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On the coloration properties of CaF_2 : Na

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Résumé. — Nous avons étudié les propriétés dichroïques et l'existence d'états excités métastables de plusieurs centres colorés créés par irradiation X dans CaF_2 : Na. Selon nos résultats les bandes d'absorption à 600, 385 et 322 nm sont associées au même centre de propriétés optiques orthorhombiques. L'absence d'observation d'un état métastable favorise le modèle du centre F^+_{2A}. D'autre part, on prouve aussi que la bande à 500 nm et une autre absorption à 322 nm appartiennent au même centre qui a des propriétés optiques tétragonales. Nous avons détecté un état métastable excité de ce centre de durée de vie 0,83 s à 77 K. Deux modèles possibles sont discutés pour ce centre.

Abstract. — We have investigated the dichroic properties and the existence of metastable excited states of several colour centres created by X-irradiation in CaF_2 : Na. According to our results absorption bands peaking at 600, 385 and 322 nm are associated to the same centre which behaves optically as orthorhombic. The lack of observation of a metastable state is in favour of the F^+_{2A} model for this centre. On the other hand the band at 500 nm and another absorption at 322 nm are proved to belong to the same centre which behaves optically as tetragonal. A metastable excited state of this centre with lifetime of 0,83 s at 77 K has been detected. Two possible models are discussed for this centre.

1. Introduction.

As is well known, X-ray irradiation effects on the optical and magnetic properties of CaF_2 are largely modified by the presence of small concentration of impurities. Particularly, the X-ray induced absorption of pure CaF_2 and Na doped CaF_2 are wholly different.

Na impurities enter the CaF_2 lattice in a Ca^{2+} substitutional position as Na^+. Local charge compensation is achieved by a F^- vacancy in one of the nearest neighbours positions [1]. X-irradiation produces several colour centres depending on the irradiation temperature [2-4]. These centres may also be produced by additive coloration procedures [5, 6]. One of the interests of the CaF_2 : Na system is its tentative usefulness as colour centre laser material because of the emission properties of one of these centres [7].

It is known that X-irradiation at 77 K produces two main absorption bands at about 385 and 433 nm. These absorption bands have been identified as due to F_A centres [2, 6]. Other absorption bands at 322, 385, 500 and 600 nm ([1]) are created by X-irradiation at room tempe-

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([1]) Through this article we will refer to the maxima of these absorption bands when they are measured at 300 K.

rature. Those at 322, 385 and 600 nm were early reported by Scouler and Smakula [8]. Rauch [3] ascribed two of them, those at 600 and 385 nm, to a F_{2A} centre and that at 500 nm to a F_{3A}^+ centre. However, M.C.D. experiments carried out recently by Doualan *et al.* [6] indicated that the centre responsible for the 385 and 600 nm bands should be a paramagnetic defect. (Following their work we shall call this defect the Y centre). Thus, they associated these bands to a F_{2A}^+ centre and tentatively assigned the 322 nm band to it, as well. Likewise these authors refused the Rauch's assignation of the 500 nm band and propose that it could correspond to a F_{2A} centre.

In order to get more information about the origin of the different bands that appear in this compound, we have carried out a series of experiments of polarized bleaching and optical detection of metastable states. Our results indicate that at least two absorption bands have their maxima at about 322 nm, one of them being associated with the 600 and 385 nm bands and the other with the 500 nm band.

With regard to the centre responsible of the 322, 385 and 600 nm bands, the Y centre, the absence of detection of a metastable excited state supports the F_{2A}^+ model. A metastable excited state corresponding to the centre that absorbs at 322 and 500 nm (the X centre) has been detected. Several experimental results are, apparently, in favour of the F_{3A}^+ model for this centre.

2. Experimental.

The samples used in our experiments were grown by a Bridgman method in our Laboratory. The Na impurity content of the samples was 1 mol % of NaF in the melt. X-ray coloration was performed either at 77 K or at 300 K by a Cu-target X-ray tube operated at 40 kV and 20 mA.

Absorption spectra were measured with a Cary 17 spectrometer in the whole 250-750 nm range. Optical bleaching experiments were performed with high-pressure Hg and Xe lamps. Monochromator and colour filters were used to select the desired wavelengths. Polarized light used in dichroism experiments was obtained with Glan-Thompson Quartz prisms.

