PHYSICAL REVIEW B VOLUME 3, NUMBER 2 15 JANUARY 1971

Optical Studies of a Photochromic Color Center in Rare-Earth-Doped CaF_2[†]

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(Received 23 July 1970)

An impurity-associated color center is found in CaF_2 doped with La, Ce, Gd, Tb, Lu, or Y. Photo-ionization by uv light leads to a reversible color change, i.e., the material is photochromic. This paper presents the results of optical experiments including (a) magnetic circular dichroism and (b) linear dichroism produced by exposure to linearly polarized light. Identification of the center's absorption spectrum, both before and after photo-ionization, is made. The simplest consistent model is two electrons trapped by a trivalent-rare-earth fluorine-vacancy nearest-neighbor complex.

I. INTRODUCTION

The study of color centers in CaF_2 has been complicated by impurities.[1,2] Only recently has positive identification[3,4] been made of simple color centers analogous to those found in alkali halides. The "four-band spectrum" (bands at 5800, 4000, 3350, and 2240 Å) was a primary result of using impure CaF_2. This was first found by Smakula[5] in CaF_2 colored by room-temperature x irradiation. It was later found that the spectrum is enhanced by the presence of Y.[6–8] O'Connor and Chen[7] suggested that the coloration is due to reduction of trivalent Y ions to the divalent state, a process normally associated with rare-earth ions in CaF_2 colored by ionizing radiation[9] or additive coloration.[10] Later, however, Gorlich[11] found by polarized-emission techniques that the two lowest energy bands of the four-band spectrum found in x-irradiated CaF_2:Y are associated with an anisotropic absorption center. They pointed out that the symmetry of this center is that of an *F* center (an electron trapped at a fluorine vacancy) associated with a nearest-neighbor Y ion.

Recent studies[12–14] have shown that an absorption spectrum strikingly similar to the four-band Y spectrum is found after additive coloration of CaF_2 containing either La, Ce, Gd, Tb, or Lu – the only rare earths that are believed to have, like Y, a single *d* electron in the divalent crystal-field ground state.[15] The colored crystals exhibit a photochromic effect; i.e., their color is reversibly changed upon exposure to light. The effect is ascribed to a photoreversible electron transfer between a rare-earth (RE) ion and a photochromic (PC) color center produced by additive coloration; absorption of uv light by the PC center transfers an electron to an isolated RE^{3+} ion; the process is reversed thermally or by absorption of visible light by the RE^{2+} ion. Schematically, this is

$$PC + RE^{3+} \underset{kT}{\overset{\text{vis}}{\rightleftharpoons}} PC^{+} + RE^{2+} .$$

For La, Ce, Gd, or Tb, the color change is stable for a day or more at room temperature. Similar photochromic effects have been observed in Y-doped CaF_2 in which the four-band spectrum was produced by additive coloration.[13,14]

The work reported in this paper is concerned with the optical properties of the above systems, i.e., additively colored CaF_2 containing La, Ce, Gd, Tb, Lu, or Y. Both linear-dichroism and circular-dichroism measurements are made. The results show that for each dopant, additive coloration forms a rare-earth-associated color center. The simplest consistent model is a trivalent-rare-earth fluorine-vacancy complex that has trapped two electrons to make a neutral center. This can be considered as a divalent rare earth associated with a nearest-neighbor *F* center or, more simply, an REF center. The experimental identification of this center is the result of a joint effort with Anderson and Sabisky. Their study of the EPR properties of this system are presented in the following paper.[16]

The experimental work presented in this paper is divided into three parts: Sec. III – the absorption spectrum produced by additive coloration; Sec. IV – linear dichromism produced by exposure to linearly polarized light; and Sec. V – magnetic circular dichromism. Section VI discusses the results in terms of the simplest consistent model, the REF center.

II. MATERIALS PROPERTIES AND PREPARATION

The samples used in this work were obtained from Optovac or grown at RCA Laboratories by Temple using a gradient-freeze method. Rare-earth impurities were introduced by adding 0.05–0.3 mole % of the rare-earth fluoride to the melt. The crystal structure of CaF_2 is a simple cubic lattice of F^- ions with every other body-center site occupied by a Ca^{2+} ion. Trivalent rare-earth (RE^{3+}) ions substitutionally occupy Ca^{2+} sites. The crystals were grown under reducing conditions so that, presumably, interstitial fluorine ions provide charge

