

Formation kinetics of $(F_2^+)_H$ centers in NaCl:OH⁻ crystals

G. Lifante, P. Silfsten,* and F. Cussó

Departamento de Física Aplicada (C-IV), Universidad Autónoma de Madrid, E-28049 Madrid, Spain

(Received 25 April 1989)

The kinetics of formation of $(F_2^+)_H$ centers in additively colored NaCl:OH⁻ crystals has been studied. The role of temperature and illuminating wavelength has been systematically investigated. It has been found that the transformation is activated above 60 K and its efficiency increases monotonously with the energy of the incident photons. The thermally activated destruction of the centers is also discussed.

I. INTRODUCTION

During the past few years color centers in alkali halides have received renewed attention because of their usefulness as laser-active centers in the near ir. In particular, the F_2^+ center (two anion vacancies bounding a single electron) has very interesting possibilities: It has shown a high quantum efficiency and can be produced, in principle, in any alkali halide host covering the emission range from 1 to 3 μm .^{1,2}

The production of F_2^+ centers in alkali halides doped with cation impurities, which act as efficient electron traps, has allowed to reach concentrations of F_2^+ centers up to 10^{18} cm^{-3} . The association with cation impurities has also improved the stability of the centers.³ But, the decisive step in order to obtain stable laser emission has been the discovery of the so-called $(F_2^+)_H$ centers, which consist of F_2^+ centers associated with double-charged anion impurities. In oxygen-doped NaCl, KCl, and KBr tunable cw operation in the 1.45–2.16- μm range has been observed.^{4,5}

The formation of the $(F_2^+)_H$ centers is particularly feasible in NaCl where the oxygen centers can be obtained from OH⁻ impurities which decompose during additive coloration. Practical concentrations of OH⁻ are within the range 10–70 ppm for coloration pressures of 20–40 Torr.⁶

The procedure for the formation of the $(F_2^+)_H$ centers in NaCl:OH⁻ has been described in the literature and consists of the following steps. (a) Additive coloration which produces O²⁻ defects and F centers. (b) Room-temperature photoaggregation in order to produce F_2^+ centers. (c) Low-temperature (77-K) illumination to obtain the perturbed $(F_2^+)_H$ centers.

The last stage which activates the transformation $F_2^+ \rightarrow (F_2^+)_H$ leading to the stable laser-active centers is not fully understood yet, and the role of different physical variables of this process has not been thoroughly studied.

In the present work the effect of temperature and illumination wavelength on the transformation $F_2^+ \rightarrow (F_2^+)_H$ has been studied. It has been found that the transformation is activated at temperatures above 60 K and its efficiency increases monotonously with the energy of the incident photons. The inverse transformation $(F_2^+)_H \rightarrow F_2^+$, thermally activated, is also discussed.

II. EXPERIMENTAL PROCEDURES

NaCl:OH⁻ crystals grown by the Czochralski method were obtained from the Crystal Growth Laboratory of Universidad Autónoma de Madrid. Merck Laboratories suprapure NaCl was used as the starting material.

Samples 4–5 mm thick were additively colored in a Van Doorn heat pipe at a temperature of 720 °C for 1 h using sodium vapor pressures in the range 20–40 Torr. To remove colloids, crystals slabs approximately $10 \times 5 \times 2 \text{ mm}^3$ in size were heated to 600 °C in air for several minutes and quenched to room temperature (RT) on a copper block.

Photoaggregation was carried out at RT using light from a 100-W arc Xe lamp, filtered through a 1-cm cell of CuSO₄ solution (“broad F band”).

The wavelength dependence of the $F_2^+ \rightarrow (F_2^+)_H$ photoconversion at low temperature (77 K) has been studied by using an Applied Photophysics (Model U.V. 90) photoradiator. In order to choose adequate irradiation times, two different illumination levels have been used, giving intensities of 13.6 or 0.64 mW/cm² at 550 nm.

