Optical absorption spectrum of x-irradiated CaF$_2$:Co

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Optical-absorption spectra of CaF$_2$:Co x-irradiated at 80 and 300 K are reported. Room-temperature x-irradiated crystals show five bands with peaks at 250, 295, 545, 715, and 780 nm which are associated with a Co-related defect. Irradiation at 80 K produces some bands at 240, 280, and 535 nm which are also associated with the presence of Co. Dichroism measurements show that the centers responsible for these bands, both in the 300-K and in the 80-K irradiated samples, have a trigonal symmetry. From dichroism and bleaching experiments a model consisting of an F center nearest to a Co^{2+} ion in a substitutional position is proposed for the defect created at 300 K. The same center, but perturbed by an interstitial, is proposed for the defect produced at 80 K. The energy levels of the room-temperature-produced center, together with the polarizations and energies of its possible electronic transitions, have been calculated using the Mulliken-Wolfsberg-Helmholtz approximation. A good agreement with the experimental results is obtained.

I. INTRODUCTION

A great deal of attention has been paid to radiation damage in fluorite-type single crystals in the last decade.[1] X irradiation of CaF$_2$ crystals at temperatures below 77 K produces an F band which disappears when we warm up the samples to room temperature (RT)[2] or by means of optical bleaching at 77 K.[3] No detectable F-band coloration has been obtained by RT x-irradiation in pure CaF$_2$ samples.

On the other hand, after RT x-irradiation yttrium-doped CaF$_2$ crystals show an absorption spectrum with four bands (Smakula's bands).[4-6] Similar spectra appear in x-irradiated and additively colored rare-earth (RE) doped CaF$_2$.[7,8] These absorption bands have been explained with a model consisting of a trivalent impurity associated with a nearest fluorine vacancy with two trapped electrons.

Radiation damage has received much less attention in transition-ion-doped CaF$_2$, if we exclude CaF$_2$:Mn due to its applications in radiation dosimetry. Irradiation effects in ionic crystals doped with iron-group impurity ions have been reported by several authors giving two main kinds of results: (i) valence changes of the impurity ions, such as those reported by Ikeya,[9] Ikeya and Itoh,[10] and Jain and Lal[11]; and (ii) changes in the oscillator strength of the 3d-ion transitions due to the formation of impurity-ion–F-center complexes as has been reported by Sibley and co-workers.[12-15] These complexes are similar to those found in RE-doped CaF$_2$ crystals.

In order to see the influence of transition-ion impurities on the colorability of CaF$_2$ crystals as well as to determine whether the observed changes in the absorption spectrum are due to valence changes of these ions or to the formation of complex centers, the study of the influence of x irradiation on the optical and EPR properties of CaF$_2$ doped with several iron-group ion impurities has been undertaken. We report in the present paper the results obtained on the absorption and EPR spectra of cobalt-doped CaF$_2$.

II. EXPERIMENTAL

The single crystals used in our experiments come from two different sources. Some of the Co-doped samples were purchased from Optovac Inc. The crystals doped with Co and La, Gd, Yb, or Na, as well as some other Co-doped crystals, were kindly made available by den Hartog (Solid State Physics Lab, Groningen, Holland). The Co content of the samples was in the range 100–20 000 ppm. Analyses were performed by neutron activation.

Some other impurities, such as Mn and Gd, were also present in very small amounts (smaller than 10 ppm). The RE impurity content of the double-doped crystals was 30% of the Co content (in the starting materials). Analysis of the grown crystals was not performed of these samples.

X irradiation was done using a Cu-cathode tube working at 40 kV and 20 mA. Temperatures, in the range of 10–300K, were obtained using an Oxford CF100 flow cryostat. The precision and stability of the temperature were within ± 0.2 K.

Absorption measurements have been taken using a Cary 17 spectrophotometer. EPR measurements were performed at the Solid State Physics Lab (Groningen, Holland) using a Varian E-3 EPR spectrometer working in the X band. Measurements were taken at RT, liquid-N$_2$ temperature and liquid-He temperature with appropriated Dewars.

Optical bleaching was performed with a 100-W

high-pressure Hg lamp and a 0.25-m high-intensi-
ty Bausch-Lomb monochromator. Polarized light
was obtained using two quartz Glan-Thomson
prisms which were also used in dichroism mea-
surements.

