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## Infrared-induced bleaching and ‘F-light’ regeneration of laser-active $(F_2^+)_{\text{H}}$ centres in NaCl:OH<sup>−</sup>

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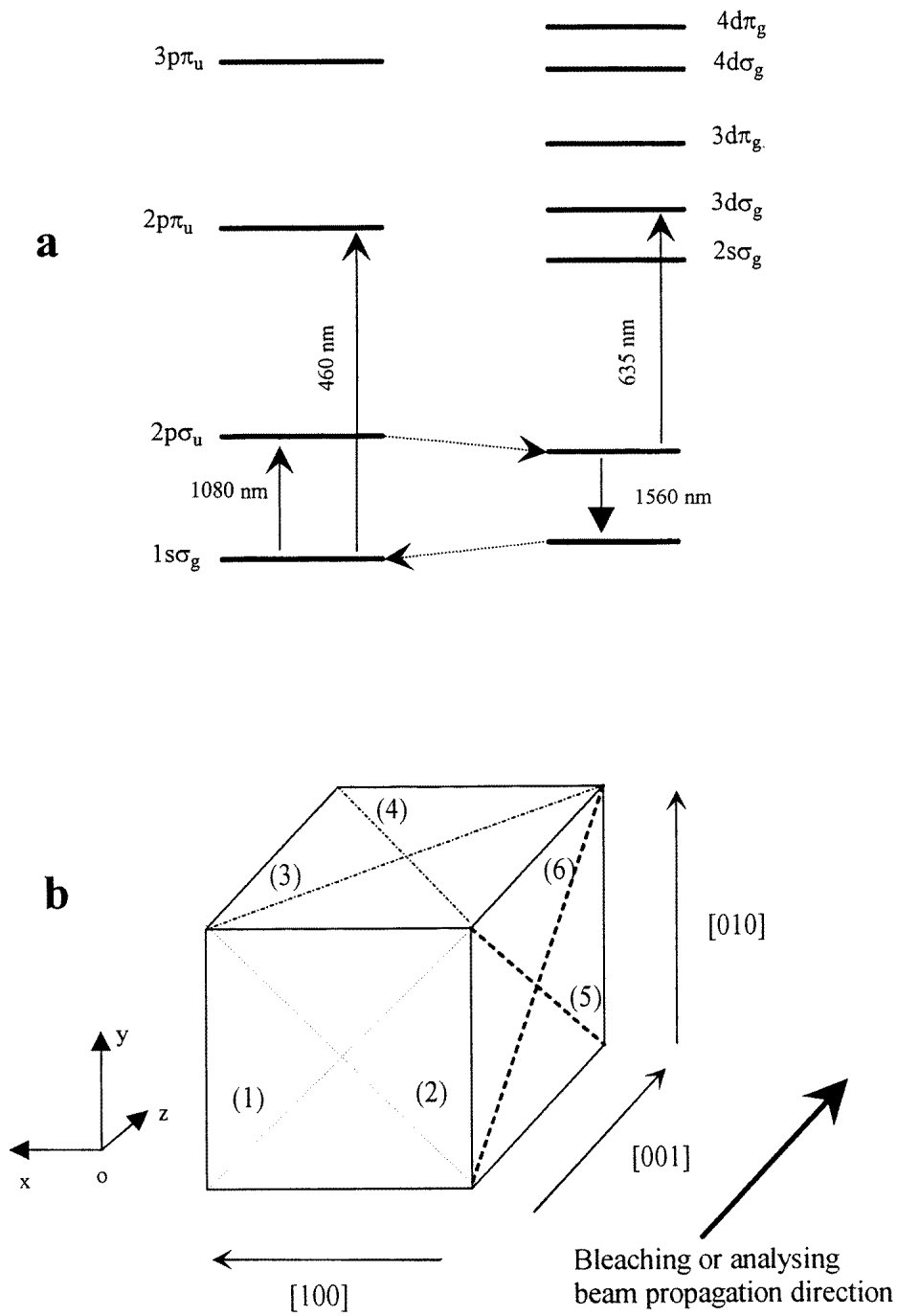
**Abstract.**  $(F_2^+)_{\text{H}}$  centres in NaCl:OH<sup>−</sup> have long been known to be bleached at 77 K by the intense infrared pumping light used in colour-centre lasers. This bleaching is generally assigned to reorientational effects. From absorption and emission measurements, we show unambiguously that, in addition to reorientation, a very significant destruction is involved in the bleaching:  $(F_2^+)_{\text{H}}$  centres are transformed into other ‘C’ centres which do not absorb in the same wavelength domain. Some suggestions are made concerning the nature of these ‘C’ centres. The  $(F_2^+)_{\text{H}} \rightarrow$  ‘C’ conversion is easily and completely reversed by irradiation at 77 K with visible or near-ultraviolet light (a well known procedure in  $(F_2^+)_{\text{H}}$ -colour-centre laser technology).

### 1. Introduction

The tunable laser emission of  $F_2^+$  centres in different alkali halides covers the very interesting 1 to 2  $\mu\text{m}$  spectral range (Gellermann 1991). But there is a rapid degradation of output power under the effect of optical pumping. This has led to the use of various substitutional impurities in order to improve the stability of intrinsic  $F_2^+$  centres. The introduction of a doubly charged chalcogen impurity ( $\text{O}^{2-}$ ) has led to the formation of a new  $F_2^+$ -like centre, the so-called  $(F_2^+)_{\text{H}}$ , which was identified for the first time by Lobanov *et al* (1978) in oxygen-doped LiF. It was later created in various other oxygen-, sulphur- and selenium-doped materials, such as KCl and NaCl. This new centre shows better thermal stability, but, in spite of the anchoring impurity, its laser emission unfortunately still suffers from fading. In NaCl at 77 K, stable laser operation is achieved only when an UV (Pinto *et al* 1986, Matts *et al* 1990) or green (German and Pollock 1987, Kurobori *et al* 1989, Carrig and Pollock 1991) light is focused on the active crystal, simultaneously with the pumping light which excites the  $1s\sigma_{\text{g}} \rightarrow 2p\sigma_{\text{u}}$  transition (see figure 1(a)). This infrared transition appears in absorption at 77 K at around 1.05  $\mu\text{m}$  for the (a) variety and 1.08  $\mu\text{m}$  for the (b) variety of  $(F_2^+)_{\text{H}}$  centres. The maximum fluorescence intensity is observed respectively at 1.485  $\mu\text{m}$  and 1.560  $\mu\text{m}$  at the same temperature. The visible absorption transition  $1s\sigma_{\text{g}} \rightarrow 2p\pi_{\text{u}}$  peaks at approximately 460 nm. *A priori*, the fading of  $(F_2^+)_{\text{H}}$  lasers in the absence of ‘regenerating’ light may arise from one of two causes: reorientation or destruction of active centres by the infrared pump beam.

