the static field would appear to be ruled out, since no such rotation is possible for a compacted powder with a binder. Further, the effect of the parallel and transverse fields is in the opposite direction for a simple correction. The fact that the single-crystal results agree with theory would argue against some peculiarity of the CMN itself (e.g., spin-lattice relaxation anomalies,[10] rare-earth impurities, etc.). Any discrepancies due to a difference between B and H should be negligible because of the small magnetization at the temperatures used here. The deviation of the experimental results on the powder from theory cannot be explained at this time.

ACKNOWLEDGMENTS

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[*] Work performed under the auspices of the U. S. Atomic Energy Commission.

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Defect Centers in Calcium Fluorophosphate

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Crystals of calcium fluorophosphate $Ca_{10}(PO_4)_6F_2$ have been grown from melts of various compositions. Optical and ESR measurements have been performed on samples before and after various treatments such as a uv irradiation and a thermal quench. Two kinds of defect centers have been detected: color centers produced by the irradiation, and more basic defects present in the samples before irradiation. The identity of two of these basic defects has been established and their role in the formation of the color centers has been deduced.

I. INTRODUCTION

Calcium fluorophosphate, often referred to as FAP, crystallizes in the hexagonal apatite structure and has a unit cell with the formula $Ca_{10}(PO_4)_6F_2$.[1] It has been investigated extensively partly because of its commercial importance as the phosphor in most fluorescent lamps and partly because of the richness of its defect structure and its color centers. Single crystals can be prepared by melt- or flux-growth techniques,[2–4] while powder samples similar to those used in lamps can be prepared by solid-state-reaction techniques. Optical measurements made on such crystals or on powders show strong absorption in the uv region of the spectra near 250 and 190 nm which is not a property of the perfect crystal since its strength is found to vary from sample to sample.[2,5] Owing to the magnitude of the absorption, it has been attributed not to trace impurities but to lattice defects or to some common impurity like oxygen or hydroxyl which might be incorporated in large amounts. Previous attempts to control its strength have been successful in powders but not in single crystals.[5]

Efforts have been made to identify the center (hereafter called the X center) responsible for the absorption at 250 nm (called the X band). Johnson,[6] Swank,[7] and Piper, Kravitz, and Swank[8] have exposed crystals of fluorapatite to radiation from an x-ray source and have been able to partially convert the X center into various new defects. ESR measurements have been very successful[8] in identifying many of the paramagnetic defects made and can also be used to reveal the complex interactions between them. Hopefully, one could work backwards from these identifications to an understanding of the properties of the X center and its structure. Prener *et al.*[5] have attempted to do this but were unable to arrive at an unequivocal identification of the X center. In spite of this, the present understanding of the defect structure in fluorapatite and the changes which occur upon exposure to ionizing radiation is fairly complete and may be summarized as follows.

(i) The primitive common defects in FAP are a fluorine-ion vacancy V, and an oxygen ion $O^=$, substituted for a fluorine ion.

(ii) These defects attract each other so that various kinds of complexes can form such as $O^=\text{-}V$ and $V\text{-}O^=\text{-}V$. Following the nomenclature of Prener *et al.*[5] these centers and those described above will be called $(O)^-$, $(V)^+$, $(OV)^0$, and $(VOV)^+$. The bracket encloses the combination of primitive defects which replaces an equal number of fluorine ions and the superscript indicates the charge of the complex relative to the fluorine ions it replaces.

(iii) Ionizing radiation creates electrons e and holes h which can be trapped at the diamagnetic defects discussed above making new centers some of which are paramagnetic. Some of the most important of these centers have been identified by ESR and include the following:

$(VOV)^0$ or $(VOV)^+ + e$, called the E(I) center (or A^{I} center)[8]
$(V)^0$ or $(V)^+ + e$, called the E(II) center (or A^{II} center)[8]
$(OVV)^0$ or $(VOV)^+ + e$, called the E(III) center (or C center)[8]
$(OV)^+$ or $(OV)^0 + h$, called the H(I) center
$(O)^0$ or $(O)^- + h$, called the H(II) center .

The E(I) and E(III) centers are formed from the same basic defects, $(VOV)^+$ and an electron, but differ in the final position of the oxygen atom after the electron is captured.

Another important paramagnetic center, the E(IV) center has not been identified.[8] An important nonmagnetic center, the B center, has been identified as $(OVV)^-$ or $(VOV)^+ + 2e$.

(iv) A moderate thermal anneal or an optical bleach releases electrons and holes from these traps and eventually leads to the mutual annihilation of the free electrons and holes.

(v) X irradiation, a moderate anneal, or an optical bleach do not change the concentration of the defect complexes but only change the number of electrons or holes trapped on them.

The purpose of this paper is to solve two of the problems which still limit our understanding of the defect structure and response to radiation of apatite. We propose, first, to identify the X center and the center, hereafter called the Y center, which absorbs near 190 nm and, second, to explain microscopically the creation of E and H centers by radiation. The investigations reported here include a study of the crystal growth conditions under which X and Y centers form, their thermal stability, their interactions with impurities, and their response to irradiation with γ and uv sources.

II. EXPERIMENTAL TECHNIQUES

The crystals discussed below have all been grown by the Czochralski technique in an argon atmosphere from a melt composed of $Ca_2P_2O_7$, CaF_2, and $CaCO_3$. The details of this growth are discussed elsewhere.[4] A stoichiometric melt is composed of these components in the ratio 3 : 1 : 3. We investigated deviations from stoichiometry by varying either the CaF_2 or $CaCO_3$ content of the melt from this ratio. It was difficult to grow good single crystals when the deviations were large for second phases, probably of CaF_2 or CaO, then formed as inclusions in the crystals. These inclusions reduced the usefulness of samples by degrading their optical and ESR properties and by stressing them. The stress was often so large that crystals would spontaneously break into a fine powder—sometimes months after their growth.