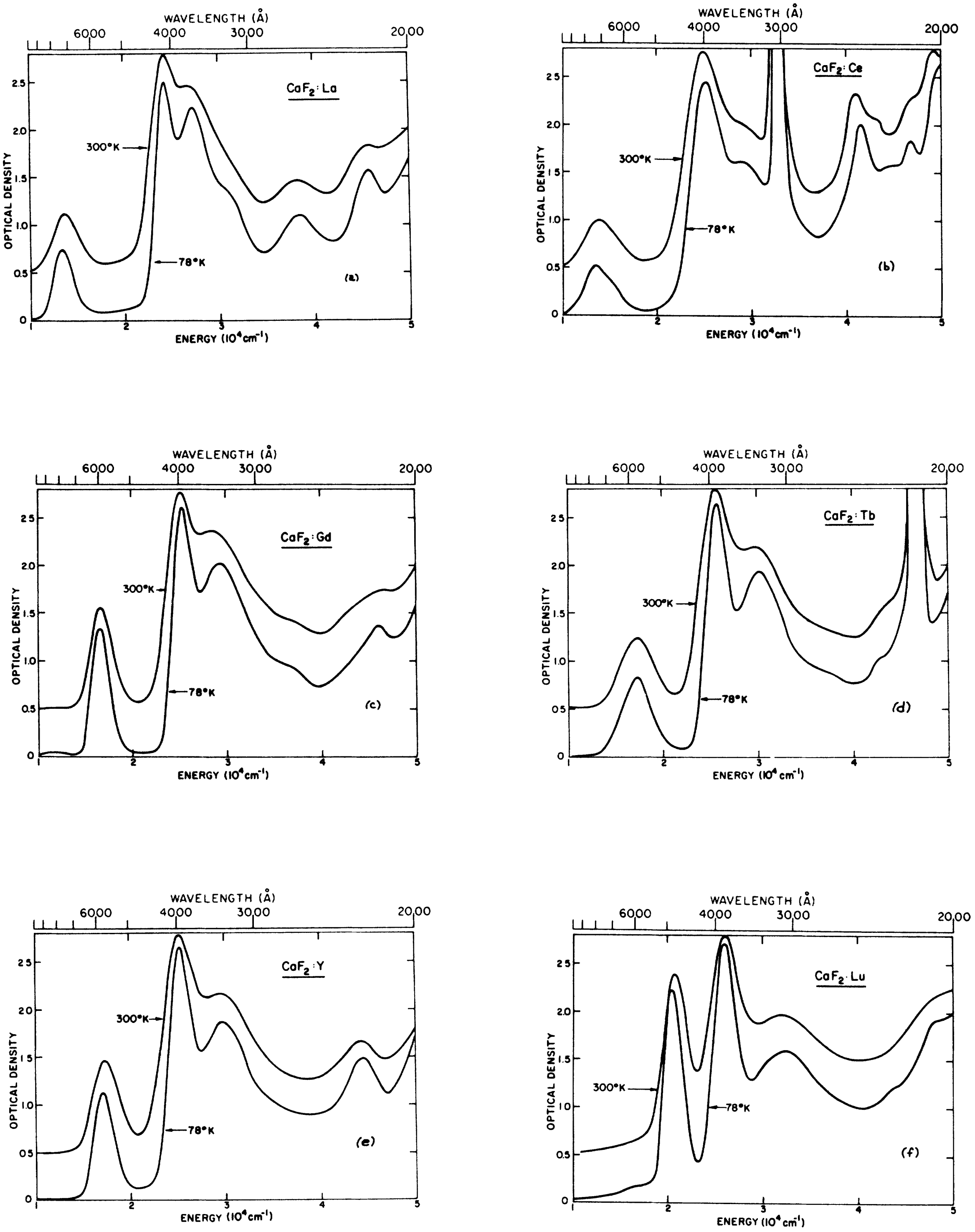

FIG. 1. Optical absorption spectrum of additively colored rare-earth-doped CaF$_2$. The 300 °K curve has been moved upward by 0.5 o.d. The intense absorption bands for Ce and Tb are due to the trivalent rare earth and are present before additive coloration. The rare-earth concentrations (in mole %) and sample thicknesses are (a) 0.1 %, 2.1 mm, (b) 0.05 %, 2.1 mm, (c) 0.1 %, 0.8 mm, (d) 0.1 %, 1.1 mm, (e) 0.3 %, 1.0 mm, and (f) 0.1 %, 0.8 mm. The absorption intensity corresponds to a PC-center concentration of roughly 10^{17}/cc.

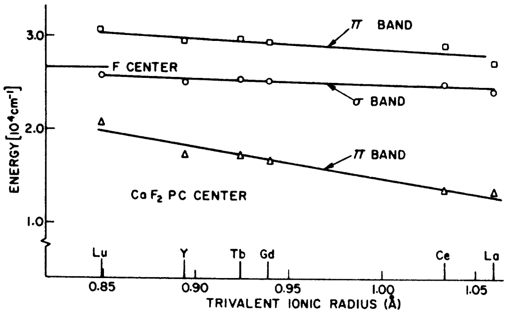

FIG. 2. Absorption-band energy as a function of the trivalent ion radius of the impurity. Only the three prominent bands below 33 000 cm^{-1} are shown. The labels refer to symmetry identifications discussed in Sec. IV. The radii used here are those obtained from the oxide of the impurity. Radii obtained from the fluorides are slightly larger, but have the same progression.

compensation.[17] The crystals, as grown, were transparent in the visible region. They were additively colored by baking in a calcium vapor.[18] Similar coloration can be produced by x [9,14] or γ [14] irradiation at room temperature.

III. ABSORPTION SPECTRA

The absorption spectra associated with the photochromic switching of these systems is shown elsewhere.[13] Of interest here is the thermally stable spectrum; i.e., that found after complete thermal decay of photochromic effects induced by uv light, since this spectrum is due to the color center produced by additive coloration. Because of its photochromic properties it will be referred to throughout most of this paper as the PC (for photochromic) center. Figure 1 shows its spectrum for each dopant. These measurements were made with a Cary 14 recording spectrophotometer using cut and polished samples mounted on the cold finger of a Hoffman Dewar. In each case, the liquid-helium temperature (~ 4 °K) spectrum is identical to the liquid-nitrogen temperature (~ 78 °K) spectrum.

A. Effect of the Dopant

The spectra contain three prominent bands below 33 000 cm^{-1} that progress towards higher energy as the impurity gets smaller. Figure 2 gives the peak energy of the three bands as a function of the ionic radius of the trivalent impurity.[19] The most intense band changes the least and, for the smallest impurity, approaches the CaF_2 F-band energy.

A similar relation of band energy to ionic size is found for analogous absorption bands[13] in additively colored SrF_2 doped with the same impurities. In this case, the analogous band approaches the energy of the SrF_2 F band.[14]

B. Effect of Temperature

The temperature dependence of these bands is similar to that of normal color centers: As the temperature decreases, the bands narrow and increase in peak intensity so as to keep the total area roughly constant. The amount of narrowing is consistent with the Debye temperature of CaF_2 (520 °C). For Ce and Tb, this narrowing emphasizes asymmetric structure on the lowest-energy band. For the other dopants, this band is symmetric but shows an anomalous temperature effect; it shifts by ~ 300 cm^{-1} to *lower* energy upon cooling from 300 °K to 78 °K. Most color centers shift in the opposite direction with temperature.[20]

C. Summary

The absorption spectrum of the PC center is similar in some ways to that of a normal color center such as the F center. However, the dopant is involved in some way; there is a slight but systematic shift of the spectrum to higher energy with decreasing trivalent ionic radius of the impurity.

IV. LINEAR DICHROISM

The PC-center spectrum has characteristics of an impurity-associated color center. Such centers, since they contain two or more defects at definite lattice sites, exhibit optical anisotropy. That is, their optical absorption properties are dependent on the direction of linear polarization. A cubic crystal that contains anisotropic centers in thermal equilibrium with the lattice, has isotropic absorption properties because the centers are equally distributed in all possible directions. Macroscopic anisotropy, i.e., linear dichroism, is induced by exposing the crystal to linearly polarized light absorbed selectively by centers in a particular direction. This disturbs the distribution of the centers by either (i) ionizing those centers or (ii) allowing them to reorient into another direction. Observations of such effects have been crucial in the identification of the M center,[4,21] two nearest-neighbor F centers, and the F_A center,[22] an F center perturbed by a nearest-neighbor impurity.