The axes of the anion bivalency can have any of six different [110]-like orientations in the NaCl lattice (figure 1(b)). For a given  $(F_2^+)_{\text{H}}$  centre, the  $1s\sigma_{\text{g}} \leftrightarrow 2p\sigma_{\text{u}}$  and  $1s\sigma_{\text{g}} \rightarrow 2p\pi_{\text{u}}$

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**Figure 1.** (a) The energy diagram of the  $(F_2^+)_{\text{H}}$  centre in  $\text{NaCl}:\text{OH}^-$  (from Georgiou *et al* 1987). (b) The six possible directions of the anionic bivalency of  $(F_2^+)_{\text{H}}$  centres.

transitions are respectively polarized parallel and perpendicular to the [110] bivacancy axis of the centre<sup>†</sup>. Both the Cornell group (Georgiou *et al* 1987) and the Utah group (Gellermann 1991) assign the fading of NaCl colour-centre lasers solely to reorientational processes: under the effect of the intense and polarized pump light,  $(F_2^+)_{\text{H}}$  centres are aligned along those of the six directions of figure 1(b) which absorb this pump light with the smallest efficiency.

On the other hand, Baldacchini *et al* (1991) report emission measurements under the combined influence of a YAG:Nd<sup>3+</sup> laser (1.064  $\mu\text{m}$ ) and a He–Ne laser (0.633  $\mu\text{m}$ ). They observe both reorientation and destruction of  $(F_2^+)_{\text{H}}$  centres at 50 K, but solely destruction at 10 K. In their experiment, the role of the He–Ne laser is to ‘greatly enhance’ the fading caused by the YAG:Nd<sup>3+</sup> laser. It is not clear from the paper by Baldacchini *et al* whether they have demonstrated and studied destruction of  $(F_2^+)_{\text{H}}$  centres under the influence of just infrared light.

The main purpose of the present work is precisely to prove unambiguously that there is some destruction of  $(F_2^+)_{\text{H}}$  centres in NaCl under excitation at 77 K solely by intense 1.064  $\mu\text{m}$  light. We have obtained evidence of this process both by absorption and by emission measurements. Of course, this destruction is observed to be fully invertible at the same temperature via the action of green–blue or UV light. (If it was not,  $(F_2^+)_{\text{H}}$ -colour-centre lasers would be far from being as successful as they are!)

Section 2 deals with the experimental procedure, and subsections 3.1 and 3.2 respectively with the absorption and emission experimental results. Section 4 contains the discussion. In subsection 4.1, we show how one may obtain from experimental data some information about the respective populations  $n_i$  of the six centre orientations  $i$  of figure 1(b): this will lead to the chief result of our paper. Subsection 4.2 deals with the limited character of the destruction of  $(F_2^+)_{\text{H}}$  centres. Subsection 4.3 speculates about the nature of the species ‘C’ into which  $(F_2^+)_{\text{H}}$  centres are converted when they are ‘destroyed’ by IR irradiation. Finally, the concluding section, section 5, makes one suggestion for further investigations.

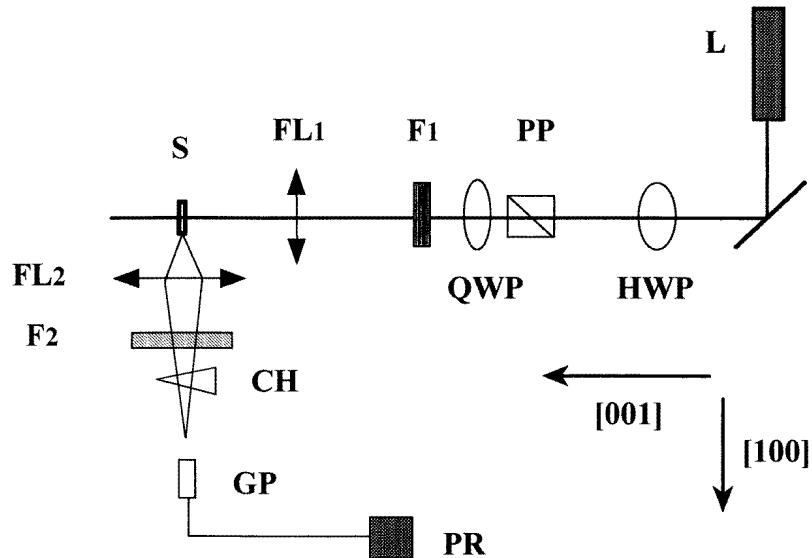
## 2. Experimental procedure

### 2.1. General features

In the experiments of subsection 3.1, a sample is bleached at 77 K by a polarized 1.064  $\mu\text{m}$  beam; subsequently its absorption spectrum is measured at the same temperature. These two phases are repeated several times in order to study the discoloration as a function of irradiation time. In the experiments of subsection 3.2, a sample is irradiated in similar conditions and its  $2p\sigma_{\text{u}} \rightarrow 1s\sigma_{\text{g}}$  fluorescence is monitored at right angles as a function of time. The absorption spectra of subsection 3.1 are recorded with a Perkin–Elmer Lambda 9 spectrophotometer, which has been equipped with a Glan–Thompson polarizing prism: this allows one to measure absorption spectra for polarized light.

Figure 2 shows the set-up which is used both for the emission measurements and for the irradiation phases of the absorption experiments. A sample **S** of coloured NaCl:OH<sup>−</sup>, 2 mm thick, is fixed (with its [100] and [001] axes in the horizontal plane) on the cold finger of a liquid nitrogen cryostat which can easily be moved from the irradiation apparatus of figure 2 to the Lambda 9 spectrometer and back, and be replaced in exactly the same position after each transfer. The useful region of the sample is restricted to a circular area, 1 mm in diameter, by a copper plate, with a small hole, which is pressed against **S**. The role of

<sup>†</sup> We discuss in appendix 1 whether these polarization rules are exact or approximate.



**Figure 2.** The experimental set-up for the bleaching experiments. **L**: YAG:Nd<sup>3+</sup> laser; **HWP**: half-wave plate; **PP**: polarizing prism; **QWP**: quarter-wave plate; **F<sub>1</sub>**: Schott RG 800 filter; **FL<sub>1</sub>**: excitation focusing lens; **S**: sample; **FL<sub>2</sub>**: fluorescence focusing lens; **F<sub>2</sub>**: filter used to cut the stray light of the YAG:Nd<sup>3+</sup> laser; **CH**: chopper; **GP**: germanium photodiode; **PR**: pen recorder.

this diaphragm and the choice of its aperture diameter are important topics which will be discussed in subsection 2.2.

The sample is cooled down to 77 K and  $(F_2^+)_H$  centres are then photoconverted (see for instance Gellermann 1991) into their so-called (b) variety, the one which is used in colour-centre lasers. We perform this operation by exciting the sample for 20 minutes with the weakly focused (spot size 0.75 cm<sup>2</sup>) unfiltered light<sup>†</sup> of a high-pressure mercury lamp (Osram HBO 100) propagating along the direction [001]. In principle, after five minutes, the photoconversion process is fully achieved. But we wait for 20 minutes in order to be certain that the conversion is completed and we excite the sample on both sides to ensure a better homogeneity.

