

EPR Studies of Photochromic CaF_2

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 (Received 23 July 1970)

The stable photochromic center CaF_2 was found to be a trivalent rare-earth ion (either La, Ce, Gd, Tb, Lu, or Y) with a fluorine-vacancy immediately next to it, plus two electrons making a neutral complex. This stable state can be ionized by irradiation with blue light ($\lambda \leq 4000 \text{ \AA}$), leaving the trivalent rare-earth ion next to a perturbed F center. The electron can be trapped by a rare-earth ion which occupies a cubic site forming a divalent rare-earth ion. Electron paramagnetic resonance (EPR) studies of all three types of centers are discussed.

I. INTRODUCTION

We have made electron paramagnetic-resonance (EPR) studies of the photochromic centers observed¹ in CaF_2 and have found the basic center to be a rare-earth F -center complex. The interaction between the rare-earth ion and F center produces a rich and interesting system which has many features yet to be understood. This is only a preliminary report outlining the basic features as obtained by EPR studies of the ground state. The work was done in close cooperation with the optical studies of Staebler and Schnatterley²; the model which is presented here must be considered a result of this joint effort.

II. BACKGROUND INFORMATION

CaF_2 proved to be a very interesting host for studying the rare-earth ions because it was found that ionizing radiation could convert those trivalent rare-earth ions located at essentially cubic sites into the divalent state.³ Later it was found that nearly all the rare-earth ions in the crystal could be converted⁴ to the divalent state by heating the crystals in a calcium atmosphere similar to the way F centers⁵ are formed in CaF_2 . However, it proved difficult to produce the divalent state in those cases where the ground state of the ion probably is the $4f^n5d$ configuration⁶ which includes the group of ions La, Ce, Tb, and Gd. Reduced crystals which contain these ions show a similar set of absorption bands and reasonably good photochromic properties.

Staebler² has shown that in the stable state (the state toward which the reduced crystals naturally decay or are thermally driven to at 100°C) the optical absorption bands are related to the F -center band and that the perturbations depend on which rare-earth ion is present. He also showed that the photochromic centers have $\langle 111 \rangle$ symmetry, and they can be polarized by suitable optical pumping. This stable state is ionized by irradiation with blue light ($\lambda \leq 4000 \text{ \AA}$) forming two new centers. The primary electron trap is probably trivalent

ions in cubic environments similar to the case when unreduced crystals are exposed to ionizing radiation. Thus, one of the centers formed after irradiation with blue light is the divalent rare-earth ion. The second center is the ionized residue of the stable state which has its own absorption bands. Staebler has shown that this center also has $\langle 111 \rangle$ symmetry.

III. MODEL FOR PHOTOCHROMIC CENTERS

The following model is strongly suggested by the optical data of Staebler and Schnatterley² and confirmed by the EPR results presented in this paper. The stable state is formed by a trivalent rare-earth ion with its $4f^n$ configuration, a fluorine vacancy immediately next to it, and two electrons making the complex neutral. The two electrons probably occupy perturbed F -center-type orbitals in the ground state⁷ which we shall designate as e^2 . When the center is ionized, the electron which is left behind occupies a perturbed F -center orbital next to the trivalent rare-earth ion with its $4f^n$ electrons. The ionized electron is captured by some trap, which in some cases has been shown to be a trivalent ion in an essentially cubic environment.

The reverse photochromic process involves removing the electron from the divalent rare earth presumably of $4f^n5d$ configuration, or whatever trap the electron is in, with longer-wavelength radiation (usually $\sim 5800 \text{ \AA}$). Our understanding of the electron trap is incomplete, but we do feel that the lack of suitable electron traps is probably a limiting factor in the switching process since 100% conversion of the stable centers to ionized centers is not obtained.

To facilitate the discussion, we will refer to the stable and ionized centers as $\text{Re}^{3+}\text{-}F'$ and $\text{Re}^{3+}\text{-}F$, respectively. That is, the stable state can be considered as an F' center next to a trivalent rare-earth ion and the ionized state as an F center next to a trivalent rare-earth ion. Under the notation of Gourary and Adrian,⁸ the stable and ionized centers would be written as $[-12e|\text{RE}^{3+}]$ and $[-1e|\text{RE}^{3+}]$, respectively. Their notation is based on the form:

TABLE I. Ground electron configurations of photochromic centers in CaF_2 . Those configurations underlined with solid lines have been identified by EPR resonance; those with dashed lines should show EPR resonance, but they have not been identified at this time. The others should not show any resonances.

| Trivalent ion | Stable center | Ionized center | Re^{2+} (trapped electron) |
|--------------------------------|---------------------------------|-------------------------------|-------------------------------------|
| La <u>$4f^0$</u> | <u>e^2</u> | <u>e</u> | <u>$5d$</u> |
| Ce <u>$4f^1$</u> | <u>$4f-e^2$</u> | <u>$4f-e$</u> | <u>$4f5d$</u> (Ref. 9) |
| Gd <u>$4f^7$</u> | <u>$4f^7-e^2$</u> | <u>$4f^7-e$</u> | <u>$4f^75d$</u> |
| Tb <u>$4f^8$</u> | <u>$4f^8-e^2$</u> | <u>$4f^8-e$</u> | <u>$4f^85d$</u> |
| Lu <u>$4f^{14}$</u> | <u>$4f^{14}-e^2$</u> | <u>$4f^{14}-e$</u> | <u>$4f^{14}5d$</u> |
| Y <u>$4d^0$</u> | <u>e^2</u> | <u>e</u> | <u>$4d$</u> (Ref. 10) |

[missing ions|trapped particles|added ions]. For the ground electron configurations, we use the notation $4f^n-e^2$ and $4f^n-e$ for the stable and ionized states, respectively. $4f^n$ is the number of $4f$ electrons of the trivalent impurity ion and e^n is the number of electrons trapped by the fluorine vacancy.

