

## Color Centers in X-Irradiated Halophosphate Crystals

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A number of new measurements have been made of the properties of the anisotropic color centers produced by x rays in single crystals of calcium fluoro- and chlorophosphate. The measurements include optical absorption, fluorescence, and photoconductivity. Transformations of the centers under thermal and optical excitation were studied. Three distinct color centers are necessary to account for all the observed color bands, and it is suggested that these are composed of appropriate combinations of halogen vacancies. Coloration results when such defects capture electrons during x irradiation. Subsequent color changes are thermally induced by diffusion of these defects and their aggregation to form new complexes.

### I. INTRODUCTION

THE recent success achieved by Johnson<sup>1</sup> in growing large single crystals of calcium fluorophosphate, opened up the possibility of making refined optical and electrical measurements on this material. A number of such measurements have already been reported by Johnson.<sup>1,2</sup> One of the interesting properties that has come to light is the rapid coloration under x rays or shortwave (1849 Å) ultraviolet.<sup>2</sup>

The crystals of calcium fluorophosphate discussed here have the apatite structure, with the empirical formula  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ . They are colorless as grown, but turn emerald-green after a short x irradiation. The green color changes slowly on standing in the dark at room temperature, first to a blue-green, and finally to blue. Johnson reported<sup>2</sup> three absorption bands in the visible spectrum, peaking at 4500, 6100, and 7500 Å, respectively. The green color comes from a transmission between the first two peaks. The first band gradually fades at room temperature, causing the visible color to shift toward the blue. Johnson also found the absorption to be anisotropic. The color bands are observed only with light polarized parallel to the *c* axis.

In addition to the optical coloration, x irradiation also produces a number of spin-resonance signals. The most predominant one observed by Segall *et al.*<sup>3</sup> was interpreted as arising from the ion  $\text{O}^-$  substituted for  $\text{F}^-$ . It was determined that this center was not responsible for any of the observed color bands.

Reflectivity spectra of halophosphate powders, showing color-center formation under ultraviolet irradiation, have been reported by Suchow<sup>4</sup> and by Apple.<sup>5</sup> Apple describes the absorption spectrum, in terms of the x-ray induced loss in reflectivity as a function of wavelength. These spectra show the peaks at 4500 and 6100 Å for calcium fluorophosphate, as observed by Johnson. Apple does not show the peak at 7500 Å, but shows a peak in

the ultraviolet at  $\sim 3700$  Å. The latter region was not investigated by Johnson.

Although some crystals of calcium chlorophosphate were grown by Johnson, they were generally non-stoichiometric as a result of the rapid loss of  $\text{CaCl}_2$  at the melting point of the crystal ( $\sim 1650^\circ\text{C}$ ). Since then, Prener of this Laboratory has succeeded in growing these crystals from a flux of  $\text{CaCl}_2$  at much lower temperatures.<sup>6</sup> These crystals ranged up to several mm on a side, sufficient for optical measurements.

The present report gives the results of some further measurements made on several of the fluorophosphate crystals grown by Johnson, and on one of the chlorophosphate crystals grown by Prener, and uses these results to deduce probable models for the color centers produced by x rays.

### II. EXPERIMENTAL METHODS

Flat platelets were sawed from the crystalline boules. The platelets were 3–5 mm on a side and about 0.7 mm thick. They were taken from single-crystal regions, ascertained by viewing the boule between crossed polaroids. Usually, the sample was cut with the *c* axis lying in the plane of the platelet, but some samples were prepared with the *c* axis perpendicular to this plane. The large faces of the platelet were polished for optical measurements.

The samples were x irradiated with a tube having a tungsten target and drawing 20 mA at 50 kV. The crystal was approximately 6.8 cm from the source of x rays. A filter of 0.010-in.-thick aluminum was used in the beam. The mean quantum energy was estimated to be about 25 keV. The mean penetration of an x-ray quantum of 25-keV energy into a crystal of calcium fluorophosphate is 0.9 mm. Hence, for the sample thicknesses used, the x irradiation was throughout the volume.

The crystal under investigation was usually mounted in a special cryostat both during x irradiation and during subsequent electrical or optical measurements. The temperature of the sample could be held at any point from liquid-helium temperature to about  $150^\circ\text{C}$ . A

<sup>1</sup> P. D. Johnson, J. Electrochem. Soc. **108**, 159 (1961).

<sup>2</sup> P. D. Johnson, J. Appl. Phys. **32**, 127 (1961).

<sup>3</sup> B. Segall, G. W. Ludwig, H. H. Woodbury, and P. D. Johnson, Phys. Rev. **128**, 76 (1962).

<sup>4</sup> L. Suchow, J. Electrochem. Soc. **108**, 847 (1961); J. H. Singleton and L. Suchow, *ibid.* **110**, 36 (1963).

<sup>5</sup> E. F. Apple, J. Electrochem. Soc. **110**, 374 (1963).

<sup>6</sup> J. S. Prener and J. D. Kingsley, Electrochem. Soc., Extended Abstracts **12**, 1 (1963).

rotating window assembly made it possible to x irradiate through a beryllium window or to transmit the beam of a spectrophotometer through quartz windows and the sample. Electrical connections were provided for a copper-constantan thermocouple, and a heating coil. A high-impedance connection was provided for the measurement of photoconductivity.

Optical absorption measurements were made in a Cary model-14 recording spectrophotometer.<sup>7</sup> A double Glan calcite polarizing prism<sup>8</sup> was placed in the sample beam ahead of the sample. Space limitations prevented placing of a matched prism in the reference arm. Hence it was necessary to subtract a background spectrum, made before the sample was x irradiated, from the spectrum of the colored crystal. This subtraction also eliminated the intrinsic absorption and reflection of the sample. All the optical absorption measurements reported here were made at 77°K. A few runs made at liquid-helium temperature showed only a marginal improvement in resolution, so that the greater difficulty of helium-temperature measurements was not justified.