The bleaching light is provided by a cw YAG:Nd<sup>3+</sup> laser **L** delivering up to 20 W on the 1.064 μm line. A combination of a half-wave plate **HWP** and a polarizing prism **PP** allows us to fix both the polarization and the power of the light incident on the sample. When we want to excite the centres with a circularly polarized beam, we add a quarter-wave plate **QWP**. We cut off the stray light from the discharge lamps exciting the YAG:Nd<sup>3+</sup> rod of **L** with a Schott RG 800 filter **F<sub>1</sub>**, in order to avoid a simultaneous regeneration of the centres during their bleaching by the intense 1.064 μm light. The exciting light is weakly focused on the sample by a lens **FL<sub>1</sub>**, with focal length of 101 mm. The choice of the spot radius will be discussed in subsection 2.2.

In the case of the fluorescence intensity measurements, the sample is excited by a circularly polarized infrared light propagating along the direction [001] (figure 2) and the fluorescence intensity is measured along the direction [100]. It is chopped (**CH**) and focused

<sup>†</sup> Hereafter called the 'F-light' for brevity.

(**FL**<sub>2</sub>) on a germanium photodiode **GP**. The signal of the **GP** is fed into a lock-in amplifier, the output of which is plotted as a function of time thanks to a pen recorder **PR**. A second filter **F**<sub>2</sub>, which transmits only wavelengths longer than 1.2  $\mu\text{m}$ , is added to cut out the scattered light of the YAG:Nd<sup>3+</sup> laser.

## 2.2. The radius of the bleaching beam

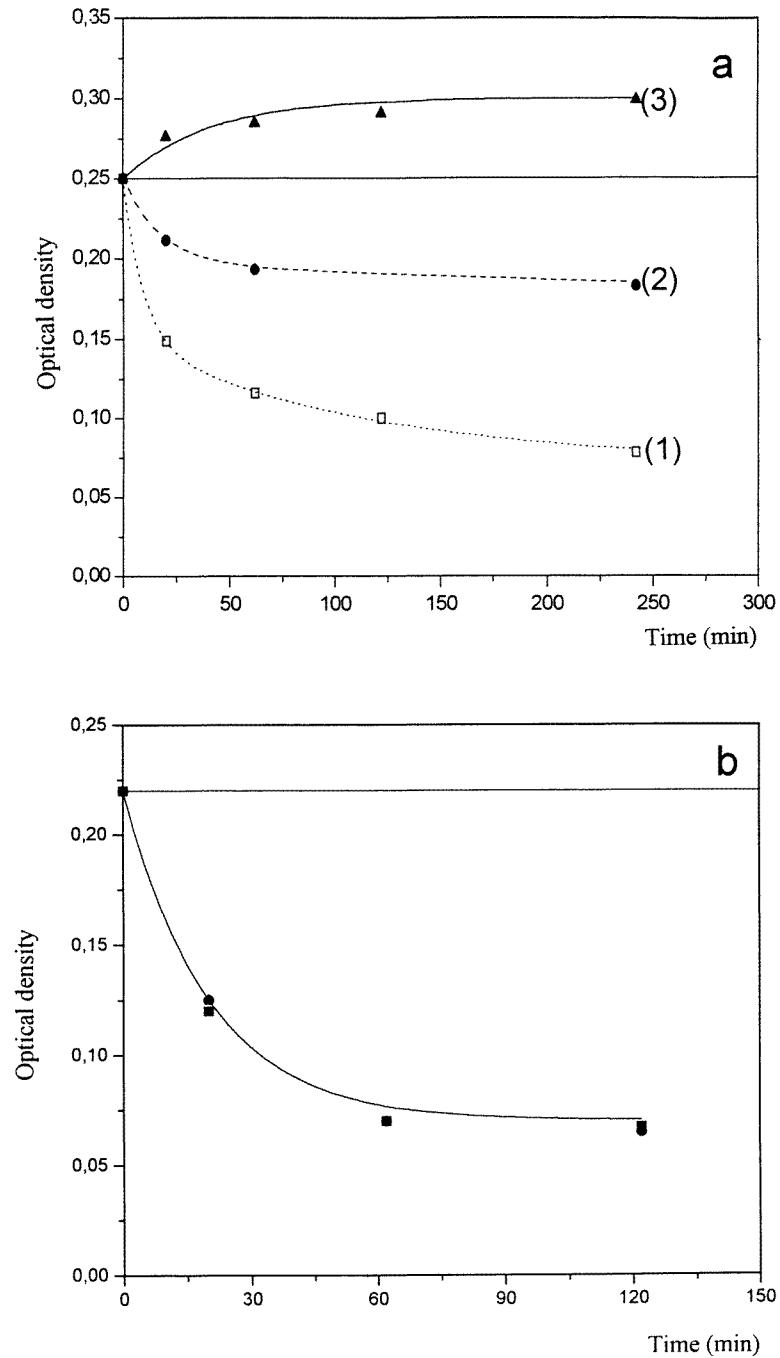
The main difficulty in a quantitative study of  $(F_2^+)_{\text{H}}$ -centre bleaching by infrared  $1s\sigma_{\text{g}} \rightarrow 2p\sigma_{\text{u}}$  light is that it is intrinsically a very weak phenomenon. Even with 20 W of 1.064  $\mu\text{m}$  light, a measurable effect would take inconveniently long to obtain if the beam was unfocused. In order to get data in a few hours, one must concentrate the infrared power on a spot with a radius  $w$  (at  $e^{-2}$  of the maximum intensity) of the order of 0.5 mm. Ideally, the sample beam of the spectrophotometer in the experiments of subsection 3.1 should have dimensions much smaller than  $w$  (since the YAG:Nd<sup>3+</sup> laser beam is gaussian, its intensity, and therefore the induced bleaching, vary considerably over a radial distance of the order of  $w$ ). Unfortunately, the Lambda 9 beam is much larger ( $\sim 2 \times 4 \text{ mm}^2$ ), so we have been obliged to place against the sample the diaphragm with radius  $r$  mentioned in subsection 2.1: it ensures that it is the same part of the crystal which is bleached by the YAG:Nd<sup>3+</sup> laser and later analysed by the spectrophotometer. However,  $r$  cannot be chosen much smaller than  $w$ , as suggested above, because with a too small diaphragm there is not enough intensity passing through the sample and reaching the detector in the spectrophotometer: the spectra become too noisy. A compromise must therefore be found between:

(i) a ratio  $r/w$  that is too large (the absorption spectra are noiseless, but only the axial part of the probed region has been bleached and therefore the variations of the centre number densities are ‘washed-out’); and