This section describes linear dichroism studies of the PC center. The results show that the center has the axis of symmetry of an F center next to a rare-earth ion. In addition, absorption bands of the ionized center are identified. Preliminary observations have already been published.[23]

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A. Experimental Procedure

Sample Preparation

Additively colored samples were cut and polished with two parallel (1$\bar{1}$0) faces. Figure 3 shows the

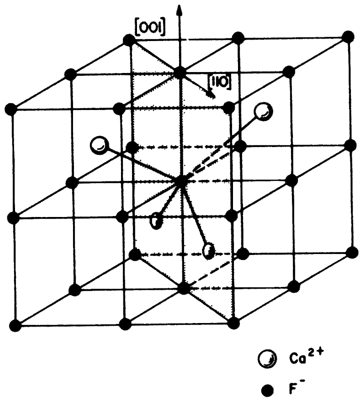

FIG. 3. Lattice structure of CaF_2 showing the sample surface plane.

crystal structure of CaF_2 and the sample surface plane. This plane was chosen since it contains the principal crystal directions, [001] nearest-neighbor fluorine direction, [110] nearest-neighbor calcium direction, and [111] nearest-neighbor fluorine to calcium direction.

Linear dichroism was produced by irradiating a sample with linearly polarized normally incident light from a 500-W high-pressure mercury lamp using Corning glass filters to select the wavelength. The light was polarized with Polaroid HNP'B uv material. All effects induced by these exposures were reversible; an experiment could be easily repeated or changed using the same sample.

Optical Measurements

The linear dichroism was measured by finding the absorption spectrum for light polarized (a) parallel and (b) perpendicular to the polarization of the initial irradiation. All spectra were taken with a Cary 14 recording spectrophotometer using Polaroid material or a Glan prism to linearly polarize the Cary light. For low temperature measurements, the sample was mounted on the cold finger of a Hoffman Dewar.

Thermal Effects

The thermal decay of the linear dichroism was measured with a heater designed by Heyman.[24] A sample was sandwiched between two spring-loaded hollow copper cylinders surrounded by a nichrome wire heater. All of this fitted into the sample compartment of the Cary and achieved temperatures up to 110 °C.

B. Linear Dichroism Results

Axis of Symmetry

Linear dichroism is found in these materials after irradiation with linearly polarized light. It will be shown that the dichroism arises from either selective reorientation or selective ionization of the PC center. However, no linear dichroism is produced by light polarized in the [001] direction. This establishes that the PC center has an axis of symmetry that can lie along any one of the four ⟨111⟩ directions, the body diagonals, through the following argument. Since these directions make equal angles with the [001] direction, each center equally absorbs the [001] polarized light and the absorption remains isotropic.

Since a ⟨111⟩ axis has a threefold rotational symmetry, the center can have electronic states of twofold orbital degeneracy. The anisotropy of the optical transitions, then, can be defined as having σ symmetry (due to a single absorption dipole along the axis of symmetry) or π symmetry (due to two orthogonal absorption dipoles both perpendicular to the axis of symmetry). If one defines the angle between the axis of symmetry and the polarization direction as θ, the angular dependence of the absorption coefficients is given by $\alpha_\sigma \sim \cos^2\theta$ and $\alpha_\pi \sim \sin^2\theta$.

Reorientation – Ionized Center

For the Lu and Y systems, absorption by the lowest-energy band (see Fig. 1) easily reorients the PC center. The linear dichroism associated with this reorientation is shown on Figs. 4(a) and 4(b). The polarization direction used, [111], is that which gives the maximum dichroism. The symmetry of the bands is identified by the following argument. Initially the centers are equally distributed among the four possible directions: [111], [$\bar{1}$11], [1$\bar{1}$1], and [11$\bar{1}$]. After a center absorbs a photon, it can reorient into another direction, perhaps while it is in an excited state. If it happens to fall into the [111] direction, it remains there; the π band does not absorb the [111] polarized light. The net result, then, is to align all of the centers into the [111] direction. This gives the maximum possible dichroism; the parallel absorption due to σ bands, the perpendicular absorption due to π bands. These identifications have been confirmed quantitatively.[14,23]

The spectrum of the ionized PC center (PC^+) is identified by then photo-ionizing the aligned PC center with uv light. Figure 5 shows the result. This was done at 78 °K because the Y and Lu systems are not photochromically stable at room temperature. The irradiation produces the following: (i) isotropic absorption in the visible and near infrared, due perhaps, to the RE^{2+} ion, the site of the trapped electron and (ii) anisotropic absorption of the aligned PC center after ionization. Schematically, the photochemical reaction may be described by

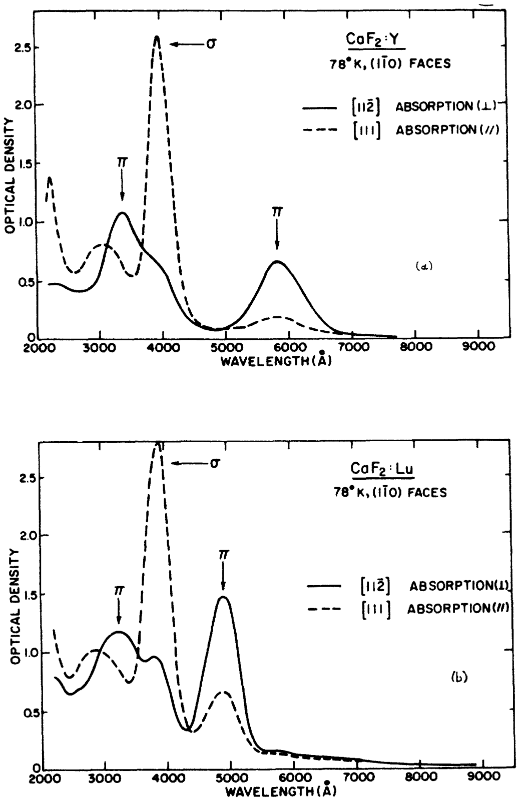

FIG. 4. Linear dichroism of the PC center after reorientation into the [111] direction by exposure to [111] polarized visible light (4500 Å < λ < 6500 Å) at 300 °K. Arrows indicate the symmetry of the three most prominent bands of the PC center. (a) $CaF_2:Y$, (b) $CaF_2:Lu$.

$$PC(\uparrow)+RE^{3+} \overset{uv}{\rightleftharpoons} PC^{+}(\uparrow)+RE^{2+} .$$

The dichroism of the PC-center spectrum, indicated by the vertical arrow, is transferred to that of the PC^+ center. Comparison of Figs. 4 and 5 shows that the two spectra are quite similar; the PC^+-center spectrum looks like the PC-center spectrum shifted slightly to higher energy.