For optical measurements samples were cut from the boules, ground to size, and polished. In some cases their optical density in the uv region was so high that very thin specimens (a few thousandths of an inch thick) had to be prepared. In these cases the samples were permanently glued to quartz plates to protect them. The quartz[9] and glue[10] used were essentially transparent to the limit of our optical measurements, 185 nm. Optical measurements were made on a Cary 14 spectrometer using either light polarized with a Polacoat[11] polarizing film or samples specially orientated so that useful measurements could be made with unpolarized light.

An oven was designed to allow the measurement of the optical properties of samples at elevated temperatures. Conventional Dewars allowed optical and ESR measurements at low temperatures. uv irradiation of the samples was usually accom-

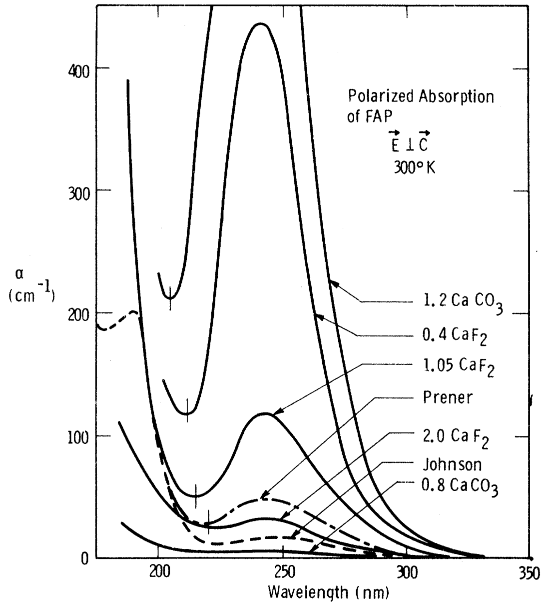

FIG. 1. Polarized absorption of several crystals at 300 K. The curves are labeled to indicate the stoichiometry of the melt from which each crystal was grown. 1.2 $CaCO_3$, for instance, means that this melt was stoichiometric except for $CaCO_3$ which was 1.2 times the stoichiometric value.

plished with a low-pressure Hg discharge lamp; interference filters were used to isolate the Hg lines at 254 and 185 nm. γ irradiation was carried out with a Cs^{137} source. The samples could be irradiated in the dewars at low temperatures and subsequent optical and ESR measurements could be performed without warming them. ESR measurements were carried out at 10 GHz in a conventional manner previously described.[12]

III. RESULTS

The experimental results will be divided into four parts. In Sec. III A (properties of the X and Y centers) data are presented on the concentrations of the X and Y centers, their dependence upon stoichiometry and impurities, and the effect on them of thermal quenching. In Sec. III B (new color-center bands) data are presented on the newly found optical bands of the E(IV) and H(II) centers. In Sec. III C (area correlation measurements) correlations are established between the areas of the X and Y bands and the various color-center bands. In Sec. III D (γ-radiation experiments) data are presented on the difference between uv and γ irradiation and this is used to identify the Y center. In Sec. III D the application of the mass action law to the primitive defects is discussed and the identification of the X center is presented. This final identification depends upon the results of Secs. III A–III C.

A. Properties of the X and Y Centers

Deviations from Stoichiometry

A series of crystals was grown from melts with varying CaF_2 or $CaCO_3$ content. Their optical properties were measured including the strength of the strongly polarized absorption found near 250 nm (X band) and additional absorption further to the ultraviolet. These bands are the same as those originally measured by Johnson[2] using unpolarized light and the spectra are essentially identical to the polarized spectrum given by Prener *et al.*[5] Figure 1 shows the polarized absorption spectra of several of our crystals and one of Prener's as well as the original unpolarized measurement of Johnson. The absorption coefficient shown is $\alpha_\perp$ (measured with $\vec{E} \perp \vec{c}$) to allow a fair comparison with Johnson's unpolarized measurement. As noted by Prener $\alpha_\parallel$ is about 7 times larger than $\alpha_\perp$ and has a somewhat different shape. The fluorescence from this center appears at about 700 nm and is also highly polarized with $\vec{E} \parallel \vec{c}$.[13] The absorption peak noted by Johnson at about 190 nm appears to be due to an impurity, as it is not noted by us or Prener. The absorption in Prener's sample is near the average of ours, i.e., we record much higher and much lower absorptions coefficients.

Figure 2 shows a plot of the strength of the X band versus the CaF_2 or $CaCO_3$ content of the melt from which a series of nonstoichiometric crystals was grown. When a crystal is labeled, e.g.,

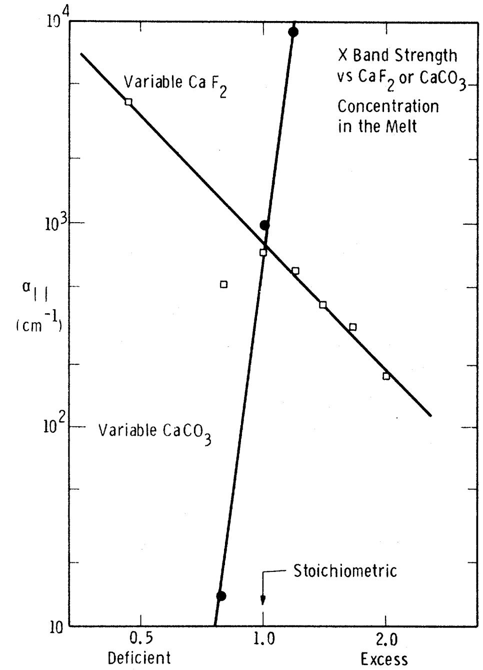

FIG. 2. Dependence of the X band upon stoichiometry of the melt.

$2\ CaF_2$, this signifies that the CaF_2 content of the melt is twice the stoichiometric value. Clearly the *X* band is very sensitive to variations in stoichiometry. Excess $CaCO_3$ and deficient CaF_2 encourage its growth. These measurements strongly suggest that the *X* center is composed of defects such as fluorine vacancies or oxygen interstitials or oxygen ions substituted for fluorine ions.