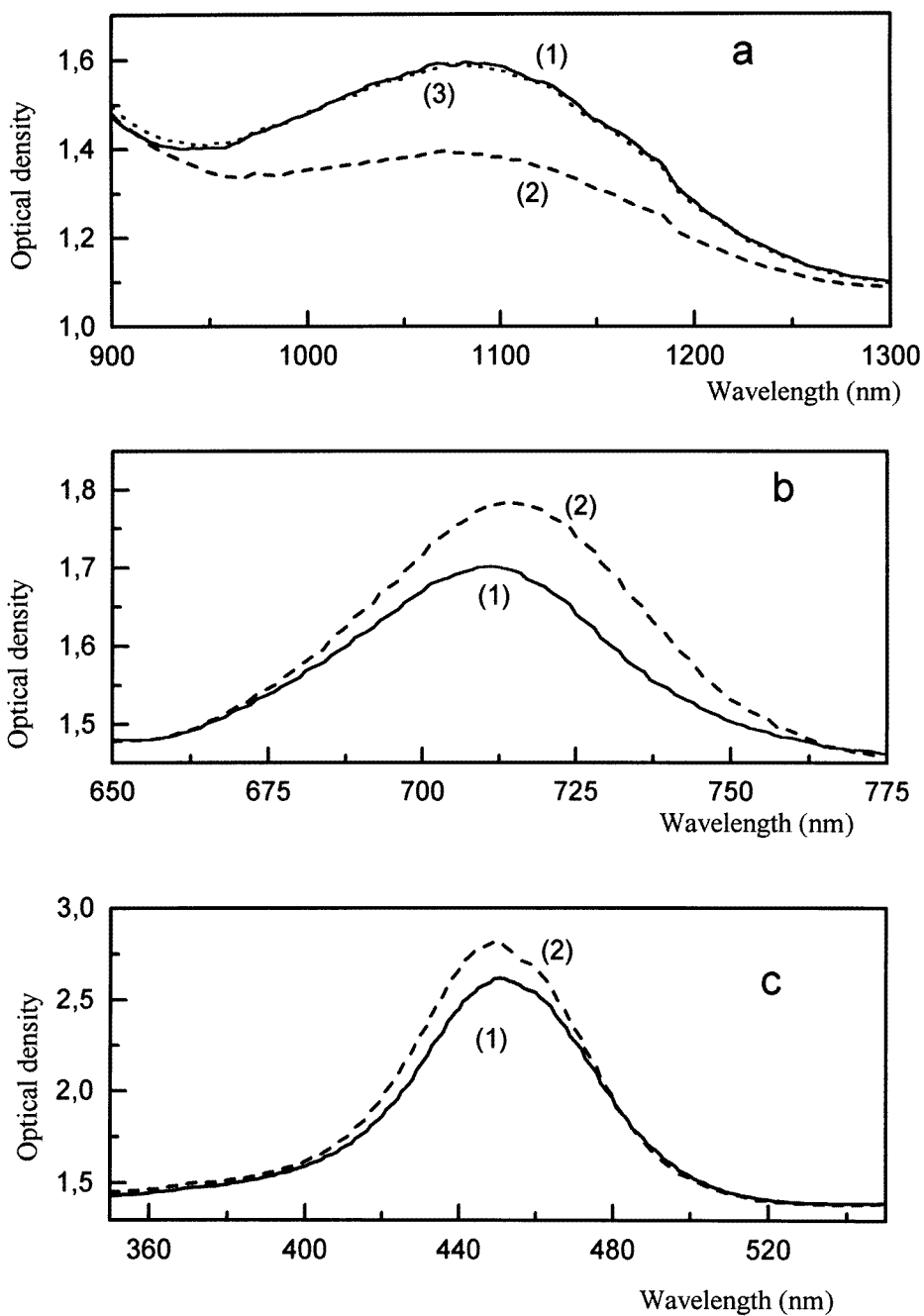
(ii) a ratio  $r/w$  that is too small (the absorption spectra should be significant, because the explored region has been nearly uniformly bleached, but they are too noisy to be really useful).

Practically, in our experiments, a hole radius of  $r = 0.5 \text{ mm}$  was used and the focusing lens **FL**<sub>1</sub> of figure 2 was located so as to make  $w$  of the order of  $r$ . The radius  $w$  was determined in an auxiliary experiment where the sample was replaced by a razor blade which we progressively translated perpendicularly to the YAG:Nd<sup>3+</sup> beam. With a Scientech 362 power-meter, we determined the evolution of the transmitted power as a function of the blade position. Fitting the derivative of this function with a gaussian, we obtained  $w = 0.52 \text{ mm}$  as the beam radius  $w$  at the location of the sample. Thus, the bleaching beam intensity varied by a factor of  $\exp(-2(0.5/0.52)^2) = 0.16$  between the centre and the edge of the diaphragm, an inhomogeneity which will be taken into account in the discussion of subsection 4.2.

Since the bleaching is thus necessarily limited to a cylinder of very small radius, it is impossible to explore the sample absorption with light propagating perpendicularly to the [001] bleaching beam. One therefore lacks information concerning the absorption for [001] polarization, a fact which will prevent full determination of the populations  $n_i$  in subsections 3.1 and 4.1 below.



**Figure 3.** The evolution of the optical density at  $1.08 \mu\text{m}$  as a function of time. (a) Excitation with 6 W of the  $1.064 \mu\text{m}$  beam of the  $\text{YAG:Nd}^{3+}$  laser polarized along the direction [100]; sample temperature: 77 K; polarization of analysing light: [100], [110] and [010] respectively for curves 1, 2 and 3. (b) Excitation with 6 W of the  $1.064 \mu\text{m}$  circularly polarized beam of the  $\text{YAG:Nd}^{3+}$  laser; sample temperature: 77 K; polarization of analysing light: [100] (squares) and [110] (circles).



**Figure 4.** Spectral changes induced by IR intense irradiation. Measurement temperature: 77 K. (a) Curve 1: before bleaching; curve 2: after 105 minutes' bleaching at 77 K; curve 3: after 20 minutes' subsequent irradiation with 'F-light'. (b), (c) Curve 1: before bleaching; curve 2: after bleaching with 7 W for 165 minutes at 77 K.



### 3. Experimental results

#### 3.1. Absorption experiments

Using a [100] linearly polarized 6 W infrared beam, we have excited the centres and subsequently measured the absorption spectra using [100]-, [110]- and [010]-polarized analysing light. We have plotted the evolution of the optical density, measured at 1.080  $\mu\text{m}$ , versus the cumulated bleaching time (see figure 3(a)). We observe a decrease of the absorption coefficient along the direction [100] (curve 1) and an increase along the direction [010] (curve 3). A number of the centres lost along the excitation polarization direction are found along the perpendicular one. This is qualitatively consistent with the usually invoked effect of reorientation.