Table I shows the electron configurations of the basic photochromic centers this model predicts for the various rare earths and the yttrium ion. Underlined are those centers identified by EPR resonance whose properties will be the main subject of the remainder of this paper. Although all the possible resonances have not been observed or identified, there is sufficient data for us to feel confident in the correctness of the model.¹¹

IV. EXPERIMENTAL PROCEDURES

Our initial experiments into the nature of these centers were made by monitoring the circular dichroism of the photochromic absorption bands while simultaneously irradiating the crystal with X-band ($\sim 0.3 \text{ cm}^{-1}$) microwaves. When the external magnetic field tuned one of the Zeeman transitions in the ground state onto resonance a change in the circular dichroism was usually observed. This procedure in the case of $\text{CaF}_2:\text{Ce}$ enabled us to find weak resonances only associated with the stable state in the midst of many resonances due to ordinary Ce^{3+} at a variety of sites. This type of double-resonance experiment also gave the first clue about the existence and properties of the ionized state associated with La, which, because of its very long relaxation time ($T_1 \sim 100 \text{ sec}$ at 1.3°K), and unusual width ($\sim 1.6 \text{ kG}$) had gone unnoticed in ordinary EPR experiments. After finding which resonances were associated with the absorption bands in this way for La and Ce, the detailed data were then taken using a standard EPR apparatus. Further identification of the resonances with the photochromic centers was provided by measuring the effects of switching and measuring the amount

of heating of the spins produced by simply optically pumping into the photochromic absorption bands. Another very useful identifying feature comes from the Staebler-Schnatterly² observation that pumping for $\frac{1}{2} \text{ h}$ at room temperature along a $\langle 111 \rangle$ axis with blue radiation tended to align the ionized centers along that axis. This provided a method for increasing the strength of the EPR resonances of one trigonal site over the other sites; in the case of La, where the lines overlap one another, this helped to pull out the details of the angular dependence of the resonances.

The majority of the crystals were grown at RCA Laboratories, using a modified gradient-freeze technique. The crystals were grown in an helium atmosphere containing approximately 10% HF gas. The concentration of the dopants varied between 0.003 and 0.3 mole %. All of the data presented in this paper were taken using crystals which were reduced by heating in a calcium atmosphere.

V. EXPERIMENTAL RESULTS

A. Lanthanum

Trivalent lanthanum has the closed-shell configuration of xenon; so in our model the stable state has the two-electron configuration e^2 . No EPR resonances are expected, and very few extraneous resonances due to other impurities are observed with the crystal in the stable state. After ionizing this center at room temperature or at 1.3°K , the divalent-lanthanum resonance first observed by Hayes and Twidell appears.¹² In addition, there appears a new spectrum shown in Figs. 1–3, also intimately associated with the La nucleus with its nuclear spin of $\frac{7}{2}$ since it has eight major hyperfine components. The data were taken at 18 GHz using a standard EPR apparatus with superheterodyne detection and field modulation. The rf power, however, was set at a mildly saturating level ($\sim 1 \mu\text{W}$) and the dc magnetic field was swept at about 1 kG/min to produce the absorptive type of signal shown

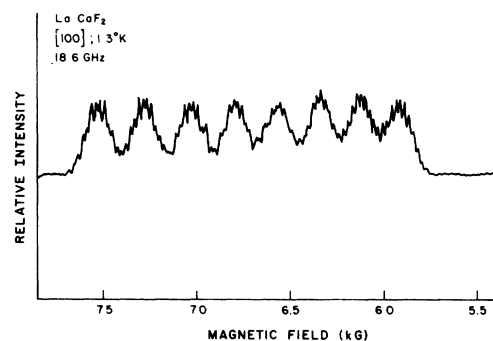


FIG. 1. EPR spectrum of the ionized center in photochromic $\text{CaF}_2:\text{La}$, H along the $[100]$ direction.

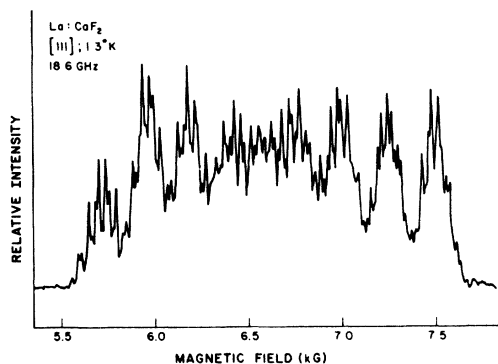


FIG. 2. EPR spectrum of the ionized center in photochromic CaF_2 :La, H along the [111] direction.

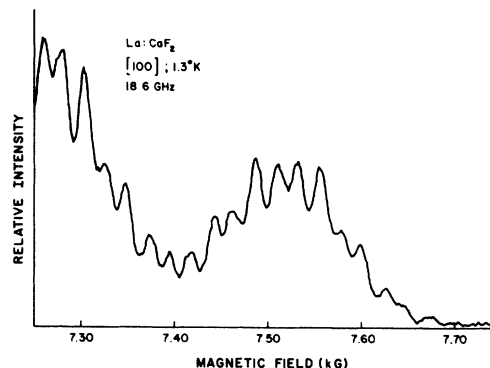


FIG. 3. Detail of the high-field end of the spectrum shown in Fig. 1.

rather than the usual derivative curve. This occurs because the saturating rf eats away at this inhomogeneously broadened line as the sweep proceeds.

The complex hyperfine structure due to the neighboring fluorine nuclei makes the angular dependence of the resonance somewhat obscure. Fortunately, with the magnetic field along a [111] axis one La hyperfine line (and its fluorine fine structure) associated with the sites parallel to that direction becomes almost completely resolved on the low-field end of the spectrum (see Fig. 2). Also, after polarizing the centers by optical pumping at room temperature, one site could be populated three times more than the other sites. This made it possible to identify the symmetry as trigonal and to obtain reasonably accurate values for the parameters of the effective spin Hamiltonian

$$H = g_{\parallel}\beta H_{\parallel}S_z + g_{\perp}\beta H_{\perp}(S_x + S_y) + A_{\parallel}I_zS_z + A_{\perp}(I_xS_x + I_yS_y). \quad (1)$$

The parameters are given in Table II along with those for La^{2+} and the F center in CaF_2 .

A preliminary analysis of the detailed fluorine hyperfine structure was not sufficient to give any quantitative details about the interaction between the electron and the neighboring fluorine nuclei.

The problem is complex since the photochromic center has ten nearest-neighbor fluorine ions which all apparently contribute to the structure. For some comparison of the interactions of the various centers with the fluorine nuclei, an approximate linewidth obtained by averaging over the fluorine hyperfine structure is given in Table II.