It would be desirable to make similar measurements of the extrinsic absorption near 190 nm versus stoichiometry, to see whether it varies in the same way as the *X* band. The question to be answered is whether this absorption (the *Y* band) is also caused by the *X* center or is due to an entirely different center (the *Y* center). We were unable to achieve measurements at this wavelength adequate for our purpose. This was for several reasons.

(a) The precipitates commonly found in many of our samples scatter light sufficiently to make the determination of an appropriate baseline for the optical measurements difficult.

(b) The glue used with the thin samples has an absorption in this region which develops when it is exposed to uv irradiation.

(c) The intrinsic absorption of the crystal in this region is unknown but may obscure the extrinsic absorption in low-absorption samples like those shown in Fig. 1.

(d) We have evidence, to be presented later, that there are several centers contributing to the absorption near 190 nm and we have not been able to unravel their relative contributions.

The data that we do have relative to the *Y* band and its variation with stoichiometry are shown in Fig. 1. We can draw the following qualitative conclusions.

(a) The *Y* band roughly follows the *X* band in strength, i.e., samples low in *X* center are low in *Y* center.

(b) The *Y* center is probably not the same as the *X* center for its strength does not vary as much with growth conditions as the *X* center. This can be seen most clearly in Fig. 1 by noting the shift in the position of the minimum in the absorption near 210 nm from sample to sample. The shift is in the direction expected if the concentration of the *Y* center varies with composition less rapidly than the *X* center.

Quenching and Temperature Effects

Two alternative models for the *X* center, which have been proposed largely on the basis of ESR data, are $(VOV)^+$ and $(VO)^0$. These models are both supported by the dependence of the *X* band upon variations from stoichiometry noted above. It is to be expected that the bonds holding these proposed complexes together are susceptibile to rupturing. Accordingly, we have made attempts to destroy the *X* center by dissociating it thermally. These attempts included two experiments: In the first, crystals were mounted in an oven and the absorption in the *X* band was measured as a function of temperature. Normally, one expects that the height of such a band will decrease with temperature and its width increase correspondingly such that the area remains constant and proportional to the concentration of the center. Figure 3 shows the area under the *X* band for three different crystals as a function of temperature. Clearly, for each of these samples the area of the absorption band decreases at temperatures above room temperature, indicating that the concentration of the *X* center decreases at these temperatures. The scatter in the data becomes large at very high temperatures because the *X* band becomes weak and broad and is difficult to separate from the base line and the *Y* band.

In the second experiment we investigated the recovery of the *X* band in samples that were thermally quenched. The sample shown in Fig. 3 labeled $1.05\ CaF_2$ (an unsupported wafer 0.006 in. thick) was first heated to 800 °C for several minutes. According to Fig. 3 this treatment should reduce

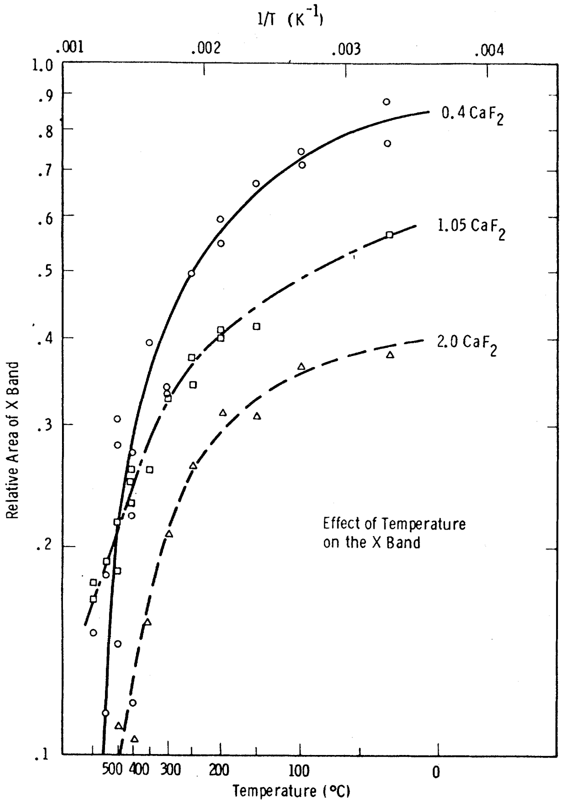

FIG. 3. Dependence of the *X* band upon temperature for three representative samples.

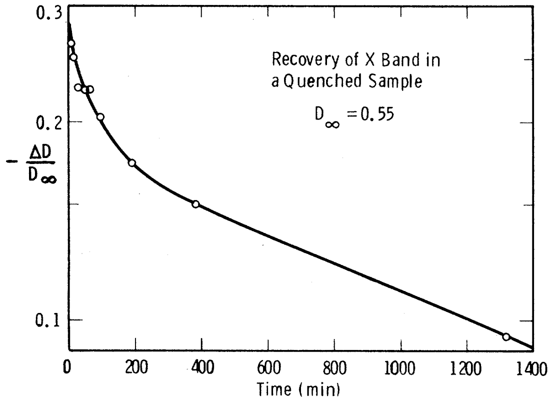

FIG. 4. Dependence of the *X* band upon time following a quench from high temperatures. Optical density is abbreviated *D*.

the area of the *X* band by more than four times. The sample was then quenched by plunging it into cold water. A series of optical absorption measurements was then performed starting about 5 min after the quench. The results are shown in Fig. 4 as $-\Delta D/D_\infty$, the fractional drop in the optical density (D) of the *X* band owing to the quench, versus time. Clearly heating has destroyed some of the *X* centers and their reformation requires several days at room temperature.

At the elevated temperatures at which the *X* center is partially destroyed the *Y* band and therefore the *Y* center appear to be relatively little affected. This is further evidence that the *X* and *Y* centers are not the same and that the *Y* center is either a monatomic center or a complex more tightly bound that the *X* center.