In the detection of transient transmittance, light from a 250 W high-pressure Xe-lamp was used as the exciting light incident upon the crystal at right angles to the measuring beam. The sample was mounted in an Oxford CF-100 continuous flow cryostat. The exciting light was chopped by means of an electromagnetic shutter. Detection was carried out by a photomultiplier RCA C31034. The signal, after amplification was analysed by a HP5480A/B signal analyser obtaining adequate signal-to-noise ratio with several tens of sweeps. Our experimental arrangement can detect transients with time constants larger than 1 ms, this limit being introduced by the shutting time. Data fitting was carried out with an exponential fitting program [9].

3. Experimental results.

3.1 Optical Absorption and dichroism. — All the optical dichroism experiments that we report in the present section were performed at 77 K and both bleaching and measuring light propagated along the [001] direction of the crystals.

When the CaF_2 : Na crystals are exposed to X-irradiation at 77 K, two bands grow at 433 and 387 nm. These bands have been associated, by optical dichroism experiments, to a F_A centre [2]. M.C.D. experiments carried out recently by Doualan *et al.* [6] support this identification. F_A centres become thermally unstable on warming up to room temperature; the initial absorption spectrum disappears giving rise to a new spectrum (see Fig. 1) consisting of three bands at 600, 385 and 322 nm. No band at 500 nm is formed by this procedure.

We have induced optical dichroism in all these bands by bleaching with 385 nm light polarized with $\mathbf{E} /\!/ [100]$. The results of this experiment are shown in figure 2. Dichroism can also be induced in the 385 and 322 nm bands bleaching with $\mathbf{E} /\!/ [110]$, while in this case no dichroism is induced in the 600 nm band (see Fig. 3). Analogous results were obtained bleaching with

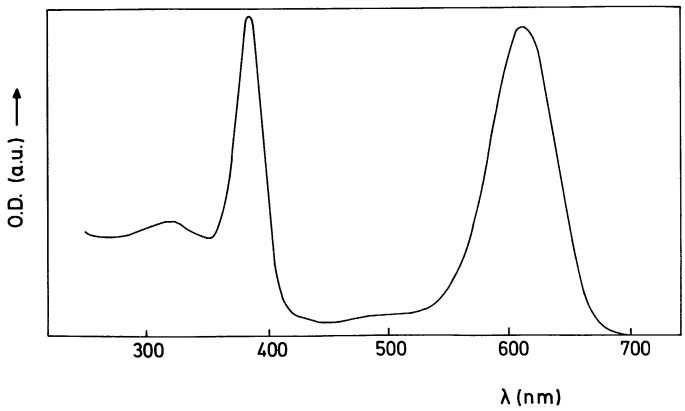

Fig. 1. — Absorption spectrum measured at 77 K of a 77 K X-irradiated sample subsequently annealed at 300 K.

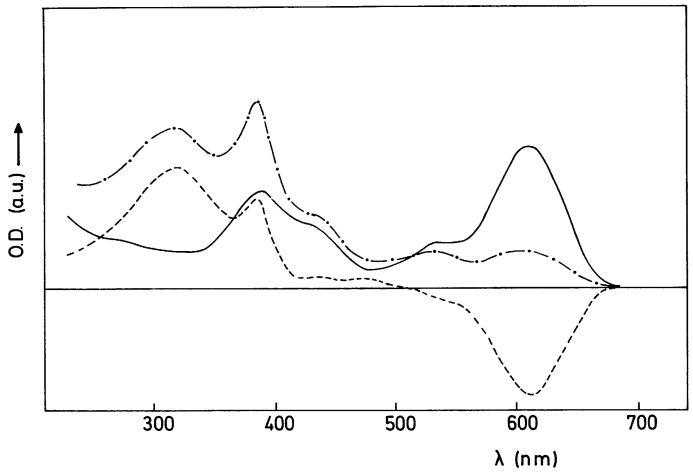

Fig. 2. — Optical dichroism induced with 385 nm light polarized with **E** // [100]. (———) After bleaching, measured with **E**// [100]. (–·–·–) After bleaching, measured with **E**// [010]. (– – – –) Resulting dichroism. The absorption at about 440 nm corresponds to a transition of F_A centres created during the bleaching. They have another transition at 380 nm. Their spectrum is not dichroic after a bleaching with polarized light with **E**// [100] and therefore they do not contribute to the observed dichroism. This is not the case when the bleaching light is polarized along the [110] direction. When this happened the spectrum of F_A centres was destroyed bleaching with unpolarized light of ~ 440 nm (see Figs. 3 and 5).