III. EXPERIMENTAL RESULTS

The RT optical-absorption spectrum of Co-
doped CaF$_2$ single crystals has been previously
reported[16-18] and is shown in Figs. 1(a) and 1(b)
together with the spectrum of a RT x-irradiated
sample, measured at RT and liquid-N$_2$ tempera-
ture.

We can see [Fig. 1(a)] that the radiation induces
some new bands, with peaks at 250, 295, 320,
450, 545, 715, and 780 nm (these are the positions
at the liquid-N$_2$-temperature spectrum). The
bands at 320 and 450 nm do not behave as the
other five do, and we will not be concerned with
these two bands. The infrared part of the spec-
trum [Fig. 1(b)] does not change after x-irradia-
tion. We also find that when measurement is made
at liquid-N$_2$ temperature the new bands narrow
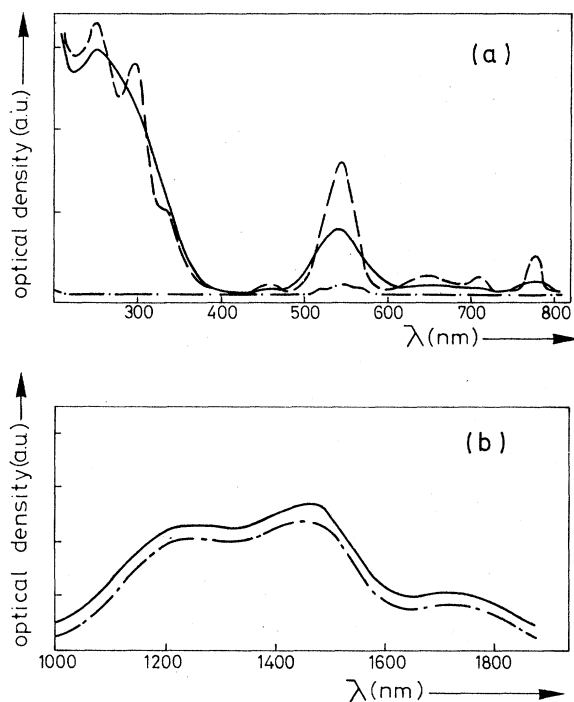and increase their heights keeping the same area.

This is the typical behavior of parity-allowed
transitions in contrast with the bands due to Co^{2+}
in unirradiated samples, which are parity for-
bidden and consequently decrease their intensities
when the samples are cooled down.

The absorption spectrum of x-irradiated samples
has been measured after different x-irradiation
times and it has been found that the five radiation-
induced bands show a constant intensity rate a-
mong them, which indicates that all of them are
due to the same center (this will be confirmed by
dichroism experiments).

The intensity of the 545-nm band as a function
of x-irradiation time at RT is given in Fig. 2.
The same evolution corresponds to the other four
bands. The broken line gives the intensity evolu-
tion corresponding to a first-order kinetics
$(dn/dt = a - bn)$.

Samples containing different Co concentrations
ranging from 100 to 20 000 ppm have been x irra-
diated to saturation at RT. The final intensity of
the new bands increases with the Co concentration.
On the other hand, no similar spectrum is found
by x-irradiation of pure CaF$_2$ or doped with Mn,
Fe, or Ni, so we attribute the 250, 295, 545, 715,
and 780 nm bands to a Co-related defect.

A Co-doped sample and some double-doped ones
containing Co and La, Gd, Yb, or Na, (all of them
with similar Co concentrations), have been x irra-
diated to saturation at RT. All of them show the
same five-band spectrum but with different inten-
sities. We show in Fig. 3 the 500–600-nm region
of the absorption spectrum of these samples before
and after x irradiation. We conclude that rare-
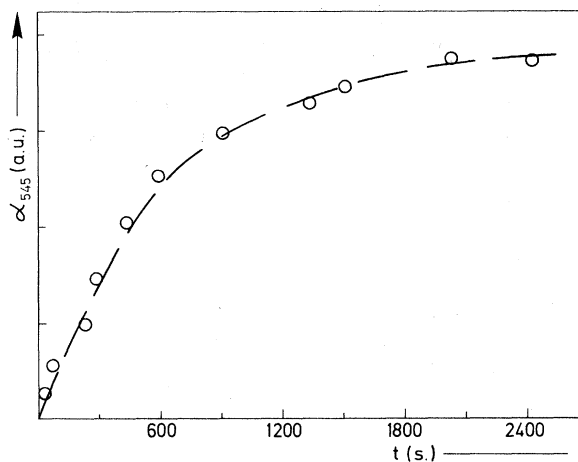earth impurities inhibit the formation of the new

FIG. 1. Optical-absorption spectrum of CaF$_2$:Co
(-·-·-) before any treatment measured at RT (—) after
RT x irradiation measured at RT and (- - -) after RT
x irradiation measured at liquid-N$_2$ temperature. (a)
uv and VIS region, (b) Near-infrared region (to facilitate
the comparison, the absorption zero has been slightly
shifted in the x-irradiated spectrum).