This broad resonance has been shown to be directly associated with the ionized center in many ways. As we have mentioned, it appears after ionizing the stable center; it has $\langle 111 \rangle$ symmetry, and the sites can be preferentially populated. The center was directly correlated with the photochromic bands by monitoring changes in the circular dichroism associated with the strong absorption bands as a function of magnetic field while the crystal was being saturated with microwave radiation. Finally, we measured an excitation curve (Fig. 4) for optically pumping the ground-state spins as a function of wavelength and obtained a pump band which is in good agreement with the optical data of Staebler and Schnatterley.²

The large hyperfine constants, and the long spin relaxation time ($T_1 \sim 100$ sec at 1.3°K) argue that this resonance is associated with an s type of electron rather than the d electron observed for La^{2+} . Although the hyperfine interaction with the La nu-

TABLE II. Parameters of spin Hamiltonian for La^{3+} , $\text{La}^{3+}\text{-F}$, $\text{Lu}^{3+}\text{-F}$, and the F center in CaF_2 . $\Delta\nu$ is the approximate linewidth of a single resonance line due to the neighboring fluorines.

| Ion | g_{\parallel} | $\frac{g_{\parallel} - g_{\perp}}{g_{\parallel}}$ | $\frac{1}{3}(g_{\parallel} + g_{\perp})$ | A_{\parallel} (10^{-4} cm^{-1}) | $\frac{A_{\parallel} - A_{\perp}}{A_{\parallel}}$ | $\Delta\nu$ line-width (G) |
|---------------------------|---------------------|---|--|--|---|----------------------------------|
| La^{2+} | 2.00 ± 0.01 | 0.048 | 1.937 ± 0.002 | 37 ± 9 | -0.67 | 30 |
| $\text{La}^{3+}\text{-F}$ | 1.99 ± 0.01 | 0.017 | 1.97 ± 0.01 | 237 ± 20 | 0.17 | 120 |
| $\text{Lu}^{3+}\text{-F}$ | 2.0 ± 0.05 | | | 300 ± 40 | | 280 |
| F center (5) | 1.9978 ± 0.0005 | 0 | 1.9978 | ... | ... | 200 |

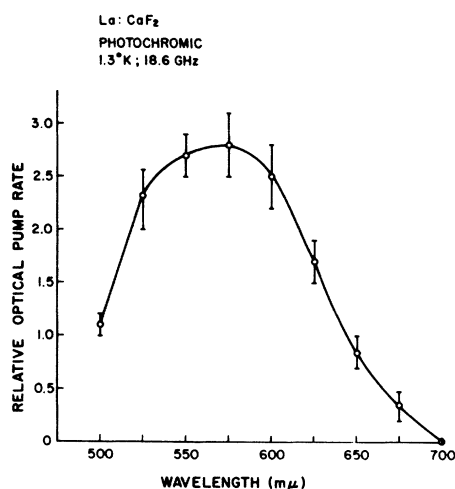


FIG. 4. Wavelength dependence of the relative spin heating induced by optically pumping the ionized center in photochromic $\text{CaF}_2:\text{La}$.

cleus is over twice as large as that observed for the d electron, we do not believe it is large enough for this resonance to be considered as a simple $6s$ electron in La^{2+} . The La III optical spectrum gives a hyperfine splitting of 1.09 cm^{-1} or a hyperfine interaction constant A of 0.27 cm^{-1} for the $6s^2 S_{1/2}$ level¹³ which is over ten times larger than that observed.

The g value and its anisotropy have been qualitatively explained by Alig.⁷ He found that the major contribution to the anisotropy comes from orthogonalizing the F -center wave function to the core states of the neighboring trivalent rare-earth ion, which has large spin-orbit-coupling parameters.

The photochromic center and the La^{2+} center were also observed using double resonance. That is, the change in the circular dichroism signal associated with the absorption bands is recorded while microwave power is applied to the crystal. The double-resonance detection of the La^{2+} center was particularly strong and is shown in Fig. 5.

B. Lutecium

Since trivalent lutecium has the $4f^{14}$ closed shell for its ground configuration, the ionized state in photochromic $\text{CaF}_2:\text{Lu}$ should also show a resonance similar to La . The two situations are also identical in that Lu^{175} is the only stable isotope and it has the same nuclear spin of $\frac{7}{2}$ as La . Also, the nuclear moments of La and Lu are similar, $+2.778$ ¹⁴ and $+2.23$,¹⁵ respectively. In Fig. 6 we show the resonance observed for the ionized state and the parameters have been given in Table II. Since the fluorine hyperfine structure is less distinct than it is for La and the over-all fluorine interaction in-

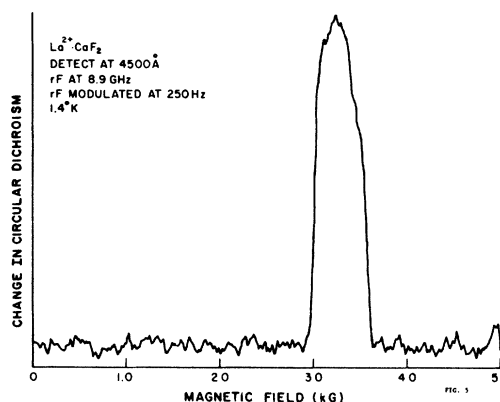


FIG. 5. EPR spectrum of the ground state of divalent lanthanum detected optically.

creased more than the corresponding Lu hyperfine interaction the parameters were obtained with much less accuracy. The one line which separates along the $[111]$ direction in the La case does not quite become sufficiently resolved for Lu to make meaningful deductions about the anisotropy factors other than to show they are similar for the two centers.

The linewidths due to interactions with the fluorine nuclei might indicate that the $\text{La}^{3+}-\text{F}$ wave function is more compact than the isolated F centers. Alig⁷ has shown that the neighboring fluorine move in closer for $\text{Lu}^{3+}-\text{F}$ than for $\text{La}^{3+}-\text{F}$, which helps explain the larger fluorine hyperfine interactions in this case. The Lu hyperfine interaction is larger for other reasons since the atomic spectra¹⁶ of doubly ionized lutecium Lu III shows the hyperfine interaction for the $6s^2 S_{1/2}$ level is 0.4 cm^{-1} as compared to 0.27 cm^{-1} for La III . Note, the ratio of $0.4/0.27 = 1.48$, while the ratio of the measured hyperfine constant for the photochromic centers is $300/237 = 1.27$. No resonance due to Lu^{2+} was identified.