Fluorescence measurements were made using a grating spectrometer with a 75-W compact xenon arc lamp<sup>9</sup> as light source. For excitation spectra, the monochromatic light from the exit slit was focused onto the sample in the cryostat. A photomultiplier, type 7102, viewed the sample through a window at 45° to the exciting beam. Filters were used in front of the photomultiplier to reject the scattered exciting light. For fluorescence spectra, the light from the xenon arc, modified only by passing through appropriate optical filters, was focused directly onto the sample. The light emitted was then focused onto the entrance slit of the spectrometer with the photomultiplier at the exit-slit end. The beam was chopped in the spectrometer in all cases, and the chopped signal was measured using a Perkin-Elmer model-107 amplifier.<sup>10</sup> A Perkin-Elmer vacuum thermocouple with fluorite window was used to monitor the monochromatic beam.

The same spectrometer used for the fluorescence measurements was also used for the measurement of photoconductivity. However, the beam was not chopped in this case, and the photoconductive currents were measured with a Cary model-30 vibrating reed electrometer.<sup>11</sup> For these measurements, the sample was sandwiched between a gridded electrode, through which the incident light passed, and a sensitive electrode, leading to the electrometer. The latter was fitted with a guard ring leading to ground, so that only volume currents were measured. The gridded electrode was connected to a voltage supply, usually operated at 500 V so as to give a collecting field of about 7000 V/cm. As is

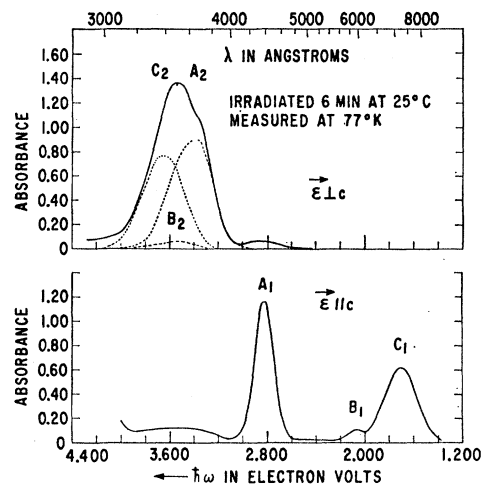


FIG. 1. X-ray-induced absorption in a calcium fluorophosphate crystal. The dotted lines indicate the approximate resolution of the ultraviolet band into three subbands.

usually the practice in making measurements of photoconductivity on insulators, no attempt was made to establish an Ohmic contact. The crystal was merely placed in physical contact with the electrodes. The photoconductive signal then arises from small displacements of charge within the crystal. These displacements also gradually polarize the crystal, so it is necessary to terminate the measurements after a certain amount of charge has been displaced.

### III. RESULTS—CALCIUM FLUOROPHOSPHATE

#### A. Absorption Spectra

Figure 1 shows the spectrum of the absorption induced in a crystal of calcium fluorophosphate by x irradiation for 6 min at 25°C. The upper spectrum was taken with light polarized perpendicular to the *c* axis ("perpendicular spectrum"), while the lower spectrum was taken with light polarized parallel to the *c* axis ("parallel spectrum"). One sees in the parallel spectrum the three peaks reported by Johnson.<sup>2</sup> For convenience in later discussions, the peaks have been labeled with the letters *A*, *B*, *C* in order of increasing wavelength. These letters will be used to identify both the absorption bands and the centers giving rise to these bands.

The band in the near ultraviolet shown by the solid line in the perpendicular spectrum was not reported by Johnson, but may be the ultraviolet band seen in reflectivity by Apple.<sup>5</sup> As a result of correlations observed under various conditions of preparation and bleaching, it has been determined that the ultraviolet band in the perpendicular spectrum is complex, consisting of three unresolved bands. Furthermore, these bands do not arise from any new centers, but are in fact transitions to higher excited states of the *A*, *B*, and *C* centers,

<sup>7</sup> Applied Physics Corporation, Monrovia, California.

<sup>8</sup> Designed and built by Dr. D. T. F. Marple and kindly loaned for these measurements.

<sup>9</sup> PEK X-75, PEK Laboratories, Inc., Palo Alto, California.

<sup>10</sup> Perkin-Elmer Corporation, Norwalk, Connecticut.

<sup>11</sup> Applied Physics Corporation.

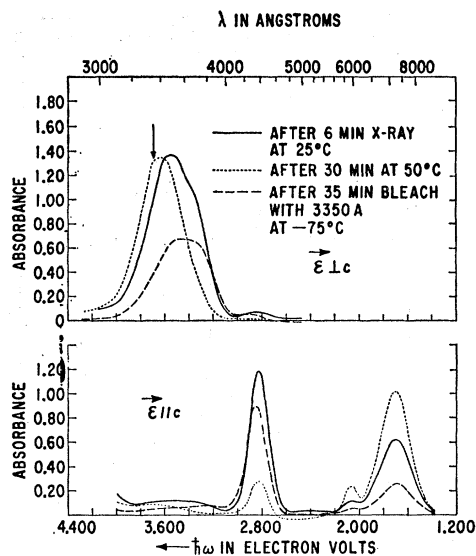


FIG. 2. Bleaching of color centers in a calcium fluorophosphate crystal.

respectively. For this reason, the three visible bands are further labeled by the subscript "1," denoting transitions to the first excited state, while the components of the ultraviolet band, shown by the dotted curves in Fig. 1, are labeled by the subscript "2," denoting transitions to the second excited states.

The wavelengths of the maxima of the  $A_1$ ,  $B_1$ , and  $C_1$  bands shown in Fig. 1 are 4400, 6000, and 7350 Å, respectively. The fact that these values are about 100 Å shorter than those reported by Johnson<sup>2</sup> results from the fact that the measurements reported here were made at 77°K, rather than at room temperature. The widths for the  $A_1$ ,  $B_1$ , and  $C_1$  bands are 0.15, 0.12, and 0.27 eV, respectively. Since the methods of resolving the perpendicular bands are indirect, the measurements made on these bands are less accurate. It was of interest to estimate the area ratios, and these were found to be, roughly: Area of  $A_2$ /area of  $A_1$ =area of  $C_2$ /area of  $C_1$ =1.6. This may be compared to the ratio of 2.0 for the statistical weights for the two levels. The corresponding area ratio for the  $B$  center looks smaller, but the accuracy is very poor in this case.