FIG. 2. Evolution of the 545-nm-band intensity with
the irradiation time. The broken line gives the theore-
tical evolution corresponding to a first-order kinetics.
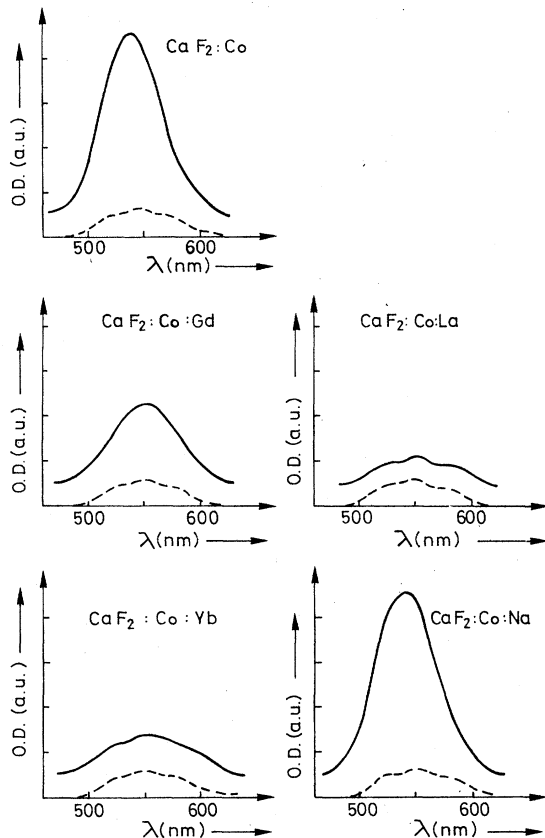α is the absorption coefficient.

FIG. 3. 500–600-nm region of the optical-absorption spectrum of CaF_2:Co, CaF_2:Co:Gd, CaF_2:Co:La, CaF_2:Co:Yb, and CaF_2:Co:Na (– – –) before any treatment and (—) after RT x irradiation to saturation. Measured at RT.

bands while Na impurity does not affect their final intensity.

The five bands are stable at RT, if the sample is kept in the dark, but they can be thermally bleached on heating the crystal at 600 K for several hours. After this treatment a new RT X ir-
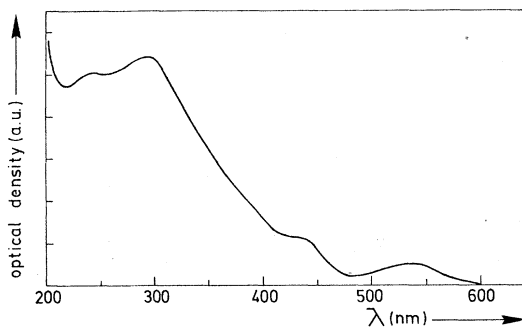

FIG. 4. Absorption spectrum of CaF_2:Co after liquid-N_2 temperature irradiation. Measured at liquid-N_2-temperature.

radiation gives the same results as if the sample was untreated, which means that the thermal bleaching has completely removed the damage created by radiation. A similar behavior is obtained by RT bleaching of an x-irradiated crystal with light of wavelengths shorter than 350 nm.

On the other hand if the bleaching with 300-nm light is performed at 80 K we get a partial destruction of these bands but if we warm up the sample to RT the five bands recover the same intensities they had before optical bleaching.

A 80-K x-irradiated CaF_2:Co sample has the absorption spectrum shown in Fig. 4 with some absorption bands at 240, 280, 435, and 535 nm. As in the RT x-irradiated sample, the 435-nm band has a different behavior from the other with respect to dichroism and evolution under radiation. We will not study this band. The spectrum saturates with an intensity much smaller than that in the RT irradiation experiments and we have not been able to detect any band in the 600–800-nm region. The 240-, 280-, and 535-nm bands are very close to the 250-, 290-, and 545-nm bands obtained by RT x irradiation and they have the same behavior in dichroism experiments.