Interaction of X Center with Impurities

The concentration of the *X* centers is drastically reduced when certain impurities are added to FAP. Examples of impurities which cause this effect are Mn, Nd, Gd, and Sb. A concentration of about 1 at.% of these ions relative to Ca is needed in each case to substantially eliminate the *X* center. This "gettering" phenomenon has been carefully investigated for Mn because of the detailed information which can be obtained with this paramagnetic ion using ESR techniques. The conclusions of this study are presented elsewhere[14] but may be summarized as follows: When crystals are grown under conditions that usually produce large concentration of *X* centers and Mn ions are added, the *X* centers disappear and a new Mn center [called Mn(II*m*)] appears. In this new center the Mn ion sits next to a complex defect. If the sample is quenched from about 800 °C the complex defect near the Mn ion changes its identity in some unknown way but slowly recovers if held at room temperature for several hours.

The similarities between this complex and the *X* center, especially the quenching behavior, make it seem likely that they are the same center and, therefore, that the "gettering" action is merely an association of the *X* center and the impurity ion.

Concentration of X Centers

We can use the "gettering" phenomenon in an indirect fashion to calculate the concentration of *X* centers in a crystal. The calculation is based upon the assumption that there is no change in the concentration of *X* centers when Mn ions are added to a crystal but that they associate one-to-one with Mn ions making Mn(II*m*) centers. Measurements have been made by ESR of the maximum concentration of Mn(II*m*) centers which can be formed in a sample. This concentration is equivalent to the *X* center concentration in that crystal and also to the *X* center concentration which would have been present even if no Mn ions had been added. Using these arguments and the ESR measurements we find an *X* center concentration in "stoichiometric" samples of $2\times10^{18}/\text{cm}^3$. We can calculate the *X* center concentration in several other different ways, such as from its absorption strength (and the assumption of unit oscillator strength), and find values in good agreement with this one. This agreement lends support to our interpretation of the "gettering" process as an association event.

The concentration of *X* centers found is very large; about 1% of the fluorine ions are replaced with *X* centers in a "stoichiometric" crystal. In the sample 1.2 $CaCO_3$ about 10% of the fluorine ions are replaced. This large defect concentration is comparable to that which has been achieved in a crystal of calcium chloroapatite, $Ca_{10}(PO_4)_6Cl_2$, by an appropriate heat treatment.[15]

B. New Color-Center Bands

The E(IV) Center

When the samples with a low concentration of *X* and *Y* centers (0.8 $CaCO_3$ and 2 CaF_2) were irradiated with 185-nm uv light a host of paramagnetic centers was generated which could be correlated with growing optical absorption bands. Two of these optical bands have not been observed before and are reported here.

We will call the first, shown in Fig. 5, the *E*(IV) band because its growth and destruction are well correlated with that of the *E*(IV) center observed by ESR. This resonance was found by Piper *et al.*,[8] but not correlated with an optical band or assigned to a specific center. We identify the *E*(IV) center as an $(OV)^0$ defect with a trapped electron, i.e., $(OV)^-$. The identification is based upon the following observations.

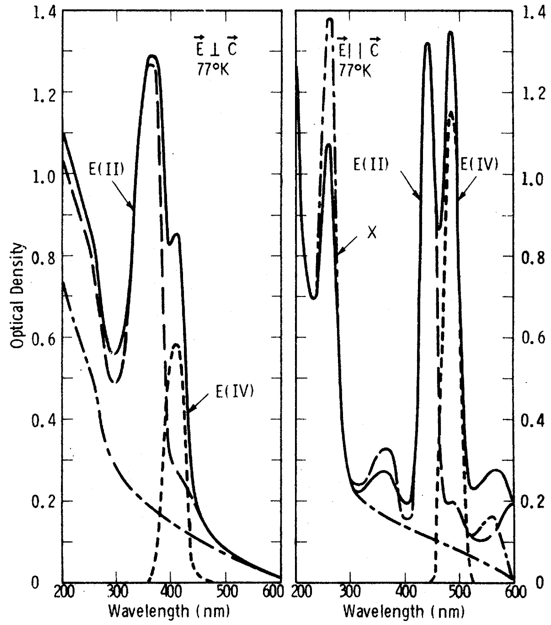

FIG. 5. Irradiation sequence for a sample deficient in $CaCO_3$, showing the optical bands of the H(II) and E(IV) centers. (Dot-dashed curve, before irradiation; solid curve, after 1-hr irradiation with 185-nm uv light; dashed curve, after warming to room temperature and recooling to 77 K; dotted curve, resolved E(IV) bands.)

(a) The observed ESR spectra can only be due to a center composed of an electron trapped by a fluorine vacancy which has some unidentified defect on only one side.

(b) The optical spectrum is similar to that of the E centers and thus its structure should be similar, i.e., an electron trapped by a fluorine vacancy with, possibly, an adjacent defect or complex.

(c) The E(IV) center, like the E(I) center, is destroyed when irradiated samples are warmed from 77 to 300 K. The destruction of the E(IV) and E(I) centers differ, however, in two important ways. First, the E(IV) center is not itself thermally unstable for it does not usually disappear completely upon warming. Second, the disappearance of the E(I) center is accompanied by the appearance of the E(III) center, i.e., the E(I) center is converted to the E(III) center. In contrast, the disappearance of the E(IV) center is accompanied by the disappearance of the H(I) center, i.e., they mutually destroy each other. It can be shown that this destruction is due to the capture by E(IV) of holes freed from the thermally unstable H(I) center. The E(IV) center is the only E center to be destroyed in this way upon warming; therefore, its hole capture cross section must be much larger than the others. This follows quite naturally if the E(IV) center has a net negative charge. The proposed model for the E(IV) center, i.e., $(OV)^-$, has this property and is the most reasonable model which also satisfies the other constraints mentioned above.