C. Terbium

The ionized state of photochromic $\text{CaF}_2:\text{Tb}$ has for its ground configuration $4f^8-e$. Because of the

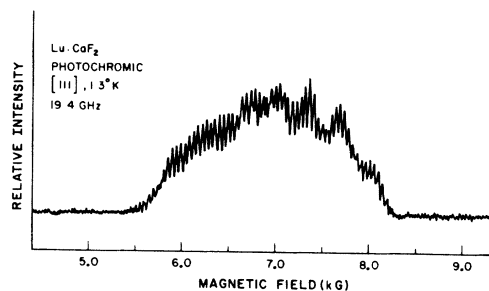


FIG. 6. EPR spectrum of the ionized center in photochromic $\text{CaF}_2:\text{Lu}$.

coupling of the F -center electron with the $4f^8$ electrons, the EPR spectrum is completely different from that of the ionized state for La and Lu. A set of lines with trigonal symmetry is observed each of which are split into four hyperfine components due to the nuclear spin of $\frac{3}{2}$ (Fig. 7). The fluorine hyperfine interactions appear to be small since no fine structure is observed. The linewidths of the resonance lines are comparable to the widths of the Tb^{3+} resonances found in the crystal. The fitted parameters to the effective spin Hamiltonian are given in Table III, along with two Tb^{3+} resonances which have been observed in these crystals and reported previously.¹⁷ The main features we have used to identify this new center with the ionized state of the photochromic center is that it increases after irradiation with blue light and disappears with red irradiation. It could be polarized so that the intensity of the resonances due to the centers along one of the $\langle 111 \rangle$ axes were an order of magnitude stronger than for the other sites, which was a much higher degree of polarization of the sites than was obtained with La or Lu.

The g and A values of this center can be understood in the coupling scheme used for the $4f^n 6s$ configuration as outlined by Wybourne.¹⁸ That is, the $^2S_{1/2}$ state of the outer electron is coupled to the lowest spin-orbit component (7F_6) of the $4f^8$ configuration to form states with total angular momentum values J of $\frac{13}{2}$ and $\frac{11}{2}$. The trigonal field then splits these states into many levels characterized by crystal-quantum numbers μ . Since g_{\parallel} is much larger than g_{\perp} , the ground state must be primarily $\mu = \pm \frac{1}{2}$ in character. An admixture of $\mu = \pm \frac{3}{2}$ character is then needed to fit the g values exactly. The details of the calculations for the g and A values are in the Appendix. The results are consistent with the ground state arising from the $J = \frac{13}{2}$ manifold and not $\frac{11}{2}$. Also, the value of the

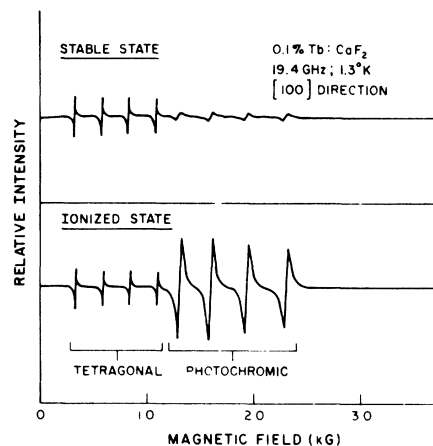


FIG. 7. EPR spectrum of the ionized center in photochromic $\text{CaF}_2:\text{Tb}$, H along the $[100]$ direction.

hyperfine constant A can be best fitted using a value for the hyperfine constant of the trapped electron which is that observed for the Lu^{3+} - F center. The calculations show that the contribution of the F -center electron to the reduced matrix elements of the g and A tensor is multiplied by a factor of $\frac{1}{13}$, which makes its effects small compared to the contribution from the $4f^8$ electrons. This is also true for the fluorine hyperfine interactions, which helps explain the lack of fine structure in the spectra.

The ground state of Tb^{3+} charge compensated by oxygen is characterized by maximum values in the quantum number μ , while the Tb^{3+} - F -center complex described above is characterized by minimum values of μ . This suggests that the distortion in the latter case is due to a net positive charge at the vacancy.

It should be possible to observe EPR resonances in the stable state associated with photochromic terbium. As will be shown for cerium in Sec. VD, the two electrons (e^2) are tightly bound and the $4f^n$ electrons of the rare-earth ion experience a simple weak trigonal distortion. The distortion for the cerium resonance is in the same direction as that produced by oxygen compensation. The stable state should therefore have resonances which appear like ordinary Tb^{3+} with a weak trigonal distortion. The ground state of Tb^{3+} in CaF_2 consists of the $\mu = \pm 6$ components of the 7F_6 spin-orbit manifold. The ground doublet is split by higher-order terms in the crystal field potential. We have made EPR measurements at 19 and 35 GHz and have not observed any resonances which can be attributed to the stable state. With the photochromic centers in the stable state, the paramagnetic circular dichroism at 6100 Å was found to be large. No resonances were observed using optical detection at 6100 Å while the crystal was being irradiated with

TABLE III. Parameters of spin Hamiltonian for three centers in Tb-doped CaF_2 .

| Center | g_{\parallel} | g_{\perp} | A_{\parallel} (10^{-4} cm^{-1}) | A_{\perp} (10^{-4} cm^{-1}), (GHz) | Δ Zero-field splitting |
|----------------------|-----------------|-------------|--|---|-------------------------------------|
| Tb^{3+} - F | | | | | |
| Trigonal symmetry | < 0.6 | 9.076 | | 1172 | 0 |
| photochromic | | ± 0.008 | | ± 7 | |
| Tb^{3+} | | | | | |
| Trigonal symmetry | 17.28 | < 0.25 | 2033 | | 31.67 |
| O^2 compensation | ± 0.01 | | ± 3 | | ± 0.02 |
| (Ref. 16) | | | | | |
| Tb^{3+} | | | | | |
| Tetragonal symmetry | 17.768 | < 0.25 | 2087 | | 5.134 |
| F^- compensation | ± 0.020 | | ± 3 | ... | ± 0.006 |
| (Ref. 16) | | | | | |

microwaves at 19 or 35 GHz. However, the magnetic field dependence of the circular dichroism associated with the absorption bands of the stable state at 1.3°K indicates that the zero-field splitting is certainly not larger than 2 kT. The magnetic field dependence of the circular dichroism is due to a center which has a large g value ($g \sim 9.4$ for the [110] direction). Since the magnitude of the transition probability varies as $(\Delta/\nu)^2$, where Δ is the zero-field splitting and ν the applied frequency, resonances due to the stable state at frequencies of 19 or 35 GHz would be weak and possibly not observable if the zero-field splitting was very small.