For the La, Ce, Gd, or Tb systems, the PC center is quite difficult to reorient directly with linearly polarized visible light. In these cases, the centers were reoriented while in the ionized state by exposure to linearly polarized uv light absorbed by the ~3300-Å band of the PC^+ center. Figures 6(a)–6(d) show the result for light polarized in the direction that gives maximum dichroism, the [11$\bar{2}$] direction. In addition to a remnant of the PC-center spectrum, two other spectra are apparent. One is the isotropic absorption of the RE^{2+} ion, the site of the released electron.[12,13,16] The other is the anisotropic absorption of the aligned ionized PC center. The symmetries of the PC^+ bands are identified by, again, the direction of polarization required to produce the largest dichroism. In this case, the centers reorient after a σ-band absorption. As a result, they are aligned into the [111] direction by exposure to light polarized in the perpendicular [11$\bar{2}$] direction. This identification agrees with the similarity of these bands to those of the Lu and Y PC^+ center.

The spectrum of aligned PC centers can now be obtained by reversing the photochromic process either thermally or optically; in other words, by releasing the electrons from the RE^{2+} ions so that they can be trapped by the aligned PC^+ centers. Schematically, this is

$$PC^{+}(\uparrow)+RE^{2+} \xrightarrow[kT]{VIS} PC(\uparrow)+RE^{3+} .$$

Figures 7(a)–7(d) show the result of the optical transfer, i.e., irradiation with visible (VIS) light, done at low temperatures to insure that no further reorientation took place. The bands of these PC centers have the same symmetries as the analogous bands of the Lu and Y PC centers; the most intense

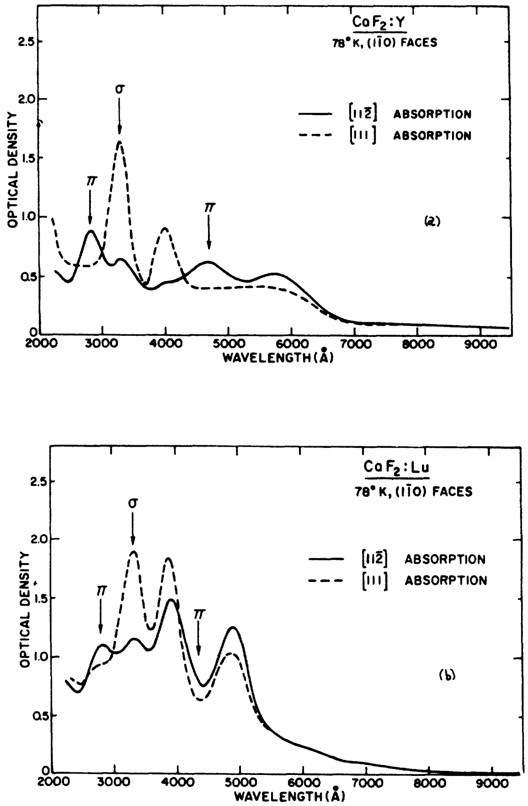

FIG. 5. Samples of Fig. 4 after exposure to unpolarized uv light (λ < 4000 Å) at 78 °K. Arrows indicate the symmetry of the three most prominent bands of the ionized PC center.

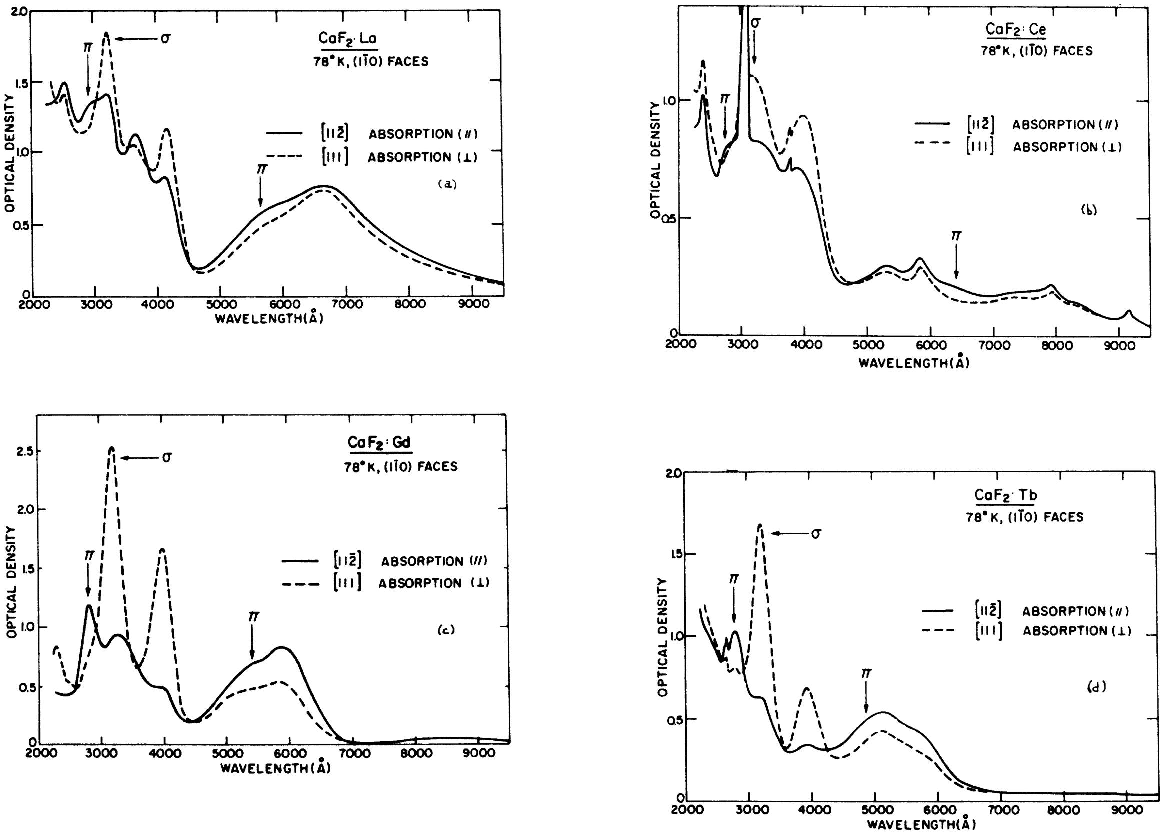

FIG. 6. Linear dichroism and symmetry identification for the ionized PC center after reorientation into the [111] direction by exposure to [112̄] polarized 3300-Å light at 300 °K. (a) CaF_2 : La, (b) CaF_2 : Ce, (c) CaF_2 : Gd, (d) CaF_2 : Tb.

band (~4000 Å) has σ symmetry, while the two bands on either side (~3450 Å and ~6000 Å) have π symmetry. Also, as for the Lu and Y systems, the spectrum of the ionized center has analogous bands at slightly higher energy.

