

Thermal and optical properties of the F_A and $(F_2^+)_A$ centers in Na-doped CaF_2 crystals

J. M. G. Tijero

*Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas (CSIC),
Universidad Autónoma de Madrid, Canto Blanco, 28049 Madrid, Spain*

F. Jaque

*Department of Physics and Applied Physics, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland
(Received 13 March 1989; revised manuscript received 3 August 1989)*

The $F_A \rightarrow (F_2^+)_A$ thermal conversion in additively colored and x-ray-irradiated Na-doped CaF_2 crystals was studied using different methods: optical absorption and luminescence, thermal-stimulated polarization, ionic thermocurrent, and photoconductivity. The experimental data show that the $(F_2^+)_A$ centers are created in the temperature range 77–300 K in two stages: The low-temperature process is associated with a short-range reorientation, while an anionic-vacancy-diffusion process operates in the high-temperature stage. The optical damage incurred at low temperatures under high-intensity light excitation was also investigated, and the bleaching mechanisms are discussed.

I. INTRODUCTION

In recent years additional interest has been generated in alkali halide and alkaline-earth fluoride crystals containing F_2^+ centers following the discovery of wavelength-tunable laser action in those materials.^{1,2} Unfortunately, under laser operation the F_2^+ centers undergo an optical-damage process which is not yet fully understood and which severely reduces the lasing efficiency.³ However, for the alkali halides it is possible to produce F_2^+ centers with greater optical stability by using crystals doped with oxygen or containing divalent cations.⁴ Similarly, in the alkaline-earth fluorides perturbed F and F_2^+ centers can be formed by additive coloration or x-ray irradiation of alkali-metal impurity-doped or oxygen-doped crystals.^{5,6} These perturbed centers are denoted F_A and $(F_2^+)_A$, where the subscript denotes the presence of the impurity ion, generally Na^+ , Li^+ , K^+ , or O^{2-} .

Although electron-paramagnetic-resonance^{7,8} (EPR) measurements have been performed on these centers, a conclusive model has not yet been defined. However, at present, it is accepted that the F_A center consists of an F center with one alkali-metal ion in a cation site, while the $(F_2^+)_A$ center is formed by one electron trapped in two anion vacancies with one alkali-metal ion in a cation site.^{9,10,8}

In Na-doped CaF_2 samples, the F_A centers are formed by electron on x-ray irradiation at low temperature or by ultraviolet illumination of additively colored samples containing F_2^+ -aggregate centers.^{11,9} On the other hand, as regards the creation of $(F_2^+)_A$ centers, although it has been reported that these centers appear on warming a sample with F_A centers to room temperature, little is known of the mechanisms involved in the $F_A \rightarrow (F_2^+)_A$ thermal conversion process.

Therefore, in order to address this problem, we present

a study of the $F_A \rightarrow (F_2^+)_A$ thermal conversion process where measurements of the thermal-stimulated polarization (TSP) and the ionic thermocurrent (ITC) have been taken in Na-doped CaF_2 crystals over the temperature range 35–300 K. In addition, the optical damage incurred at low temperature under high-intensity light excitation was also investigated.

II. EXPERIMENTAL PROCEDURE

Sodium-doped CaF_2 single crystals were grown by the Bridgman method in graphite crucibles at the Laboratoire de Spectroscopie Atomique at Caen (France) and the Departamento de Física de la Materia Condensada at Zaragoza (Spain). Typically the Na impurity concentration was 1 mol % in the melt. The coloration of the crystals was then performed either by exposure to x rays from a Mb target x-ray tube operated at 50 kV and 30 mA or by additive coloration using apparatus previously described.¹²

Absorption spectra were measured with a Cary 17 spectrophotometer and EPR spectra were recorded at 77 K using a quartz-walled immersion Dewar in an E-112 Varian X-band spectrometer. An E-257 gas-flow temperature controller was used to allow sample temperatures between 80 and 300 K in the cavity. ITC measurements were performed with the equipment described elsewhere.¹³

A closed-cycle cryostat (Cryogenic CRT) was used in optical absorption, thermoluminescence (TL), TSP, and photoconductivity (PC) measurements in the temperature range 30–300 K. The ITC, TSP, and PC detection was performed by a Cary 401 electrometer. The TL signal was detected by a Cary 9789Q photomultiplier. The PC spectra were corrected for the optical absorption of the sample by the correction factor $D_{\text{opt}}(\lambda)(1-10^{-D_{\text{opt}}(\lambda)})^{-1}$, where D_{opt} represents the optical density of the sample.