If we warm up to RT a crystal irradiated to saturation at 80 K we get an absorption spectrum similar to the one obtained if we irradiate to saturation the same crystal at RT. The change from one spectrum to another takes place at about 270 K.

Dichroism experiments have been performed with samples irradiated both at RT and 80 K. We will describe only the results corresponding to RT irradiated samples because they are similar to these obtained with the samples which have been irradiated at 80 K.

Polarized bleaching at 80 K, with light of 250, 290, 545, 715, or 780 nm propagating along the [001] direction and having $\vec{E} \parallel [100]$, does not induce any dichroism. Bleaching with light propagating along [001] and with $\vec{E} \parallel [110]$, gives the dichroism shown in Fig. 5, when we bleach in 290, 545, 715, or 780 nm, and the opposite when we bleach in the 250-nm band. These results show[1] that the center responsible for these bands are oriented along the ⟨111⟩ directions. On the other hand, we see that when we polarize in the 545-nm band we get a dichroism of almost 100% which will be useful to distinguish between σ and π transitions.

Thermal reorientation of these centers takes place at about 160 K. We show in Fig. 6(a) lnΔ versus, time (Δ is the dichroism) for five different temperatures between 158 and 166 K. The theoretical evolution (solid line) is given by
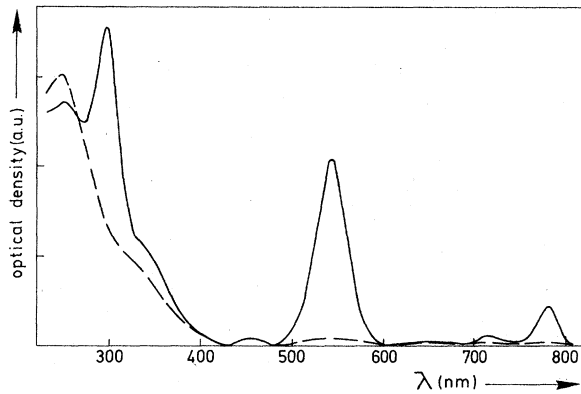
$$\Delta = \Delta_0 e^{-2t/\tau(T)} \tag{1}$$

FIG. 5. Optical dichroism in RT x-irradiated CaF$_2$: Co after bleaching at liquid-N$_2$ temperature in the 545-nm band with light propagating along the [001] axis with $\vec{E} \parallel$ [110]. (– – –) measured with $\vec{E} \parallel$ [110] (—) measured with $\vec{E} \parallel$ [1$\bar{1}$0].

with

$$1/\tau(T) = \nu_0 e^{-\Delta E/k\,T} \cdot \qquad (2)$$

Δ_0 being the initial dichroism, and ΔE the activation energy for the reorientation process.

Figure 6(b) shows $\ln(1/\tau)$ vs. $1/T$. The solid line gives the theoretical evolution with $\nu_0 = 1.7 \times 10^{14}$ sec^{-1}; $\Delta E = 0.57$ eV.
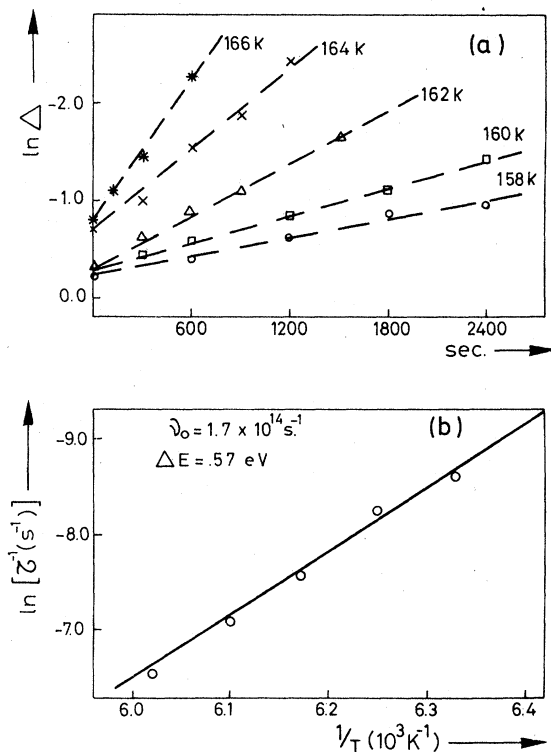

FIG. 6. (a) lnΔ vs time at five temperatures [see Eq. (1)]. (b) $\ln(1/\tau)$ vs $1/T$ [see Eq. (2)].