Absorption spectra in the range 13–300 K were taken with the crystals mounted in a closed-cycle He cryostat coupled to the chamber of a Cary 17 spectrophotometer.

The thermally stimulated depolarization (TSD) setup, described elsewhere,⁷ operates in the range liquid-nitrogen temperature (LNT) to RT. The depolarization currents are measured with a Cary 401 electrometer with a time constant lower than 1 s. Polarizing fields of 10^4 V cm^{-1} and linear heating rates of 2.5 K min^{-1} have been used.

III. EXPERIMENTAL RESULTS

A. Photoconversion: $F_2^+ \rightarrow (F_2^+)_H$

The optical absorption of an additively colored crystal of NaCl:OH⁻ taken at LNT immediately after quenching to RT shows the characteristic F band (445 nm) and two additional bands (225 and 280 nm) associated with oxygen centers.⁸ After RT photoaggregation the F band diminishes and F -aggregate bands appear, specifically those associated with F_2 , F_2^+ , F_3 , and F_3^+ . In particular, the F_2^+ band appears at 1.045 μm at LNT and its intensity reaches 20% of the F band (see Fig. 4, dashed line).

After additional illumination (broad F band) for 5 min at 77 K, the F_2^+ band is broadened and shifted to 1.09 μm (Fig. 1). This band corresponds to the fundamental absorption of the $(F_2^+)_H$ center, i.e., F_2^+ perturbed by oxygen impurities.^{5,6} Longer illuminations do not further increase the shift.

In accordance with previous observations,^{5,6} this treatment also causes a displacement in the F -band region (which coincides with the $1s\sigma_g \rightarrow 2p\pi_u$ transition of the F_2^+ center), and the energy shift (0.04 eV) is the same as that observed for the fundamental F_2^+ band ($1s\sigma_g \rightarrow 2p\sigma_u$ transition) (Fig. 1).

The effect of temperature on the photoconversion $F_2^+ \rightarrow (F_2^+)_H$ is shown in Fig. 2, where the position of the F_2^+ absorption band is given for different illumination temperatures. It can be seen that there is no photoconversion for temperatures below 60 K, and above 70 K it is fully accomplished within 5 min of exposure. A similar temperature dependence is observed for the F -band shift.

In order to investigate the photoconversion kinetics and its wavelength dependence, the liquid-nitrogen temperature has been chosen, which is convenient from the experimental point of view and where, as seen in Fig. 2, the photoconversion is already operative. In fact, this is the photoconversion temperature selected in most studies of $(F_2^+)_H$ centers.^{5,6}

The photoconversion kinetics can be studied following the shift of the absorption peaks as a function of irradiation time under different illuminating wavelengths. These results are given in Fig. 3 where the solid symbols correspond to the F_2^+ band and the open symbols to the F band. It can be seen that both photoconversion processes follow similar kinetics.

The F_2^+ and F bands shift monotonously to longer wavelengths with the irradiation time, and the peak positions can be empirically fitted to an exponential law:

$$\lambda(t) = \lambda_{in} + (\lambda_{fin} - \lambda_{in}) \{1 - \exp[-t/\tau(\lambda)]\}, \quad (1)$$

where λ_{in} and λ_{fin} represent the initial and final peak positions, respectively, and $\tau(\lambda)$ an experimentally deter-

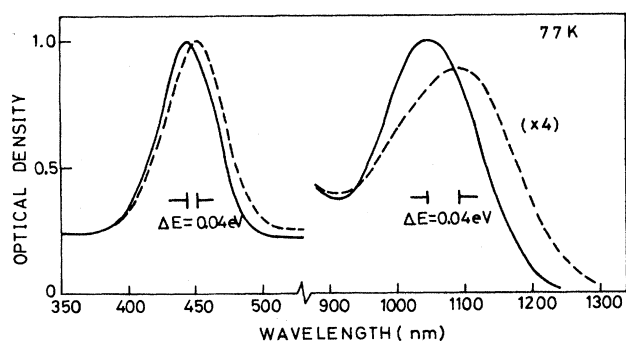


FIG. 1. Effect of low-temperature illumination on the F and F_2^+ bands in $\text{NaCl}:\text{OH}^-$ additively colored. Solid line corresponds to the absorption of samples photoaggregated at RT and the dashed line is obtained after 5 min exposure to F -band light at 77 K.