No resonances associated with Tb^{2+} were identified.

D. Cerium

The stable state of the photochromic center associated with cerium has the electron configuration $4f-e^2$. The (e^2) electrons are coupled strongly together so the $4f$ electron is observed by itself and the resonances appear like a new Ce^{3+} center in CaF_2 with trigonal symmetry. However, the resonances are clearly associated with the photochromic center for the following reasons: (i) The intensity of the resonances are reduced after irradiation with blue light and are increased after red. (ii) The lines were first found by monitoring changes in the circular dichroism of the photochromic absorption bands while saturating the crystal with rf radiation (Fig. 8). (iii) One of the $\langle 111 \rangle$ sites could be preferentially populated by the procedure used for the other centers.

The resonance observed for g_{\parallel} is shown in Fig. 9 where, similar to other Ce^{3+} resonances, a set of satellite lines due to the simultaneous flip of neighboring fluorine nuclei are observed.¹⁹ The g values are given in Table IV along with those for Ce^{3+} in trigonal sites due to oxygen compensation and interstitial fluoride compensation.^{20,21}

In Fig. 10, we show the wavelength dependence of the change in the circular polarization signal as

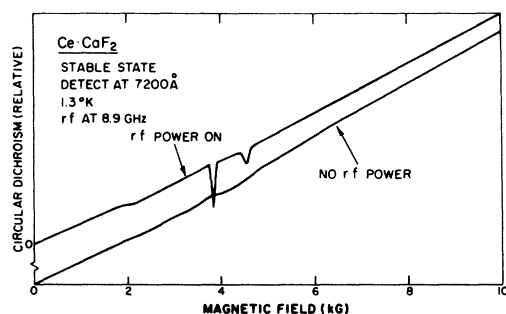


FIG. 8. Optical detection of the EPR spectrum of the stable state in photochromic $\text{CaF}_2:\text{Ce}$.

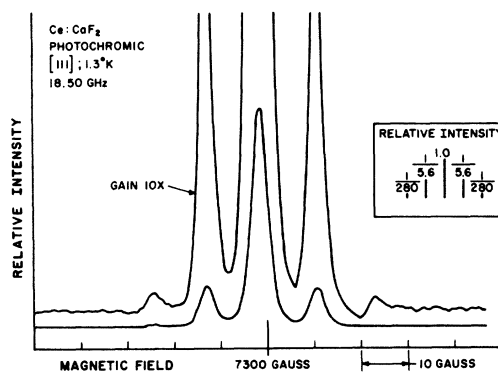


FIG. 9. EPR spectrum of the stable state of photochromic $\text{CaF}_2:\text{Ce}$.

obtained by irradiating the crystal with microwave radiation. The data were obtained by first fixing the magnetic field at an EPR line. The change in the absorption of circularly polarized light by the sample was then detected with a lock-in amplifier while the crystal was being irradiated with modulated microwave radiation.

The $^2F_{5/2}$ spin-orbit manifold of the $4f$ electron is split in a cubic potential into two levels $G_{3/2}(\Gamma_8)$ and $E_{5/2}(\Gamma_7)$. In CaF_2 , the quartet state is lowest. The quartet state for the $J = \frac{5}{2}$ manifold for the z axis taken as the $[111]$ direction can be characterized by the wave functions

$$|\pm \frac{3}{2}\rangle \text{ and } \pm \sqrt{\frac{4}{9}} |\pm \frac{1}{2}\rangle \pm \sqrt{\frac{5}{9}} |\mp \frac{5}{2}\rangle.$$

The trigonal distortion splits the quartet into two doublets. The experimental g values of the ground doublet are $g_{\parallel} = 1.803$ and $g_{\perp} = 1.76$ which are close to those expected for a mild perturbation of the $(\pm \frac{1}{2}, \mp \frac{5}{2})$ doublet of the quartet state. A small admixture of the $E_{5/2}$ level into the ground state by

TABLE IV. g values for different centers in Ce-doped CaF_2 .

| Center | g_{\parallel} | g_{\perp} | $\frac{1}{3}(g_{\parallel} + 2g_{\perp})$ |
|--|-----------------|-------------|---|
| $\text{Ce}^{3+} - \text{F}^{\text{I}}$ | | | |
| Trigonal symmetry | 1.803 | 1.176 | 1.39 |
| photochromic | ± 0.004 | ± 0.002 | |
| Ce^{3+} | | | |
| Trigonal Symmetry | 2.38 | < 0.1 | 0.79 |
| F^- compensation (Ref. 19) | ± 0.03 | | |
| Ce^{3+} | | | |
| Trigonal symmetry | 3.673 | < 0.3 | 1.23 |
| O^{2-} compensation (Ref. 20) | ± 0.002 | | |

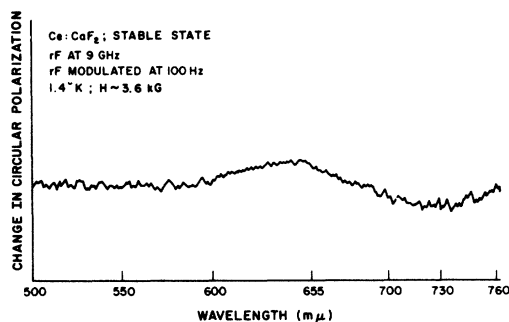


FIG. 10. Wavelength dependence of the paramagnetic circular dichroism of photochromic $\text{CaF}_2:\text{Ce}$ detected by modulating the ground-state population with microwave radiation.

the trigonal field makes the agreement even better. If there is no admixture of the $^2F_{7/2}$ spin-orbit component, then the trace of the g tensor is 1.43, which is in good agreement with the observed value of 1.39.

The linewidth of the photochromic center, as measured peak to peak on a derivative curve, for the singlet resonance line along the $[111]$ direction was 4.0 G at 4.2°K and 18.86 GHz. The linewidth was measured along the $[111]$ direction as a function of temperature and was found to broaden very rapidly. The width at 1.25°K was 47 G. The increase in linewidth converted to megacycles can be fitted by the equation

$$\Delta\nu = 4.8 \times 10^5 e^{-90/T} \text{ MHz.}$$

According to the Orbach relaxation process, this temperature-dependent linewidth suggests that the other doublet state of the quartet lies 90°K or 63 cm^{-1} above the ground state.

