 is kept fixed, $K(\lambda_1, \lambda_2)$ versus λ_1 is the excitation spectrum. In the integrand of equation (1), the first bracket represents the excitation light intensity at depth x inside the crystal, the last bracket accounts for the fluorescence light absorption along the exit path. We have corrected all our emission and excitation spectra, multiplying the observed result I_2/I_1 by the factor $l(k_2 - k_1) / [\exp(-k_1 l) - \exp(-k_2 l)]$, known from the absorption spectrum. The correction is valid if the light of wavelength λ_1 directly excites fluorescence at wavelength λ_2 ; it would be only approximate in the case of a more complex process, for instance if two different C.C.'s were involved, with a radiative transfer at some intermediate wavelength λ' between them. This is not the case of the spectra discussed below, but we have clearly observed such transfers in the excitation spectrum of « F_{2A} » centres whenever the sample also contained other kinds of C.C.'s.

3. Optical spectra of f and g centres.

C.C.'s in additively coloured $\text{CaF}_2 : \text{Na}^+$ are not stable, they reversibly change into one another under the influence of luminous irradiations at various wavelengths (even at very low temperatures) and also in the dark, at least when $T \gtrsim 150$ K. Several centres are simultaneously present with various concentrations, their absorption and emission bands are fairly broad (typically 35 to 70 nm at half-height), they are often poorly resolved or wholly unresolved which makes the interpretation of observed spectra more difficult. However, we have empirically found experimental procedures that enhance certain C.C.'s at the expense of others, thus enabling us to determine the lineshapes of the excitation and emission bands of these centres.

3.1 f CENTRES.

3.1.1 General. — When a sample is kept several days in the dark at room temperature, a very conspicuous absorption band grows around 490 nm. It corresponds, at low temperatures, to a green fluorescence centred on 550 nm, the intensity of which

decreases by a factor of 7 between 5 and 105 K and has nearly completely vanished at 195 K. These facts were described by Rauch [4] who attributed them to the « F_{3A}^+ » centre. We shall therefore refer below to this state of the crystal as an « F_{3A}^+ » enriched sample⁽¹⁾.

But, on closer examination, it appears that several different centres contribute to the above reported absorption and fluorescence : the emission spectrum of the same « F_{3A}^+ » enriched sample is clearly different when the excitation is from the 483 nm (Fig. 2 α) or the 531 nm line (Fig. 2 β) of the Kr^+ laser. Let us now turn to the excitation spectrum. Its maximum continuously shifts to the blue when the monitoring wavelength decreases from 568 to 542 nm (in this spectral region, there is no emission from b centres, see table I, which could be confusing for the interpretation). Let us try to explain these experimental facts with the simplest scheme : two poorly resolved kinds of C.C.'s, the « F_{3A}^+ » centres to the shorter wavelengths and the f centres to the longer. Figure 2 α is essentially the fluorescence of « F_{3A}^+ » centres (with a moderate contribution of f centres on the red wing), figure 2 β corresponds to f centres, with a contribution of b- and g centres at longer wavelengths.

Fig. 2. — Fluorescence spectra at 5 K : α : Of an « F_{3A}^+ » enriched sample, with 483 nm excitation. β : Of the same sample, with 531 nm excitation. γ : Of an f enriched sample, with 531 nm excitation. Vertical scales are arbitrary, those of curves β and γ have been chosen in order to obtain coincidence of the short wavelengths wings. The dotted profile is the difference $\beta - \gamma$, it is due to the emission of other centres present in the « F_{3A}^+ » enriched sample, chiefly b and to a smaller extent g centres. The vertical arrows show the location of the emission bands of the chief C.C.'s.

⁽¹⁾ In reference [7], we called it a sample in the « violet » state.

Both « F_{3A}^+ » and f centres slowly grow at room temperature in the dark at the expense of « F_{2A}^+ » centres. However, after heating at 110 °C for 45 min, f centres are much enhanced. We shall call f enriched sample a crystal which has thus been heated. Figures 2 γ , 3 and 4 α respectively show the fluorescence, excitation and absorption spectra at 5 K of an f enriched sample.