On the other hand, with a circularly polarized exciting light, we observe a large decrease of the absorption coefficient along both directions [100] and [110] (see figure 3(b)). This strongly suggests that destruction of  $(F_2^+)_{\text{H}}$  centres is occurring together with reorientation, but the evidence is not fully conclusive since there remains a linearly independent polarization direction [001] which cannot be explored in the present work.

When the experiment was finished, the sample, still at 77 K, was irradiated for about 20 minutes with 'F-light'. The absorption spectrum was then observed to be restored exactly to its initial state, in the 0.95–1.20  $\mu\text{m}$  range of the  $(F_2^+)_{\text{H}}$  band (figure 4(a), curves 1 and 3), as well as in all of the other spectral regions. This proves that the modifications of the sample induced by the IR beam (reorientation and eventually destruction of  $(F_2^+)_{\text{H}}$  centres) are completely reversed by the action of the mercury light and this allows us to perform a number of different experiments using the same portion of the sample, since it can be restored to its primitive state as often as we wish.

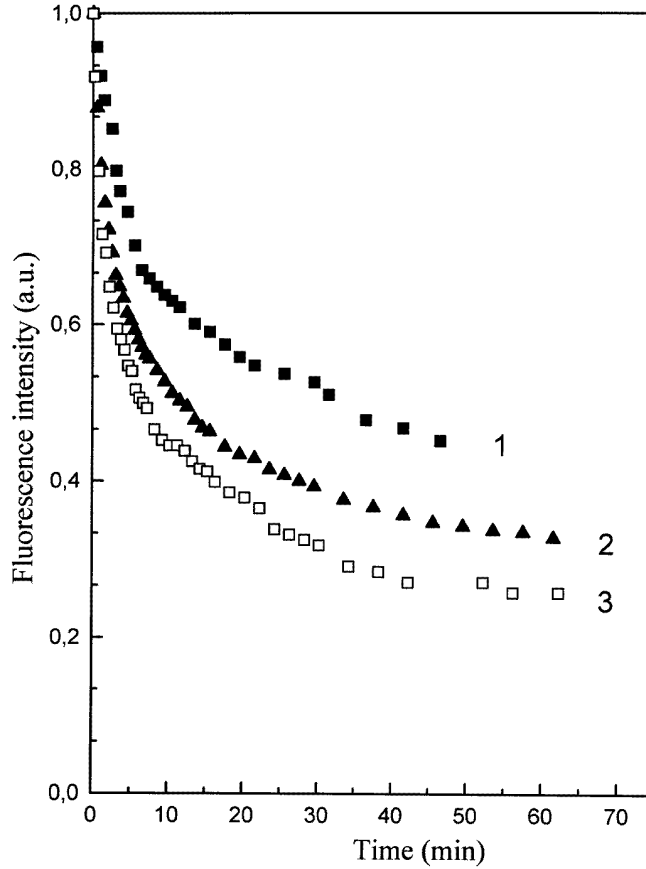
#### 3.2. Emission experiments

The 1 mm diameter diaphragm was kept in front of the sample, although it is useless for this kind of measurement. The infrared laser beam was much better focused than in subsection 3.1 ( $w \sim 0.1$  mm), so the whole gaussian beam passed through the hole. The experiment was performed with a circularly polarized bleaching beam propagating along direction [001]. Its power was chosen in four consecutive experiments to be 4, 6, 8 and 9.8 W. In each case, we measured the fluorescence intensity emitted in the [100] direction, without inserting any polarization analyser. As could be expected from the results of absorption experiments (subsection 3.1), we observed an important decrease of the fluorescence intensity as a function of time, the decay being quicker for higher IR powers (see figure 5). An auxiliary measurement verified that only a negligible amount of stray light reached the photodiode **GP** of figure 2. Thus, the zero-intensity line of figure 5 is meaningful.

## 4. Discussion

#### 4.1. Populations of the six orientations of centres

We shall take advantage of the following fact: we observe changes in the intensity of the  $(F_2^+)_{\text{H}}$  infrared absorption band, but no shift or broadening which would disclose the creation of some new species absorbing in the same spectral range (compare, for instance, curves 1 and 2 of figure 4(a)). Therefore, the (b) variety of  $(F_2^+)_{\text{H}}$  centres is the only source



**Figure 5.** Evolution of the fluorescence intensity as a function of time for different pump powers. The pump power  $P_L = 4$  W, 8 W and 9.8 W respectively for curves 1, 2 and 3. For each curve, the observed intensities have been divided by the corresponding initial value.

of the absorption spectra at around  $1.1 \mu\text{m}$ †. Assuming that the infrared transition is 100% polarized parallel to the axis of the anionic bivacancy (assumption 1), the optical density of the sample can be written as follows, for a given polarization of the analysing beam:

$$\text{OD}(\lambda) = a(\lambda) \sum_i n_i \cos^2 \theta_i \quad (1)$$

where  $a(\lambda)$  is the absorption shape;  $n_i$  is the number per unit volume of centres with orientation  $i$  (see figure 1(b));  $\theta_i$  is the angle between the polarization of the analysing light and the axis of the bivacancy. In table 1, we list the values of  $\cos^2 \theta_i$  for the polarizations which will be useful below.

To eliminate  $a(\lambda)$ , we compare the optical density OD of the bleached sample with the original optical density  $\text{OD}^0$ . But, in order to reach conclusion, we must know the initial values  $n_i^0$  of the populations  $n_i$ , following the preparation of the sample by irradiation with unpolarized mercury light propagating along [001]. Let us assume, for this 'F-light', the selection rule of the  $1s\sigma_g \rightarrow 2p\pi_u$  transition, i.e. absorption by each class  $i$  of centres with

† More precisely, of the absorption spectra corrected by subtracting a general background which remains the same before and after bleaching.

**Table 1.** Values of  $\cos^2 \theta_i$ : column 1 contains the polarizations of light and line 1 the orientations of anionic bivacancies, according to the labelling of figure 1(b). The last line, which refers to unpolarized or circularly polarized light propagating along [001], is the half-sum of the lines corresponding to polarizations [100] and [010].