In order to perform optical bleaching in the low-energy absorption band of the $(F_2^+)_A$ centers the $\lambda = 647.1$ -nm line of a Kr^+ laser (Spectra Physics 171) was used. A xenon lamp (150 W) was used in photoconductivity measurements as well as in the optical-bleaching treatments in the range 280–640 nm.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. $(F_2^+)_A$ -center formation in additively colored samples

Samples with perturbed F_A centers were obtained by the exposure of additively colored Na-doped CaF_2 crystals containing F -aggregate centers to ultraviolet illumination (in the 280–340-nm wavelength region) at 77 K. The samples were then warmed, causing thermal bleaching of the F_A centers to produce $(F_2^+)_A$ centers and the temperature dependence of this process over the range 100–260 K is shown in Fig. 1. The concentrations of the F_A and $(F_2^+)_A$ centers were calculated from the absorption intensities of the corresponding low-energy absorption bands ascribed to both centers, 430 and 600 nm, respectively. From Fig. 1 it can be seen that the F_A -center thermal bleaching occurs in two steps with the maximum slopes at 160 and 200 K. Similarly, the rate of creation of the $(F_2^+)_A$ centers also consists of two stages which show close correlation with the F_A decreases, thus indicating that the $(F_2^+)_A$ centers are formed from the F_A centers.

Using the model already described for the F_A and $(F_2^+)_A$ centers, the conversion process $F_A \rightarrow (F_2^+)_A$ would only require the addition of an anion vacancy at the F_A site. Therefore, it is important to note that the first slope of the $F_A \rightarrow (F_2^+)_A$ conversion process occurs

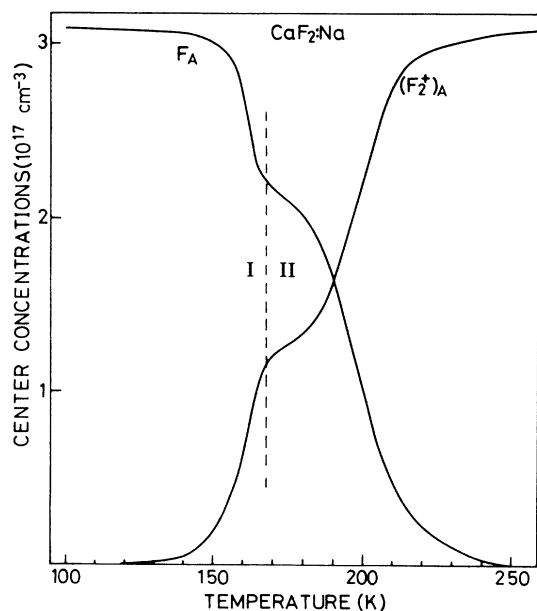


FIG. 1. Thermal evolution of the F_A - and $(F_2^+)_A$ -center concentrations under linear heating (5 K/min) in the temperature range 100–260 K of additively colored Na-doped CaF_2 samples.

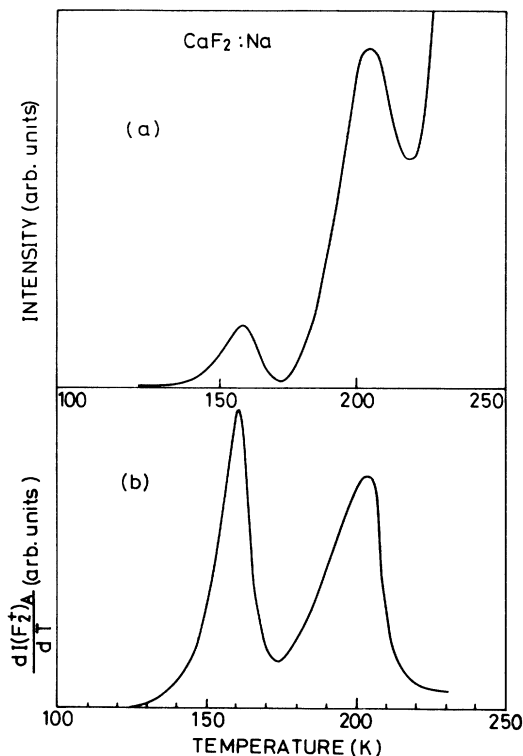


FIG. 2. (a) Thermal-stimulated-polarization spectrum ($\epsilon = 1000$ V/nm) corresponding to additively colored $CaF_2:Na$. (b) Formation rate $dI(F_2^+)_A/dT$ of the $(F_2^+)_A$ centers obtained from Fig. 1.

at temperatures below 150 K where the diffusion of anion vacancies do not take place.