### B. Bleaching of Color Centers

As mentioned above, the  $A$  bands fade in the dark at room temperature. This fading is strongly temperature-dependent: below 200°K the fading is small; above 100°C it is almost instantaneous. The  $B$  and  $C$  bands are more stable, but some fading occurs here also. All three centers can be completely bleached in  $\frac{1}{2}$  h at 125°C. Thus it is possible to carry out many experiments on a given sample by bleaching and re-irradiation. Usually the bleaching was carried out for  $\frac{1}{2}$  h at 500°C to ensure complete restoration of the crystal to its

TABLE I. Peak heights of color bands of some fluorophosphate crystals x irradiated for 5 min at  $-25^\circ\text{C}$ .

Crystal	$A_1/C_1$	$A_1+C_1$	$-\Delta C/\Delta A^a$
73-A	4.3	1.51	0.71
125-1-1	1.5	1.50	0.70
112-1-1	1.0	1.58	0.43
131-1-1	0.7	1.66	0.33
118-1-1	0.6	1.80	0.34

<sup>a</sup>  $\Delta C$  and  $\Delta A$  are the changes of the respective bands on heating at  $25^\circ\text{C}$  for 30 min.

original form. One crystal was bleached and re-colored more than 50 times without any evidence of progressive changes in properties. The speed with which a given band bleaches at a given temperature is very much dependent on the sample used, and even varies throughout the volume of a particular sample. The bleaching rate may be related to strain, since more rapid bleaching was observed near small cracks.

The centers can also be bleached by irradiation with light in one of their absorption bands. In general, the higher energy transitions are more efficient in producing bleaching. Irradiation in the  $C_1$  band does not produce any detectable bleaching, while irradiation in the  $C_2$  band produces bleaching with high efficiency. Lower efficiencies are found for the  $A_1$  and  $B_1$  bands than for the  $A_2$  or  $B_2$ .

Some of these bleaching effects are illustrated in Fig. 2, which shows the absorption induced into a crystal by x irradiation for 6 min at room temperature (solid line). Later, the  $A$  bands were bleached by heating for 30 min at  $50^\circ\text{C}$  (dotted line). Finally, the  $B$  and  $C$  bands were bleached with 3350-Å ultraviolet radi-

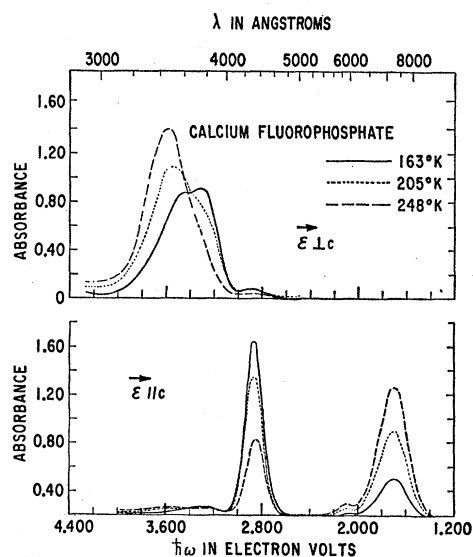


FIG. 3. Effect of temperature of x irradiation of a crystal of calcium fluorophosphate.

tion (indicated by arrow in figure). When the  $A$  bands were bleached, the  $B$  and  $C$  bands were enhanced. Conversely, when the  $B$  and  $C$  bands were bleached, the  $A$  bands were partially restored. The slight shift in the peak of the reconstructed  $A_1$  band will be discussed later. The correlations between the perpendicular spectrum and the parallel spectrum clearly reflect the assignment of the  $A_2$  and  $C_2$  component bands indicated in Fig. 1.

### C. Variation Among Samples

Samples from seven different boules were investigated. All samples showed the same x-ray-induced absorption bands. However, the relative heights, particularly of the  $A$  and  $C$  bands, varied considerably among the various samples. Also, the rate of bleaching of the  $A$  bands at room temperature differed. The two effects were correlated, i.e., the crystals which showed the smallest  $A$  bands initially also showed the most rapid bleaching of those bands. Table I shows the results for five crystals. It is interesting that the ratio of the band heights  $A_1/C_1$  varies by a factor of nearly 10, while the sum  $A_1 + C_1$  varies only about 20% among the samples. The ratio  $\Delta C/\Delta A$  is a measure of the increase of the  $C_1$  band for a given decrease in the  $A_1$  band.

### D. Effect of Temperature of Irradiation

Figure 3 shows the results of x irradiation of a particular crystal at three different temperatures. One sees that the  $A$  centers are favored at low temperatures,

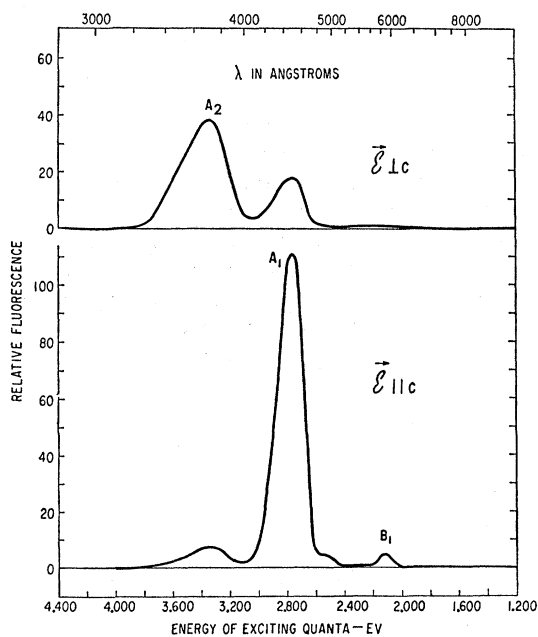


FIG. 4. Fluorescence excitation spectrum of color centers in a crystal of calcium fluorophosphate x rayed 3 min at  $-25^\circ\text{C}$  and measured at  $77^\circ\text{K}$ .