Selective Switching

The identification of the ionized center spectrum was confirmed with selective ionization experiments.[20] For example, consider the results for CaF_2 : Tb shown on Fig. 8. A sample in the thermally stable isotropic state was irradiated with linearly polarized light around 4000 Å. (The exposure time was only a few seconds, as compared to the typical exposure of more than a minute required for reorientation effects.) The irradiation decreases the ~4000-Å band of the PC center and produces the ~3300-Å band of the PC^+ center. The important point is that the two bands have equal and opposite linear dichroism. This effect is described schematically as

$$\mathrm{PC}(\uparrow\rightarrow)\xrightarrow{\mathrm{uv}}\mathrm{PC}(\uparrow)+\mathrm{PC}^{+}(\rightarrow)\,.$$

Initially, the absorption is isotropic because the centers are uniformly distributed in all possible directions. This is represented by the two orthogonal arrows. When centers in particular directions are ionized, the horizontal centers for example, two linear dichroism spectra are produced: one of the vertical PC centers and one of the horizontal PC^+ centers. The dichroism of the two σ bands, then, are equal and opposite; the parallel absorption is minimum for the ~4000-Å PC band and maximum for the ~3300-Å PC^+ band. This dichroism is consistent with an ionization process directly associated with absorption by the 4000-Å σ band. Similar effects have been observed for the higher-energy π band.[14] In both cases, the ionization efficiency is larger than 0.1%[13] and is approximately independent of temperature down to 4 °K.[14]

Thermal Decay

Linear dichroism produced by selective ionization decays as the RE^{2+} traps are thermally ionized. That is, the electrons are retrapped by the PC^+ centers so that the sample returns to its original state, the isotropic absorption of the PC center.

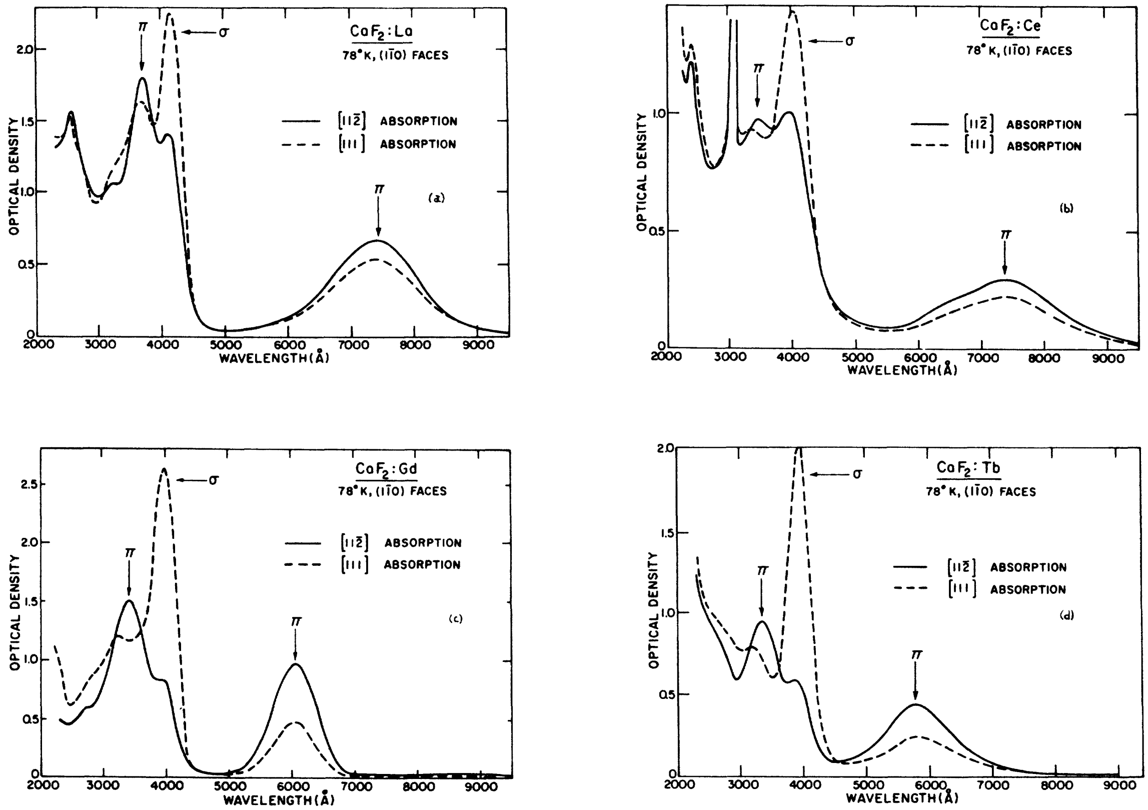

FIG. 7. Linear dichroism and symmetry identification for the PC-center spectrum. These are the samples of Fig. 6 after exposure to unpolarized visible light at 78 °K.

Thus, both the linear dichroism and the RE^{2+} absorption bands decay at the same rate. This decay is a complex function of time.[13] A much simpler decay function is found for the linear dichroism of realigned PC centers. In this case, the linear dichroism decays exponentially during thermally induced reorientations of the centers. This proceeds until the centers are uniformly distributed in all possible directions. Generally, the room-temperature reorientation decay time is much longer than the photochromic decay time.

As shown in Fig. 9, the time constant of the thermal reorientation depends on the impurity and the temperature. The temperature dependence is consistent with a thermal reorientation process that involves an activation energy. That is, the reorientation rate ν has the following form:

$$\nu = \nu_0 e^{-E_a/kT} ,$$

where ν_0 is a frequency factor (the attempt rate), E_a is the activation energy (the height of the barrier), k is Boltzmann's constant, and T is the temperature. The time constant is given by $1/\nu$. Table I lists the activation energies and frequency factors for the different impurities. Within experimental error, the activation energy decreases with decreasing impurity size.