322 nm light, polarized with **E**// [100] and **E**// [110] (see Figs. 4 and 5). The dichroism is thermally destroyed at about 210 K.

In figure 6 we show the absorption spectrum of a CaF_2 : Na sample X-irradiated at 300 K. It can be seen that besides the bands that appear by annealing at 300 K a sample irradiated at 77 K, a band peaking at 500 nm is formed. On annealing for several minutes at 373 K, the 385 and 600 nm bands are almost destroyed (and there is a decrease in the optical absorption in the spectral region of about 322 nm). Bleaching at 300 K with 322 nm light, the spectrum transforms into that shown in figure 1. When the bleaching is performed at 77 K, no subsequent

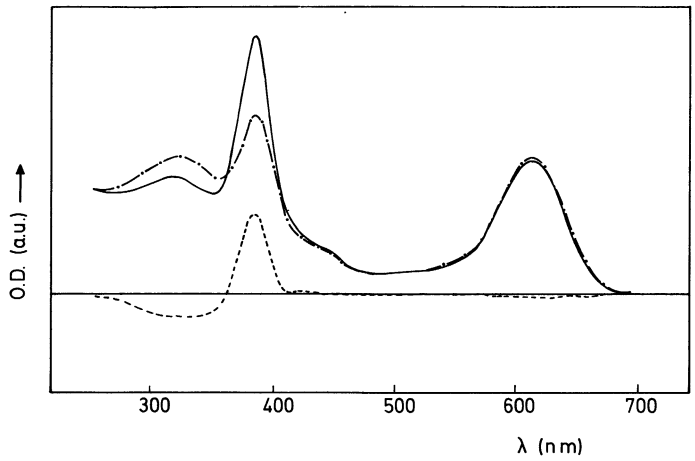

Fig. 3. — Dichroism induced with 385 nm light polarized with $\mathbf{E}/\!/[110]$. (———) After bleaching, measured with $\mathbf{E}/\!/[110]$. (–·–·–) After bleaching, measured with $\mathbf{E}/\!/[1\bar{1}0]$. (– – – –) Resulting dichroism.

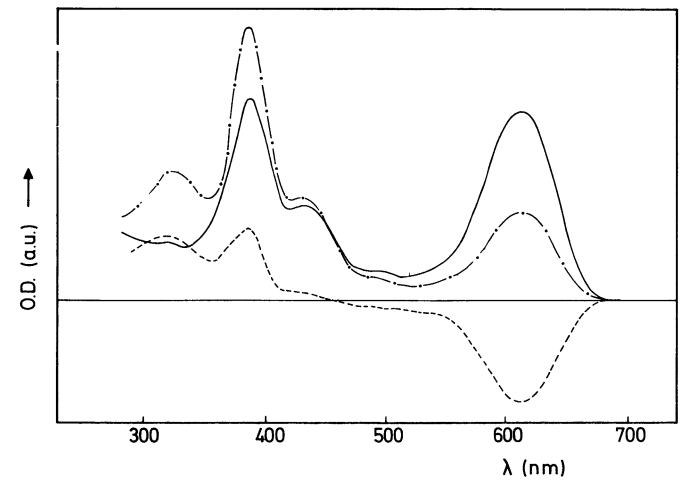

Fig. 4. — Dichroism induced with 322 nm light polarized with $\mathbf{E}/\!/[100]$. (———) After bleaching, measured with $\mathbf{E}/\!/[100]$. (–·–·–) After bleaching, measured with $\mathbf{E}/\!/[010]$. (– – – –) Resulting dichroism.

formation of the 385 and 600 nm band is observed. However the bands are formed by a subsequent annealing up to 300 K.