The data for the Ce photochromic stable state are described by a large cubic field potential with a small negative trigonal distortion. The $\text{Ce}^{3+}\text{-O}^{2-}$ compensated center is described by a very large negative trigonal distortion so that the ground state is simply the $\pm \frac{5}{2}$ part of the $^2F_{5/2}$ manifold. Thus, the sign of the trigonal distortion in the stable state is the opposite of that observed for the ionized state of the terbium F -center complex.

There is no reason to expect the ionized state to necessarily show EPR resonances. Following terbium we would expect the F -center electron to couple to the $^2F_{5/2}$ spin-orbit component of the $4f$ electron to form states of $J = 2$ and 3. In either case, if the sign of the trigonal distortion is the same as for the ionized state of terbium, we would then expect the single $\mu = 0$ state to be the ground state.

There should be resonances for Ce^{2+} since the optical data and theoretical calculations show that the ground state is a triplet with $g \approx 1.25$.⁹ It is

very likely that this line is extremely broadened by inhomogeneous strains or the Jahn-Teller effect. It has eluded attempts by us to find it by ordinary EPR and by double resonance. In the double-resonance experiments the circular dichroism associated with the divalent-cerium optical-absorption bands was monitored while the crystal was irradiated with microwaves at 9 and 19 GHz.

E. Gadolinium

There is every reason to expect that both the stable state and ionized state associated with Gd should show EPR resonances. The stable state would consist of the $^8S_{7/2}$ component of the $4f^7$ electrons under the two electrons (e^2) and should appear as a new Gd^{3+} resonance with trigonal symmetry. The ionized state would be characterized by the $J = 3$ and 4 states resulting from the coupling of the F -center electrons with the $^8S_{7/2}$ state. In this case, because of the S character of both states the effect of the trigonal crystal field will be small and so, even though the ground state in zero field will be the $\mu = 0$ level, the other levels should be close enough to be readily observable by EPR.

A sample of $\text{CaF}_2:\text{Gd}$ was studied at 1.3°K and 19 GHz. Many resonance lines were observed between 0 to 10 kG and a large number of these lines switched with optical radiation. The large number of resonance lines and their complexity makes this case one which requires much more careful study than the others in order to sort out all the resonances.¹¹

F. Yttrium

A few experiments were done on CaF_2 crystals grown with 0.3% and 0.02% YF_3 and then colored as were the other crystals described in this paper. All the samples contained a number of resonances near $g = 2$ which made it difficult to clearly identify the switching centers. Figure 11 shows the EPR

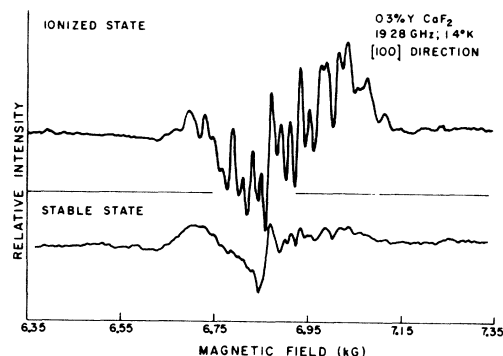


FIG. 11. EPR spectrum of photochromic $\text{CaF}_2:\text{Y}$ in both the stable and switched states.

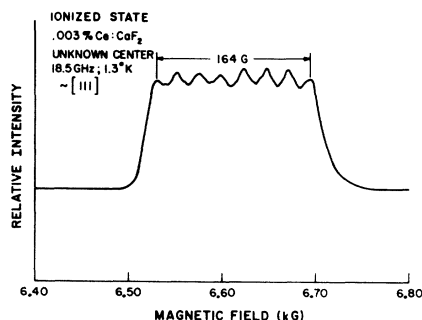


FIG. 12. EPR spectrum of an unidentified trapped electron in photochromic $\text{CaF}_2:\text{Ce}$.

spectra observed in the stable and ionized states. There is an indication in the switched state of a resonance about 170 G wide with complex fluorine hyperfine structure somewhat like that observed in the ionized states for the La and Lu photochromic centers. This resonance line has a g value of 1.99 ± 0.01 and a spin-lattice time of a few seconds.

The 100% abundant yttrium isotope Y^{89} has a nuclear spin of $\frac{1}{2}$, but a very small nuclear moment (-0.1368) compared to that of La or Lu. Thus the hyperfine splitting of the F -center resonance due to the Y nuclei is expected to be much smaller than the broadening due to the fluorine hyperfine interactions. In addition there are the four magnetic inequivalent sites which add to the confusion. The net effect is to make any useful measurements of the Y F -center complex very difficult.

G. Electron Traps

The electrons freed upon ionizing the stable centers are trapped at a moderately deep level in order for these materials to be good photochromics. We have identified most clearly in the lanthanum case that the electron combines with La^{3+} ions at cubic sites to form La^{2+} . Optical studies have shown in the case of Ce that again the free electron forms a divalent rare-earth ion.² At the present time, we have not observed any EPR resonances which could be positively identified with the trapped electron for Tb, Gd, Lu, and Y. However, we have generally noted changes in resonances around $g = 2$ upon switching the crystals which may be due in part shallow traps which are stable at 1.3°K .

In one particular sample which contained 0.003% Ce, a distinct resonance was observed which can be attributed to the trapped electron. In this particularly clean crystal, one-third of the cerium was found to be the stable photochromic center, while the remaining cerium was Ce^{3+} in tetragonal sites. Measurements showed at room temperature and at 1.3°K that about 10% of the stable photochromic centers could be switched. This means

impurities with concentrations as low as 10^{16} ions cm^3 could form the electron trap. The resonance occurs at $g = 2.0$, it is isotropic, and has a relaxation time of several seconds at 1.3°K . The eight equally spaced hyperfine components show it is associated with an element which consists 100% of an isotope with spin $\frac{7}{2}$. The total width of the resonance however is only 160 G as compared to the 1.6 kG for the La^{3+} F -center resonance. The possibilities besides La and Lu are Co, Sc, Ta, Nb, or Cs. We favor the model that this trap is a F center next to Cs.

VI. SUMMARY

These EPR studies provide the most convincing data for the correctness of the model of the photochromic centers in rare-earth-doped calcium fluoride. The stable state has only been positively identified in the cerium-doped samples, but it should be possible to identify this center for gadolinium- and terbium-doped samples using EPR techniques. The ground state of the stable center with its $4f^n-e^2$ configuration should be properly viewed according to Alig's calculation⁷ as a trivalent rare-earth ion next to a F' type of center (two electrons centered in the vacancy) rather than a divalent rare-earth ion next to an F center. It could result when an M center²² (two F centers) combined with a trivalent rare-earth ion charge compensated by an interstitial fluoride ion.