EPR measurements of a CaF$_2$:Co sample have been performed at liquid-N$_2$ temperature, and liquid-He temperature before and after x irradiation. The signal due to Co^{2+} ions is only visible in the liquid-He temperature measurement as it has been already reported.[19] There is also a Mn^{2+} signal due to some Mn impurities present in all our samples. We have not found any change in the EPR signal after x irradiation, which means either that the center responsible for the new absorption bands is not paramagnetic, or that its concentration is too low to be detected with our experimental setup.

Emission measurements of unirradiated and x-irradiated samples have been reported elsewhere.[20]

IV. DISCUSSION

From the experimental results reported in Sec. III we can conclude that since the absorption spectrum shown in Fig. 1, which corresponds to RT x-irradiated CaF$_2$:Co, appears only in Co-doped samples, and its intensity is proportional to Co-concentration for samples from the same batch, the center responsible for these bands is a kind of Co-related defect.

Optical and EPR properties of some transition ions in ionic crystals after irradiation with ionizing particles have been reported. Ikeya,[9] Ikeya and Itoh,[10] and Jain and Lal[11] working with alkali-metal halides have found that irradiation produces valence changes in the transition ions. On the other hand Sibley and co-workers[12–15] working with perovskites have found an enhancement of the spin-forbidden transitions of the ion. This enhancement is produced by a radiation-induced F center close to the impurity ion.

In our case, since the dichroism experiments show that the center responsible for the five-band absorption spectrum has trigonal symmetry, we have taken into account two different kinds of models.

The first one would consist of ions Co$^+$ or Co^{3+} created by the x irradiation and having a trigonal Jahn-Teller distortion similar to the one observed by Zaripov et al.[21] for Ni^{2+} and Fe^{2+} ions in CaF$_2$.

With this model we cannot explain the recovery of the absorption spectrum of a RT x-irradiated sample after bleaching at 80 K with uv light. If we assume that we cannot create Co^0 or Co^{4+}, the bleaching would be due to a new valence change from Co$^+$ or Co^{3+} to Co^{2+}. On warming up to RT we would not recover the RT x-irradiated sample but the unirradiated one.

The other kind of model we have studied has been a Co^{2+} ion perturbed by a radiation-induced lattice defect.
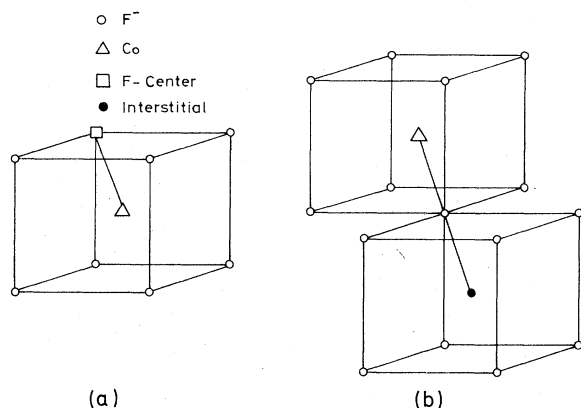
FIG. 7. Two possible models for the center having trigonal symmetry. (a) An F center nearest to a Co^{2+} ion. (b) An interstitial close to a Co^{2+} ion.

Two simple centers of this type are consistent with the observed trigonal symmetry. A fluorine interstitial close to a Co^{2+} ion giving a kind of H_A center and a F center nearest to a Co ion. We show these two models in Fig. 7.

Due to the absence of an EPR signal which can be associated with this defect, it is difficult to distinguish between these two models. We can get some insight into this problem by studying the spectrum induced in crystals doped with Co and some rare-earth (RE) ions or with Na. The RE ions go into CaF_2 in substitutional positions and introduce fluorine interstitials as charge compensators.[22,23] The Na ions also go in a substitutional position but they introduce fluorine vacancies as charge compensators.[24] From the results given in Fig. 3 we see that the saturation intensity of the x-ray-induced 545-nm band is smaller in the Co-RE-doped samples. Since these samples have an excess of interstitials we conclude that the center probably does not involve any interstitial and so the model we propose for the center consists of an F center nearest to a Co^{2+} ion (F-Co center) (Fig. 7). This model is similar to the one proposed by Sibley and co-workers for the centers they found in transition-ion-doped perovskites and in doped MgF_2.[12-15]

In our case, although in unirradiated CaF_2:Co there is an absorption band in the 550-nm region associated with the parity-forbidden $^4A_{2g}(^4F)$ $\rightarrow {}^4T_{1g}(^4P)$ Co^{2+} transition, the increase of the intensity in this region is probably not due to the lifting of the parity selection rule by the presence of an F center, because, as we have seen in Fig. 1(b) the ir band due to the $^4A_{2g}(^4F) \rightarrow {}^4T_{1g}(^4F)$ Co^{2+} transition is not affected on irradiation.