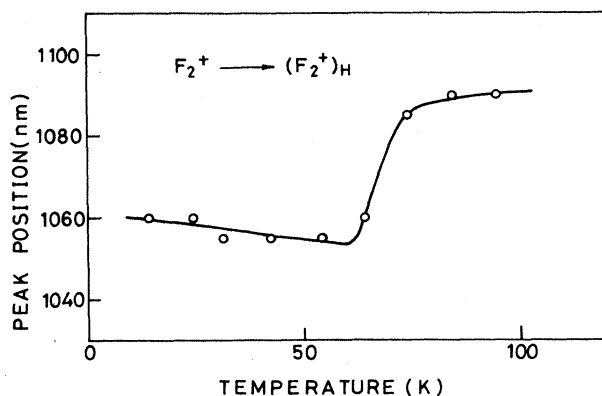


FIG. 2. Effect of the temperature of illumination on the $F_2^+ \rightarrow (F_2^+)_H$ transformation.

mined time constant dependent on the illumination wavelength, the inverse of which, $\eta(\lambda) = 1/\tau(\lambda)$, gives a measure of the photoconversion efficiency.

It is clear from Fig. 3(a) that this photoconversion efficiency increases as the illumination wavelength decreases from 550 to 400 nm. For this last wavelength the transformation is completed within a few minutes. Therefore, to continue this study at wavelengths lower than 450 nm, the illumination intensity has to be reduced in order to proportionally lower the conversion rates. It has been verified that, at the intensities used in this work,

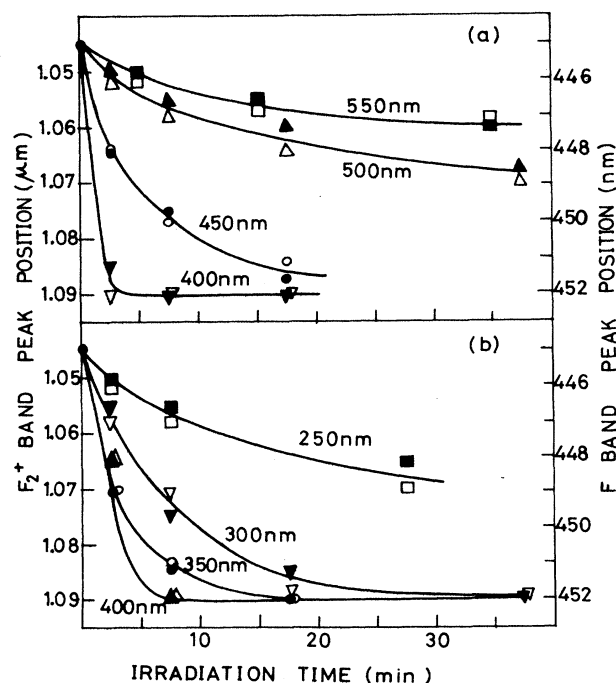


FIG. 3. Displacement of the F (open symbols) and F_2^+ (solid symbols) bands as a function of time at different irradiation wavelengths.

the photoconversion is proportional to the number of incident photons and that such reduction in light intensity increases by the same factor as the time constant $\tau(\lambda)$.

It can be seen in Fig. 3(b) that the photoconversion rate is now reduced when the wavelength decreases from 400 to 250 nm. The most efficient conversion, $F_2^+ \rightarrow (F_2^+)_H$, seems to take place around 400 nm (approximately the *F* band). Nevertheless, it has to be taken into account that data in Fig. 3 are determined not only by the intrinsic efficiencies, but also by the experimental conditions. In fact, the spectral distribution of the illuminating source (arc Xe lamp) has a strong wavelength dependence which has to be corrected in order to isolate the intrinsic parameters.