	1	2	3	4	5	6
[100]	0.5	0.5	0.5	0.5	0	0
[110]	0	1	0.25	0.25	0.25	0.25
[010]	0.5	0.5	0	0	0.5	0.5
[001]	0	0	0.5	0.5	0.5	0.5
Unpolarized or circular	0.5	0.5	0.25	0.25	0.25	0.25

an efficiency proportional to  $\sin^2 \theta'_i$ , where  $\theta'_i$  is the angle between the polarization of the ‘F-light’ and the axis of the bivacancy (assumption 2). Let us also suppose that an  $(F_2^+)_H$  centre in its  $2p\pi_u$  state reorientates randomly and that the dose of ‘F-light’ irradiation is sufficient for reaching the steady state (assumption 3). In these conditions, the initial populations are expected to be inversely proportional to the absorption efficiencies  $\sin^2 \theta'_i = 1 - \cos^2 \theta'_i$ :

$$n_1^0(1 - \cos^2 \theta'_1) = n_2^0(1 - \cos^2 \theta'_2) = \dots \quad (2)$$

Using the last line of table 1, because of the unpolarized character of the ‘F-light’ beam, we obtain from (2)

$$\begin{aligned} n_1^0 = n_2^0 &= \frac{3}{14} N^0 \\ n_3^0 = n_4^0 = n_5^0 = n_6^0 &= \frac{2}{14} N^0 \end{aligned} \quad (3)$$

where  $N^0$  is the total number density of  $(F_2^+)_H$  centres in the initial crystal. The corresponding optical density is:

$$OD^0(\lambda) = (5/14)N^0 a(\lambda) = 0.357N^0 a(\lambda) \quad (4)$$

for any analysing light with the [001] propagation direction. From relations (1) and (4), we have

$$OD(\lambda)/OD^0(\lambda) = \left( \sum_i n_i \cos^2 \theta_i \right) / 0.357N^0. \quad (5)$$

On bleaching with a [100]-polarized YAG:Nd<sup>3+</sup> laser for 240 minutes, one obtains from the three curves of figure 3(a)

$$0.5(n_1 + n_2 + n_3 + n_4) = 0.109N^0 \quad (6a)$$

$$n_2 + 0.25(n_3 + n_4 + n_5 + n_6) = 0.258N^0 \quad (6b)$$

$$0.5(n_1 + n_2 + n_5 + n_6) = 0.427N^0. \quad (6c)$$

According to table 1, with the [100]-polarized YAG:Nd<sup>3+</sup> laser, centres along directions 1, 2, 3 and 4 are excited in the same way and those along directions 5 and 6 are not excited at all<sup>†</sup>. Therefore, at any time during excitation, one should have

$$n_1 = n_2 = n_3 = n_4 \quad \text{and} \quad n_5 = n_6.$$

<sup>†</sup> In fact, one currently does not know what the microscopic mechanism of the fading of  $(F_2^+)_H$  centres under intense infrared excitation is. We assume here that it has the same symmetry properties as the well understood  $1s\sigma_g \rightarrow 2p\sigma_u$  linear absorption of the same infrared light.

Thus, equation (6a) leads to  $n_1 = 0.054N^0$  and equation (6c) to  $n_5 = 0.372N^0$ . Using these calculated values of  $n_1$  and  $n_5$ , the first member of equation (6b) equals  $0.267N^0$  which is in fair agreement with the observed  $0.258N^0$ . The total number of centres after bleaching is

$$N = 4n_1 + 2n_5 = 0.960N^0. \quad (7)$$

This suggests a weak destruction of centres by the polarized infrared beam, but since 0.960 is close to unity, the evidence is far from being conclusive.

On the other hand, in the experiments with circular polarization of the YAG:Nd<sup>3+</sup> laser, the symmetry of the excitation leads to

$$n_1 = n_2 \quad \text{and} \quad n_3 = n_4 = n_5 = n_6.$$

The measured absorption coefficient (figure 3(b)) and formula (5) lead to  $n_1 + n_3 = 0.109N^0$  at  $t = 120$  min. The total number of centres is  $N = 2n_1 + 4n_3$ , so

$$N = 2n_1 + 4n_3 = 0.436N^0 - 2n_1 \leq 0.436N^0. \quad (8)$$

In this case, the observed population is quite significantly less than  $N^0$ . We can conclude that the bleaching effect of the  $(F_2^+)_{\text{H}}$  centres under intense infrared irradiation is not only due to reorientation but also to a destruction of these centres. Why is this destruction of centres more conspicuous with circularly polarized IR light (equation (8)) than with linearly polarized light (equation (7))? Most probably because circularly polarized light is absorbed by all classes of centres and can therefore transform them all, while with [100]-linearly-polarized light some classes of centre ( $i = 5$  and  $6$ ; see table 1) are not pumped and therefore not destroyed. On the contrary,  $n_5$  and  $n_6$  are increased because for centres of sites 1, 2, 3 and 4, together with destruction, there is reorientation, which converts some of them into centres of sites 5 and 6. The reverse conversion is impossible since sites 5 and 6 do not absorb the [100]-polarized bleaching light.

Georgiou *et al* (1987) state that 'The  $F_2^+ : O^{2-}$  center is stable at 77 K and is not destroyed under intense optical excitation. Any observable decrease of its absorption after hard pumping at  $1.06 \mu\text{m}$  is due to reorientation of the centers. . .'. However, in the same paper, the authors show what is probably the first evidence of destruction of  $(F_2^+)_{\text{H}}$  centres by IR light: from the curves a, b and c of their figure 12, one calculates via our formula (5)  $N = 0.825N^0 - 2n_1 \leq 0.825N^0$ .

Let us turn now to the emission experiments of subsection 3.2. Using table 1, the fluorescence intensity  $I$  is expected to be

$$I = \alpha[1 \times 0.5(n_1 + n_2) + 0.5 \times 0.5(n_3 + n_4) + 0.5 \times 1(n_5 + n_6)] \quad (9)$$

where  $\alpha$  is a constant. The first angular factor of each term in the sum between square brackets accounts for excitation and the second factor for emission. The sample had been prepared by photoconversion at 77 K with mercury light propagating along the direction [001]. Using equation (3) for the initial populations of centres, one calculates, from formula (9) that, at the beginning of a fluorescence experiment,

$$I^0 = (6/14)\alpha N^0 = 0.429\alpha N^0. \quad (10)$$

Taking into account the symmetry of excitation ( $n_1 = n_2$  and  $n_3 = n_4 = n_5 = n_6$  at any time), equation (9) becomes

$$I = \alpha(n_1 + 1.5n_3). \quad (11)$$

Using 9.8 W incident power, we observed after 62 minutes (figure 5, curve 3)  $I = 0.259I^0$ . Comparing with relations (10) and (11), we have

$$n_1 + 1.5n_3 = 0.429 \times 0.259N^0 = 0.111N^0.$$

The total population is then

$$N = 2n_1 + 4n_3 = 0.296N^0 - 0.666n_1 \leq 0.296N^0. \quad (12)$$

This is further proof that there is some destruction of  $(F_2^+)_H$  centres by intense infrared light.

One may raise the objection that the conclusions of the present subsection rest on assumptions 1, 2 and 3. The two former ones are probably approximate as discussed in appendix 1. Assumption 2 appears to be especially questionable because the preparation beam contains a number of widely distant spectral lines, which may induce several phenomena with various symmetries, instead of only the  $1s\sigma_g \rightarrow 2p\pi_u$  transition that we have considered. But the anisotropies induced by different phenomena are expected to compensate one another partially and therefore the initial optical density and fluorescence intensity should not be higher than the values of equations (4) and (10). They should be intermediate between these values and the ones calculated under the hypothesis of an isotropic initial distribution of centres ( $n_i^0 = N^0/6$ )<sup>†</sup>:  $OD^0(\lambda) = 0.333N^0a(\lambda)$  and  $I^0 = 0.417\alpha N^0$ . But, if one substitutes respectively 0.333 and 0.417 for the coefficients 0.357 and 0.429 of equations (5) and (10), one obtains  $N \leq 0.407N^0$  instead of equation (8) and  $N \leq 0.288N^0$  instead of equation (12). The conclusion is thus reinforced rather than weakened.