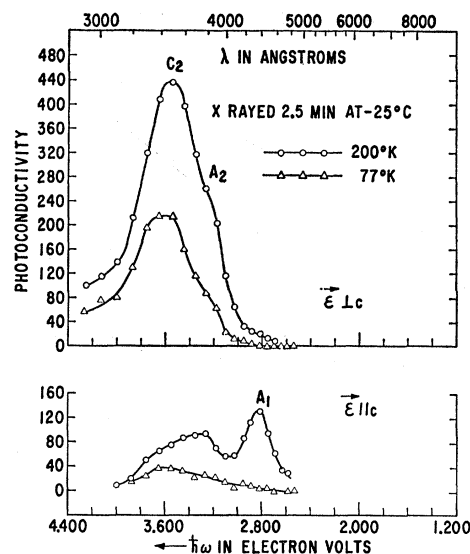


FIG. 5. Excitation spectrum of photoconductivity from color centers in a crystal of calcium fluorophosphate.

while the  $B$  and  $C$  centers are favored at high temperatures. Over a range of  $85^\circ\text{K}$  the  $A_1/C_1$  ratio changes by a factor of 8. Figure 3 also shows the correlations between the first excited states in the parallel spectrum and the second excited states in the perpendicular spectrum.

A more subtle effect of irradiation temperature is seen in the position of the  $A_1$  band.  $A$  centers produced near  $200^\circ\text{K}$  give an absorption peak at  $4335 \text{ \AA}$ , while centers produced at room temperature show a peak at  $4394 \text{ \AA}$ . A gradual shift of the peak occurs between these limits. On cooling centers already made, there is no change in the peak position; but if centers made at low temperature are then warmed to room temperature for half an hour, in addition to bleaching considerably, the peak of the  $A_1$  band will shift to  $\sim 4400 \text{ \AA}$ . Smaller variations have been observed in the  $B$  and  $C$  bands.

### E. Fluorescence of Color Centers

Figure 4 shows an excitation spectrum of one of the crystals at  $77^\circ\text{K}$ . The polarization and wavelengths refer to the exciting light. The crystal was lightly x rayed so that the excitation spectrum should be a faithful reproduction of the absorption spectrum for any given band. Peaks corresponding to the  $A_1$  band and the  $B_1$  band are seen in the parallel spectrum, and a peak corresponding to the  $A_2$  band is seen in the perpendicular spectrum. The polarization is not as complete here as in the absorption spectrum, owing to the fact that the exciting light was incident at  $45^\circ$  to the surface of the crystal in this case, rather than normal to the surface as in the absorption measurements.

There was no indication of fluorescence from the  $C$  center. However, the photomultiplier used did not de-

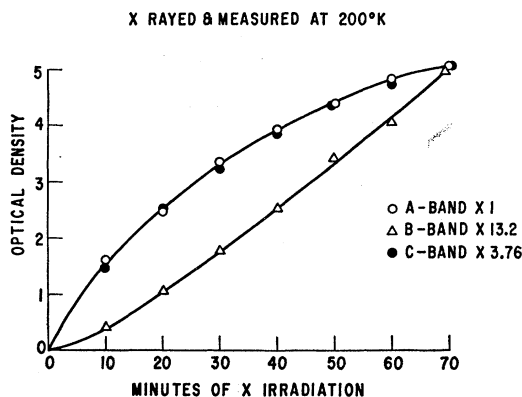


Fig. 6. Plot of band height versus x-ray dose for the  $A_1$ ,  $B_1$ , and  $C_1$  bands in a crystal of calcium fluorophosphate.

tect radiations longer than  $1.2 \mu$  in wavelength. Another point of interest is the fact that the excitation peak for the  $A_1$  band occurs at a slightly longer wavelength than the absorption peak.

Some observations were made on the polarization of the luminescence. Again the polarization was not complete. However, the fluorescence was predominantly polarized parallel to the  $c$  axis, not only when excited in the  $A_1$  and  $B_1$  peaks, but also when excited in the  $A_2$  peak. In the last case, the excitation must be internally converted to the lower state before emission.

The efficiency of the  $A$ -center fluorescence at  $77^\circ\text{K}$  was estimated to be approximately 5%. This decreases with increasing temperature to about 1% at room temperature. The  $B$  center shows a smaller variation with temperature.

Although the luminescence was examined with the spectrometer, no spectra were recorded. At the light intensities needed for detection of the spectrally analyzed emission, the centers were rapidly bleached by the exciting light. However, repeated experiments established the emission of the  $A$  center in the neighborhood of  $6900 \text{ \AA}$  and the  $B$ -center fluorescence peak at about  $9000 \text{ \AA}$ .

### F. Photoconductivity

Several samples were examined for photoconductivity. The magnitude of this effect was very small. For example, with a field of  $7000 \text{ V/cm}$ , the product of the ionization efficiency  $\eta$  and the mean drift distance  $w$  was of the order of  $10^{-8} \text{ cm}$ . In order to get usable signals ( $10^{-15}$ – $10^{-14} \text{ A}$ ), it was necessary to use very high light levels. With the xenon arc lamp and a bandwidth of  $30 \text{ \AA}$  on the monochromator, sufficient intensities were available, but as few as ten readings of the photoconductivity would bleach the sample significantly. For this reason, photoconductivity measurements were not made extensively.

Figure 5 shows some typical measurements, plotted in the form of a sensitivity spectrum at two tempera-

tures. At  $200^\circ\text{K}$  the  $A_1$  band is clearly seen, but at  $77^\circ\text{K}$  it is frozen in. In the perpendicular spectrum a large peak is seen at  $3500 \text{ \AA}$  with a shoulder at about  $3800 \text{ \AA}$ . These could be the unresolved  $C_2$  and  $A_2$  bands. This photoconductivity decreases, but does not disappear at  $77^\circ\text{K}$ . There seems to be some photoconductivity in the ultraviolet portion of the parallel spectrum, but interference from the unknown depolarized contribution from the perpendicular spectrum prevents accurate measurement here. No photoconductivity was observed with irradiation in the  $B_1$  or  $C_1$  bands. No measurements were made on the  $B_2$  band, because of the difficulty of making this band large compared to the  $C_2$  band.

Some investigation was made in regard to possible anisotropy of the photoconductivity with respect to the field direction. Since it was necessary to cut separate samples for measurements with the field parallel to the  $c$  axis, the comparison was only approximate. Several samples were investigated in each case and no dependence on the field direction was noted. The difference in photoconductivity (i.e., in mobility) would have had to be greater than 20% in order to be detected.