The conversion efficiency per incident photon as function of the irradiation wavelength is given in Fig. 4, together with the absorption spectrum of the samples at LNT. It can be seen that the conversion efficiency per incident photon increases monotonously to higher energies.

The possibility of photoconversion at the fundamental F_2^+ absorption has also been examined. The samples have been irradiated with the 1.06- μm line of a pulsed Nd:YAG (yttrium aluminum garnet) laser. After a dose of 100 J/cm² at LNT, no trace of photoconversion has been detected. It indicates a negligible conversion efficiency at this wavelength (Fig. 4).

B. Thermal conversion: $(F_2^+)_H \rightarrow F_2^+$

Although the $(F_2^+)_H$ centers exhibit cw stable laser emission at low temperatures,⁵ they are destroyed when warmed to RT, even in the dark, and the F_2^+ center is recovered. This decomposition can be detected through the different luminescence properties of the "pure" and "perturbed" F_2^+ centers. It has been reported that the $F_2^+ + (F_2^+)_H$ emission shows a continuous shift in its peak position, which is attributed to a relative change in the populations of F_2^+ and $(F_2^+)_H$ centers. The transformation between the centers seems to be operative in a remarkably broad temperature range (120–270 K) and it

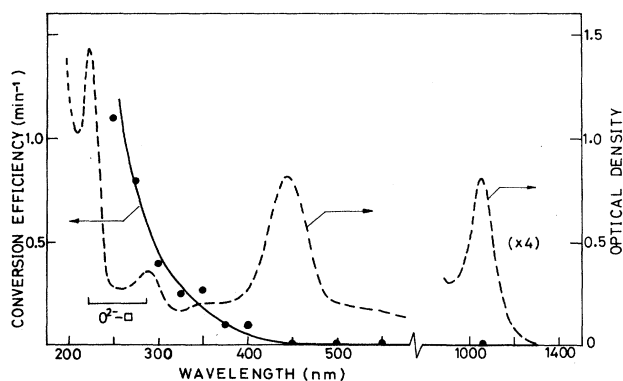


FIG. 4. Wavelength dependence of the $F_2^+ \rightarrow (F_2^+)_H$ conversion efficiency, per incident photon (solid circles), compared to the absorption spectrum (dashed line). All data are taken at LNT.

has been associated with a decomposition of the $(F_2^+)_H$ centers.⁶

In order to investigate further the mechanism of the $(F_2^+)_H \rightarrow F_2^+$ transformation, it has been alternatively studied following the shift of the absorption spectrum when the crystal is heated in the dark.

When the sample containing the $(F_2^+)_H$ centers is warmed from LNT to RT, the absorption band shows, starting at 100 K, a continuous shift to higher energies, and at around 250 K the band appears at the position of the unperturbed F_2^+ centers. Although one could be tempted to attribute such displacement to a progressive transformation of the $(F_2^+)_H$ into F_2^+ centers, it is necessary to consider the (unknown) $(F_2^+)_H$ absorption's own shift with temperature.

It is known that the F_2^+ center in KCl shifts towards higher energy when the temperature increases⁹ and a not very different behavior would be expected for $(F_2^+)_H$ centers. Therefore, the absorption-band displacement will be only partially due to center interconversion. In order to distinguish between both processes, a careful examination of the experimental data is necessary.

The peak energy of the $F_2^+ + (F_2^+)_H$ band (triangles) and that of the unperturbed F_2^+ band (circles) are plotted as a function of temperature in Fig. 5. It can be seen that the peak energy of the pure F_2^+ centers in NaCl shows a linear increase similar to that found for this center in KCl. By contrast, the evolution of the peak energy of the $(F_2^+)_H$ centers is more complicated. Its position at 13 K remains constant up to about 100 K, from which it shifts to higher energy a little faster than the pure F_2^+ centers. This shift is further accelerated above 210 K, and at 240 K the position and subsequent evolution are coincident with those of the pure F_2^+ centers.