Dichroism is induced in both 500 and 322 nm band bleaching with 322 nm light polarized with $\mathbf{E}/\!/[100]$. The results of these experiments are given in figure 7. The dichroism is thermally destroyed at about 260 K. No dichroism can be induced by bleaching with 322 nm light polarized along the [110] direction.

On the other hand, it is not possible to destroy this spectrum bleaching with 500 nm light at 77 K. Bleaching at 77 K with light of 500 nm polarized either [100] or [110] does not induce any polarization in the absorption spectrum.

3.2 TRANSIENT TRANSMITTANCE EXPERIMENTS. — It is well known that the F_2 centre in CaF_2 and SrF_2 has a spin triplet state a few tenths of electron-volts above the ground state [10]. The

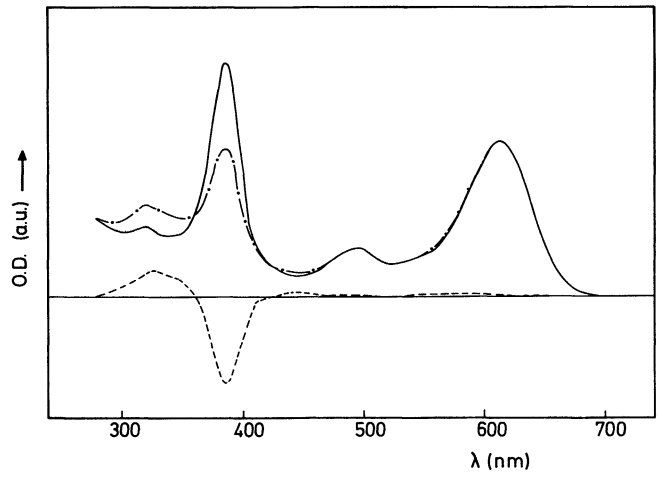

Fig. 5. — Dichroism induced with 322 nm light polarized with **E**//[110]. (———) After bleaching, measured with **E**//[110]. (– · – · –) After bleaching, measured with **E**//[1$\bar{1}$0]. (– – – –) Resulting dichroism.

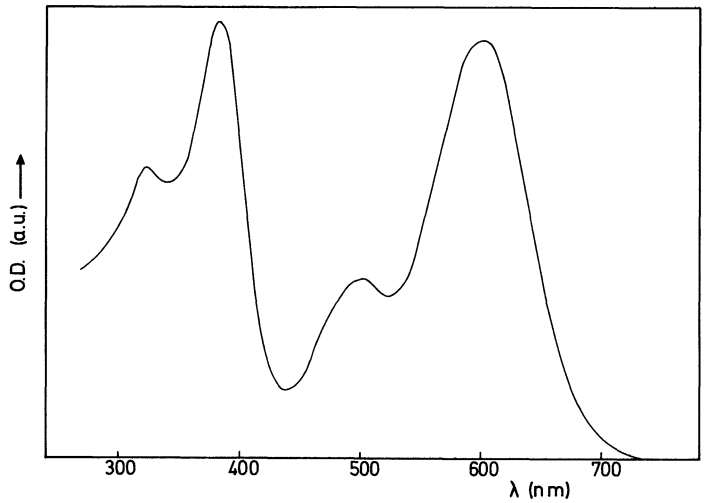

Fig. 6. — Absorption spectrum of a sample of CaF_2 : Na irradiated at 300 K. Measured at 300 K.

presence of this state has been observed by the detection of transient effects, induced by optical pumping, in the transmittance. Transients arise by depopulation (pumping light induced) and subsequent repopulation of the ground state in the assembly of centres. In some cases, optical population of this metastable state allows the detection of paramagnetic resonance associated to it. Characteristic relaxation times of the transients are rather long. (In CaF_2, where most of the F_2 centres are $\langle 100 \rangle$ type it was found a lifetime of 1.7 s at 77 K for the recovery of the M band. See Ref. [10] for other references.)