Let us suppose now that assumption 1 is only partly true, i.e. that the  $1s\sigma_g \rightarrow 2p\pi_u$  transition is polarized only approximately (and not exactly) parallel to the bivacancy axis (see appendix 1). Then, for each line of table 1, the entries will be closer to their average value 0.333 and the anisotropy of optical spectra will be somewhat 'washed-out'. In this hypothesis, decay curves such as those of figures 3(b) and 5 would correspond to even more significant destruction of  $(F_2^+)_H$  centres than estimated above.

#### 4.2. The limited character of the $(F_2^+)_H$ -centre destruction

One remarks in figures 3(a) and 3(b) that the limit for very long irradiation times does not seem to correspond to a total discoloration for the polarization parallel to the bleaching beam. This means that the destruction of centres is only partial. One may think either of an experimental artefact or of a real physical phenomenon.

The most obvious cause of an artefact is the spatial inhomogeneity of the bleaching beam. In addition to the transverse inhomogeneity mentioned in subsection 2.2, one must consider the longitudinal one, since the pumping beam becomes weaker as it propagates inside the 2 mm thick sample (an inhomogeneity that decreases in the course of time as the front part of the sample is bleached). Let us call the cylindrical volume whose absorption is measured  $V$ . Its different points are not bleached at the same rate, which could lead to a very nonexponential decay of the measured absorption, with a rapid fall at the beginning and a much slower decrease afterwards. The latter might be experimentally mistaken for a horizontal nonzero asymptote, such as the one of figure 3(b).

We made computer simulations of this effect by solving rate equations in order to obtain the populations  $n_i$  of the six orientations of  $(F_2^+)_H$  centres as a function of bleaching time  $t$  and of the location within  $V$ . Then, we calculated the transmission of the spectrophotometer probe beam across this nonuniformly coloured crystal and therefore the apparent optical density OD to be compared with the measurement results. In order to perform this calculation, we had to make hypotheses concerning the bleaching mechanisms (the relative

<sup>†</sup> The argument would be qualitatively the same if assumption 3 was wrong, i.e. if the dose of 'F-light' was insufficient.

importance of reorientation and of destruction of centres, the order  $\alpha$  of these processes). But, whatever hypotheses we assumed, the qualitative results remained the same: if the adjustable parameters of the model were chosen to account for the initial part of the decay curve, the tail of the OD versus time curve was indeed calculated to be lingering, but much less than observed experimentally.

In view of these unsuccessful model calculations of experimental artefacts, we believe that the destruction of  $(F_2^+)_{\text{H}}$  centres by IR light is really limited:

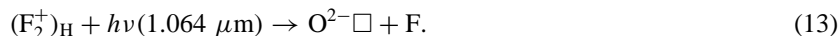
- (i) either because of some reaction inverse of (13), (14) and/or (16) of the next subsection, subsection 4.3, inducing a dynamical equilibrium under irradiation; or
- (ii) because of the existence of two slightly different varieties of  $(F_2^+)_{\text{H}}$  centre, one of which would be totally proof against destruction by intense IR beams.

#### 4.3. What do $(F_2^+)_{\text{H}}$ centres become when they are 'destroyed'?

In the experiments of subsection 3.1, we also looked at how intense  $1.06 \mu\text{m}$  irradiation modifies absorption spectra in domains other than that of the  $(F_2^+)_{\text{H}}$   $1s\sigma_{\text{g}} \rightarrow 2p\sigma_{\text{u}}$  transition. The two chief alterations are observed at around 700 and 450 nm. The red absorption is increased and shifted by  $\sim 2$  nm towards long wavelengths (figure 4(b)), while the blue one is also increased and very slightly shifted towards short wavelengths (figure 4(c)). These spectral changes are observed to be fully reversible under the action of the same 'F-light' as restores the  $(F_2^+)_{\text{H}}$  centres to their initial number density.

The absorption bands of figures 4(b) and 4(c) are both known to be composite: in NaCl at 77 K,  $F_2$  absorbs at 715 nm,  $F_3^+$  at 700 nm, F at 450 nm. In the vicinity of the F band lies one transition of a number of aggregate centres among which are the  $(F_2^+)_{\text{H}}$  centres themselves: their  $1s\sigma_{\text{g}} \rightarrow 2p\pi_{\text{u}}$  absorption peaks at 458 nm. The shift observed in figure 4(c) may be due to the removal of  $(F_2^+)_{\text{H}}$  centres (which absorb at a slightly longer wavelength than F centres), but the intensity increase shows that there is simultaneously growth of another type of centre, possibly F centres themselves. However, one cannot be wholly positive since so many different species have an absorption in the F-band domain.

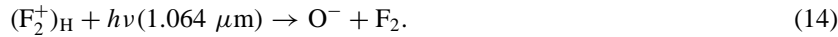
Let us suggest a first hypothesis concerning the bleaching process. One knows (even if one ignores the detailed mechanism) that infrared irradiation is able, with a very low probability, to displace one of the anion vacancies which are building blocks of the  $(F_2^+)_{\text{H}}$  centre, thus leading to the reorientation of this defect without altering its nature. Why should this vacancy motion not take place sometimes in a direction away from the other vacancy? One would thus obtain an  $\text{O}^{2-}\square$  centre and an F centre, close to one another, but with a practically negligible interaction:



It has not been possible to test this hypothesis by looking for an increase of the  $\text{O}^{2-}\square$ -centre absorption. The latter occurs at around 290 nm (Wandt *et al* 1987). In this spectral domain, a general absorption background (with a pronounced slope increasing towards short wavelengths) prevents accurate measurements of the intensity of the  $\text{O}^{2-}\square$  band. Hypothesis (13) accounts for the observed increase of the F band (figure 4(c)), as well as for the reversible character of the bleaching: 'F-light' may, of course, be absorbed by an F centre bringing it to its relaxed excited state, where the potential barrier separating it from the neighbouring  $\text{O}^{2-}\square$  defect may be easy to recross, thus restoring the  $(F_2^+)_{\text{H}}$  centre.