C. Summary

The PC center has the symmetry of an F center associated with a rare-earth impurity; i.e., its

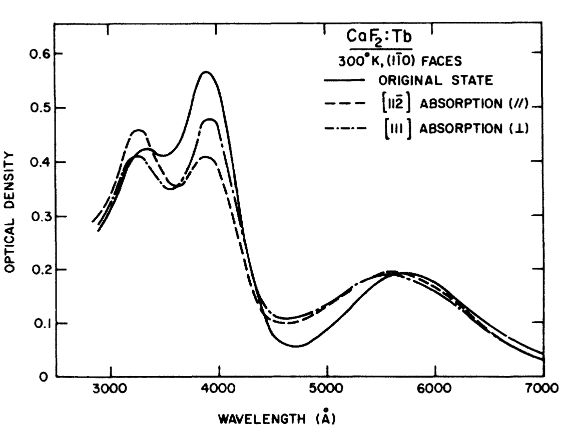

FIG. 8. Selective ionization of the PC center in CaF$_2$: Tb. The sample was exposed to [11$\bar{2}$] polarized 4000-Å light at 300 °K.

axis of symmetry is in the direction between an F^- site (the position of an *F* center) and a nearest-neighbor Ca^{2+} site (the position of a rare-earth impurity). The absorption bands are identified as a singlet (σ band) or a doublet (π band), consistent with the center's threefold rotational symmetry. The similarity of the spectrum from rare earth to rare earth is confirmed by these identifications; each spectrum contains a strong band at ~4000 Å with σ symmetry between two less intense bands with π symmetry. In addition, absorption for wavelengths shorter than 3000 Å is predominantly of σ symmetry. This is particularly evident for the Y system [see Fig. 4(a)]; the 2250-Å band of the Y four-band spectrum and a broader band at ~3000 Å both have σ symmetry. These results confirm that the entire four-band spectrum of CaF_2 : Y is associated with a single center. This does not agree with the results of Theissing *et al.*[25]

Reorientation of the center from one direction to another occurs thermally or after optical absorption. The thermal process follows an Arrhenius relation with an activation energy that, within experimental error, decreases with decreasing radius of the trivalent rare earth.

Absorption by the σ band or the higher-energy bands photoionizes the center with an efficiency that is apparently temperature independent. The absorption spectrum of the ionized center is similar, in intensity and structure, to the original spectrum shifted slightly to higher energy. Photoionization of the PC^+ center has not been observed.

IV. CIRCULAR DICHROISM

In Sec. III, it was shown that the lowest-energy band of the PC center is a π band. That is, it involves twofold orbital degeneracy. When a magnetic field is applied, such a band is expected to show circular dichroism; absorption of light propagating in the field direction depends upon whether it is right- or left-handed circularly polarized. This section presents circular dichroism studies of the PC center. The results confirm that the center contains a rare-earth ion, consistent with the rare-earth *F*-center model.

TABLE I. Reorientation parameters of the PC center.

Impurity[a]	Activation energy (eV)	Frequency factor[b] (sec^{-1})
La	1.23 ± 0.05	5×10^{14}
Ce	1.25 ± 0.05	2×10^{15}
Gd	1.27 ± 0.05	3×10^{15}
Tb	1.26 ± 0.02	3×10^{15}
Y	1.17 ± 0.03	6×10^{15}
Lu	1.13 ± 0.03	8×10^{14}

[a] Listed in order of decreasing trivalent radius.
[b] Within a factor of 5.

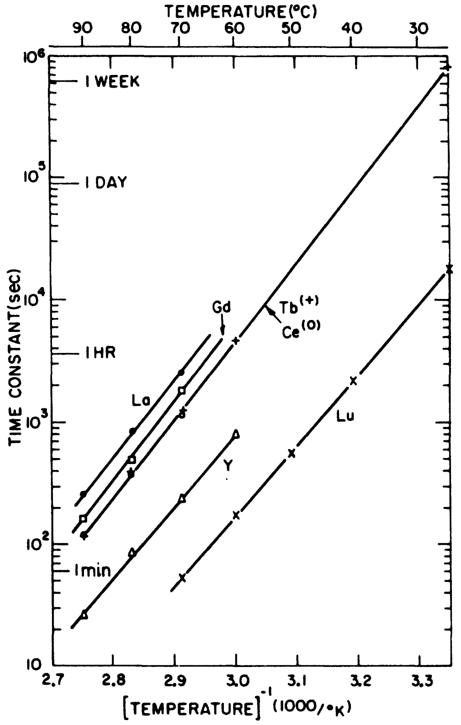

FIG. 9. Temperature dependence of the decay of linear dichroism of aligned PC centers.

Henry and Slichter[26] give a review of circular dichroism associated with color centers, the *F* center in particular. Effects associated with rare-earth ions[27] are generally more complex.

A. Experimental Procedure

Cut and polished samples with (111) faces, the cleavage plane, were mounted inside the core of a superconducting magnet immersed in pumped helium (~ 2 °K). Absorption measurements were made with a Cary 14 spectrophotometer. The Cary light passed longitudinally through the magnet, normal to the sample surface, after being circularly polarized with a Glan prism and Soleil compensator. Absorption curves were taken for left or right circular polarization. In the convention used here, the *E* vector of left-polarized light rotates in a direction that advances a right-hand screw in the propagation direction.

B. Experimental Results

Using the above techniques, circular dichroism was observed only for the Ce-, Gd-, or Tb-doped CaF_2 systems. Figures 10(a)–10(c) show the π-band absorption for right-hand and left-hand polarization for these three cases. The Ce circular dichroism, i. e., the difference between the two absorption spectra on Fig. 10(a), increased linearly

