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Ni^+ and Ni^{3+} centers in X-irradiated CaF_2

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Résumé. — Nous montrons des mesures optiques et de RPE sur CaF_2 : Ni avant et après être irradié par radiation X. Une bande d'absorption à 255 nm grandit lors de l'irradiation X. L'évolution thermique de cette bande et quelques expériences de blanchiment à 15 K sur des échantillons irradiés par radiation X et contenant des centres V_K indiquent que la bande de 255 nm est due aux centres Ni^+.
Quelques signaux de RPE associés aux centres Ni^+ ont été observés. Les mesures à basse température prouvent qu'il y a deux classes de centres légèrement différentes, l'une avec une symétrie tétragonale ($g_{\parallel} = 2{,}569 \pm 0{,}005$, $g_{\perp} = 2{,}089 \pm 0{,}005$) et l'autre avec presque les mêmes valeurs de $g_{\parallel}$ et $g_{\perp}$, et une petite distorsion rhombique. Les deux signaux montrent une structure hyperfine due à l'interaction avec quatre ions fluorure.
Le modèle proposé pour le centre Ni^+ est un ion moléculaire $(NiF_4)^{3-}$ constitué par un ion Ni^+ déplacé vers une des faces du cube des fluors.
De même, nous avons observé sur quelques échantillons irradiés un autre signal de RPE qui montre une symétrie cubique ($g = 2{,}003$) avec une structure superhyperfine bien due à l'interaction avec huit fluors équivalents. Le modèle proposé pour le centre responsable de ce signal est un centre Ni^{3+} avec une position substitutionnelle du Ca^{2+}.

Abstract. — Optical and EPR measurements of CaF_2 : Ni before and after X-irradiation are reported. An absorption band at 255 nm grows during X-irradiation. The thermal evolution of this band and some bleaching experiments in 15 K X-irradiated samples containing V_K centers indicate that the 255 nm band is due to Ni^+ centers. Some EPR signals associated with the Ni^+ centers are also observed. Low temperature measurements show that there are two slightly different kinds of centers one of them having tetragonal symmetry ($g_{\parallel} = 2.569 \pm 0.005$, $g_{\perp} = 2.089 \pm 0.005$) and the other one with about the same values of $g_{\parallel}$ and $g_{\perp}$ and a small rhombic distortion. Both signals show a superhyperfine structure due to interaction with four fluoride ions.
The proposed model for the Ni^+ center is a $(NiF_4)^{3-}$ molecular ion formed by a Ni^+ ion displaced toward one of the faces of the cube of fluorines.
Another EPR signal showing cubic symmetry ($g = 2.003$) with a well resolved superhyperfine structure due to the interaction with eight equivalent fluorines is also observed in some irradiated samples. The proposed model for the center responsible of this signal is a Ni^{3+} center in a Ca^{2+} substitutional position.

1. **Introduction.** — In fluorite crystals doped with 3d-ions several kinds of impurity related defects have been detected after X-irradiation. In Co doped CaF_2, Co^+ ions as well as Co^{2+}-F center complexes are produced [1, 2]. Optical studies of Mn doped CaF_2, show that Mn^{2+} centers are reduced to Mn^+ by X-irradiation at LNT (P. J. Alonso and R. Alcalá, unpublished). In Cu-doped $SrCl_2$, Cu ions enter the lattice as Cu^+. During X-irradiation Cu^{2+} ions close to one of the faces of the chloride cubes are formed [3].

In the present work radiation effects of CaF_2 : Ni are reported.

2. **Experimental.** — The crystals used were prepared by means of the Bridgman technique employing a 25 kW high frequency generator. The nickel impurities were added to the starting material as NiF_2 ; the nominal concentrations were about 0.4 mol %.

Optical absorption experiments were performed with a Cary 17 spectrophotometer. Low temperature measurements were taken in an Oxford Instruments CF-100 continuous flow cryostat.