On the other hand, the other radiation-induced bands do not correspond to the positions of the Co^{2+} electronic transitions calculated with the

data given.[16] Hence the appearance of these lines is not due simply to a lifting of the spin and parity forbiddeness of Co^{2+} transitions, due to F-center interaction, but to the formation of a $Co^{2+}-F$-center complex.

Using this model, the experimental result we have reported in Sec. III, can be explained.

Since the F-Co center has not a center of symmetry, the electronic transitions associated with it are parity allowed. This is consistent with the thermal evolution of the absorption spectrum given in Fig. 1.

The first-order kinetics shown in Fig. 2 corresponds to the following process. During RT x irradiation some of the F centers formed are stabilized by some Co^{2+} ions. The number of the unperturbed Co^{2+} ions does not change in a measurable way because both the infrared part of the spectrum [Fig. 1(b)] and the EPR signal do not change after x irradiation. The rate of F-Co center production in these conditions can be assumed to be constant. On the other hand, some of the F-Co center created can also be destroyed by the radiation, by a mechanism similar to that of the optical bleaching with uv light described below, giving a destruction rate proportional to the number of existing centers. This gives the found kinetics.

The dependence of the saturation intensity of the absorption bands with the Co concentration is obvious with our model. The influence of RE impurities has already been explained.

Thermal bleaching at 600 K and RT optical bleaching with uv light are due to the ionization of the F-Co center followed by the diffusion of the vacancy. When we bleach at low temperature, the vacancy is not mobile and the Co^{2+}-vacancy complex remains stable. On warming up the sample, electrons are removed from some electron traps and retrapped by the Co^{2+}-vacancy complex giving back the $Co^{2+}-F$-center complex.

The spectrum obtained by 80-K x irradiation can be associated with a $Co^{2+}-F$-center complex perturbed by a close interstitial. When we warm the sample up, the interstitial migrates and the unperturbed F-Co center is formed. A similar behavior has been found by Lee and Sibley[15] in irradiated $KMgF_3$:Mn and by Hayes and Lambourn[25] in the interstitial perturbed F centers detected by EPR measurements in CaF_2 irradiated at low temperature.

Dichroism results correspond to the reorientation (bleaching with light of wavelength longer than 350 nm) or preferential destruction (bleaching with uv light) of the F-Co center. The almost total dichroism obtained in the 545-nm band shows that this band must be associated with a σ transi-

TABLE I. Energy levels and transition energies for the F center in CaF_2 calculated by several authors. The experimental value of the transition energy is 3.3 eV.

Ground state (eV)	First excited state (eV)	Transition energy (eV)	Zero-energy level	Reference
−7.66	−4.08	3.59	Vacuum level	30
−9.41	−5.90	3.51	Vacuum level	31
−6.64	−2.79	3.85	Bottom of the conduction band	1

tion (dipolar moment along $\langle 111 \rangle$ directions) because the maximum dichroism that can be obtained in our experiments for a π transition is 25%. Since the bands at 295, 715, and 780 nm show the same type of dichroism as the 545-nm band band we conclude that all of them are preferentially σ polarized. The 250-nm band, which shows an opposite dichroism is π polarized.

The activation energy (0.57) eV) obtained for the thermal reorientation of the center is within the energy range corresponding to the motion of vacancies in CaF_2.[26]

The absence of an EPR signal which can be associated with the F-Co center can be due to the small number of these centers (the Co^{2+} concentration does not change in a measurable way) together with a very short spin-lattice relaxation time (as it is found for Co^{2+}). It can also be explained if the ground state of the F-Co center is not paramagnetic.

In order to make a final check of our model we have performed a calculation of the energy levels associated with the $Co^{2+} - F$-center complex following the same procedure used by Alig in his calculation of the energy levels of photochromic centers in CaF_2.[27] In order to do this we have used the molecular-orbital theory within the Mulliken-Wolfsberg-Helmholtz (MWH) approximation.[28] We have started with the Co^{2+}-ion and F-center single-electron orbitals.