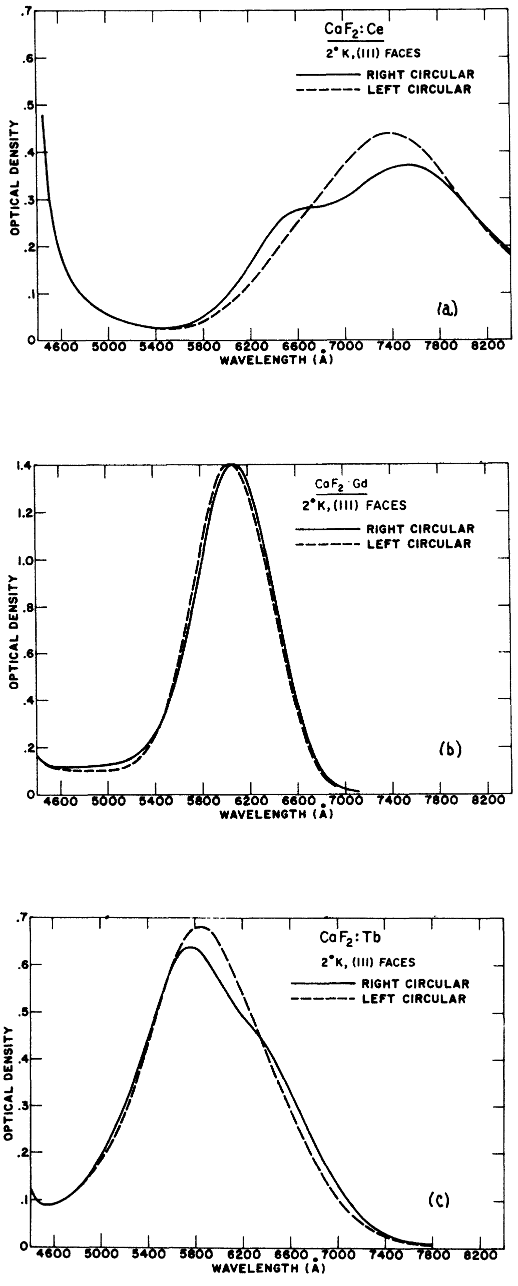

FIG. 10. Magnetic circular dichroism of the lowest-energy π band for the PC center in (a) $CaF_2:Ce$ at 25 kG, (b) $CaF_2:Gd$ at 10 kG, and (c) $CaF_2:Tb$ at 10 kG.

up to the highest field used (~ 25 kG). The Gd and Tb circular dichroism saturated at ~ 10 kG. In each case, the shape of the difference curve appeared to be independent of the field.

For Gd, the dichroism involves a nearly rigid shift of ~ 100 cm^{-1}. For Ce and Tb, the dichroism accentuates asymmetric structure [see Figs. 1(b) and 1(d)] in a similar manner; the left-hand spectrum is a single band, the right-hand spectrum contains at least two bands.

The above circular dichroism confirms the identification of the π band as having orbital degeneracy. In particular, the dichroism is like that expected for electronic transitions from an orbital-singlet paramagnetic ground state to an orbitally degenerate excited state split by a spin-orbit interaction. The identification of the ground state as an orbital singlet is best shown by the nearly rigid shift of the Gd band; circular dichroism associated with an orbitally degenerate ground state, the *R* center[28] for example, typically involves large changes of the integrated absorption at low temperature.

The rare earth has a large influence on the circular dichroism in a manner consistent with the results of Anderson and Sabisky.[16] They found that the EPR of the PC center is best correlated with the tightly bound well-shielded $4f$ electrons of a trivalent rare-earth ion involved in the center. Our results are consistent with the above in that we observe no paramagnetic circular dichroism for La, Y, or Lu – those rare earths with a closed-shell nonparamagnetic trivalent ground-state configuration. To be consistent, then, the circular dichroism of the PC center involving the other impurities must be associated with electrons in the unfilled $4f$ shell of the trivalent rare earth; $Ce^{3+}-4f$, $Gd^{3+}-4f^7$, and $Tb^{3+}-4f^8$. From the magnetic field for saturation of the circular dichroism, ignoring directional effects, we estimate the paramagnetic g values to be less than 2 for Ce and roughly 9 for Gd and Tb. Measurements at higher temperatures on the Gd and Tb systems are consistent with the $g = 9$ value.[14]

C. Summary

Circular dichroism measurements confirm the identification of the lowest-energy band as having π symmetry and suggest that the ground state is an orbital singlet. Unlike the absorption properties, the magnetic properties of the PC center are quite dependent on the rare earth. In particular, no paramagnetic-circular dichroism is observed for the PC center that involves La, Lu, or Y; the rare earths with a nonparamagnetic closed-shell trivalent configuration. This is consistent with the EPR result of Anderson and Sabisky[16] that the paramagnetism of the PC center is directly associated with the trivalent rare-earth ion. Their results, in conjunction with the results presented in this paper, allow us to present the following model with full confidence.

VI. DISCUSSION-A MODEL

The simplest model for the PC center, consistent with the experimental results, is pictured in

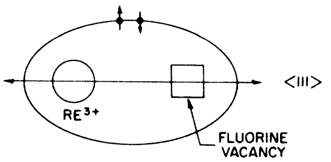

FIG. 11. Schematic model of the PC center.

Fig. 11 – two electrons trapped by a complex core consisting of a trivalent rare-earth ion (RE^{3+}) next to a fluorine vacancy. This can be considered as a divalent rare-earth ion (RE^{2+}) ion next to an F center, or more simply, a REF center. It is neutral and has C_{3v} point symmetry. A schematic energy-level diagram for the two electrons (one from the RE^{2+} ion, one from the F center) is shown in Fig. 12. Transitions of one of these electrons from the orbital-singlet ground state (A_1) lead to the absorption bands having both σ and π symmetry. Transitions to an excited state above the lowest-energy E level can transfer the electron to the conduction band with no or very little phonon assistance, perhaps after lattice relaxation. After the center is photo-ionized, transitions of the remaining electron to excited states relatively unchanged by the ionization lead to similar absorption bands.

Alig has shown[29] that defect-impurity orbitals composed of F-center functions centered at the vacancy and 6s and 5d functions centered on the rare earth give qualitative agreement to the ordering of the energy levels and the relative oscillator strengths of the bands. In particular, this model predicts that "molecular" mixing of F center and rare-earth E symmetry functions lowers the energy of the π band from that of the F band and reduces its oscillator strength. The anomalous temperature shift of this band may be associated with variations of the mixing with temperature, perhaps through changes of the rare-earth to F-center separation. Strain studies should prove interesting. The general shift of the absorption bands with the impurity size is as yet not understood.[29]

Although this center is much more complex than a simple F_A center, the reorientation process may be quite similar – hopping of the F center (or vacancy) about the impurity.[22] At least, this process is consistent with the observed dependence of the activation energy for reorientation on the impurity; as the impurity gets smaller, the F center can more easily move about it.

Since the two outer electrons in the defect-impurity ground-state orbitals apparently have oppositely paired spins, the magnetic properties of the center must be directly associated with the tightly bound 4f electrons in the RE^{3+} "core." These electrons are well shielded by 5s and 5p closed shells and thus play a smaller role in the defect-impurity orbitals. The circular dichroism can be attributed to an exchange interaction between the defect-impurity electrons in the excited state and the 4f electrons. This explanation qualitatively predicts the difference in structure between the two circular polarizations, but does not account for the asymmetry. More experiments are needed, particularly on the circular dichroism of aligned centers.