Most of the R.T. EPR experiments were performed under Q-band conditions. For the low temperature measurements we used the X-band set-up. The experiments at 80 K were carried out with an insertion type liquid nitrogen cryostat with the crystals located in the liquid nitrogen.

3. **Experimental results and discussion.** — 3.1 OPTICAL EXPERIMENTS. — Unirradiated CaF_2 : Ni shows two absorption bands at 482 nm and 555 nm which have been associated with Ni^{2+} in a Ca^{2+} substitutional position [4]. A small band at 255 nm is also detected in some of the samples (Fig. 1).

After R.T. X-irradiation an absorption band is found at 255 nm (Fig. 1). This band narrows keeping the same area when we cool the sample down from

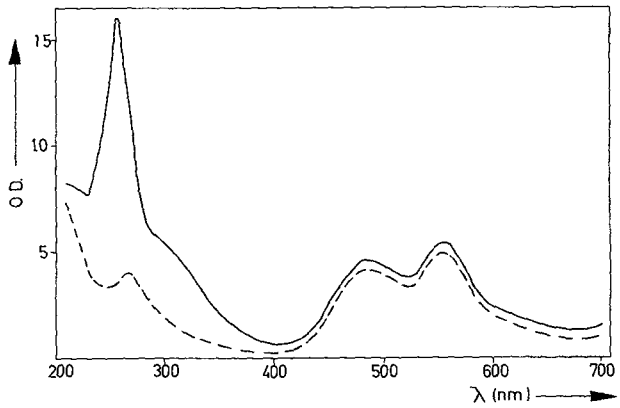

Fig. 1. — R.T. Optical absorption spectrum of CaF_2 : Ni. ------ Before X-irradiation. —— After R.T. X-irradiation.

RT to LNT. This behaviour is typical of transitions which are not parity forbidden. The 255 nm band also appears after 80 K and 15 K X-irradiation. In the 15 K X-irradiated samples V_k-centers, which give an absorption band at 315 nm [5], are also created (Fig. 2). Optical bleaching at 15 K either with 315 nm or with 255 nm light produces a simultaneous decrease of the 315 nm and 255 nm bands (Fig. 2). Dichroism can be induced by bleaching at 80 K with 255 nm light propagating along the [001] direction and having $E \parallel [100]$. No dichroism can be induced by bleaching with [110] polarized light.

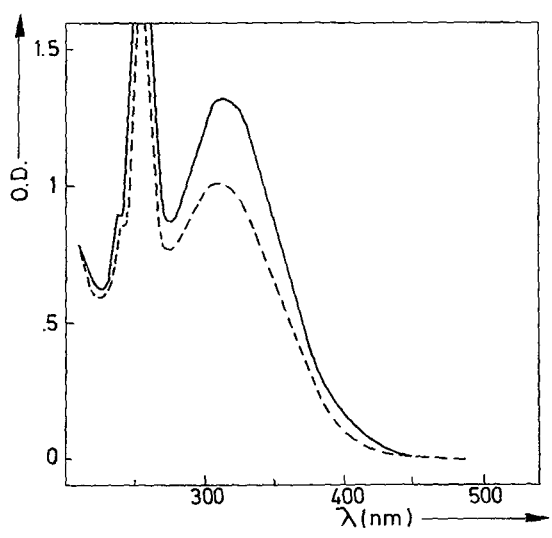

Fig. 2. — 15 K Optical absorption spectrum of CaF_2 : Ni. —— After X-irradiation at 15 K. ------ As the previous one but after optical bleaching with 255 nm light. A similar result is obtained by bleaching with 320 nm light.

Since the 255 nm band appears in Ni doped samples but it does not in pure CaF_2 or doped with Mn, Fe, or Co we conclude that it is associated to Ni impurities. The decrease of this band during bleaching with V_K light suggests that it is due to a center with trapped electrons. Holes removed by bleaching in the V_K band recombine with the extra electrons and the center becomes destroyed. Dichroism experiments show that the electric dipole corresponding to the 255 nm band is directed along one of the ⟨ 100 ⟩ directions. Finally we point out that the electronic transition associated with that band is not parity forbidden.

