Speculation on the Formation of F-Centers During Irradiation*

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It is suggested in this paper that x-ray and radium radiation cause three effects on alkali halide crystals, namely, to produce free electrons, free holes, and single-ion vacancies. It is further assumed that the single-ion vacancy results from a local distortion of the lattice rather than a diffusion of vacancy pairs from outside the crystal. This postulate explains qualitatively various color center phenomena observed at low temperatures and leads to no obvious contradictions. Some rough calculations on this model have been made. Further experimental verification is required.

I. INTRODUCTION

At present we have a satisfactory model of the F-center based on a suggestion of de Boer.[1,2] This model assumes that an F-center is an electron trapped in a negative-ion vacancy and that an F'-center is two electrons trapped in such a vacancy. It is generally believed that the number of incipient single-ion vacancies is too small to account for the number of F-centers formed during x-radiation. The most convincing evidence, in the author's opinion, regarding the absence of vacancies will be given in the next section (paragraphs 9 and 10).

At present the problem remains as to how lattice vacancies occur during irradiation. One suggestion is that vacancy pairs diffuse into the crystal.[3] A new mechanism suggested by Seitz[4–6] is that ion vacancies are generated at dislocations[7] within the crystals. Recent low temperature data by Dutton, Heller and Maurer,[8] Dorendorf,[9] and others[10] cast doubt on the idea that vacancy pairs diffuse from the surface. This difficulty has prompted a re-examination of the low temperature data on color centers in alkali halides. The re-examination lends strong support to the idea that vacancies are generated at dislocations during x-raying.

In the next section we shall list various low temperature phenomena relating to this problem. Then the data by Pick[11,12] will be re-examined and reinterpreted. Finally, the model suggested by Seitz will be considered and the idea of local heating examined.

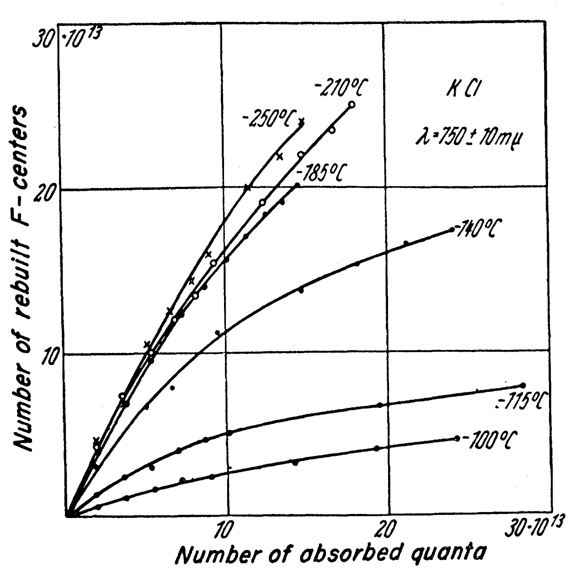

FIG. 1. Plots of the number of rebuilt F-centers as a function of the quantum absorbed in the F'-band. The data was taken by Pick, reference 12. The notation of the y axis corresponds to the present day interpretation (see reference 2).

II. SUMMARY OF LOW TEMPERATURE DATA

We start by listing some of the more interesting properties of color centers in alkali halides:

(1) A very important set of experiments was done by Pick[12] on the formation of F-centers from F'-centers exposed to light. The data were taken on additively colored synthetic crystals[13] with 80 percent of the F-centers converted to F'-centers. In the experiment the crystals were exposed to the light in the F'-band resulting in the rebuilding of the F-centers. Figure 1 is a set of curves taken from Pick, giving the number of

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[1] An experimental review of this subject has been given by R. W. Pohl, Proc. Phys. Soc. (London) **49** (extra part), 4 (1937).

[2] A theoretical review has been given by F. Seitz, Revs. Modern Phys. **18**, 384 (1946). We shall refer to some of the figures in this review since it may be more readily available than the original papers.

[3] As far as the author knows, the diffusion idea was proposed by F. Seitz, reference 2. Calculations on the energy involved in the diffusion process have been made by G. J. Dienes, J. Chem. Phys. **16**, 620 (1948). The local heating idea, to be referred to, was suggested by D. L. Dexter, Science **115**, 199 (1952).