In the course of making measurements of photoconductivity, dark currents in the range  $10^{-12}$ – $10^{-14} \text{ A}$  were observed at temperatures near room temperature or above. In addition to being temperature dependent, the dark currents were highly anisotropic, being at least an order of magnitude larger when the field was parallel to the  $c$  axis than when it was perpendicular. The dark current was approximately the same whether or not color centers were present. Photoconductivity measurements were restricted to lower temperature regions, where the dark currents were very small.

### G. Oscillator Strengths

One sample was prepared in such a way as to have primarily only  $C$  centers. This sample was then bleached with polarized monochromatic light near the peak of the  $C_2$  band. By noting the change in absorbance and measuring the number of absorbed photons, the quantity of  $n_0/\eta_B$  was calculated, where  $n_0$  is the number of centers per  $\text{cm}^3$  and  $\eta_B$  is the quantum efficiency for bleaching. Then from the total area under the  $C_1$  and  $C_2$  and absorption bands, the quantity  $n_0f$  was calculated from Smakula's equation<sup>12</sup>:

$$n_0f = 0.821 \times 10^{17} \frac{n}{(n^2 + 2)^2} \int \alpha(E) dE,$$

where  $f$  is the oscillator strength,  $n$  is the refractive index,  $\alpha(E)$  is the absorption coefficient in  $\text{cm}^{-1}$ , and  $E$  is the quantum energy in electron volts. The value  $n = 1.633$  was used. From these calculations the product

<sup>12</sup> A. Smakula, Z. Physik **59**, 603 (1930); D. L. Dexter, Phys. Rev. **101**, 48 (1956).

$\eta_B f = 0.25$  was obtained. Since one expects a maximum of unity for each of the factors, one can say that each lies between 0.25 and 1.00. A similar experiment was performed on the  $A$  center by bleaching in the  $A_1$  band, but the above product was much lower, so probably the bleaching efficiency was low in that case.

### H. Symmetry Investigations

All three centers show one excited state whose transition moment is polarized parallel to the  $c$  axis and one perpendicular. If the center has lower symmetry than the crystal, the perpendicular state may be further resolvable into two different directions in the plane perpendicular to  $c$ . This anisotropy would probably not be visible in the crystal as x rayed because centers oriented in different directions would tend to produce an over-all isotropy. If, however, these centers are bleached with light polarized in a given direction perpendicular to  $c$ , anisotropic absorption may arise through selective bleaching. A wavelength of 3500 Å was chosen, because this would hit one side of both the  $C_2$  and  $A_2$  bands. It would be better to irradiate in one side of a band than in the center, for if the band is a doublet, as one hopes it will be, then one should irradiate only one member of the doublet. This experiment was carried out several times, but no asymmetry in absorption in the plane perpendicular to  $c$  could be produced.

### I. Effect of X-Ray Dose

Figure 6 shows the relative optical density of a sample as a function of the time of x irradiation at 200°K. Because of the difficulty of measuring the highest densities, the peak values were calculated from the optical densities at wavelengths removed from the peak, and a constant band shape was assumed. Some results carried out with a thinner crystal were consistent with results obtained by the above procedure. For convenience, the curves for the different bands have been normalized to the same value at the last point.

The behavior of the  $A_1$  and  $C_1$  bands is quite similar except for magnitude, i.e., the  $A_1/C_1$  ratio remains nearly constant during exposure. The optical density of these two bands increases linearly with dose at low exposures and levels off to a nearly constant value at about 200 min exposure corresponding to an  $A_1$  band density of 6 or about  $10^{18}$  centers/cm<sup>3</sup>.

The behavior of the  $B_1$  band is entirely different from the  $A_1$  and  $C_1$  bands. It starts out in a superlinear manner reducing to linear or less at higher exposures. Figure 7 shows similar data for the  $A_1$  and  $B_1$  bands plotted in a different way, using log-log coordinates. The straight line corresponds to a quadratic relationship. The fit is very good. This relationship was investigated somewhat less completely for several other crystals and at various temperatures. The quadratic relationship was found in all cases, although the coefficient relating  $[B]^2$

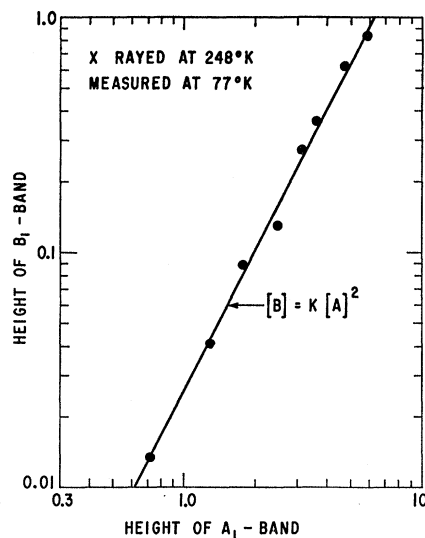


FIG. 7. Relationship between optical absorbance of the  $A_1$  and  $B_1$  bands for various x-ray doses in a crystal of calcium fluorophosphate.

to  $[A]$  was quite temperature-dependent and varied with the sample.

An experiment was carried out to see whether any defects created by the x rays could influence subsequent coloration. The crystal was x irradiated at 200°K until the  $A_1$  band had reached its saturation density. Then the crystal was cooled to 77°K and bleached for one hour with a high-pressure mercury arc. An absorption spectrum showed all the color bands to be bleached. The temperature was again brought up to 200°K and x irradiation was again carried out until the absorbance versus dose curve of the  $A_1$  band was repeated. The second curve was nearly identical to the first, being just slightly lower.

### J. B Band Measurements

In the previous figures, the  $B$  bands were very small. Owing to their quadratic relationship to the other bands, plus their greater thermal stability, it is possible to obtain spectra where the  $B$  bands are much more prominent. Such a spectrum is shown in Fig. 8. It has not been found possible to eliminate the  $C$  bands in such cases. However, in Fig. 8, for comparison, another spectrum is shown in which the  $C_1$  band is nearly the same as in the first spectrum but in which the  $B_1$  band is very small. Since the contribution of the  $C_2$  band to the perpendicular spectrum in the two cases should be nearly the same, the difference in the two perpendicular spectra should approximate the  $B_2$  band.