A tentative model for the center responsible of the 255 nm band, that accounts for all these facts, and that is also confirmed by EPR experiments, consists of a Ni^+ ion displaced a way from the Ca^{2+} substitutional site toward one of the faces of the cube of fluoride ions (Fig. 3).

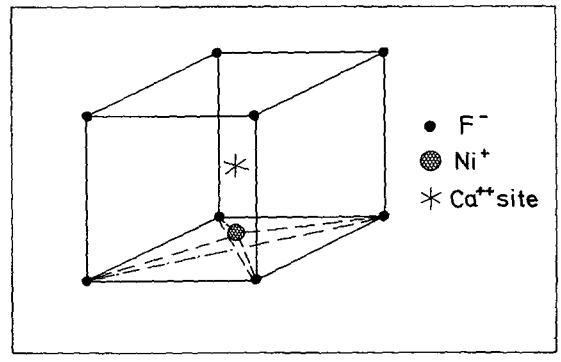

Fig. 3. — The proposed model for the Ni^+ center in CaF_2.

3.2 EPR OF Ni^+ IONS. — In as grown crystal we observed a Q-band EPR signal as shown in figure 4*a*. This signal was taken with $H \parallel [100]$ at R.T. We see two resolved patterns which, can be associated to Ni^+ centers such as the one given in figure 3. Ni^+ ions in a tetragonally distorted octahedral field such as that of the model have a ground state that can behave like a spin doublet. The two patterns observed correspond to centers having the tetragonal axis parallel or perpendicular to the magnetic field. The splitting of each of these patterns can be explained by superhyperfine interaction with four fluorine nuclei. After R.T. X-irradiation a big increase of the Ni^+ signal is observed. At the same time some unresolved lines grow in the same positions as the resolved Ni^+ spectrum (Fig. 4*b*). Bleaching with 255 nm light the two signals are destroyed. This indicates that the EPR signal and the 255 nm band are due to the same center.

If the EPR measurements are taken at 80 K under X-band conditions we obtain, in R.T. irradiated CaF_2 : Ni, the spectrum given in (Fig. 5*a*) which shows that two types of Ni^+ centers are present. After R.T. irradiation both signals have incresed and one of them becomes dominant (Fig. 5*b*). Upon bleaching with 255 nm light the two groups of lines decrease. Those marked with a star, that are the ones that show a bigger growth during X-irradiation, are also more drastically affected by the bleaching light (Fig. 5*c*). The rotational diagram of the marked lines shows a tetragonal symmetry (C_4) around one of the [100] axis.

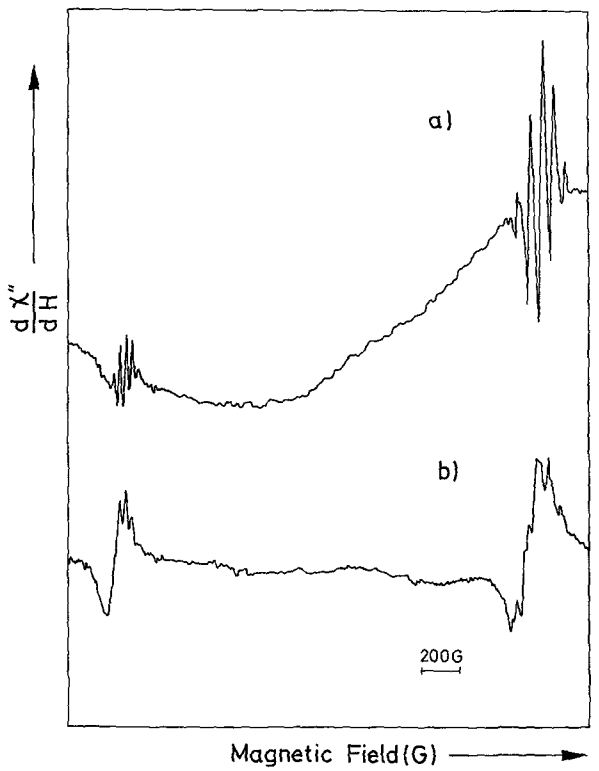

Fig. 4. — *a*) Q-band EPR spectrum of an as grown CaF_2 : Ni sample. *b*) As in *a*) but after R.T. X-irradiation. The spectra were taken at R.T. with H ∥ [100].