The H(II) Center

The second new optical band detected and assigned an identity is the H(II) band. This label is used to indicate its correlation with the H(II) paramagnetic center observed by Piper *et al.*,[8] and identified by them as $(O)^-$ plus a hole, i.e., $(O)^0$. As shown in Table I the H(II) paramagnetic center is found in all of our samples before irradiation and grows with irradiation at different rates in different samples. Its concentration before irradiation is not sensitive to variations in stoichiometry. The optical band which we call H(II) has a shape which is poorly revealed by our measurements. This is because it lies under the X and Y bands. Its existence and shape are inferred from data like that shown in Fig. 5. Figure 5 shows the optical absorption of 0.8 $CaCO_3$ before and after extensive irradiation at 77 K with 185-nm uv light. Aside from the growth of the E bands a decrease in the X band can be noted and a general increase in

TABLE I. Properties of three crystals of FAP grown from different melts. The values of $\alpha_{\parallel}$, the optical absorption of the X band, and $H(\mathrm{II})_0$, the concentration of the H(II) center (from ESR), are obtained before irradiation. Also given are the growth in the H(I), H(II), E(I), E(II), and E(IV) ESR signals after irradiation. The experimental error in the ESR measurements is ± 25%. The growth of all the H centers equals the growth of all the E centers within experimental error.

	Before irradiation			After 1-h irradiation at 77 K				
Sample	$\alpha_{\parallel}(X)$ (cm^{-1})	$H(\mathrm{II})_0$ ($10^{16}/cm^2$)	Type irradiation	$\frac{\Delta H(\mathrm{II})}{H(\mathrm{II})_0}$	$\frac{H(\mathrm{I})}{\Delta H(\mathrm{II})}$	$\frac{E(\mathrm{I})}{\sum E}$	$\frac{E(\mathrm{IV})}{\sum E}$	$\frac{E(\mathrm{II})}{\sum E}$
0.97 $CaCO_3$	1200	13	uv	5.2	1.7	0.9	<0.03	<0.06
0.97 $CaCO_3$	1200	13	γ	0.4	6.3	0.9	<0.03	0.1
2.0 CaF_2	120	7.5	uv	5.4	1.2	0.3	0.6	0.1
2.0 CaF_2	120	7.5	γ	•••	•••	•••	•••	•••
0.8 $CaCO_3$	13	20	uv	0.6	1.8	0.1	0.6	0.3
0.8 $CaCO_3$	13	20	γ	0.5	1.0	0.2	0.6	0.2

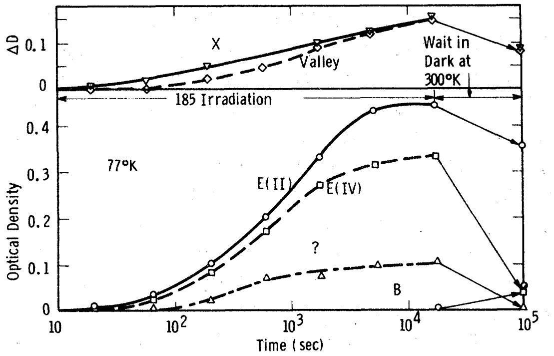

FIG. 6. Change in ESR spectra of an approximately stoichiometric sample due to irradiation at 185 and 250 nm.

the region around the X and Y bands, especially for the polarization $\vec{E} \perp \vec{c}$. Irradiation with light in this region, around 250 nm, causes a drop in this broad, general absorption. We call this absorption the H(II) band. Indirect information about its shape can be derived from ESR measurements. They show that the concentrations of the H(II) center and the E centers are always roughly equal. The height of the H(II) optical band, however, is only a fraction of that of the E bands. Thus, assuming equal oscillator strengths, the H(II) band must be broad, i.e., 5–10 times wider than the E bands.

The identification of the H(II) optical band with the H(II) ESR center is based upon the following factors.

(a) The H centers must have absorption bands and, since they do not appear in the visible or near ir, they should be found to the short wavelength side of the E bands near the intrinsic absorption edge.

(b) Irradiation with 185-nm uv light increases the H(II) paramagnetic center and the H(II) optical band proportionately.

(c) An irradiation with light absorbed by the H(II) band, i.e., near 250 nm, reduces the ESR signal of the H(II) center, as is shown in Fig. 6, as well as the strength of the H(II) band.

(d) Holes are released by such an irradiation near 250 nm. This conclusion is reached after observing the rapid destruction, primarily of E(IV) and B centers, that results from such an irradiation. These centers can be destroyed by holes and since they alone have a net negative charge they have a large capture cross section for holes. In samples like that shown in Fig. 6 containing few E(IV) or B centers, those nuetral E centers present, i.e., E(I), E(II), or E(III), are destroyed by the holes instead. In samples containing no E centers at all, i.e., unirradiated samples, the holes are trapped by $(OV)^0$ centers forming H(I) centers and the H(II) centers are destroyed.

(e) The H(II) band cannot be assigned to the only other known hole center, H(I), because the H(II) band forms at 300 K while the H(I) center is unstable at 300 K. Furthermore, the H(I) center is not strongly affected by radiation into this band, as is shown in Fig. 6.

C. Area Correlation Measurements

Mobility of Defects

If samples are irradiated at 300 K with uv light to create E and H centers and are then stored in the dark at room temperature, the concentration of most of the defects changes. This is shown, for instance, in Fig. 7—a plot versus time of the optical density of several centers in the crystal 0.8 $CaCO_3$ as a result of prolonged irradiation with 185-nm uv light followed by a long wait in the dark, all at 300 K. These measurements were made with unpolarized light and the crystal was cut so that the light sampled both polarizations equally. Most apparent from Fig. 7 are the reduction of the E(II) band and the growth of the E(III) and B centers during the wait in the dark. Also plotted are the change in the peak height of the X band at 250 nm and the valley at about 200 nm. It is apparent that the radiation causes both to rise. This increase in absorption is caused by the growth of the H(II) band beneath them. If these measurements are repeated at 77 K, no changes are observed after prolonged holding periods in the dark.