In the case of the additively colored alkali halides, the formation of the $(F_2^+)_A$ centers has been found to occur at temperatures as low as 10 K.¹⁴ The mechanism involved there has been correlated with a nonradiative excitation process which causes an ionic reorientation. Thus, in order to determine the influence of reorientation phenomena as well as the role of diffusion of the anion vacancies in the formation of these centers, the TSP and ITC were studied. The TSP spectrum corresponding to additively colored $CaF_2:Na$ samples containing F_A centers is shown in Fig. 2(a). Two peaks at 162 and 205 K appear together with an exponential increase above 220 K. This increase has also been observed in uncolored $CaF_2:Na$ samples and is attributed to anionic conductivity as in Na-doped samples the free anion-vacancy concentration seems to be strongly increased.¹⁵ In contrast to the TSP the ITC spectrum of additively colored samples presents only a single peak at 162 K, the same temperature as the TSP peak.

The ITC spectrum of an uncolored sample is shown in Fig. 3; in this case it consists of a unique peak that is centered at 153 K, a temperature very close to the ITC peak seen in the additively colored samples. This suggests that the 162-K ITC and TSP peak is due to a Na-vacancy dipole reorientation probably perturbed by a nearby F

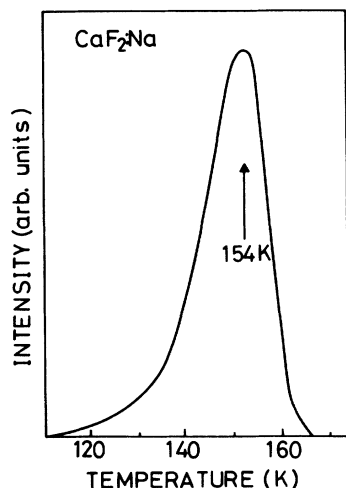


FIG. 3. Ionic thermocurrent spectrum corresponding to uncolored Na-doped CaF_2 .

center. The presence of these F centers (reciprocally perturbed by Na-vacancy dipoles) can account for the small temperature shift observed compared with the unperturbed dipole reorientation in uncolored samples.

The second TSP peak at approximately 205 K is only detected when an additively colored sample containing F -aggregate centers is illuminated at 77 K with ultraviolet light. The nature of this peak is related to the diffusion of the anion vacancies which become mobile at around 200 K. The appearance of this peak only after low-temperature illumination indicates that free anion vacancies are created during the ultraviolet irradiation. By increasing the temperature, these anion vacancies can be trapped in F_A centers forming the $(F_2^+)_A$ centers as will be discussed further.

Figure 2(b) shows the rate of $(F_2^+)_A$ -center formation with the temperature $[dI(F_2^+)_A/dT]$, obtained from Fig. 1. Two peaks are seen in this figure, both very close to the corresponding TSP peaks. Therefore, the first stage of the $(F_2^+)_A$ formation must be related to a reorientation process, while the second stage is attributed to an anion-vacancy (V_F^-) trapped by the F_A centers, thus forming the $(F_2^+)_A$ centers according to the reaction $F_A + (V_F^-) \rightarrow (F_2^+)_A$.

B. $(F_2^+)_A$ -center formation in x-ray-irradiated samples

The thermal evolution of the F_A and $(F_2^+)_A$ -center concentrations in 77-K x-ray-irradiated samples is shown in Fig. 4. The annealing of the F_A centers occurs in two stages, similar to those found for additively colored samples. In fact, the second stage also presents the maximum slope at 206 K. In contrast, with the additively colored samples, however, the formation of the $(F_2^+)_A$ centers only takes place during the second F_A thermal-annealing stage.