Fig. 3. — Excitation spectrum of f centres at 5 K. Monitoring wavelength 575 nm. Vertical scale is arbitrary. The insert gives an enlarged view of the zero-phonon line domain.

3.1.2 Fluorescence. — Let us compare the emission profiles 2 β and 2 γ which were obtained in the same experimental conditions, the former with a « F_{3A}^+ » enriched sample, the latter with an f enriched one. They are obviously very similar on the blue wing and rather different on the red one. The difference (dotted curve of Fig. 2) is attributed to the fluorescence of b (and to a smaller extent g) centres : these C.C.'s are present in the « F_{3A}^+ » enriched sample, but they are in very small concentration in the f enriched one, as evidenced by the absorption spectrum (Fig. 4 α) which falls nearly to zero at wavelengths greater than 540 nm. The similarity of the blue wings of figures 2 β and 2 γ strongly suggests that they both arise from f centres with no contamination at all from « F_{3A}^+ » centres, even in the case of figure 2 β which corresponds to a crystal with a large concentration of these centres. The reason is that the 531 nm Kr⁺ line does not excite at all the fluorescence of « F_{3A}^+ » centres because it lies to the red of the 521.6 nm zero-phonon transition of these

Fig. 4. — α : Absorption spectrum of an f enriched sample at 5 K. β : Absorption spectrum of the same sample after a 50 min irradiation with the 531 nm line of a Kr⁺ laser (power = 50 mW, on a surface of approximately 0.25 cm²). Temperatures of irradiation and measurement = 5 K.

centres⁽²⁾. From the above discussion, we conclude that figure 2 γ , with its peak at 573 nm and its 34 nm FWHM, is the true fluorescence profile of f centres, reasonably free from distortions due to other centres.

3.1.3 Excitation. — Let us turn to the excitation profile (Fig. 3). It was obtained by monitoring the 575 nm emission of an f enriched sample. As discussed in section 3.1.2, contamination from b and g centres (on the red wing) should be very small for such a sample. On the other hand, one may fear the blue wing to be distorted because of « F_{3A}^+ » centres. We therefore registered several curves similar to the one of figure 3, but with different monitoring wavelengths in the 560-585 nm range. They could be analysed as the sum of two components : the chief one, due to f centres, with exactly the shape of figure 3, and a small one on the blue wing, attributed to « F_{3A}^+ » centres. The maximum intensity of the latter component was only 3 % or 10 % of the chief one when we monitored

(2) Rauch [4] locates the zero-phonon line of « F_{3A}^+ » centres at 521.7 nm. It is obviously a misprint for 521.7, both in the Russian original and in the american translation. Indeed, we have clearly observed the zero-phonon line of « F_{3A}^+ » centres in absorption, excitation and emission. We have also observed its satellites corresponding to one and two 143 cm⁻¹ phonons, in nice agreement with the 141 cm⁻¹ vibrational frequency quoted by Rauch [4].

the fluorescence at 568 and 560 nm respectively. When monitoring at 585 nm, the observed excitation profile was exactly the same as the one of figure 3 within the experimental uncertainties. All these observations make us confident that figure 3 is the excitation profile of f centres with little contamination from foreign centres. It peaks at 510 nm and has a 41 nm FWHM.

3.1.4 Absorption. — On the other hand, we have not been able to obtain a pure f centre absorption spectrum. In figure 4 α , the chief maximum corresponds to the superposition of « F_{3A}^+ » and of f centres absorptions. It is distinctly shifted to the red with respect to the absorption spectrum of pure « F_{3A}^+ » centres (503 nm instead of 490), but not so much shifted as we would expect for pure f centres (510 nm from the excitation spectrum of figure 3).