[4] F. Seitz, Phys. Rev. **80**, 239 (1950).

[5] F. Seitz, Revs. Modern Phys. **23**, 328 (1951).

[6] F. Seitz, Advances in Physics **1**, 43 (1952).

[7] Some reviews of the theory of dislocations are A. H. Cottrell, *Progress in Metal Physics* (Interscience Press, Inc., New York, 1949), Vol. 1, p. 77; F. Seitz, "The Theory of Plastic Flow in Single Crystals," in: *A Symposium on the Plastic Deformation of Crystalline Solids, Mellon Institute*, Carnegie Institute of Technology and the Department of the Navy, Office of Naval Research, Pittsburgh, May 19–20, 1950; NAVEXOS-P-834, U.S. Government Printing Office, Washington 25, D. C., 1950, pp. 1–36.

[8] Dutton, Heller, and Maurer, Phys. Rev. **84**, 363 (1951).

[9] H. Dorendorf, Z. Physik **129**, 317 (1951).

[10] W. H. Duerig and J. J. Markham, Conference on the Electrical and Optical Properties of Ionic Crystals, Illinois (1951); Phys. Rev. to be published.

[11] H. Pick, Ann. Physik **31**, 365 (1938).

[12] H. Pick, Ann. Physik **37**, 421 (1940).

[13] That KCl and KBr were additively colored crystals was inferred from reference 11.

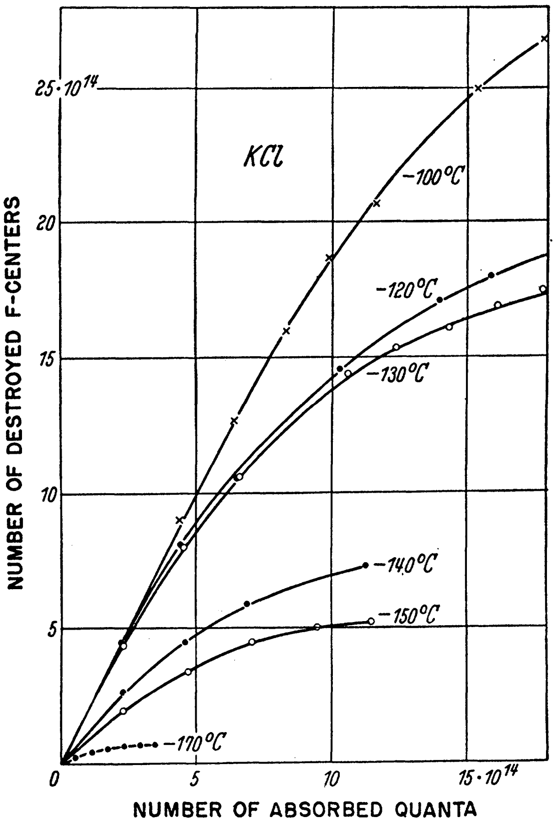

FIG. 2. Plots of the number of destroyed F-centers as a function of the quantum absorbed in the F-band. The data was taken by Pick, reference 11.

rebuilt F-centers as a function of the number of quanta absorbed. The slope of the curves gives the quantum yield $\eta(F'\rightarrow 2F)$, which we define as the number of F-centers formed per quantum absorbed by the F'-band. Our notation does not agree with references 2, 11, and 12. The conclusion we would like to stress is that the slope of the curve, i.e., $\eta(F'\rightarrow 2F)$, varies with time of exposure. The following variation can be estimated from Fig. 1:[14]

At 170°K $\eta(F'\rightarrow 2F)$ drops from 0.3 to 0.1;

at 130°K $\eta(F'\rightarrow 2F)$ drops from 1.4 to 0.4;

and at 23°K $\eta(F'\rightarrow 2F)$ drops from 2 to 1.2.

We shall assume that η changes because the F-center concentration varies with exposure.