We have used this technique to detect the existence of metastable states in the centres responsible for the different absorption spectra in X-irradiated CaF_2 : Na and we have obtained the following results :

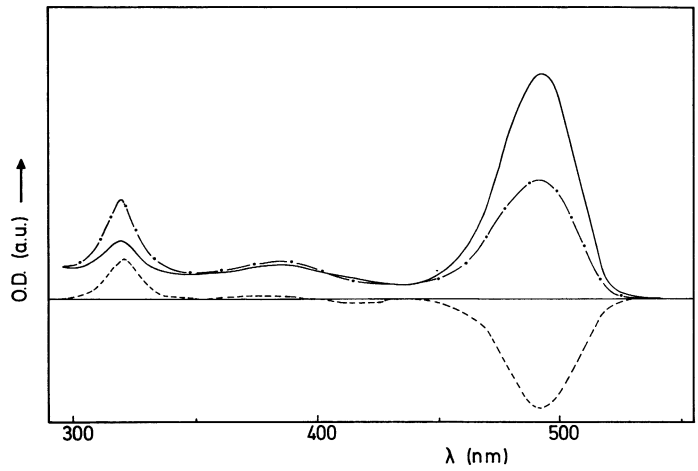

Fig. 7. — Dichroism induced in the absorption spectrum of the X centres bleaching with 322 nm light polarized with $\mathbf{E}/\!/[100]$. (———) After bleaching, measured with $\mathbf{E}/\!/[100]$. (–·–·–) After bleaching, measured with $\mathbf{E}/\!/[010]$. (– – – –) Resulting dichroism. The band at 390 nm grows during the bleaching with 322 nm light. (See below.)

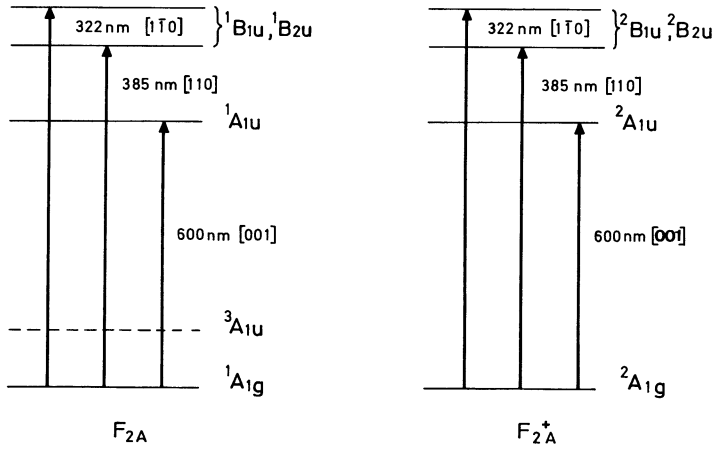

Fig. 8. — Energy level diagram for the F_{2A} and F_{2A}^+ centres according to our dichroism experiments. The optical transitions and the corresponding polarizations are indicated as well. Our results do not allow to distinguish the relative positions of the B_{1u} and B_{2u} levels.

a) In a sample with the absorption spectrum of figure 1, we have investigated the transmittance in 600 nm and 385 nm at 77 K pumping with light in the 600 nm band. In all cases we did not observe any transient with relaxation time longer than 1 ms.

b) In a sample with the spectrum of figure 6, pumping with light in the 500 nm band, we observed a transient in the transmittance of 500 nm. Its relaxation time is $\tau = 0.83 \pm 0.08$ s at 77 K.

4. Discussion.

4.1 THE BANDS AT 600, 385 AND 322 nm. — The dichroism experiments carried out in the spectrum of figure 1 indicate clearly that the 600, 385 and a band at 322 nm belong to the same centre. This confirms the suggestions made by Doualan *et al.* [6] on the basis of their M.C.D. experiments. Furthermore our dichroism experiments also show that the centre is not optically axial, the transition corresponding to the 600 nm band must be polarized along the $\langle 100 \rangle$ directions and those at 385 and 322 nm must be polarized along $\langle 110 \rangle$ direction mutually perpendicular and perpendicular to the polarization of the 600 nm transition.

These results are in opposition to the conclusions of the work carried out by Rauch [3] using the polarized luminescence method.

Two models have been proposed for the centre responsible of the 600 and 385 nm bands, the Y centre, which according to our results must have another transition at 322 nm. Rauch [3] ascribed it to a F_{2A} centre (a F_2 centre close to a Na^+ impurity). Doualan *et al.* [6] propose the model of a F_{2A}^+ centre in view of their M.C.D. experiments. Our dichroism experiments do not allow to decide between these two models. Both are compatible with the observed results.