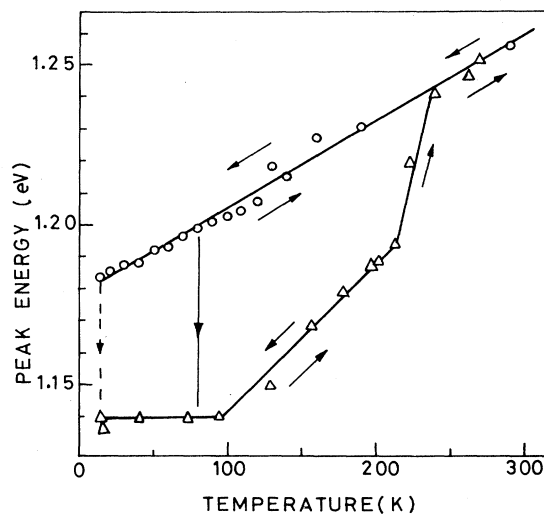


FIG. 5. Temperature dependence of the F_2^+ (circles) and $(F_2^+)_H$ (triangles) peak absorption bands. The arrows indicate the reversible and irreversible character of the process. Oblique arrows correspond to thermally activated processes and vertical arrows to light-induced transitions.

It seems clear then that at 240 K the transformation $(F_2^+)_H \rightarrow F_2^+$ has been completed, but the beginning of the transformation does not appear equally evident. Nevertheless, the different rates of peak-energy change observed in Fig. 5 suggest that a major change is taking place in the range 210–240 K, which could be probably due to center transformation, whereas the shift between 100 and 200 K would correspond to thermal displacement of the $(F_2^+)_H$ absorption band.

This hypothesis is confirmed by two additional effects: the reversible character of the peak energy shift, and its time dependence.

The shift of the F_2^+ centers is, as indicated by the small oblique arrows in Fig. 5, reversible throughout the whole temperature range. This is the expected behavior for a single-center evolution. The same reversibility is observed for $(F_2^+)_H$ centers within the range 13–210 K, which indicates that in this case, too, we are dealing with a single center, the $(F_2^+)_H$, whose peak position shifts to higher energy with temperature in a very similar way to the F_2^+ centers. The different rate change, as compared with the pure F_2^+ centers, could be probably attributed to the presence of perturbing O^{2-} impurities.

The reversible character of the shift is lost above 210 K. Beyond this point, if the crystal is cooled down the absorption peak exhibits a permanent shift, indicating that now we are dealing with a true center transformation. If it has been completed, i.e., if the temperature has been raised above 240 K, the absorption band follows the F_2^+ behavior.

Further confirmation can be achieved through the time evolution of the absorption bands. Storage of the samples within the temperature range 13–210 K for arbitrarily long times does not show any peak-energy shift, as would be expected if a thermally activated center transformation would be operative at these temperatures.

Therefore we can conclude that the thermally activated $(F_2^+)_H \rightarrow F_2^+$ transformation takes place in the narrow temperature interval 210–240 K.

Let us finally remark that the $F_2^+ \rightarrow (F_2^+)_H$ transformation can be reactivated immediately after the thermal "dissociation" of the $(F_2^+)_H$ centers. This indicates that the F_2^+ configuration is the same after RT aggregation

and before low-temperature illumination.

A similar behavior is also observed for the thermal recovery of the F centers. At temperatures close to 100 K the 445-nm band begins to shift and the position of the pure F band is recovered at around 240 K. In this case, it has to be considered that the F band shifts to lower energy with temperature.