3.1.5 Zero-phonon transition. — We observed several sharp lines in the spectral region at the boundary of the emission and excitation profiles of f centres (Table II). 541.8 nm is the only one to appear simultaneously in absorption, in fluorescence and in the excitation spectrum of the 573 nm f emission (see

the insert in Fig. 3)⁽³⁾. Moreover, its intensity in the absorption spectrum greatly increases when one transforms an « F_{3A}^+ » enriched sample into an « f enriched » one. Therefore, we identify the 541.8 nm line as the zero-phonon transition of f centres. The 537.4 nm broader transition ($\Delta\lambda \sim 0.8$ nm) which appears both in absorption and in excitation is a satellite of 541.8 nm. It corresponds to a vibrational frequency of 151 cm^{-1} . One also observes in emission the symmetrical satellite at 546.3 nm ($\Delta\lambda = 0.75$ nm).

3.1.6 Bleaching. — Both « F_{3A}^+ »- and f centres are destroyed, at room temperature, by 365 nm irradiation which regenerates « F_{2A} » and b centres. Moreover, while « F_{3A}^+ » centres are reasonably stable against bleaching at low temperatures, f centres are easily destroyed, even at 5 K, by irradiation with the 531 nm light of the Kr^+ laser : figure 4 β shows the absorption spectrum of an f enriched sample after 50 min irradiation.

⁽³⁾ In figure 3, the breadth (~ 1 nm) of the 541.8 nm line is instrumental (the slits of monochromator M_1 of figure 1 β have been widely opened to get enough light). The real breadth of the 541.8 nm line is only ~ 0.1 nm as observed both in emission and absorption spectra.

Table II. — *Sharp lines in $\text{CaF}_2 : \text{Na}^+$ at helium temperatures*

λ (nm)	$\Delta\lambda$ (nm)	Sample state	Observation mode	Remarks
473.7	0.05	4	A	S
474.5	0.1	4	A	
508.6	0.1	2	F	
515.3	0.15	3, 4	A	
521.6	0.15	3, (4)	A, E, F	
523.4	0.2	2	F	« F_{3A}^+ », S
530.5	0.1	3, 4	A	
540.0	0.05	3, 4	A	
540.0	0.1	2	F	
541.8	0.1	3, 4	A, E, F	
555.3	0.1	2	F	(1)
568.7	0.05	2	F	S, (1)
571.8	0.05	1, 2, (3)	E, F	f, S
577.4	0.1	1, 2, (3)	E, F	b ?
612.9	0.1	4	A	b ?, S
615.1	0.8	3	A	(2)
618.6	1.1	3	A	
682.3	0.2	(2), 3	A	
684.6	0.15	1, 2, (3), (5)	A, E, F	
710.6	0.6	3	A	
737.9	0.2	3	A	« F_{2A} », S

In the column « Sample state », 1 means « F_{2A} » enriched (I), 2 : « F_{2A} » enriched (II), 3 : « F_{3A}^+ » enriched, 4 : f enriched, 5 : b-g enriched.

In the column « Observation mode », A means absorption, E excitation and F fluorescence.

In the column « Remarks », S means that the line has one or several vibrational satellite(s). The name of a centre indicates that the line is identified as the zero-phonon transition of this particular centre. (1) In spite of their common wavelength, we doubt that the 540.0 nm lines are the same in absorption and in emission, because they appear in different states of the crystal. (2) The 618.6 nm « line » may be a poorly resolved blend of two transitions.

tion at 5 K by approximately 200 mW cm^{-2} of 531 nm light. f centres have almost totally disappeared, as evidenced by the vanishing of their 541.8 nm zero-phonon line, while the « F_{3A}^+ » centres remain unaffected, since they do not absorb the 531 nm radiation, which is on the red side of their own zero-phonon transition.

Comparison of figures 4 α and 4 β suggests that the bleaching of f centres at 5 K creates both F_A centres (or, at least, C.C.'s absorbing in the same 390-435 nm domain) and new centres with an absorption maximum at 645 nm. The low temperature bleach of f centres is presently the only method we know to generate these 645 nm centres. The latter are thermally unstable, they are destroyed in the dark at some temperature between 105 and 150 K. They are currently under investigation in our laboratory and we shall report more completely about them later.

3.1.7 Discussion. — We do not know presently the microscopic structure of f centres. They might be of related nature to « F_{3A}^+ » centres since they are formed simultaneously by thermal evolution of « F_{2A} », b and g centres and destroyed simultaneously by U.V. irradiation at room temperature. We hope to obtain more precise informations on this point in a near future by a study of the polarization of fluorescence and by magnetic circular dichroism experiments.