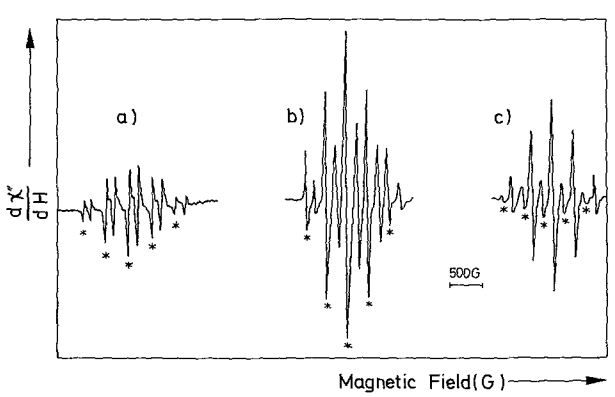

Fig. 5. — *a*) X-band EPR spectrum of an as grown CaF_2 : Ni sample. *b*) As in *a*) but after R.T. X-irradiation. *c*) As in *b*) but after R.T. bleaching with 255 nm light. All the spectra were taken at 80 K with H ∥ [100]. Only the lines corresponding to the lower field pattern in figure 4 are shown.

From the EPR spectra taken by rotating the magnetic field the magnetic parameters as given by the spin hamiltonian

$$\mathcal{H} = \mu_\beta[g_\parallel H_z S_z + g_\perp(H_x S_x + H_y S_y)] + \\ + \sum_{i=1}^{4} [(S_{x'} I^i_{x'} + S_{y'} I^i_{y'}) A_\perp + S_{z'} I^i_{z'} A_\parallel]$$

(where the z' axis for each ligand is along the Ni-F line) are :

$$g_\parallel = 2.569 \pm 0.005 \; ; \quad g_\perp = 2.089 \pm 0.005 \; ;$$
$$A_\parallel = 81 \; (10^{-4} \; \mathrm{cm}^{-1}) \; ; \quad A_\perp = 36 \; (10^{-4} \; \mathrm{cm}^{-1}) \, .$$

The rotational diagram of the unmarked pattern is similar to that of the marked one but with small differences which show that the symmetry of the associated center is slightly lower than tetragonal.

A study of the temperature dependence of the spectrum in the range from RT to LNT shows that the tetragonal signal broadens very drastically with T at about 200 K while the other signal broadens more slowly. These results allows us to explain R.T., Q band data. The unresolved line is due to the tetragonal center which gives a broad band at R.T. and the resolved pattern is due to the orthorhombic center.

We conclude that there are at least two kinds of Ni^+ centers in our samples. Both of them correspond basically with the model given in figure 3 but one of them is slightly perturbed.

3.3 EPR OF Ni^{3+} IONS. — After X-irradiation and at the same time that the Ni^+ signal we can observe, in some of the purest samples used, another signal showing cubic symmetry. It was observed only at R.T. under Q-band conditions. This signal taken with H ∥ [100] is given in figure 6. It has an isotropic g-factor ($g = 2.003$) very close to the free electron value an it shows nine equidistant lines with an intensity ratio of approximately 1 : 8 : 28 : 56 : 70 : 56 : 28 : 8 : 1 which can be associated with a super-hyperfine interaction with eight equivalent fluorine nuclei. The magnetic parameters of this center as given by the spin hamiltonian

$$\mathcal{H} = g\mu_\beta \mathbf{HS} + \sum_{i=1}^{8} \times \\ \times \{[A_s + A_p(3\cos^2\theta_i - 1)] S_z I_z \\ + 3 A_p S_z I_x \sin\theta_i \cos\theta_i\}$$