(2) Pick[11] has produced F'-centers in additively colored synthetic KCl and KBr by exposing F-centers to light. Here he obtains curves for the number of F-centers destroyed as a function of the number of quanta absorbed. A typical set of curves taken from reference 11 is shown in Fig. 2. For the production of F'-centers from F-centers we define $\eta(2F\rightarrow F')$ as the number of F-centers destroyed when a quantum is absorbed in the F-band. As the concentration of F'-centers increases $\eta(2F\rightarrow F')$ decreases. The concentration dependence is much more pronounced at lower temperature; indeed at 100°K, $\eta(2F\rightarrow F')$ decreases from 0.5 to zero after a short period of radiation.

(3) F-centers form in large concentration at 5°K during an exposure to x-rays.[8,10]

(4) Growth rate curves, i.e., plots of F-center concentration against time of exposure, have been obtained by several observers. Typical growth rate curves for an exposure to x-rays are shown in Fig. 3. The figure is based on observations by Harten[15] on synthetic KCl at temperatures between 90°K and 330°K and by Duerig[10,16] on synthetic NaCl, KCl, and KBr at 5°K, 80°K, and 300°K. From Harten's work, one may assume that a transition in the form of the curve occurs in KCl at about 160°K. Leitner[17] has exposed NaCl at room temperature to x-rays, γ-rays, and β-rays. These data support Fig. 3 with one possible exception. Only a small amount of curvature was observed when a thinner crystal (0.125 cm) is exposed to x-rays from a 130-kv source. For a thicker crystal (0.296 cm) a curvature appears. Growth rate curves have been obtained for the irradiation of natural NaCl (Belar) and natural KCl (Urbach) by a radium source at room temperature.[18] Belar's radium source was shielded by an 0.5-mm glass which should absorb all the α-rays. Urbach's source was in a glass tube so that his crystals were shielded from α-rays. The radium data agree with the high temperature curve.

The actual data are not sufficient at present to establish the complete validity of Fig. 3. Probably the difference is a question of degree.

(5) It has been shown[9,10] that the F'-band is formed upon x-ray bombardment of KCl and KBr at 80°K. While the number of F'-centers is not large, they play

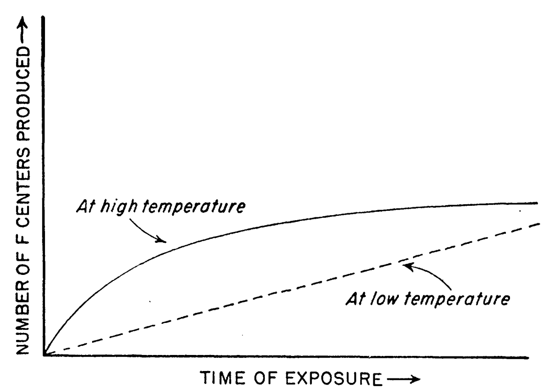

FIG. 3. Schematic plot of the concentration of F-centers as a function of the x-raying time.

[14] Temperatures will be given only approximately.

[15] H. Harten, Z. Physik **126**, 619 (1949).

[16] W. H. Duerig (private communication).

[17] Irmberta Leitner, Wien. Ber. IIa **145**, 407 (1936). A correction to this paper appears in footnote 1 of a paper by K. Przibram, Z. Physik **107**, 709 (1937).

[18] Maria Belar, Wien. Ber. IIa **132**, 45 (1923) and **135**, 186 (1926); F. Urbach, Wien. Ber. IIa **135**, 149 (1926).

a very important role in the formation of color centers under the foregoing conditions. By cooling KBr and KCl to 80°K, Duerig[16] has obtained growth rate curves for the F'-centers. The curves are approximately a linear function of time, indicating that the F'-centers grow simultaneously with the F-centers. We may conclude that the formation of F'-centers requires only a very small concentration of F-centers.

(6) The F'-band has not appeared in KCl during x-raying at 5°K. It has also been observed[10] that the F'-band appeared in x-rayed NaCl at 5°K if the rate of radiation (number of photons per second) is large but not if the rate is small. KBr seems to behave like NaCl, although the F'-band is very small.