The F-center orbitals we used are these corres-

TABLE II. Single-electron energy levels for the F-Co center.

Irreducible representation of the C_{3v} group corresponding to each level	Energy of the level (eV)
$1a_1$	−9.1
$1e$	−8.5
$2a_1$	−7.8
$3a_1$	−6.2
$2e$	−5.7
$3e$	−5.6
$4a_1$	−3.4

ponding to the ground state and to the first excited state, of which the energy difference is known.[1] These orbitals in the unperturbed F-center transform according to the A_1 and T_2 irreducible representations of the T_d symmetry group. In the C_{3v} symmetry of the Co-F center the ground state transforms according to the A_1 representation and the first excited state according to $A_1 + E$.

The environment of the unperturbed Co^{2+} in CaF_2 has O_h symmetry. We have used the $3d$ and $4s$ orbitals because the $4p$ are too high in energy.[29] The $3d$ orbitals in O_h symmetry split into e_g and t_{1g} orbitals, while the $4s$ ones transform according to a_{1g}. We have placed these $4s$ orbitals 4.8 eV higher than the ground level e_g according to Stahl-Brada and Low data.[16]

In the C_{3v} symmetry the a_{1g} and e_g orbitals transform, respectively, according to the A_1 and
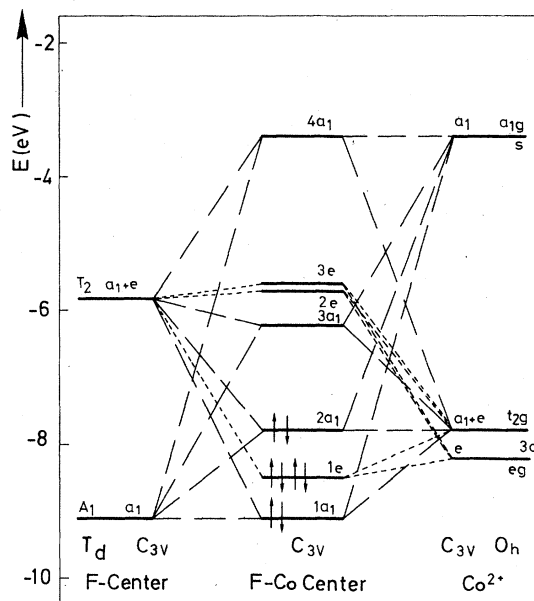

FIG. 8. Calculated energy-level diagram of the F-Co center (central part). The left-hand part shows the energy levels of an isolated F center and the right-hand part gives the energy levels for an isolated Co^{2+} ion in CaF_2.

TABLE III. Single-electron transitions for the F-Co center in RT x-irradiated CaF_2.

Single-electron transition	Calculated energy (eV)	Observed energy (eV)	Predicted polarization	Observed polarization
$(1a_1)^2(1e)^4(2a_1)^2 \rightarrow (1a_1)^2(1e)^4(2a_1)^1(3a_1)^1$	1.6	1.6	σ	σ
$(1a_1)^2(1e)^3(2a_1)^2(2e)^1$	1.9	1.7	σ, π	σ
$(1a_1)^2(1e)^3(2a_1)^2(3e)^1$	2.2	2.3	σ, π	σ
$(1a_1)^2(1e)^4(2a_1)^1(4a_1)^1$	4.4	4.3	σ	σ
$(1a_1)^2(1e)^3(2a_1)^2(4a_1)^1$	4.5	4.9	π	π

E representations and the t_{1g} orbital splits in $A_1 + E$.

In the MWH approximation the matrix elements of the Hamiltonian for the F-Co center are the following: H_{ii} are taken as the energy levels of single electron orbitals in the Co^{2+} and in the F center, while the H_{ij} are taken as

$$H_{ij} = \tfrac{1}{2} S (H_{ii} + H_{jj}),$$
(3)

S being a parameter which accounts for the overlapping of F-center and Co^{2+} orbitals. We have taken a value $S = 0.15$ in the range of those reported in the literature.[28] The calculations are not very sensitive to this value.

Other data we need for the MHW approximation are the relative positions of F-center and Co^{2+} energy levels. Several calculations have been made for the F-center levels in CaF_2. We give three of them in Table I. On the other hand Sabatini et al.[32] have found, using a semiempirical method, a value of 8.2 eV for the ionization energy of Co^{2+} in CaF_2.