Ionizing the stable photochromic center with short-wavelength light ($\lambda \leq 4000 \text{ \AA}$) leaves a perturbed F center next to the trivalent rare-earth ion ($4f^n-e$), which has been clearly identified for La-, Lu-, and Tb-doped samples. Because of experimental difficulties it was not identified for Y and Gd samples. The electron, which is freed, can be trapped on trivalent rare-earth ions at cubic sites forming the divalent rare-earth ion, which probably has the ground configuration $4f^n5d$ for these rare-earth ions.

With our present understanding of these centers the $5d$ electron does not play an important role in stabilizing the ground-state energy. So probably the other rare-earth ions also form similar centers and our observations in a γ -irradiated $\text{BaF}_2:\text{Tm}^{2+}$ crystal might be an example.²³ We observed that short-wavelength excitation ($\lambda \leq 4000 \text{ \AA}$) could convert a substantial part of the cubic EPR spectrum of divalent thulium into a trigonal spectrum, and long-wavelength excitation could convert it back. This behavior could be explained if the divalent thulium at cubic sites could be ionized with the blue light leaving nonparamagnetic trivalent thulium at the cubic sites. The electron could then be trapped at sites where the divalent thulium ions are next to an F center. The resulting center would be a paramagnetic center ($4f^{13}-e^2$) with an EPR

spectrum of divalent thulium with a trigonal distortion. The sign of the distortion would be that due to a negative charge next to the divalent thulium, which is that observed.

If this explanation is correct, then those divalent rare-earth ions with the ground configuration of $4f^n$ in the crystal keep the same configuration when an F center is moved next to them. This is in contrast to those divalent rare-earth ions with the $4f^n 5d$ configuration where the $5d$ electron moves onto the vacancy with the F center. Using this as a guide, there should be a number of other centers yet to be observed.

ACKNOWLEDGMENTS

We are particularly indebted to Dr. D. L. Staebler for supplying a wealth of information on this subject prior to his publication. We appreciate the crystals of Ce-doped CaF_2 supplied by Dr. R. C. Duncan. The many interesting discussions with Dr. R. Alig were very helpful. We thank J. Beherall for his able experimental assistance.

APPENDIX: CALCULATIONS OF g AND A FOR Tb^{3+} - F CENTER

The ionized state of this center can be considered as a trivalent rare-earth ion with its $4f^8$ core coupled to an s -like electron. Following Wybourne,¹⁸ the energy levels that result from the addition of an s electron to the low-lying states of the f^n configurations exhibit close $J_1 j$ coupled states. The $^2S_{1/2}$ level of the electron of the F center is coupled to the 7F_6 manifold of the $4f^8$ core of the terbium to form states of total angular momentum $J = \frac{11}{2}$ and $\frac{13}{2}$. A state for this coupling scheme is written as $\langle (S_1 L_1) J_1; (s l) j; J |$. The trigonal crystal field potential due to the fluorine vacancy and the trapped electron splits these levels into states which are characterized by the magnetic quantum number μ .

Because $g_1 \gg g_n$, the ground state must be primarily of $\mu = \pm \frac{1}{2}$ character. The perpendicular splitting factor g_1 is defined by

$$g_1 = (J + \frac{1}{2})g(J_1 j J), \quad (\text{A1})$$

where

$$J = J_1 \pm \frac{1}{2},$$

$$g(J_1 j J) = g(S_1 L_1 J_1) \pm \frac{g(s l j) - g(S_1 L_1 J_1)}{2J_1 + 1}, \quad (\text{A2})$$

$g(S_1 L_1 J_1)$ and $g(s l j)$ are the LS -coupling Lande g factors for the 7F_6 manifold of terbium and the trapped electron, respectively. $g(S_1 L_1 J_1) = 1.50$ and $g(s l j) = 2.00$. For the $\mu = \pm \frac{1}{2}$ states, $g_1 = 8.76$ for the $J = \frac{11}{2}$ state and $g_1 = 10.75$ for the $J = \frac{13}{2}$ state. The value of $g_1 = 8.76$ for the $J = \frac{11}{2}$ state is deceptively close to the measured value of 9.076. Admixtures of other components within the same J

manifold allowed by the trigonal field can only reduce the value from 8.76. To increase the value to fit the experimental value of 9.076 a substantial admixture of the $\mu = \pm \frac{1}{2}$ states within the $J = \frac{13}{2}$ manifold is required. To fit the experimental result $g_n < 0.6$, a further increase in the number of admixed states is required. Therefore, we have rejected the possibility of the $J = \frac{11}{2}$ manifold since the $J = \frac{13}{2}$ manifold by itself is sufficient to fit all the data.

To fit g values, we take the wave function,

$$\left(\frac{1}{1 + \alpha^2} \right)^{1/2} \left[\left| \frac{13}{2}; \pm \frac{1}{2} \right\rangle \pm \alpha \left| \frac{13}{2}; \mp \frac{5}{2} \right\rangle \right]. \quad (\text{A3})$$

Fitting $g_1 = 9.076$ requires that $\alpha^2 = 0.185$ which gives $g_n = 0.097$. This calculated value for g_n is within the experimental result of $g_n < 0.6$. The ground state also has admixtures of the states $\mu = \pm \frac{7}{2}$, $\mp \frac{11}{2}$ and $\pm \frac{13}{2}$, but from the limited experimental data the above simple description is adequate.