3.2 g CENTRES.

3.2.1 The b-g enhancing treatment. — One of the chief problems in the study of C.C.'s which fluoresce in the red (b, g) is the intense emission of « F_{2A} » centres which generally dominates that part of the spectrum.

A similar remark holds concerning the absorption spectra of the same C.C.'s. We have therefore searched for a technique allowing to increase the concentration ratio of b and g centres *versus* « F_{2A} » centres and we have called this technique b-g enhancing treatment (although it is rather an « F_{2A} » depressing treatment).

The starting point is a F_A enriching treatment, i.e. an irradiation of the sample at 105 K by the U.V. lines of mercury (Osram HBO 100 W/2 lamp through a Schott UG 11 filter during ~ 75 min). This bleaches all absorption bands in the long wavelength region of the spectrum, especially the « F_{3A}^+ », f, b, g and « F_{2A} » bands, creating C.C.'s which absorb in the blue, violet and ultraviolet ⁽⁴⁾: at least the F_A centre (390 and 435 nm) and another centre, the absorption band of which overlaps the long wavelength component of the F_A absorption.

After this F_A enhancing treatment, the sample is illuminated at 105 K by the 436 nm line of mercury (HBO 100 W/2 lamp through a Schott Monochromat 436 filter during ~ 100 min). This does not affect the F_A centres but bleaches the second 435 nm absorption band and regenerates b, g and « F_{2A} » centres.

Figure 5 shows the absorption spectrum at 5 K of a crystal after this b-g enhancing treatment. One remarks that the absorption of « F_{2A} » centres is small ($kl < 0.4$), which allows the b centre band at 530 nm to be partly resolved, whereas it is generally completely hidden by the « F_{2A} » absorption blue wing. As for the g centres, their absorption is unresolved in the spectrum of figure 5, but they are how-

⁽⁴⁾ In reference [7], we spoke of the « yellow » state of the sample.

Fig. 5. — Absorption spectrum at 5 K of a b-g enriched crystal. The arrows show the location of the absorption bands of the chief C.C.'s.

ver present, as evidenced by the observations of sections 3.2.2 and 3.2.3 below.

3.2.2 Fluorescence spectrum of g centres. — Figure 6 shows in solid line the emission spectrum of a b-g enhanced sample excited at 5 K by the 568 nm line of the Kr^+ laser. The chief peak is the fluorescence of « F_{2A} » centres, but there is an obvious partly resolved component on the short wavelength side. The emission profile of « F_{2A} » centres (obtained from an auxiliary experiment with a sample chiefly containing these latter centres) was multiplied by a suitable factor (dotted curve of Fig. 6) and subtracted from the solid line, yielding the broken curve which is obviously the sum of two components : on the left the g centre emission, peaking at 681 nm, and on the right an infrared band. We have already observed such infrared fluorescence of $\text{CaF}_2 : \text{Na}^+$ on several different occasions, but we have not yet studied it. As for the emission profile of the g centre, it may be somewhat distorted in figure 6 by inaccuracies in the subtraction procedure for the long wavelength wing and by a small contribution of b centres on the short wavelength side. (The laser light at 568 nm excites b centres, but with a poor efficiency since it is fairly distant from their absorption maximum.)

3.2.3 Excitation spectrum of g centres. — When one registers excitation spectra of a b-g enriched sample with various monitoring wavelengths in the 600-700 nm range, one obtains noticeably different profiles which can be explained only by the effect of at least three different C.C.'s. As an example, figure 7 shows

Fig. 7. — Excitation spectrum of the g centre at 5 K. Monitoring wavelength : 680 nm. Full line : observed spectrum. Dotted line : excitation spectrum of b centres as obtained when monitoring the 600 nm emission (multiplied by a suitable factor). Broken line : difference between the two previous spectra, attributed to the g centres.