(7) Domanic[19] has measured the photoconductivity of F'-centers in KCl as a function of the temperature. His data extend to 20°K. The electrical conductivity depends in part on cross sections, as does the formation of various centers. The essential point of these data is that there is no indication of an abrupt discontinuity in the properties of the material between 80°K and 20°K. Let us therefore assume that the properties remain continuous from 20°K to 5°K, so that conclusions reached at 20°K can be extended to 5°K.

(8) Glaser[20] and others have measured photoconductivity from F-centers between 20°K and 500°K. These data support the conclusion regarding continuity in the low temperature region stated just above.

(9) Smakula[21] has studied the production of F-centers during the irradiating of the crystal (synthetic KBr, KI, RbCl, and RbBr) at the edge of the fundamental ultraviolet absorption region. During this radiation excitons are created which in turn produce F-centers. Two features are to be stressed. First, the number of F-centers produced is very small compared to the number of centers produced by x-rays. Smakula's equation [reference 2, Eq. (1)] indicates that the number of F-centers per unit surface exposed to the radiation is proportional to $\ln I_0/I$, where I_0 is the intensity of the transmitted light before radiation and I is the transmitted light after radiation. An estimate using $\ln I_0/I$ shows that the saturation value of the number of F-centers in crystals colored at liquid air temperature by excitons is about 1 percent of the value obtained by x-radiation. Since the thickness of coloration is unknown, it is impossible to translate this figure into F-center concentrations. The second effect to be noticed is that the growth rate curves in KBr at 300°K and at 90°K resemble the high temperature curve in Fig. 3. The saturation value of the concentration at 90°K is a third of the saturation value at 300°K. The fact that excitons can produce only a small number of F-centers supports the assumption that the number of virgin[22] single-ion vacancies is small.

Schröder[21] performed similar experiments on synthetic and natural NaCl at 300°K. A curve on one synthetic sample is similar to Smakula's. In general the curves on the natural samples do not resemble the high temperature curve of Fig. 3. Schröder shows that past history influences the growth rate cruves. If the crystals are colored uniformly (this is not stated in the paper), then the densities are about 1 percent of the densities obtained by x-rays.[10] An important point to be noted is that some synthetic crystals could not be colored by excitons. Schröder believed these crystals to be exceptionally pure.

(10) Delbecq, Pringsheim, and Yuster[23] have explored and interpreted the α- and β-bands in KI. The α-band is caused by the presence of a negative-ion vacancy. Since the α-band does not appear before the irradiation of the crystals, we must conclude that the number of virgin single-ion vacancies is very small. Further work at 190°K and 80°K indicates that the α-bands appear during x-irradiation, i.e., a number of negative-ion vacancies are frozen into the lattice. At 300°K, however, the α-band, even after irradiation, is hardly visible and the number of vacancies frozen into the lattice must be considerably smaller.

(11) Observations by Harten[15] and Duerig[16] show that by heating the crystal one can remove the ion vacancies formed during irradiation, i.e., one obtains identical growth rate curves on a virgin specimen and on one which has been subject to appropriate heat treatment. Harten heated his crystal (KCl) at 620°K for 5 minutes. Duerig has bleached KBr by exposing it to light at room temperature for 10 hours and KCl by exposing it to light at 600°K for $\frac{1}{2}$ hour. We shall refer to this phenomenon as healing.

In the next section we shall interpret Pick's data and then later we shall speculate on what happens during the x-raying.

III. AN INTERPRETATION OF PICK'S DATA

Let us now use the conventional model[2] of the F- and F'-centers to interpret Pick's results. It will appear that the η's are not unique functions of the temperature, but depend on the concentrations. We will first show that the F-centers formed during the above experiments are produced by two steps: capture of the electron in the excited state, followed by a transition to the ground state. The following notations will be used:

[19] F. Domanic, Ann. Physik **43**, 187 (1943); reference 2, Fig. 12.

[20] G. Glaser and W. Lehfedt, Nachr. Akad. Wiss. Göttingen, Math-physik. Kl. **2**, 91 (1936–37); G. Glaser, Nachr. Akad. Wiss. Göttingen, Math-physik. Kl. **3**, 31 (1937); reference 2, Figs. 6 and 7.