When a crystal containing  $B$  centers was strongly irradiated with 6000-Å light at 77°K, the  $B_1$  band was bleached and the  $A_1$  and  $C_1$  bands were enhanced. On warming to room temperature for  $\frac{1}{2}$  h, the  $A_1$  and  $C_1$

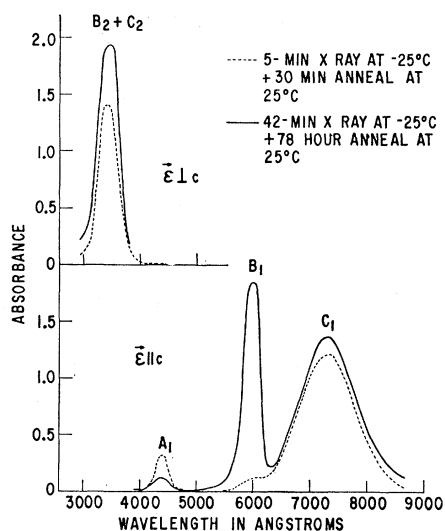


FIG. 8. Absorbance (plotted on a wavelength scale) induced in a crystal of calcium fluorophosphate by x rays. Conditions were chosen for the solid curve such that the  $B$  bands were maximized.

bands faded and the  $B_1$  band was restored to about 94% of its original value.

In another experiment, the  $B$  and  $C$  bands were bleached with ultraviolet at 77°K, creating a very large  $A_1$  band. On warming to room temperature for 1 h, the  $A_1$  band faded and the  $B_1$  and  $C_1$  bands were partly restored. For comparison, a crystal was x irradiated at 77°K until an  $A_1$  band of the same size as the one mentioned above was generated. On warming to room temperature for one hour, the  $A_1$  band faded, and  $B_1$  and  $C_1$  bands were generated. In this case, the generation of  $B$  centers was smaller by a factor of 6.6 than in the first case. Evidently, after the  $B$  centers were bleached at 77°K, the  $A$  centers generated "remembered" that they had come from  $B$  centers and regenerated these centers with high efficiency upon being heated. On the other hand,  $A$  centers made directly by x rays at 77°K produced far fewer  $B$  centers on heating.

### K. Chemical and Electrical Coloration

Several attempts were made to color crystals by chemical and electrical means: (1) crystals were heated in the range 1000 to 1300°C in calcium vapor. This resulted in a reduction of the phosphate near the surface, producing a brown deposit. The central part of the crystal remained colorless. (2) A voltage was applied to nickel electrodes across the crystal, the cathode being a sharp point pressed into the crystal, the cathode being a sharp point pressed into the crystal face. Temperatures up to 600°C and voltages up to 10 000 V/cm were used. Breakdown sometimes occurred, but no color centers were formed. (3) Metallic lithium was deposited on the surface of the crystal and then heated in vacuum at various temperatures up to 700°C. Below 500°C there was

no reaction, while above that temperature phosphate reduction similar to that obtained with calcium vapor was observed. In no case were any anisotropic color centers formed.

### L. Natural Crystals

A specimen of natural apatite from Durango, Mexico, was investigated. Johnson had previously found<sup>13</sup> that these crystals, which are straw-colored in nature, could be bleached by heating, and that color could be partially restored by x irradiation. The crystal used here was heated to 1000°C for  $\frac{1}{2}$  h. The spectrum at 77°K showed no visible color, but a sharp rise in absorption below 3100 Å. X irradiation for 6 min at 77°K produced an absorption in the near ultraviolet which had the effect of extending the monotonic rise to longer wavelengths, i.e., to about 3800 Å. A subsequent irradiation for 135 min at 77°K greatly extended the coloration into the visible. The crystal had now reverted to its straw-colored appearance, somewhat paler than originally. No evidence of the three absorption bands seen in the synthetic crystals was detected.

### IV. EXPERIMENTAL RESULTS: CALCIUM CHLOROPHOSPHATE

Figure 9 shows the absorption introduced into a crystal of calcium chlorophosphate by 5 min of x irradiation at  $-25^\circ\text{C}$ . The solid curve is the absorption measurement just after irradiation. The dashed curve was made later, after the crystal had been heated to  $75^\circ\text{C}$  for 90 min. Figure 10 shows the development of some of the bands with increasing x-ray dose.

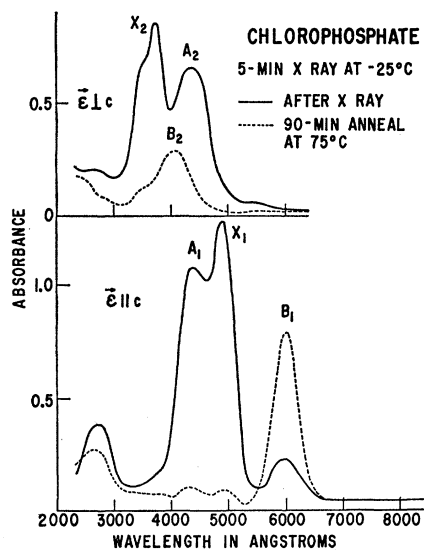


FIG. 9. X-ray-induced optical absorbance versus wavelength<sup>13</sup> for a crystal of calcium chlorophosphate. Dashed line shows the effect of thermal bleaching at  $75^\circ\text{C}$ .

<sup>13</sup> P. D. Johnson (unpublished results).

An attempt has been made to identify the bands in Fig. 9 with corresponding bands in the fluorophosphate. The most probable correspondence has been indicated by using the same labels. The  $B_1$  band is the most clear-cut case, because of its superlinearity with x-ray dose and a quadratic relationship to the other bands. Also, the  $B_1$  band occurs at the same wavelength in the two materials. In addition, the bleaching properties are very similar in the two cases.

The identification of the  $A$  bands in the chlorophosphate is less positive. The justification for labeling the  $A_1$  and  $A_2$  bands as shown is: (1) the wavelength of the  $A_1$  band is the same as in the fluorophosphate; (2) the splitting is the smallest of the three pairs of bands shown, being almost zero in this case; (3) the thermal bleachability at room temperature is similar to the  $A$  band; (4) the dependence of the band height on temperature of x irradiation is qualitatively similar.