Fig. 6. — Fluorescence spectrum at 5 K of the b-g enriched crystal of figure 5. The excitation is by the 568 nm line of the Kr^+ laser. The arrows show the location of the fluorescence peaks. Full line : observed spectrum. Dotted line : fluorescence profile of « F_{2A} » centres. Broken line : difference spectrum.

the spectrum recorded when monitoring 680 nm fluorescence. After having subtracted the dotted curve representing the contribution of b centres, one is left with a bell-shaped curve peaking at 564 nm, which we associate with the excitation of g centres. 680 nm has been chosen for the detection because it is just below the wavelength (684.6 nm) of the « F_{2A} » centres zero-phonon line, so that the profile of figure 7 is not perturbed at all by these centres. For 695 nm monitoring wavelength, the red wing of the spectrum is very different from the one of figure 7; one observes two poorly resolved maxima of approximately equal amplitudes : at 565 nm, due to g (and b) centres, and at 615 nm, arising from « F_{2A} » centres.

For monitoring wavelengths shorter than 680 nm, profiles similar to the one of figure 7 are observed, with the excitation peak shifting smoothly to the blue as expected from the growing of the b component and decrease of the g one. For instance, when observing at 650 nm (Fig. 8), the excitation peak is found at 544 nm instead of 558 nm on figure 7. However, the decomposition of the observed curve into two components does not yield perfectly satisfactory results : the broken curve of figure 8, attributed to g centres, is found to be slightly different from the one of figure 7, its maximum is shifted to 559 nm (instead of 564) and its width is reduced to 45 nm (instead of 48).

Fig. 8. — Same as figure 7, but with monitoring wavelength = 650 nm. The broken line profile is similar, but not exactly proportional to the one of figure 7 (see discussion in the text).

We do not know presently whether these differences are due to experimental errors and inaccuracies in the subtraction procedure, or if they indicate that there exist several different kinds of g centres with similar, but not exactly equal, spectral properties.

We ignore, until now, whether g centres are associated with some sharp line spectrum. In the positive alternative, this (or these) line(s) should lie around 615 nm, at the intercept of the red wing of the excitation and of the blue wing of the fluorescence spectra.

3.2.4 Discussion. — We believe g and b centres to be closely related to « F_{2A} » centres because of their similar creation and destruction properties. The spontaneous evolution of samples in the dark at room temperature (section 3.1.1) destroys g centres as well as « F_{2A} » and b. Conversely, b, g and « F_{2A} » centres may be restored by room temperature irradiation with U.V. (the result of this treatment is called an « F_{2A} » enriched (I) sample ⁽⁵⁾). U.V. irradiation at 105 K (i.e. F_A enhancing treatment of section 3.2.1) simultaneously destroys b, g and « F_{2A} » centres. We shall try to obtain in the future better proofs of the structural relationship of these three kinds of C.C.'s as well as ideas about the nature of their differences, but this project is expected to be more difficult than in the similar case of « F_{3A}^+ » and f centres (section 3.1.7) because of the impossibility to get optical signals of g centres sufficiently well resolved from those of other C.C.'s (see sections 3.2.2 and 3.2.3).

4. Sharp transitions in $\text{CaF}_2 : \text{Na}^+$.

4.1 OBSERVATION CONDITIONS. — At helium temperatures, we observe a number of narrow lines in coloured $\text{CaF}_2 : \text{Na}^+$ (Table II). Some of them appear in states of the sample we have already introduced above (« F_{3A}^+ » enriched, f enriched, b-g enriched, « F_{2A} » enriched (I)). Others are observed in a fifth state of the sample that we have not yet had the occasion to describe.

In its « F_{2A} » enriched (I) state (section 3.2.4), the sample shows prominent bands of the « F_{2A} » centre at 387 and 620 nm but also a residual absorption of « F_{3A}^+ » centres at 490 nm. In an attempt to obtain a sample with purer « F_{2A} » centres, we devised the following scheme : we start with an F_A enriched sample (section 3.2.1) and we heat it to 195 K for one hour, which regenerates the « F_{2A} », b and g centres, but not the « F_{3A}^+ » for which several days at room temperature would be necessary. This treatment leads to a so called « F_{2A} » enriched (II) sample. In fact it certainly generates many other centres besides « F_{2A} », judging from the great number of new sharp fluorescence lines which appear under laser excitation.