[21] A. Smakula, Z. Physik **63**, 762 (1930); H. J. Schröder, Z. Physik **76**, 608 (1932).

[22] The term "virgin" will be used for vacancies which are in the lattice before the crystal is exposed to the radiation. The term "incipient vacancy" will be reserved for the type of vacancies considered by Seitz, reference 4. This does not agree with the nomenclature recently employed by the author [Phys. Rev. **86**, 433 (1952)] where the term "incipient" means that the vacancies remain as single-ion vacancies, i.e., virgin vacancies in the sense of this paper.

[23] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951); see also E. Burstein and J. J. Oberly, Phys. Rev. **79**, 903 (1950).

$\sigma(F)$—capture cross section for an electron to form a stable F-center from a negative-ion vacancy; $\sigma(F')$—capture cross section for an electron to form and F'-center from an F-center; n_-—number of negative-ion vacancies per unit volume; n_f—number of F-centers per unit volume; and $n_{f'}$—number of F'-centers per unit volume.

The probability that a free electron forms an F-center can be defined as

$$P(F)=\sigma(F)n_-/[\sigma(F)n_-+\sigma(F')n_f], \quad (1)$$

while the probability that a free electron forms an F'-center is

$$P(F')=\sigma(F')n_f/[\sigma(F)n_-+\sigma(F')n_f]. \quad (2)$$

Since $P(F)+P(F')=1$, we are assuming that the electrons, at low temperatures have only two choices in additively colored crystals. This assumption underlies Pick's work.

If $P(F')$ is unity, then every electron released from an F-center ends up in an F'-center. This destroys two F-centers, the one which released the electron and the second one which captured the electron to form an F'-center. If every photon releases an electron and $P(F')=1$, $\eta(2F\rightarrow F')=2$. If $P(F')$ is smaller than unity, less than two F-centers will be destroyed for every electron released, i.e., $\eta<2$. Likewise if $P(F)=1$, then $\eta(F'\rightarrow 2F)$ will be 2, because every electron released from an F'-center (this forms one F-center) is captured by a vacancy to form a second F-center. In general, $\eta(2F\rightarrow F')=2\varphi(T)P(F')$ and $\eta(F'\rightarrow 2F)=2P(F)$, where φ is the probability of dissociating an excited F-center. The temperature, T, dependence of φ is seen from paragraph 8 of Sec. II. We shall assume that it depends only on T. Thus changes of η during irradiation are due to changes in the P's.

To begin with, we would like to show with the use of Pick's experiments on making F'-centers from F-centers (paragraph 2 of Sec. II) that at high temperatures (about 170°K for KCl), $\sigma(F)$ is very small compared to $\sigma(F')$. At these temperatures the initial value $\eta(2F\rightarrow F')$ is two (see Fig. 2), i.e., $\varphi=P(F')=1$; further, $P(F')$ changes only slightly with irradiation. This means that $\sigma(F')n_f/\sigma(F)n_-$ is large. If $\sigma(F')/\sigma(F)$ is not large, (i.e., n_f/n_- is large), $P(F')$ would start out by being one (since $n_f\gg n_-$) but would decrease with irradiation as n_f/n_- decreases and cause a drop in $\eta(2F\rightarrow F')$. Since there is only a small change in $\eta(2F\rightarrow F')$ during irradiation at these temperatures, it is plausible to assume that $\sigma(F)\ll\sigma(F')$.[24]

At 130°K in KCl the initial value of $\eta(F'\rightarrow 2F)$ is about 1.5 (see Fig. 1) i.e., $P(F)\approx 0.7$ because n_- is large. During the irradiation in the F'-band, n_f increases at the expense of n_- so that $P(F)$ soon drops. As stated, the value of $\eta(F'\rightarrow 2F)$ for KCl at 130°K drops several fold during the radiation. The drop in the η's which occurs when one creates F-centers from F'-centers seems to be due to the drop in n_- during the radiation, i.e., we assume that $n_f+n_{f'}+n_-$ is not affected by the irradiation and that there is no diffusion of vacancies into or out of the crystals.