The wavelength shift in the F -band region as a function of temperature is given in Fig. 6. It can be seen that this difference begins to diminish at around 100 K and disappears at 240 K. The rate of change recalls that of the F_2^+ centers: First, a slow variation appears at low temperatures (100–200 K), and a second part, much faster, follows between 200 and 240 K.

This similarity suggests that in this case also the differences below 200 K are due to a different thermal evolution of the pure and perturbed bands, whereas the true center transformation takes place in the upper temperature region (200–240 K).

IV. MECHANISM OF TRANSFORMATION OF CENTERS

The accepted model for the $(F_2^+)_H$ center consists of an oxygen-vacancy dipole bound to an F center, which can be described alternatively as an F_2^+ center perturbed by a neighboring oxygen impurity.^{5,6} Different relative orientations between the three components of the center (oxygen impurity, anion vacancy, and F center) would produce different configurations with slightly different optical transitions. The presence of the perturbing O^{2-} ion is thought to be responsible for the observed increase in the F_2^+ -center stability.

Although the structure of the centers is generally accepted, the possible mechanism of center transformations has not been thoroughly discussed. The two processes $F_2^+ \rightarrow (F_2^+)_H$ and $(F_2^+)_H \rightarrow F_2^+$ show distinctive characteristics, the latter thermally activated in the dark, and the former activated by illumination at lower temperatures. The possible mechanisms will be discussed next.

Let us first consider the mechanism of $(F_2^+)_H$ destruction: $(F_2^+)_H \rightarrow F_2^+$. As the F_2^+ center seems to be recovered when the $(F_2^+)_H$ center is heated in the dark, a decomposition $F_2^+ \cdot O^{2-} \rightarrow F_2^+ + O^{2-}$ has been proposed.⁶ Assuming that this is the process and that the shift of the $(F_2^+)_H$ band is entirely due to the change of relative populations, a binding energy between O^{2-} and F_2^+ centers of $U=0.22$ eV has been calculated.⁶ However, this binding energy seems too low to arise from the attractive between defects with a net charge (F_2^+ and O^{2-}) and, in addition, it seems difficult to imagine a migration mechanism for isolated O^{2-} ions through the lattice.

It seems more plausible to imagine that the $(F_2^+)_H \rightarrow F_2^+$ conversion corresponds to a short-range rearrangement of the center causing a transition between O^{2-} positions of high or low perturbation of the F_2^+ .⁵ The mechanism of this process would probably be caused by the O^{2-} -vacancy dipole reorientation.

Figure 7 shows the thermally stimulated depolarization (TSD) of O^{2-} -vacancy dipoles in additively colored

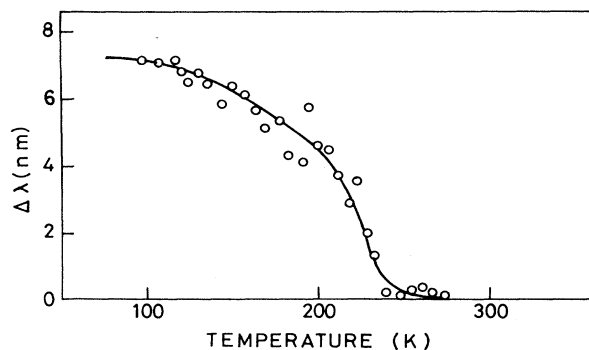


FIG. 6. Temperature dependence of the wavelength shift of the F absorption band.

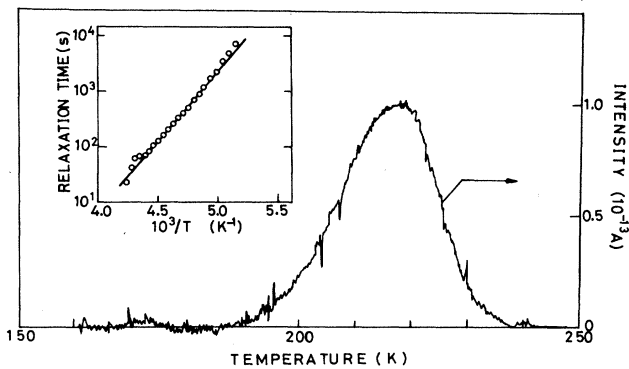


FIG. 7. Thermally stimulated depolarization of oxygen-vacancy dipoles in additively colored NaCl:OH⁻ crystals. The inset shows the plot of the relaxation time as a function of the inverse of temperature, from which an activation energy $U=0.51$ eV is obtained.