With these values we have found, for the Co-F center, using the MWH approximation, the single-electron energy levels given in Table II.

We show in Fig. 8 the energy-level diagram for the F-Co center. The arrows indicate the

occupation of these levels with spin-up and spin-down electrons in the ground-state configuration of the center. This ground state is not paramagnetic.

Finally we give in Table III the transitions in a single-electron model, the calculated and observed energies for each transition, and the calculated and observed polarizations. The agreement is satisfactory if we take into account the roughness of the approximation.

From all this we conclude that x irradiation of Co doped CaF_2 single crystals creates some new absorption bands in 250, 295, 545, 715, and 780 nm which can be associated with a $Co^{2+} - F$-center complex.

X-irradiation at 80 K induces three absorption bands at 240, 280, and 535 nm which are associated with a $Co^{2+} - F$-center complex perturbed by interstitials.

[1]W. Hayes and A. M. Stoneham, in Crystals with the Fluorite Structure, edited by W. Hayes (Clarendon, Oxford, 1974).

[2]A. Muckerji, G. A. Tanton, and J. E. Williams, Phys. Status Solidi 22, K19 (1967).

[3]J. Arends, Solid State Commun. 6, 421 (1968).

[4]A. Smakula, Phys. Rev. 77, 408 (1950).

[5]J. Barile, J. Chem. Phys. 20, 297 (1952).

[6]D. Messner and A. Smakula, Phys. Rev. 120, 1162 (1960).

[7]D. L. Staebler and Z. J. Kiss, Bull. Am. Phys. Soc. 12, 670 (1967).

[8]D. L. Staebler and Z. J. Kiss, Appl. Phys. Lett. 14, 93 (1969).

[9]M. Ikeya, Phys. Status Solidi B 51, 407 (1972).

[10]M. Ikeya and N. Itoh, J. Phys. Soc. Jpn. 29, 1295 (1970).

[11]J. C. Jain and K. Lal, Cryst. Lattice Defects 1, 165 (1970).

[12]W. E. Vehse and W. A. Sibley, Phys. Rev. B 6, 2443 (1972).

[13]L. A. Kappers, S. I. Yun, and W. Sibley, Phys. Rev. Lett. 29, 943 (1972).

[14]K. M. Lee and W. A. Sibley, Phys. Rev. B 12, 3392 (1975).

[15]W. A. Sibley and M. Koumvakalis, Phys. Rev. B 14, 35 (1976).

[16]R. Stahl-Brada and W. Low, Phys. Rev. 113, 775 (1959).

[17]G. Schwotzer and W. Ulrici, Phys. Status Solidi B 64,

K115 (1974).

[18]P. J. Alonso and R. Alcalá, Phys. Status Solidi B <u>81</u>, 333 (1977).

[19]M. Dvir and W. Low, Proc. Phys. Soc. <u>75</u>, 136 (1960).

[20]P. J. Alonso and R. Alcalá (unpublished).

[21]M. M. Zaripov, V. S. Kropotov, L. D. Livanova, and V. G. Stepanov, Sov. Phys.-Solid State <u>9</u>, 2344 (1968).

[22]C. H. Anderson, in *Crystals with the Fluorite Structure*, edited by W. Hayes (Clarendon, Oxford, 1974).

[23]J. M. Barker, in Ref. 22.

[24]A. S. Nowick, in *Point Defects in Solids*, edited by J. H. Crawford and L. M. Slifkin (Plenum, New York, 1972), Vol. 1.

[25]W. Hayes and R. F. Lambourn, J. Phys. C <u>6</u>, 11 (1973).

[26]A. B. Lidiard, in Ref. 22.

[27]R. C. Alig, Phys. Rev. B <u>3</u>, 536 (1971).

[28]M. Wolfsberg and L. Helmholtz, J. Chem. Phys. <u>20</u>, 837 (1952).

[29]E. Loh, J. Phys. C <u>10</u>, 1987 (1977).

[30]R. H. Bartram, A. M. Stoneham, and P. Gash, Phys. Rev. <u>176</u>, 1014 (1968).

[31]R. H. Bartram, A. L. Harmer, and W. Hayes, J. Phys. C <u>4</u>, 1665 (1971).

[32]J. F. Sabatini, E. Salwin, and D. S. McClure, Phys. Rev. B <u>11</u>, 3832 (1975).