However, the modifications of absorption in the red spectral range (figure 4(b)) are not explained by reaction (13). We may therefore modify this hypothesis by assuming that, simultaneously with the move of the vacancy, an electron is transferred from the oxygen

to the empty vacancy, yielding a substitutional  $O^-$  ion and a neighbouring  $F_2$  centre, again with a negligible mutual interaction:



Like (13), process (14) is plausible from the electrostatic point of view: the  $O^-$  ion and  $F_2$  centre are both neutral with respect to the NaCl lattice (as are  $(F_2^+)_{\text{H}}$ , F and  $O^{2-}$ ). Therefore, they are more easily separated than charged entities like a substitutional  $O^{2-}$  ion and an  $F_2^+$  centre which would attract one another. The  $O^-$  substitutional ion is associated with an absorption band at 185 nm in KCl (Fischer *et al* 1966), and presumably at an even shorter wavelength in NaCl, i.e. out of the range of our absorption spectra. Thus, we can obtain no direct proof of the postulated creation of  $O^-$  ions. On the other hand, the observed growth of the  $F_2$  band is obviously accounted for by mechanism (14). As for the spectral modifications of figure 4(c), they may be explained by the transition of  $F_2$  centres to their second excited state which does occur in the F-band domain. This same transition could also explain the regenerating action of the 'F-light', which would induce the reaction that is the inverse of (14) by exciting the  $F_2$  centre, thus lowering the potential barrier which separates it from the  $O^-$  ion.

Another class of hypotheses about the origin of bleaching involves no motion of ions, but rather changes in the ionization states of the various species present in the sample. For instance, Baldacchini *et al* (1991) suggest



and



to explain the results of experiments where they destroy  $(F_2^+)_{\text{H}}$  centres by the combined action of 1.064 and 0.633  $\mu\text{m}$  radiations. A similar process could be invoked here, but the source of electrons would remain to be specified (in the case of Baldacchini *et al*, it was the 0.633  $\mu\text{m}$  radiation). Moreover, it seems somewhat dubious that an entity like  $(F_2)_{\text{H}}$ , which is negatively charged with respect to the NaCl lattice, should be stable enough to account for the very significant observed  $(F_2^+)_{\text{H}}$  destruction.

Equations (13), (14) or (15) and (16) are not the only possible explanations for the  $(F_2^+)_{\text{H}}$ -centre bleaching–restoring phenomena. Moreover, several independent microscopic mechanisms may contribute to the observed effect. A final answer to the title question of the present subsection obviously needs further experimental investigation.

An extra clue for solving this problem could be the knowledge of the number  $\alpha$  of infrared photons necessary to achieve destruction of one  $(F_2^+)_{\text{H}}$  centre. The bleaching efficiency should be proportional to  $P_L^\alpha$ , where  $P_L$  is the infrared pump power. The fluorescence experiments of subsection 3.2 afford an opportunity to determine  $\alpha$ . The result is  $1.58 \pm 0.17$ , i.e. very different both from 1 (a one-photon process) and from 2 (a two-photon process). This suggests that the observed decay curves of figure 5 are the results of several phenomena involving different numbers of infrared photons (reorientation and destruction, several destructive processes, ...).

## 5. Conclusion

We have obtained strong evidence that at 77 K, under the action of an intense 1.06  $\mu\text{m}$  beam,  $(F_2^+)_{\text{H}}$  centres in NaCl:OH<sup>-</sup> are not only reorientated, but also a significant fraction of them are transformed into some other centre(s) 'C'. This fact is proved independently by

absorption and by emission measurements, using in each case a simple numerical analysis of the experimental data. The assumptions underlying this analysis have been critically examined and found to be reliable. The transformation of  $(F_2^+)_{\text{H}}$  centres into centres 'C' is totally reversed by irradiating the sample at 77 K with the unfiltered light of a high-pressure mercury lamp. Three suggestions have been made concerning the nature of 'C' ( $F + O^{2-}$ ,  $F_2 + O^-$  and  $(F_2)_{\text{H}}$ ). However, a reliable decision concerning the identity of 'C' necessitates further studies.

It is well known that the regenerating power needed by an  $(F_2^+)_{\text{H}}$ -centre laser is a rapidly increasing function of the sample temperature. It would therefore be of interest to repeat the present experiments at a much lower temperature (for instance 10 K); the results might be different, even qualitatively. From the work of Baldacchini *et al* (1991), one may expect that reorientation disappears at these very low temperatures and that only destruction of  $(F_2^+)_{\text{H}}$  centres remains. But, if such is the case, this destruction must necessarily be quite limited, much more so than at 77 K. Otherwise, it would not be possible to operate, with 60% output power, a NaCl:OH<sup>-</sup> laser at 40 K without a regeneration beam, as reported by Girard *et al* (1993). In any case, one may expect to observe simpler phenomena at 10 than at 77 K (some of the microscopic processes would be frozen out) and perhaps to obtain a significant power law  $P_L^\alpha$ , with an integer  $\alpha$ , unlike in the case of the present work (see the end of subsection 4.3).

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### Appendix 1. Polarization of the optical transitions of the $(F_2^+)_{\text{H}}$ centres

The interpretation of our present experiments relies on assumptions 1 (the infrared  $1s\sigma_g \leftrightarrow 2p\sigma_u$  transition of  $(F_2^+)_{\text{H}}$  centres is 100% polarized parallel to the axis of the anionic bivacancy) and 2 (the visible  $1s\sigma_g \rightarrow 2p\pi_u$  transition of  $(F_2^+)_{\text{H}}$  centres is 100% polarized perpendicularly to the same axis). It is therefore of interest to discuss the validity of these two widespread assumptions.

Let us consider first the case of an intrinsic  $F_2^+$  centre. Its point symmetry is  $D_{2h}$ , so, from group theory, the radiative transitions are expected to have well-defined linear polarizations: for  $1s\sigma_g \leftrightarrow 2p\sigma_u$  parallel to the [110] bivacancy axis, and for  $1s\sigma_g \rightarrow 2p\pi_u$  a close doublet of transitions polarized in two directions both perpendicular to this [110] axis. And this was indeed experimentally shown to be the case (see, for instance, Aegerter and Lüty 1971).

In the case of an  $(F_2^+)_{\text{H}}$  centre, the  $O^{2-}$  substitutional impurity lowers the point symmetry to a subgroup of  $D_{2h}$ , which depends on the exact location of  $O^{2-}$ , but which does not include as a twofold rotation axis the line joining the two  $Cl^-$  vacancies, at least in all physically reasonable hypotheses about  $O^{2-}$  position. Thus, there is no theoretical reason to assume that the lowest  $1s\sigma_g \leftrightarrow 2p\sigma_u$  and  $1s\sigma_g \rightarrow 2p\pi_u$  transitions of the  $(F_2^+)_{\text{H}}$  centre are polarized respectively along the bivacancy [110] axis and perpendicular to it. However, several sets of polarized excitation and emission measurements (Pinto *et al* 1986, Georgiou *et al* 1987, Wandt *et al* 1987) are consistent with these polarizations: everything looks as if the oxygen, which shifts the optical transitions of the  $F_2^+$  centre, had little effect on their polarizations. However, to the best of our knowledge, nobody has investigated whether some deviations



from 100% polarization of  $(F_2^+)_H$ -centre transitions are experimentally perceptible. We have therefore to be cautious in using assumptions 1 and 2 in the present paper.

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