During the low-temperature irradiation of the Na-doped CaF_2 samples, both F_A centers and hole centers (V_K) are formed,^{5,16} thus, it is possible that recombina-

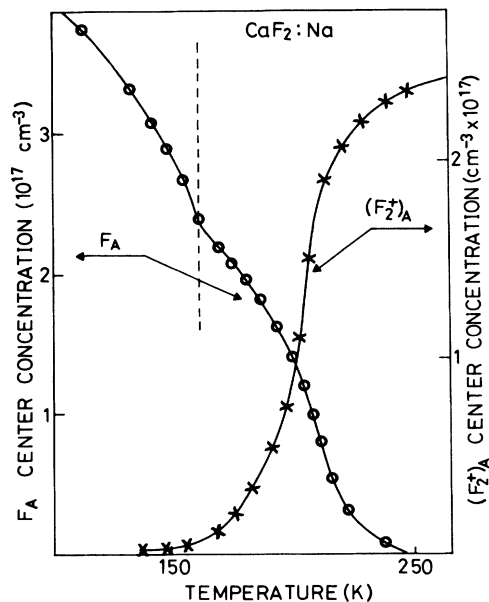


FIG. 4. Thermal evolution of the F_A - and $(F_2^+)_A$ -center concentrations under linear heating (5 K/min) of x-ray-irradiated $\text{CaF}_2:\text{Na}$ at 77 K.

tion of the V_K - F_A centers can occur during the heating stage, and TL peaks associated with this V_K - F_A recombination can be observed. Figure 5(a) shows the F_A -center concentrations as a function of increasing temperature together with the corresponding thermolumines-

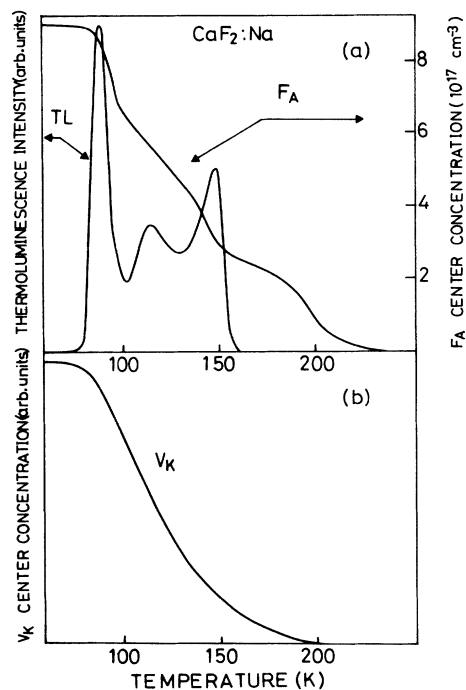


FIG. 5. (a) Thermal annealing of the F_A -center concentrations together with the thermoluminescence spectrum of x-ray-irradiated samples at 77 K. (b) Thermal annealing of the V_K -center concentrations. [Measurements were performed at 77 K after isochronal annealing (75 s) at each temperature.]

cence spectrum. It can be seen that the annealing of the F_A centers occurs in several stages which correlate with the TL peaks seen in the temperature range 50–160 K. The concentration of the V_K centers, measured by the V_K EPR signal during this thermal-annealing process, is given in Fig. 5(b). For the V_K centers, different steps were not observed in the decay of the concentration and most of the V_K centers destroyed over the same temperature range as the TL emission peaks.

The emission spectrum found for the TL peaks is similar to the emission band associated with the electron intrinsic recombination¹⁷ suggesting that the V_K - F_A recombination is responsible for the TL peaks observed at low temperature.

In conclusion, the experimental data obtained from additively colored and x-ray-irradiated samples show that the $(F_2^+)_A$ centers are created in two stages: the low-temperature stage is associated with a short-range reorientation, while an anionic-vacancy-diffusion process operates in the high-temperature zone. Finally, the V_K - F_A recombination observed in the first stage can explain the difficulty in the formation of $(F_2^+)_A$ centers at low temperatures.

C. Optical damage

It is shown that $(F_2^+)_A$ centers are destroyed when colored samples are exposed to light in the region of the absorption bands, this optical bleaching being particularly evident when photon energies corresponding to the high-energy absorption are used.^{9,18,19} Although different mechanisms such as photoionization, photodissociation, and two-photon processes have been considered as possible causes of this optical damage, the ac-

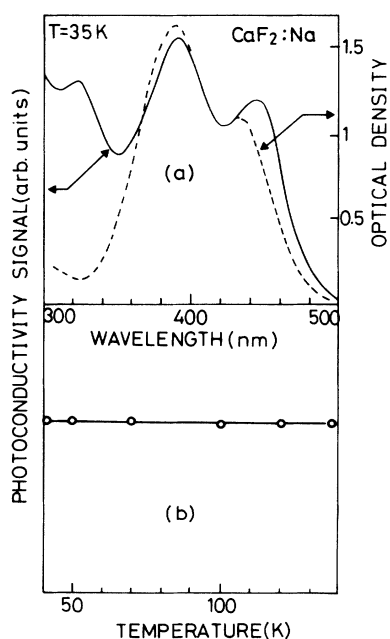


FIG. 6. (a) Photoconductivity and absorption spectra at 35 K of Na-doped CaF_2 samples containing F_A centers. (Thickness is 1.5 mm.) (b) Temperature dependence of the photoconductivity signal in the 35–160-K range.