Two explanations can be put forth to explain the changes observed at 300 K in the dark. Either electrons and holes are freed from certain defects and are trapped by others, or some of the color centers are mobile and diffuse and combine with others. Now since the electron excess centers, E(III) and B, have grown in the dark, motion of holes is ruled out. Electron motion can also be ruled out, for in this sample the E(II) center is the only possible donor. Piper *et al.*[8] have shown,

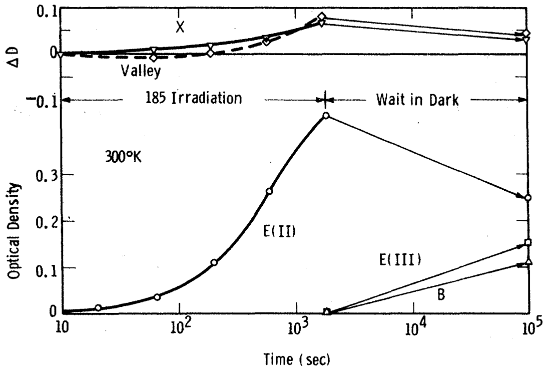

FIG. 7. Growth of color-center absorption bands in a sample deficient in $CaCO_3$ at 300 K.

however, that the electron is bound very strongly to this center so that it is very stable. After considering various alternatives, we are led to the conclusion that the E(II) center $(V)^0$ is mobile at 300 K. This can occur most readily along the chain of fluorine ions by the interchange of a fluorine ion and an electron trapped at the adjacent fluorine vacancy. The quenching experiments suggest and more direct experiments by Tse *et al.*[16] show that an undecorated fluorine vacancy can move in this way rather easily. If the vacancy and E(II) centers are mobile at room temperature some of the important reactions which one would expect to occur are the following:

$$E(\mathrm{II}) + (\mathrm{O}V)^0 \rightarrow E(\mathrm{I}) \rightarrow E(\mathrm{III})\,, \quad \text{growth of } E(\mathrm{III}) \text{ center}$$

$$E(\mathrm{II}) + E(\mathrm{III}) \rightarrow B + (V)^+\,, \quad \text{growth of } B \text{ center}$$

$$E(\mathrm{II}) + H(\mathrm{II}) \rightarrow (\mathrm{O}V)^0\,, \quad \text{destruction of } E(\mathrm{II}) \text{ and } H(\mathrm{II}) \text{ centers}$$

$$(V)^+ + (\mathrm{O})^- \rightarrow (\mathrm{O}V)^0,$$

$$(V)^+ + (\mathrm{O}V)^0 \rightarrow (V\mathrm{O}V)^+\,.$$

Evidence for the first three reactions can be found in Fig. 7. The last two reactions suggest that $(\mathrm{O})^-$ and $(V)^+$ defects as well as all kinds of complexes like $(\mathrm{O}V)^0$ and $(V\mathrm{O}V)^+$ are being consumed and/or produced constantly at 300 K until their relative concentrations approach some kind of equilibrium relationship. If the concentration of any member of this group is disturbed, for instance by capturing charges released by uv radiation, the concentration of all of the others will also change to reestablish their equilibrium. This is in contrast to the simple model proposed by Piper *et al.*,[8] in which the concentrations of the primitive defects and the complexes are never changed by irradiation—the only change being their net charge. As a consequence of this complication attempts made to correlate the growth of the E and H centers with the loss of the X or Y centers must not be carried out at room temperature but at lower temperatures, like 77 K, where the diffusion of the defects does not occur so rapidly. Such correlation studies appears to be a useful way to establish an identification of the X and Y centers.

We have performed studies at 77 K to attempt to correlate the growth of the E and H bands with changes in the X and Y bands. Typical results of such optical experiments are shown in Fig. 8. The experiment was identical to that described above (and shown in Fig. 7) except that the temperature during irradiation was 77 K instead of 300 K. ESR measurements were also made on this sample; the results are shown in Table I. The paramagnetic centers produced by irradiation were largely those revealed by the optical measurements, i.e., the E(II) and E(IV) centers, and the H(I) and H(II) centers. Other paramagnetic centers were observed at lower concentrations. The simultaneous growth of the absorption at 250 and 210 nm (called the X band and the valley) is due to the underlying H(II) band. Assuming that the oscillator strengths of the X, E, and H bands are roughly equal, we calculate from Fig. 8 that the drop in the area of the X band after extensive irradiation is very low—lower by at least an order of magnitude than the growth of the E(II), E(IV), or H(II) bands. The drop however is approximately the same as the much slower growth of the E(I) band inferred from the ESR data. Thus the E(I) center may grow from the X center by electron capture, but not the E(II), E(IV), or H(II) centers. Since we know the identity of the E and H centers we can conclude that the X center is not $(\mathrm{O})^-$, $(V)^+$, or $(\mathrm{O}V)^0$ but may be $(V\mathrm{O}V)^+$.

Since the E and H centers must be formed from some center which exists before irradiation, and since the Y band usually decreases during such irradiations, the Y center is a likely candidate. Un-

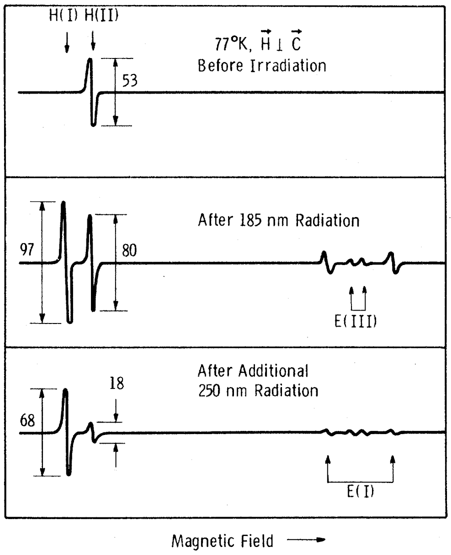

FIG. 8. Growth of color-center absorption bands in a sample deficient in $CaCO_3$ at 77 K.

fortunately, its dependence upon radiation cannot be assessed accurately so a correlation of its area with that of the *E* and *H* bands cannot be tested as was done for the *X* center.