⁽⁵⁾ In reference [7] we said more simply that the sample was in its « blue » state.

4.2 SATELLITE LINES. — Some lines in table II are accompanied by broader satellites in absorption, in emission, or in both. Two of the measured vibrational frequencies appear for several different transitions : $141 \pm 3 \text{ cm}^{-1}$ is observed for « $\text{F}_{3\text{A}}^+$ » centres (both in absorption and emission) and for the unidentified 508.6 and 540.0 nm lines in emission. Similarly the $152 \pm 2 \text{ cm}^{-1}$ frequency is found in three one-phonon spectra, those of f centres (in absorption and in emission) and of the unidentified 508.6 and 577.4 nm lines (in emission). These two frequencies are similar to those observed for satellite lines of C.C.'s in pure CaF_2 by Beaumont *et al.* [8-10] and Görlich *et al.* [11]; they are somewhat smaller than the peak in the density of states for transverse acoustic phonons in CaF_2 , 161 cm^{-1} according to Elcombe and Pryor [12].

4.3 DISCUSSION. — Three lines in table II (521.6, 541.8 and 684.6 nm) are unambiguously identified as zero-phonon transitions associated with definite centres (« $\text{F}_{3\text{A}}^+$ », f and « $\text{F}_{2\text{A}}$ »). There presently remains a doubt concerning the zero-phonon line(s) to be associated with the b centre : 571.8, 577.4 or both.

The 682.3 line is very close to the « $\text{F}_{2\text{A}}$ » zero-phonon transition. However, it is definitively not associated with the « $\text{F}_{2\text{A}}$ » centre as evidenced by its quite different creation and destruction conditions : it is seen chiefly in « $\text{F}_{3\text{A}}^+$ » enriched samples and is easily bleached at 5 K by irradiation with 531 nm light, which has no effect on the « $\text{F}_{2\text{A}}$ » centre and on its 684.6 zero-phonon line. Rauch [13] previously arrived at the same conclusion by different arguments.

The 682.3 nm line, as well as the other unidentified ones of table II, might belong to other, still unknown C.C.'s of $\text{CaF}_2 : \text{Na}^+$. They might also arise from rare-earth ions present as impurities in our samples. The various treatments may cause changes in the ionisation state of the rare-earths ($\text{RE}^{3+} + \text{e}^- \rightarrow \text{RE}^{2+}$

or the reverse). Thus, rare-earth lines may appear or disappear according to the state of the sample, as observed. However, we have used crystals grown from a Merck Optipur grade CaF_2 powder, in which a spectrographic analysis performed by Cogema failed to detect any rare-earth (minimum detectable concentration = 20 p.p.m.). Therefore it seems somewhat dubious that our samples may have contained enough rare-earth ions to yield observable intensity for the sharp $4\text{d}^n \rightarrow 4\text{d}^n$ transitions, the oscillator strengths of which are quite low. Moreover, in the particular case of the 682.3 nm line, the same impurity would have had to be present in sizeable amounts both in Rauch [13]'s crystals and in ours.

Another possibility would be that some of the observed narrow lines would belong to pure CaF_2 C.C.'s. We have compared our measured wavelengths with all those reported in the literature for C.C.'s in nominally pure fluorite [8-11] and we were unable to find any coincidence, except perhaps between our 540.0 nm fluorescence line and the 539.6 nm zero-phonon transition of F_2 [110] centres [9]. However this appears to be purely fortuitous, since the 539.6 nm line of pure CaF_2 F_2 centres should be accompanied by a much more intense fluorescence band at 585 nm, which is clearly not the case in our spectra. The lack of any coincidence between sharp lines observed in pure CaF_2 and in $\text{CaF}_2 : \text{Na}^+$ confirms the fact, stated in the introduction, that doping by Na^+ completely modifies the spectrum by suppressing every pure CaF_2 C.C., or, at least, by lowering its concentration below our experimental detection limit.

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