The third set of bands is marked  $X$  because they do not correspond closely to any of the bands seen in the fluorophosphate. They behave somewhat like the  $A$  bands in regard to bleaching properties, but the splitting is larger. The  $X_2$  band is unique in that it appears to have structure in the form of a shoulder on the high-energy side. This could be a distinct band, but so far the shoulder has always changed in proportion to the main peak. An example of the behavior of the  $A$  and  $X$  bands under optical bleaching is shown in Fig. 11, which shows progressive bleaching by  $A_2$  light. An analogous set of curves is obtained when the bleaching is done with  $X_2$  light, i.e.,  $X_1$  and  $X_2$  decrease while  $A_1$  and  $A_2$  increase.

There is no band in this material which has characteristics similar to the  $C$  band in the fluorophosphate. Very heavy irradiation produced a weak band at 7700 Å, but the width of this band was much smaller than the  $C$  band in the fluorophosphate.

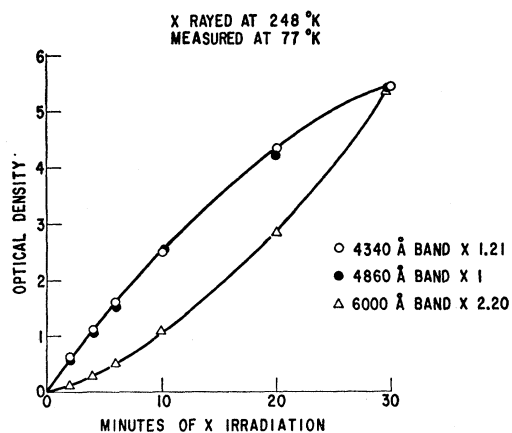


FIG. 10. Plot of absorption band heights versus x-ray dose for a crystal of calcium chlorophosphate. Curves are normalized to coincide at the last point.

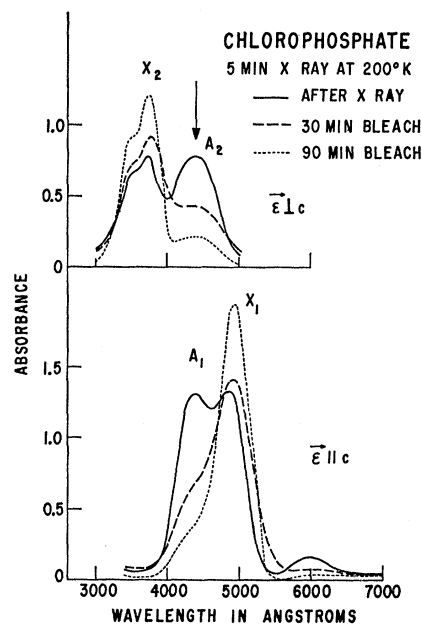


FIG. 11. Optical bleaching of a chlorophosphate crystal. Arrow shows wavelength and polarization of bleaching light.

## V. INTERPRETATION OF RESULTS

### A. Center Formation by X Rays

There are two probable methods by which x rays may produce color centers: (1) reduction or oxidation of existing point defects which have captured electrons or holes or which have been ionized by excitons; (2) creation of point defects from knock-on by electrons or as a secondary result of ionization, as in the mechanism proposed by Varley.<sup>14</sup> The tendency of the dose curves, shown in Fig. 6, to saturate at high dose, and the lack of any enhancement of coloring rate when the dose curve was repeated following an optical bleach, shows that mechanism (1) is the dominant one in this case. Since x rays do not destroy the charge neutrality of the crystal, electron centers and hole centers must be generated in equivalent numbers. When the crystal is heated to a sufficiently high temperature, the oppositely charged centers annihilate one another, restoring the crystal to its original condition. Since the color centers observed here can be transformed into one another and back again, it follows that they must all be the same type of center, i.e., all electron centers or all hole centers. Although no information obtained here positively identifies these centers as either electron centers or hole centers, an over-all model has been devised that is consistent with all the observations. In this model, the observed color centers are interpreted as electron centers. The  $O^-$  center studied by Segall *et al.*<sup>3</sup> can be classified as a hole center. Indeed, it may be the dominant anticenter for the color centers.

<sup>14</sup> J. H. O. Varley, *J. Nucl. Energy* **1**, 130 (1954).



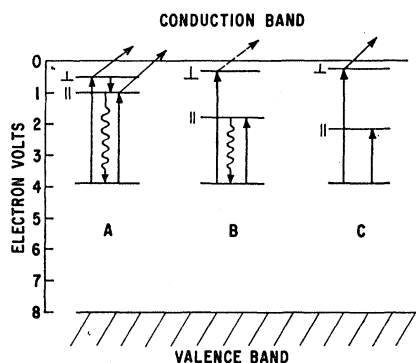


FIG. 12. Energy diagram of the three color centers seen in x-rayed calcium fluorophosphate, superimposed upon the band levels of the crystal. Solid arrows show the processes directly observed in this work.

### B. Energy-Level Diagrams

On the assumption that we are dealing with trapped-electron centers, many of the optical and electrical processes observed here may be summarized by the energy-level diagram in Fig. 12. The band gap of the crystal is approximately 8 eV as determined by Johnson.<sup>1</sup> The processes which have been observed are indicated by arrows on the diagram.

### C. Crystal Structure

In order to discuss any detailed models for the observed color centers, it is necessary to refer to the details of the crystal structure.<sup>15</sup> Figure 13 shows some of these details. The lower part of the figure shows a schematic view of one of the crystal planes perpendicular to the  $c$  axis. For simplicity, circles have been used to represent a repeated group of atoms. The top part of the figure shows the atoms in one of these groups. The plane represented by the circles is a mirror plane of the crystal. The crystal is made up by stacking these planes, with a layer of  $\text{Ca}^{++}$  ions, the  $\text{Ca}_I$  ions, between each plane. In each successive mirror plane the atoms within the circle are rotated by  $60^\circ$  about the center of the circle. The  $\text{Ca}_I$  ions are shown in the figure, although they are not in the plane of the circles. The dashed rhombus outlines the unit cell, which contains 42 atoms.