D. γ-Radiation Experiments

Identification of Y Center

It is clear that if the temperature of a sample is low enough, color centers produced by uv radiation are created solely by the capture of charges by intrinsic defects like the *X* and *Y* centers. Color centers produced by γ or x irradiation are created largely by the same process but some centers can be produced from new defects which are themselves formed by the energetic radiation. This process is usually unimportant for short irradiations such as these. There is another more important difference between uv and γ or x radiation: γ or x radiation is sufficiently energetic to simultaneously produce free electrons and free holes, while uv irradiation at 185 nm, which is absorbed by the *Y* center, does not have energy greater than the band gap energy of about 7.75 eV (160 nm), and thus is capable of freeing only electrons *or* holes. If we can decide which is the case for the *Y* center, i.e., whether electrons or holes are released, we have also determined the charge of the ionized *Y* center left behind. If only one or, at worst, a small number of color centers of that charge have been produced, we may be able to conclusively identify the ionized *Y* center as that color center. The identity and structure of the neutral *Y* center will then readily follow from our knowledge of the structure of the different color centers.

We proceed to carry out this plan in the following manner: We have irradiated three samples with varying *X* and *Y* center concentrations with 185-nm uv light at 77 K and have also irradiated two of the same crystals at 77 K with Cs^{137} γ rays. We have measured by ESR the concentrations of the centers produced. The results are shown in Table I. The entries to be noted are the last four rows which show, respectively, the ratio of the *H*(I) to *H*(II) centers produced by the irradiation and the fraction of the *E*(I), *E*(IV), and *E*(II) centers produced. The data can be summarized as follows: The mixture of *E* centers produced varies from crystal to crystal but is the same for uv and γ irradiation. The mixture of *H* centers is roughly constant for all crystals for uv irradiation $[H(\mathrm{I})/H(\mathrm{II}) \cong 1.5]$ but very different and sample-dependent for γ irradiation.

This result is exactly what one expects if electrons are freed from *Y* centers by the uv irradiation, and quite different from the case if holes were freed. The mix of *E* centers is the same for uv and γ radiation because the electrons in each case are free to be trapped where they will. The mix is different in different crystals because the mix of trapping sites is different. The mix of hole centers is the same in all crystals for uv radiation because the creation of the hole centers is the primary result of absorption of uv by the *Y* center and is thus independent of the concentrations of any of the defects or traps. The hole center concentrations for γ radiation differ from crystal to crystal and differ from the uv radiation case because the holes created with γ radiation are free to diffuse through the crystal to be trapped where they will.

The ionized *Y* center must therefore be positively charged, i.e., a hole center. Unfortunately, there are two hole centers produced, *H*(I) and *H*(II). It is possible that the *Y* band is actually composed of two subbands, one owing to $(OV)^0$ and the other $(O)^-$, and that each is converted to the corresponding hole center, *H*(I) and *H*(II), upon uv irradiation. This possibility seems to be unlikely since the mixture of *H* centers produced by uv would then be expected to vary from crystal to crystal. Instead it is essentially the same in all crystals. A more likely explanation is that the *Y* center is $(OV)^0$ and that when it is ionized by uv the resulting center is *H*(I) in an excited state. This excited center then partially (~0.4) dissociates into *H*(II) plus a vacancy. That this dissociation is not thermally activated at 77 K has been demonstrated by carrying out the irradiation at 4 K. The mixture of *H* centers produced is unchanged. Thermal dissociation of the *H*(I) center does occur at room temperature in the dark; thus the *H*(I) center is relatively unstable and the proposed partial dissociation after ionization appears to be reasonable.

Mass Action Law

In addition to leading to an identification of the *Y* center, the irradiation experiments described above give us information about the other intrinsic defects present in the various crystals. In particular, we find that once an electron has been freed from a *Y* center it can be trapped at three different centers: $(V)^+$, $(OV)^0$, or $(VOV)^+$ producing *E*(II), *E*(IV), or *E*(I). The relative production of these three centers gives us some useful information about the relative concentrations of the three undecorated defects. Table I shows the information we need. In the crystal with the largest *X* band, 0.97 $CaCO_3$, the *E*(I) center is the dominant center, showing that $(VOV)^+$ defects capture most of the electrons. In the intermediate crystal, 2.0 CaF_2, the *E*(IV) center is the strongest with the *E*(I) center having roughly $\frac{1}{2}$ of its concentration. Thus $(OV)^0$ is the main electron trap in this crystal. In the crystal with the least *X* band, 0.8 $CaCO_3$, the *E*(IV) center is the strongest center with

E(II) about $\frac{1}{2}$ as strong. Thus $(OV)^0$ is the main trap but $(V)^+$ has become more important. The mixture of hole centers produced by γ rays gives this same kind of information—the crystal 0.97 $CaCO_3$ contains mainly H(I) centers, i.e., decorated $(OV)^0$ centers, while the crystal 0.8 $CaCO_3$ has a more even distribution of H(I) and H(II) centers, i.e., decorated $(OV)^0$ and $(V)^+$ centers.

The most reasonable way to explain data of this sort is to assume that the primitive defects, $(O)^-$ and $(V)^+$, are introduced into the crystals in equal concentrations, and that the concentrations of these isolated defects as well as clusters of two, i.e., $(OV)^0$, or more, i.e., $(VOV)^+$, are governed by a mass action law. Following this line of reasoning the complex involving the most parts, $(VOV)^+$, will be most important as the highest concentration of the primitive defects; the complex with fewer parts, $(OV)^0$, will be most important at an intermediate concentration of defects; and the isolated $(O)^-$ and $(V)^+$ defects will be most important at low concentrations of defects. The kinds of color centers produced in the different crystals are in agreement with these predictions of the mass action law and substantiate the models for the different centers and the process by which color centers form.