VII. SUMMARY AND CONCLUSIONS

Additive coloration of $\mathrm{CaF_2}$ doped with La, Ce, Gd, Tb, Lu, or Y does not produce the "normal" result, i.e., reduction of the trivalent ion to the divalent. Instead, the coloration produces an impurity-associated color center that can be described as a divalent rare-earth ion next to an F center, or REF. This is a molecularlike complex in which two electrons, one from the F center, one from the rare-earth ion, occupy defect-impurity orbital states, discussed in another paper by Alig.[29] The two electrons pair their spins so that the magnetic properties of this REF center are directly associated with the RE^{3+} core ion. This has been confirmed by the EPR studies of Anderson and Sabisky.[16] The center has optical-absorption bands that arise from transitions of one of the defect-impurity orbital electrons to excited states. Interaction between this electron and the 4f core electrons leads to quite complex circular-dichroism spectra.

The optical properties of this REF center are highly anisotropic. As a result, linear dichroism can be produced by exposing a sample to linearly polarized light. The dichroism arises from selectively ionizing centers in a particular direction or from reorientation of the center, perhaps while in an excited state. The symmetry of the linear dichroism is consistent with the threefold rotational symmetry of the center.

When the center is photo-ionized by absorption of uv light, the released electron can be trapped at

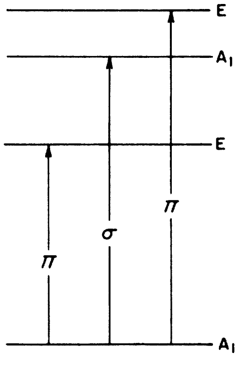

FIG. 12. Energy levels occupied by the two electrons. Labels refer to the appropriate irreducible representations in C_{3v} point symmetry.

an isolated RE^{3+}. This produces two new absorption spectra, one of the divalent rare earth, another of the ionized REF center. The latter spectrum arises from transitions of the remaining electron.

The observation of this general class of impurity-associated color center is consistent with the difficulty of producing *F* centers in CaF_2. That is, when La, Ce, Gd, Tb, Lu, or Y impurities are present, attempts at producing *F* centers result, instead, in the formation of this rare-earth *F*-center complex. However, it is as yet not understood why the coloration does not reduce these impurities to the divalent state as is the case for most other rare earths.

ACKNOWLEDGMENTS

We would like to thank R. C. Alig, C. H. Anderson, W. Burke, R. C. Duncan, P. M. Heyman, W. Phillips, E. S. Sabisky, W. Zernik, and many others at RCA Laboratories for discussions and helpful suggestions throughout the course of this research. Special thanks go to Z. J. Kiss for initially stimulating our interest in this subject. The circular-dichroism apparatus was kindly loaned to us by H. Weakliem. Many experiments were carried out with the able assistance of W. Prindle.

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†Research reported in this paper was jointly sponsored by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contract No. F19628-68-C-0087, and RCA Laboratories, Princeton, N. J., but the report does not necessarily reflect endorsement by the government sponsor.

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[1] F. Lüty, Z. Physik. 134, 596 (1953).

[2] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon, New York, 1963), p. 275.

[3] J. Arends, Phys. Status Solidi 7, 805 (1964).

[4] J. H. Beaumont and W. Hayes, Proc. Roy. Soc. (London) A309, 41 (1969).

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

[6] W. J. Scouler and A. Smakula, Phys. Rev. 120, 1154 (1960).

[7] J. R. O'Connor and J. H. Chen, Phys. Rev. 130, 1790 (1963).

[8] P. Gorlich, H. Karras, W. Ludke, H. Mothes, and R. Reimann, Phys. Status Solidi 3, 478 (1963).

[9] J. L. Merz and P. S. Pershan, Phys. Rev. 162, 217 (1967).

[10] Z. J. Kiss and P. N. Yocom, J. Chem. Phys. 41, 1511 (1964).

[11] P. Gorlich, H. Karras, G. Kötitz, and P. Ullman, Phys. Status Solidi 23, 313 (1967).

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

[13] D. L. Staebler and R. C. Duncan (unpublished).

[14] D. L. Staebler, Ph.D. thesis, Princeton University, 1970 (unpublished).

[15] D. S. McClure and Z. J. Kiss, J. Chem. Phys. 39, 3251 (1963).

[16] C. H. Anderson and E. S. Sabisky, following paper, Phys. Rev. B 3, 527 (1971).

[17] M. J. Weber and R. W. Biering, Phys. Rev. 134, A1492 (1964).

[18] W. Phillips and R. C. Duncan, Met. Trans. (to be published).

[19] R. D. Shannon and C. T. Prewitt, Acta. Cryst. B25, 925 (1969).

[20] For example, see I. S. Jacobs, Phys. Rev. 93, 993 (1954).

[21] W. D. Compton and H. Rabin, Solid State Phys. 16, 121 (1964).

[22] F. Lüty, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), p. 181.

[23] D. L. Staebler, S. E. Schnatterly, and W. Zernik, IEEE J. Quantum Electron. QE-4, 575 (1968).

[24] P. M. Heyman, Ph.D. Thesis, Princeton University, 1970 (unpublished).

[25] H. H. Theissing, T. F. Ewanizky, P. J. Caplan, and D. W. Grosse, J. Chem. Phys. 50, 2657 (1969).

[26] C. H. Henry and C. P. Slichter, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York 1968), p. 351.

[27] For example, see C. H. Anderson, H. A. Weakliem, and E. S. Sabisky, Phys. Rev. 143, 223 (1966).

[28] W. Burke, Phys. Rev. 172, 886 (1969).

[29] R. C. Alig, following paper, Phys. Rev. B 3, 536 (1971).

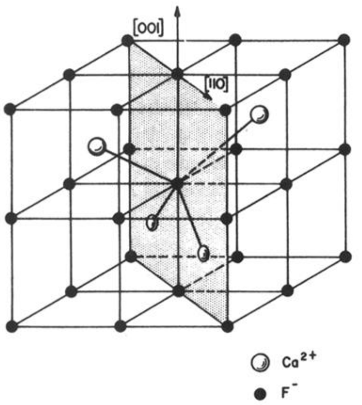

FIG. 3. Lattice structure of CaF_2 showing the sample surface plane.