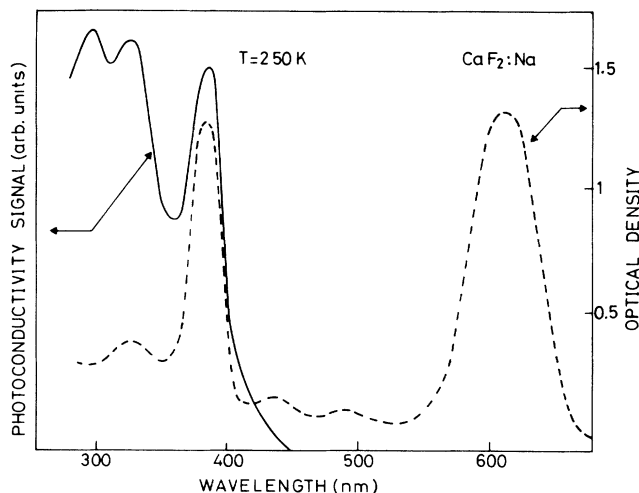


FIG. 7. Photoconductivity and absorption spectra of Na-doped CaF_2 samples containing $(F_2^+)_A$ centers. (Thickness is 1.5 mm.)

tual processes involved are not fully understood. In order to investigate the nature of this damage, photoconductivity measurements and optical-bleaching experiments with high-intensity light have been carried out.

The photoconductivity and optical-absorption spectra of Na-doped CaF_2 samples with F_A centers are shown [Fig. 6(a)]. In agreement with Rauch *et al.*,¹⁸ the PC spectrum obtained is similar to the F_A absorption spectrum, although an additional weak absorption band was observed at 325 nm. Figure 6(b) shows the PC temperature dependence for the range 40–160 K below that required for the $(F_2^+)_A$ -center formation. Over this range, the PC signal remains constant, thus indicating that the excited-state levels of the F_A centers are very near or within the conduction band.

The PC and absorption spectra for samples containing $(F_2^+)_A$ centers are shown in Fig. 7. It is important to note that while illumination in the high-energy absorption bands of the $(F_2^+)_A$ centers allows a PC signal to be detected, no signal is observed under irradiation in the low-energy absorption band. This result proves that the higher excited-state levels of the $(F_2^+)_A$ centers are also within the conduction band, but not the lower excited-state level. Therefore, in optical-damage experiments using red-light excitation, single-photoionization mechanisms cannot be considered. The PC signal under high-photon-energy excitation can explain that anion vacancies are created under ultraviolet illumination at the same time as F_A centers in samples containing $(F_2^+)_A$ centers. Indeed, since ionized $(F_2^+)_A$ centers could be unstable, it is plausible to think that free dipoles and anion vacancies are formed by breaking these ionized centers with F_A centers resulting when the photoionized electrons are trapped by free dipoles.

A typical optical-bleaching curve under 647-nm high-intensity irradiation is shown in Fig. 8(a). It presents a nonsimple kinetic decay. The role of the light intensity

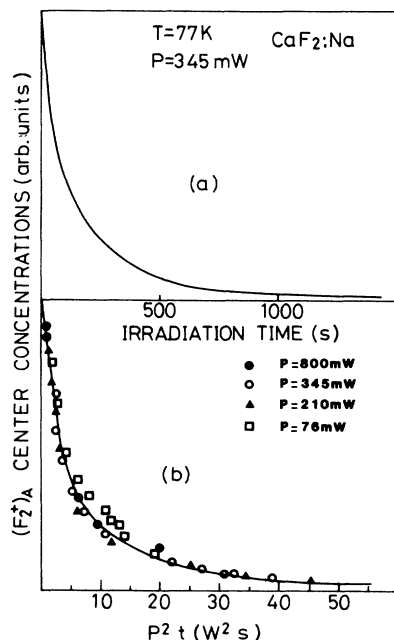


FIG. 8. (a) Optical bleaching at 77 K of the $(F_2^+)_A$ centers under 647-nm high-intensity light. (b) Optical-bleaching curves obtained by different 647-nm light intensities.

has been examined over the range 80–800 mW, and although the optical-bleaching curve is not a simple decay function, the experimental points obtained can be approximated by a unique curve when the concentration of the destroyed $(F_2^+)_A$ centers is plotted versus P^2t , where P is the light intensity (in W) and t is the irradiation time

[Fig. 8(b)]. This result suggests that the optical damage under illumination in the low-energy absorption band of the $(F_2^+)_A$ centers is due to a two-photon process.