NaCl:OH⁻ crystals. The samples have been polarized at RT, cooled down to LNT where the polarization field is switched off, and then heated to RT. The depolarization current given in Fig. 7 appears only after additive coloration and confirms that O²⁻-vacancy dipoles are produced from the decomposition of OH⁻ centers.¹⁰ The analysis of the TSD peak, inset in Fig. 7, gives an activation energy $U=0.51$ eV, in reasonable agreement with previous determinations.¹¹ These measurements set the temperature range for dipolar reorientation within the limits 200–250 K. This range is the same as that of the faster shift in the $(F_2^+)_H$ peak position (Fig. 5), and attributed to the $(F_2^+)_H \rightarrow F_2^+$ transformation. Thus, it is confirmed that at this temperature the reorientation of the defect is activated. The fact that it is in this range where the $(F_2^+)_H$ band is shifted to the F_2^+ position indicates that the rearrangement induced is enough to suppress the perturbation of the F_2^+ center.

Nevertheless, these temperatures are low enough to preclude significant diffusion of the defects and therefore, the ions are likely in nearby positions. This proximity can also be induced from the thermal dependence of the optically induced $(F_2^+)_H$ formation (Fig. 2). The temperature range at which it takes place is even lower (< 70 K) which definitely rejects the possibility of any

long-range migration of the centers.

The fact that $(F_2^+)_H$ formation is activated, by illumination, at temperatures much lower than those of vacancy mobility can be understood if one considers that dipolar reorientations are strongly dependent on the electronic distribution around the defects. In fact, it is well known that the activation energy for impurity-vacancy reorientation is strongly reduced by excitation of the impurity to upper electronic levels.^{12,13}

The role of the upper electronic levels in the reorientation of F_2^+ centers has been recently studied and its occurrence through excitation to the $2p\pi_u$ energy level (second excited state) demonstrated.⁶ However, the wavelength dependence of the photoconversion efficiency given in Fig. 4 indicates that this process is not a particular property of the $1s\sigma_g \rightarrow 2p\pi_u$ transition of the F_2^+ centers (F -band region), but it also seems to be more efficient in the high-energy region of the spectrum. Although the experiment cannot reveal a detailed structure, this spectral range corresponds to the oxygen absorption bands, suggesting that their excitation is also effective in activating the center reorientation. This would explain the fact that 365-nm as well as F -band light have been used to produce and maintain stable laser emission from $(F_2^+)_H$ centers.^{4,5,14} All these facts again support that the oxygen impurities are already close to the F_2^+ center after RT aggregation and before the low-temperature illumination which produces the perturbed and laser stable $(F_2^+)_H$ configuration.

Let us finally indicate that F -light excitation at very high intensities (2.66 eV, blue-green lines of a 3-W argon-ion laser) seems to be more efficient in allowing the center reorientations, which in this way can be activated even at 10 K.¹⁵ This result could be connected with non-linear effects, although more experimental work is required to explore this possibility.

ACKNOWLEDGMENTS

The authors would like to acknowledge stimulating discussions with Professor F. Jaque, and financial support from the Comisión Interministerial de Ciencia y Tecnología (CICYT, Spain). One of us (P.S.) is also indebted to the Ministerio de Asuntos Exteriores (Spain) and the Wihuri Foundation (Finland).

*Permanent address: Department of Physics, University of Joensuu, Joensuu, Finland.

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