An important aspect of the crystal structure is the arrangement of the halogen ions. These are essentially in rows parallel to the  $c$  axis. The distance between rows is 9.37 Å, while the distance between ions in a given row is only 3.44 Å.

This geometrical arrangement very probably results in a striking property of these crystals: diffusion of halogen-ion vacancies will be one dimensional, being confined to motion along the halogen chains parallel to

the  $c$  axis. This factor may account for the anisotropic dark conductivity, and may play an important role in the interactions of color centers.

The chlorophosphate differs from Fig. 13 in that the chloride ions are believed to be located between the mirror planes rather than in them. Otherwise, the crystal structures are identical.

### D. Models for the Centers

Johnson<sup>2</sup> suggested the  $F$ -center model as one of the likely possibilities for one or more of the color centers in calcium fluorophosphate. This model will be pursued further in the present discussion. The justification for this is based on a number of similarities between the properties of the centers under discussion and those in alkali halide crystals.

It is proposed that the  $A$  center is the analog of the  $F$  center in alkali halides, i.e., an electron trapped at a halogen ion vacancy.

The  $A$  centers, formed preferentially at low temperatures, are considered to be the primary centers. The  $B$  and  $C$  centers, formed from  $A$  centers when the temperature is raised, are interpreted as aggregate centers. That the  $A$  center is not destroyed by thermal ionization follows from the deep trap depth of this center. Although the quantum energy of absorption is not a measure of trap depth, the quantum energy of fluorescence should represent a lower limit on this depth. Even using this value (1.8 eV) the lifetime for thermal ionization at room temperature is more than  $10^{10}$  years.

The quadratic relationship between the  $B_1$  band and the  $A_1$  band immediately points to the  $B$  center as the dimer of the  $A$  center, i.e., the analog of the  $M$  center in alkali halides. Since the  $C_1$  band varies linearly with the  $A_1$  band, the  $C$  center must be an aggregate of the  $A$  center with a defect already present in large concentration. It is proposed that this second defect is the halogen ion vacancy, i.e., the  $C$  center is the equivalent to the ionized  $B$  center ( $B^+$  center). These models will be used here to interpret the experimental observations.

The excited state of the  $F$  center in alkali halides is threefold degenerate owing to the cubic lattice. When the symmetry is lowered as in the  $F_A$  center,<sup>16</sup> the excited state splits into two parts, one with its transition moment polarized parallel to the axis of symmetry and the other, still twofold degenerate, with its transition moment polarized perpendicular to the symmetry axis. In the halophosphate crystal this lower symmetry is already present in the crystal, so the  $A$ -center transition is split into parallel and perpendicular components relative to the symmetry axis of the crystal.

When two  $F$  centers unite to form an  $M$  center in KCl, the first absorption band is split into three components<sup>17</sup>; the two transitions orthogonal to the line

<sup>15</sup> St. Náráy-Szabó, *Z. Krist.* **75**, 387 (1930); S. B. Henricks, M. E. Jefferson, and V. M. Moseley, *ibid.* **81**, 352 (1932); C. A. Beevers and D. B. McIntyre, *Mineral. Mag.* **27**, 254 (1946).

<sup>16</sup> F. Lüty, *Z. Physik* **165**, 17 (1961).

<sup>17</sup> F. Okamoto, *Phys. Rev.* **124**, 1090 (1961).

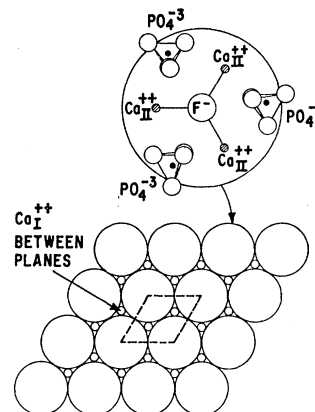
joining the two vacancies are nearly unperturbed in energy from the original  $F$  centers, while the transition polarized parallel to this line is lowered in energy by a factor of 1.48. Similarly, when two  $A$  centers unite to form a  $B$  center in calcium fluorophosphate, the energy of the perpendicular spectrum is hardly changed, while the transition energy in the parallel spectrum (parallel to the line joining the two vacancies) is lowered by a factor of 1.39.

The  $C$  center does not have any analog in the alkali halides, but the model indicated above is suggested by the following simple analysis. Let the  $F$  center (or  $A$  center) be represented by an electron trapped in a cubical box. Now the first excited state will be threefold degenerate with the three transition moments polarized parallel to the three axes of the cube. If now one of the dimensions of the box is increased, the energy of the transition polarized in that direction will be reduced, while the other two transitions will remain degenerate with unchanged energy. This is roughly what happens when a second vacancy is added to the  $A$  center. The  $C$  center differs from the  $A$  center only slightly in regards to the perpendicular spectrum, but the energy of the parallel transition is lower by a factor of 1.7.

The results for the chlorophosphate crystal support the idea that the halogen site is involved in the color centers. The change in lattice parameters between the two crystals is about 2%. Yet the  $B_2$  band, for example, differs in energy by about 10% in the two cases.

The optical bleaching of  $B$  and  $C$  centers, with the resultant formation of  $A$  centers, can take place in two ways. Either an electron can be released from the aggregate center and be trapped elsewhere to form an  $A$  center, or the aggregate center may, upon being excited, dissociate into its elements. The latter is probably the case when the  $B$  bands are bleached. It was found, for example, that the  $A$  band formed by bleaching  $B$  centers reformed the  $B$  band, upon heating, with six

FIG. 13. Diagram showing some features of the fluorapatite structure. The lower drawing shows a plane of atoms perpendicular to the  $c$  axis. Each circle represents the group of atoms shown above. The  $\text{Ca}_I$  ions shown are behind the plane of the circles. The dashed rhombus outlines the unit cell. Alternate planes have the group of atoms in the circle rotated by  $60^\circ$ .



times the efficiency of a similar  $A$  band prepared directly from x irradiation. It would appear that each  $B$  center split into two  $A$  centers, which remained close together. Upon heating, the  $A$  centers reformed  $B$  centers with high efficiency.

Although the models proposed here are far from proved, and are speculative in some respects, they are built up from simple and reasonable elements, and they are consistent with the salient features of the experimental data. They may be useful in suggesting further experiments.

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