In figure 8 we show an energy level schema for both centres with the corresponding transitions according to the dichroism results. We have labelled the energy levels assuming that the point symmetry group of the defect is D_{2h} with the main binary axis along the molecular axis. In fact the pure geometrical symmetry is lower (C_{2V}) and the binary axis is along the Ca^{2+}-Na^+ line. However, if we label the energy levels according to the C_{2V} group with the quantization axis along the Ca^{2+}-Na^+ line, the observed polarizations of the transitions do not agree with those expected. So we have to conclude that the quantization axis is along the line joining the vacancies and the centre exhibits D_{2h} symmetry, although there is no geometrical invariance under a rotation of 180° around the axis joining the vacancies.

Our transient transmittance experiments are in favour of the F_{2A}^+ centre model, since this centre does not own any metastable state. Unfortunately, the experimental results are not fully conclusive. It could happen that the relaxation time for the F_{2A} centre would be beyond our detection ability (shorter than 1 ms). This is possible although it does not seem very likely that the relaxation time of a perturbed F_2 centre may be three orders of magnitude shorter than the unperturbed centre.

Very recently, Rauch [11] has investigated the effect of bleaching at 77 K with 385 nm light the spectrum of figure 1. According to his results, during this bleaching a new centre is formed with absorption bands at 440 and 325 nm, its emission (peaking at 635 nm) being polarized along the $\langle 100 \rangle$ directions. He argues that this spectrum should belong to a F_{2A}^+ centre, produced by ionization of what he assumes are F_{2A} centres. His results, however can be better interpreted assuming that this new centre is in fact a F_{2A} centre created by trapping at a F_{2A}^+ centre an electron released from another F_{2A}^+ centre. This mechanism would explain his experimental results, mainly the point that cannot be fully understood with his model : the new centres are created randomly oriented across all the space directions.

Moreover, this interpretation accounts for the other experimental results (low temperature X-irradiation, dichroism, growth of the concentration of the Y centre during the thermal decay of these new centres).

4.2 THE BANDS AT 500 AND 322 nm. — When a crystal X-irradiated at R.T. is annealed at $\sim$ 370 K, two bands peaking at 500 and 322 nm remain. Our dichroism experiments show that these bands must belong to the same centre. Consequently, when a CaF_2 : Na crystal is irradiated at R.T., two bands belonging to different centres grow at 322 nm. Our results also demonstrate that the centre behaves optically as if it were axial with a four-fold axis along the $\langle 100 \rangle$ directions, one transition being π type and the other one σ type. The experiments do not allow to distinguish the character of each band.

Again, two different models have been proposed for this centre (the X centre). Rauch [3] and Arkhangelskaya and Shcheulin [5] propose a linear F_{3A}^{+} centre in view of their results of polarization luminescence. Doualan *et al.* [6] tentatively propose a F_{2A} centre.

Both models are compatible with our dichroism results again. On the other hand, the observation of a metastable excited state cannot decide between these two models, provided that both should have such a state. (This result, however, leaves out other possibilities such as a F_{2A}^{+} or a F_{3A}^{2+} centre.)

However, there are other results that may be in favour of the linear F_{3A}^{+} model : if we bleach at 77 K a sample containing X centres with 322 nm light, a new band peaking at 390 nm grows during the destruction of the X centres. (See Fig. 7.)

Heating the sample up to 300 K, the spectrum corresponding to the Y centres is formed. If the X centre were a F_{2A} centre, we would expect the formation of F_{2A}^{+} centres if the F_{2A} centre were ionized during the bleaching. If the centre were dissociated the formation of F and F_A centres could be expected. In fact, we do not observe any of these results. The band that grows at 390 nm could be assigned to F_{3A}^{2+} centres formed by ionization of F_{3A}^{+} centres, although there are other possibilities.

On the other hand, as we have already discussed, the results of Rauch in the study of the photobleaching of Y centres at 77 K could be interpreted assuming the formation of F_{2A} centres, that would absorb at 440 and 325 nm.

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