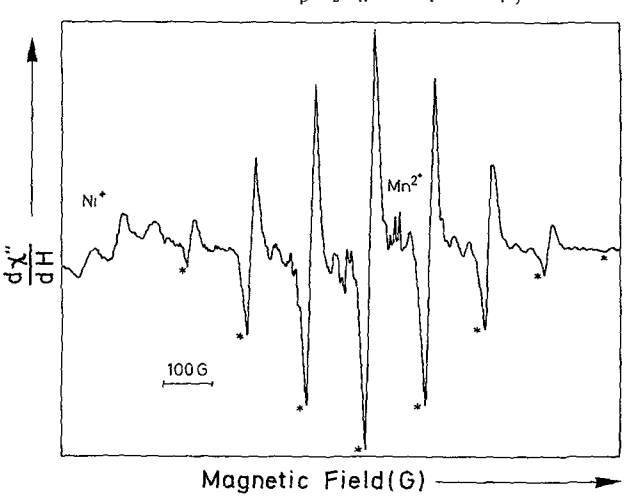

Fig. 6. — The marked lines correspond to the Ni^{3+} center. The spectrum was taken at R.T. under Q band conditions with H ∥ [100].

(with θ_i the angle between the magnetic field and the line joining the impurity center and the fluoride ions) are :

$$g = 2.003 \quad A_s = 110.8 \pm 1\ \mathrm{G} \quad A_p = 41.6 \pm 1\ \mathrm{G}\,.$$

Since the Ni ions are the predominant impurities we tentatively propose that this signal is due to Ni^{3+} ions in a Ca^{2+} substitutional position. Ni^{3+} can provide the charge compensation for Ni^{+} ions in pure CaF_2 : Ni crystals. On the other hand Ni^{3+} is d^7 ion which, in an eightfold cubic coordination, has a ground state that can be thought of as an effective spin $s = 3/2$ state. A strong crystal field, and consequently a big splitting of the levels, can be expected for Ni^{3+} ions because of its extra positive charge which attracts the eight neighbouring F-ions. This strong crystal field splitting together with some covalent bonding with the fluorines can account for the very small g-shift observed and for the high values of the SHF constants. No optical signal which can be correlated to Ni^{3+} EPR signal has been observed.

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DISCUSSION

Question. — O. SCHIRMER.

1. What are the g-values of your centres ? Are they consistent with the model given ?

2. Can you give an assignment of the optical absorption to your model ?

Reply. — R. ALCALÁ.

1. The g-values for the Ni^{+} centre are $g_{\parallel} = 2.569$ and $g_{\perp} = 2.089$. They are in the range of those given in the literature for Ni^{+} ions in similar environments.

2. We cannot at this moment give an assignment of the optical band. It appears that its oscillator strength is big because, since we do not see any decrease in the absorption bands associated to Ni^{2+}, the number of Ni^{+} ions should be rather small. We have speculated on the possibility of an interconfigurational transition.

References

[1] ALCALÁ, R. and ALONSO, P. J., *Phys. Rev. B* **18** (1978) 5506.

[2] ALCALÁ, R. and ALONSO, P. J., *J. Lumin.* **20** (1979) 1.

[3] BILL, H., *Phys. Lett.* **44A** (1973) 101.

[4] ZOROARSKAYA, E. I., MALKIN, B. Z., STOLOV, A. L. and YAKOVLEVA, Zh. S., *Sov. Phys. Solid State* **10** (1968) 255.

[5] BEAUMONT, J. H., HAYES, W., KIRK, D. L. and SUMMERS, G. P., *Proc. Roy. Soc.* **A 315** (1970) 69.