Identity of X Center

The identification of the X center is more difficult than that of the Y center because irradiation in the X bands does not form new centers. The identification is based upon the following evidence accumulated from the results reported above.

(a) The concentration of the X and Y centers depends upon crystal growth conditions in the same way indicating that they are composed of the same parts, $(V)^+$ and $(O)^-$.

(b) One result of the mass action law is that the concentration of $(VOV)^+$ (and more complicated centers) should change more rapidly with total defect concentrations than does $(OV)^0$, i.e., the Y center. The X center behaves in this way.

(c) The X center dissociates thermally indicating it is a complex more loosely bound and, therefore, probably more complicated than the Y center.

(d) There is no ESR or other evidence for the existence of defects composed of $(O)^-$ and $(V)^+$ containing more than three parts. Their existence is doubtful for their stability should steadily decrease with size.

(e) Another hypothetical three part complex that might be stable is $(OVO)^-$. It must form by the association of isolated $(O)^-$ and $(V)^+$ during the cooling of the crystal after growth like the other complexes do. Its formation, however, should be much more difficult for it involves the motion of $(O)^-$ while the other complexes can form by the much easier motion of $(V)^+$. Thus its concentration is expected to be very low. No evidence for its existence has been found.

(f) The area of the X band decreases only slightly under uv irradiation. This drop is much less than the growth of most color-center bands. The E(I) band is an exception. Because of this the X center cannot be $(O)^-$, $(V)^+$, or $(OV)^0$ but can be $(VOV)^+$.

The conclusion drawn from this evidence is that with high probability the X center is $(VOV)^+$.

IV. CONCLUSIONS

FAP crystals grow with a defect structure consisting of equal concentrations of $(O)^-$ and $(V)^+$. Their concentration can be controlled during growth by adjusting the stoichiometry of the melt. Upon cooling these defects partially associate forming $(OV)^0$ and $(VOV)^+$, the former causing the Y band and the latter the X band. At room temperature all of these defects are in equilibrium with each other such that if the concentration of one is altered that of the others will slowly shift in compensation.

Irradiation in the Y band at low temperatures frees electrons from the $(OV)^0$ center forming H(I) in an excited state. In returning to its ground state about 0.4 of the H(I) centers decompose into the H(II) center and an isolated vacancy $(V)^+$. The electrons freed from the Y center are trapped by the centers $(V)^+$, $(OV)^0$, and $(VOV)^+$ forming the related E centers. Irradiation with γ radiation creates free holes in addition to free electrons. The holes are captured by $(O)^-$ and $(OV)^0$, forming the related H centers. Upon warming several of these centers become unstable and either convert to new centers or are destroyed. Holes can be freed from the H(II) center by irradiating the sample near 200 nm where this center absorbs. The holes are most likely to be trapped by negative centers, i.e., E(IV) and B.

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Compton Profile of LiH[†]

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A Compton-profile measurement of polycrystalline LiH has been made using 59.54-keV γ rays of ^{241}Am. Fairly good agreement is found with a previous Compton-profile measurement at 17 keV using Mo$K\alpha$ x rays. A simple two-parameter theory is used in which a radial phase dependence is introduced for each of the two H^- electrons. Good agreement is obtained with the measured Compton profile and previously measured scattering factors. This is in contrast with previous theories which, though obtaining good agreement with the measured scattering factors, consistently predicted narrower Compton profiles than were experimentally measured. A tight-binding calculation of the Compton profile of LiH was also made using Kunz local-orbital wave functions, which in contrast to previously used simple screened-hydrogenic wave functions have the important feature that first-order overlap has been taken into account. The previously neglected Li^+-Li^+ overlaps are shown to be non-negligible and are included. This *ab initio* calculation, similar to previous theories, predicts a narrower Compton profile than experimentally measured.

I. INTRODUCTION

There has been considerable recent interest in the theoretical and experimental analysis of LiH. Hurst[1] assumed a model in which the crystal is entirely ionic with no exchange between the charge clouds of adjacent ions. The wave function of the H^- ion was minimized with respect to the energy in the field of point charges and the process was repeated for Li^+ as the central ion. Calder *et al.*[2] measured x-ray scattering factors and found that the Hurst wave functions gave good agreement with the measurements. Phillips and Weiss,[3] on the other hand, measured the Compton profile and found marked disagreement with the Hurst wave functions. In order to improve the fit they added d-like wave functions to the isotropic s-like wave functions of Hurst. A best fit to both the scattering factors and the Compton profile required an unrealistic 60% addition of the d-like wave functions; the fit still being poor. Very recently, a number of theoretical attempts have been made to reconcile the Compton-profile and scattering-factor data. Brandt[4] used self-consistent electron wave functions in the cell approximation, while Berggren and Martino[5] used tight-binding wave functions. While the scattering factors calculated from the self-consistent-cell and tight-binding wave functions are in good agreement with experiment, the Compton profiles calculated from these wave functions are appreciably narrower than the experimental data. The possibility thus exists that the Compton-profile data[3] using Mo$K\alpha$ x rays (~ 17 keV) might be in error. Section II describes a new Compton-profile measurement using 59.54-keV γ rays, the results of which are in fairly good agreement with those of Phillips and Weiss.[3] In Sec. III the results are analyzed. First, a simple two-parameter theory is presented which gives good agreement with both the experimental scattering factors and the Compton profile. Secondly, in order to explore the possibility of whether an improved tight-binding calculation might be in better agreement with the experimental results, a calculation to sixth order in the tight-binding approximation is presented using Kunz[6] local-orbital wave functions. Whereas in the tight-binding calculation of Berggren and Martino[5] simple screened-hydrogenic wave functions were used, the Kunz wave functions have the important feature that first-order overlap is taken into account.

II. EXPERIMENT

The LiH sample used was polycrystalline. The results can be compared with the spherically aver-