Finally, it is important to comment that during the high-intensity optical bleaching, absorption bands at 388 and 428 nm, close to the F_A bands, were observed. These bands have recently been attributed to the $F_A(1)$ center.²⁰ The structure of these centers could be related to an F center weakly perturbed by a nearby Na-vacancy dipole. Let us remark that a short-range reorientation of this dipole as proposed in this work could transform the complex F -center dipole into the $(F_2^+)_A$ center and could account for the first stage of the $(F_2^+)_A$ formation observed at low temperature, although more experimental work is required to confirm this model.

ACKNOWLEDGMENTS

This work was partially supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT, Spain). F. Jaque is a visitor at Strathclyde and is supported by the Science and Engineering Research Council (U.K.) (SERC). The authors are indebted to M. Gilmartin for a critical reading of the manuscript. We wish to thank Professor J. Margerie [Laboratoire de Spectroscopie Atomique, Centre National de la Recherche Scientifique (CNRS), Caen, France] for kindly supplying the additively colored samples and Dr. J. Casas-González (Departamento de Física de la Materia Condensada, Universidad de Zaragoza, Spain) for supplying the crystal and performing the EPR measurements.

¹L. F. Mollenauer, *Opt. Lett.* **1**, 164 (1977).

²V. A. Arkhangelskaya, A. A. Fedorov, and P. P. Feofilov, *Opt. Commun.* **28**, 87 (1979).

³L. F. Mollenauer and D. H. Olson, *J. Appl. Phys.* **46**, 3109 (1975).

⁴E. Georgiou, J. F. Pinto, and C. R. Pollock, *Phys. Rev. B* **35**, 7636 (1987).

⁵R. Rauch, *Izv. Akad. Nauk. SSSR Ser. Fiz.* **37**, 595 (1973).

⁶V. A. Arkhangelskaya and A. S. Shcheulin, *Opt. Spektrosk.* **50**, 1142 (1981) [*Opt. Spectrosc. (USSR)* **50**, 629 (1981)].

⁷A. Hamaïdia, A. Hachimi, J. Margerie, and J. F. Hemidy, *Phys. Status Solidi B* **137**, 47 (1986).

⁸A. Hamaïdia, *Phys. Status Solidi B* **150**, 323 (1988).

⁹J. L. Doualan, J. Margerie, F. Martin-Brunetière, and E. Rzepka, *J. Phys. (Paris) Lett.* **44**, L375 (1983).

¹⁰J. M. G. Tijero and J. Casas-González, *J. Phys. (Paris) Lett.* **46**, L861 (1985).

¹¹V. M. Lisitsyn and V. F. Shtanko, *Opt. Spektrosk.* **42**, 760

(1977) [*Opt. Spectrosc. (USSR)* **42**, 433 (1977)].

¹²J. L. Doualan, A. Hamaïdia, J. Margerie, and F. Martin-Brunetière, *J. Phys. (Paris)* **11**, 1779 (1984).

¹³F. Cussó, J. L. Pascual, and F. Jaque, *J. Electrostatics* **3**, 125 (1977).

¹⁴B. Williamson, M. Gilmartin, G. Lifante, F. Jaque, B. Henderson, and F. Cussó, *Solid State Commun.* **69**, 717 (1989).

¹⁵R. W. Ure, *J. Chem. Phys.* **26**, 1363 (1957).

¹⁶J. M. G. Tijero, J. Casas-González, and F. Jaque, *J. Lumin.* **40-41**, 109 (1988).

¹⁷J. Beaumont, W. Hayes, D. L. Kirk, and G. P. Summers, *Proc. R. Soc. London, Ser. A* **315**, 69 (1970).

¹⁸R. Rauch and G. Schwotzer, *Phys. Status Solidi A* **74**, 123 (1982).

¹⁹R. Rauch, *Phys. Status Solidi B* **123**, 93 (1984).

²⁰A. Hamaïdia and A. Hachimi, *Phys. Status Solidi B* **149**, 711 (1988).