To understand the hyperfine splitting, we may express the reduced matrix element of the magnetic hyperfine interaction in $J_1 j$ coupling for the $f^n s$ configuration as

$$A_R(J_1 j J) = A_R(S_1 L_1 J_1) \pm \frac{a_s(s l j) - A_R(S_1 L_1 J_1)}{2J_1 + 1}, \quad (\text{A4})$$

where

$$a_s = \frac{16}{3} \pi \beta \beta_N (\mu_I / I) |\psi(0)|^2,$$

$$A_R(S_1 L_1 J_1) = 2\beta \beta_N (\mu_I / I) \langle r^{-3} \rangle \langle J_1 || N || J_1 \rangle.$$

a_s is the hyperfine interaction of the outer electron and $A_R(S_1 L_1 J_1)$ is the reduced hyperfine interaction for the 7F_6 level of trivalent terbium. If the ground state belongs primarily to one J manifold, the values for A_R can be obtained from the experimental values of g and A using

$$A_R(J) = (A_{\text{exp}} / g_{\text{exp}}) g(J), \quad (\text{A5})$$

where $g(J)$ is given by Eq. (A2). A value of $A_R \times (S_1 L_1 J_1) = 177 \times 10^{-4} \text{ cm}^{-1}$ can be obtained from the experimental data on Tb^{3+} in tetragonal and trigonal sites. From the experimental data on the photochromic center given in Table III, $A_R(J) = 198$ and $189 \times 10^{-4} \text{ cm}^{-1}$ for the $J = \frac{13}{2}$ and $\frac{11}{2}$ states, respectively. Using Eq. (A4) to obtain a value for a_s , we find that $a_s = 450$ and $21 \times 10^{-4} \text{ cm}^{-1}$ for the $J = \frac{13}{2}$ and $\frac{11}{2}$ states, respectively.

We can obtain an estimate of a_s for terbium by scaling the values from data on the La and Lu centers. Thus, we obtain

$$a_s(\text{Tb}) = \frac{\mu_{\text{Tb}}}{\mu_x} \frac{I_x}{I_{\text{Tb}}} a_s(x), \quad (\text{A6})$$

where μ and I are the respective nuclear magnetic

moments and nuclear spins, while $a_s(x)$ is the hyperfine constant for either La or Lu. Using the accepted values of μ and I and the data in Table II for $a_s(x)$, we find that the derived value for $a_s(\text{Tb})$ is 303 and $476 \times 10^{-4} \text{ cm}^{-1}$ obtained using the data for La and Lu, respectively. These values are in

good agreement with the value of $450 \times 10^{-4} \text{ cm}^{-1}$ obtained from the data on the Tb center provided the $J = \frac{13}{2}$ manifold is taken as the ground state. Therefore, we conclude from both the g and A values that the ground state of the ionized center in Tb doped CaF_2 arises from the $J = \frac{13}{2}$ manifold.

¹D. L. Staebler and Z. J. Kiss, Appl. Phys. Letters **14**, 93 (1969); Z. J. Kiss, IEEE J. Quantum Electron. **QE-5**, 12 (1969).

²D. L. Staebler and S. Schnatterley, preceding paper, Phys. Rev. B **3**, 516 (1971).

³W. Hayes and J. W. Twidell, J. Chem. Phys. **35**, 1521 (1961).

⁴Z. J. Kiss and P. N. Yocom, J. Chem. Phys. **41**, 1511 (1964).

⁵J. Arends, Phys. Status Solidi **7**, 805 (1964); W. Hayes and J. P. Stott, Proc. Roy. Soc. (London) **A301**, 313 (1967).

⁶D. S. McClure and Z. J. Kiss, J. Chem. Phys. **39**, 3251 (1963).

⁷R. Alig, following paper, Phys. Rev. B **3**, 536 (1971).

⁸Barry S. Gourary and Frank J. Adrian, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1960), Vol. 10, p. 127.

⁹In these materials, D. Staebler and Z. J. Kiss have observed the presence of optical absorption bands due to Ce^{2+} after the crystals have been irradiated with blue light ($\lambda \leq 400 \text{ \AA}$). The energy levels of Ce^{2+} in CaF_2 have been reported by R. Alig, Z. J. Kiss, J. P. Brown, and D. S. McClure, Phys. Rev. **186**, 276 (1969).

¹⁰ Y^{2+} has not been identified by us in these crystals. EPR of Y^{2+} has been reported by J. R. O'Connor and J. H. Chen, Appl. Phys. Letters **5**, 100 (1964).

¹¹An EPR spectrum recently observed in irradiated $\text{CaF}_2:\text{Gd}^{3+}$ is probably that due to the stable center associated with Gd. A. J. Bevelo and S. Lee, Phys. Rev. Letters **24**, 1276 (1970).

¹²W. Hayes and J. W. Twidell, Proc. Phys. Soc. (London) **82**, 330 (1963).

¹³Halis Odabasi, J. Opt. Soc. Am. **57**, 1459 (1967).

¹⁴N. F. Ramsey, in *Handbook of Physics*, 2nd ed., edited by E. U. Condon and H. Odishaw (McGraw-Hill, New York, 1957), pp. 9-98.

¹⁵G. J. Ritter, Phys. Rev. **126**, 240 (1962).

¹⁶A. Steudel, Z. Physik **152**, 3 (1958).

¹⁷P. A. Forrester and C. F. Kempstead, Phys. Rev. **126**, 923 (1962).

¹⁸B. G. Wybourne, *Spectroscopic Properties of Rare Earth* (Interscience, New York, 1965).

¹⁹J. M. Baker, W. Hayes, and M. C. O'Brian, Proc. Roy. Soc. (London) **A254**, 273 (1960).

²⁰M. S. Weber and R. W. Bierig, Phys. Rev. **134**, A1492 (1964).

²¹S. D. McLaughlan and P. A. Forrester, Phys. Rev. **151**, 311 (1966).

²²J. H. Beaumont and W. Hayes, Proc. Roy. Soc. (London) **A309**, 41 (1969).

²³E. S. Sabisky and C. H. Anderson, Phys. Rev. **159**, 234 (1967).

Theory of Photochromic Centers in CaF_2

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(Received 23 July 1970)

On the basis of recent optical and EPR work, it has been suggested that the ionized and thermally stable photochromic centers in CaF_2 consist of one and two electrons bound at an anion vacancy adjacent to a trivalent impurity cation. For the ionized center, we have shown that the energy levels and wave functions of the isolated F center are not strongly perturbed by the introduction of the impurity ion. Since the divalent ions of the impurities which are found to form these centers, i.e., Y, La, Ce, Gd, Tb, and Lu, have low-lying s and d valence orbitals which overlap the F -center wave functions, we have investigated the defect-impurity orbitals which may be formed from a linear combination of F electron orbitals and these impurity orbitals. The predictions based on this defect-impurity orbital description are found to be consistent with the optical and EPR data for the stable and ionized photochromic centers.

I. INTRODUCTION

During the past few years there have been a number of studies of the optical properties of colored CaF_2 crystals containing impurity cations. One of

the earliest of these studies was that of Scouler and Smakula¹ in which the optical absorption of CaF_2 doped with YF_3 and NaF was measured after coloration by electron irradiation at selected temperatures; in a number of cases new absorption bands