Pick's experiments (paragraphs 1 and 2 of Sec. II) suggest that $\sigma(F)$ has a marked temperature dependence. Figure 1 shows that $\eta(F)$ changes very little during irradiation below 100°K (approximately) but decreases rapidly with rising temperatures between 100°K and 170°K. The variation in η indicates that the capture cross section in KCl for a vacancy is constant until 100°K and that it decreases rapidly above this temperature. The photoconductivity experiments of Dominic and Glaser (paragraphs 7 and 8 of Sec. II) support this conclusion. The variations in $\sigma(F)$ suggest that the negative-ion vacancy captures the electron in the excited state. When the lifetime of the electron in this state is short, it frees itself and $\sigma(F)$ is small. On the other hand, if the lifetime is long, transitions to the ground state are more probable and $\sigma(F)$ increases. If the electron were captured in the ground state, $\sigma(F)$ could not be small at 170°K for one would strongly expect the F-centers to be stable at these temperatures in KCl.

The above analysis indicates that Pick's quantum yield curves depend on the ratio of n_f to n_-. The composite plots of $\eta(2F\rightarrow F')$ and $\eta(F'\rightarrow 2F)$ against temperature[25] should be used with caution, since the data were not taken under the same condition. (For $\eta(2F\rightarrow F')$, n_f/n_- is large while for $\eta(F'\rightarrow 2F)$, n_f/n_- is small).

Further, we may conclude from Pick's data and the work of Smakula on excitons (paragraph 9 of Sec. II) that the number of vacancies at low temperatures are not affected by irradiation of visible or near visible light. This causes the partial saturation of $\eta(F'\rightarrow 2F)$ at low temperatures.

IV. AN INTERPRETATION OF THE DATA AT LIQUID HELIUM TEMPERATURE

In this section we shall consider the effect x-rays may have on crystals. First, the hypothesis will be stated and its ability to explain low temperature color-center phenomena explored; next, the difficulty with the vacancy diffusion idea will be given; finally, this difficulty will be considered.

The author suggests that energetic ionizing radiation generates:

(1) free electrons;
(2) free holes;
(3) single-ion vacancies.

The new suggestion is the production of vacancies

[24] A complication occurs when making F'-centers from F-centers As pointed out by Pick, during irradiation with F-light, one destroys some F'-centers as well as F-centers. This leads to a saturation of the F'-center concentration (see Fig. 2 for the temperature of 100°K). Part of the curvature observed at 170°K must be due to this effect.

[25] Reference 2, Fig. 9.

by the irradiation and not by the diffusion of vacancies into the crystals. It is to be stressed that the creation of vacancies without diffusion from grain boundaries was first made by Seitz.[4] Here we explore the consequences of the idea and its relation to recent low temperature data. The exact mechanism of vacancy production by irradiation will not be specified in this section but will be considered in detail in the next. The only hypothesis made here is that vacancies are produced by a local perturbation of the lattice. They must be surrounded by a fairly regular lattice, for otherwise F-centers in x-rayed crystals would not be similar to those found in additively colored crystals. Further, since the crystal heals at relatively low temperatures compared to the temperature of melting (paragraph 11 of Sec. II), the vacancies can be removed by a relatively simple process. The perturbation might heal itself by local diffusion at room or slightly higher temperatures. If this is true, vacancies might be produced more efficiently at low temperatures.

We shall use Pick's data on additively colored crystals to arrive at conclusions on x-rayed crystals. Data taken by Duerig[16] indicate that holes combine with F'-centers to reform F-centers during the irradiation. This tends to keep the F'-centers' concentration small. Nevertheless, if Pick's data at 20°K can be extended to 5°K, we would expect F'-centers to form whenever n_- becomes much smaller than n_f and that the absence of F'-centers indicates that n_- is not negligible compared to n_f.

The following observed facts can be explained using the assumption that vacancies form during x-raying.

(1) Formation of F-band and of F'-band at liquid-helium temperature (paragraphs 3 and 6 of Sec. II). The small concentration of F'-centers at liquid helium temperature can be explained on the assumption that enough ion vacancies are produced to keep n_- from getting small. The presence of the α-band at low temperatures, as indicated in paragraph 10 of Sec. II, supports this assumption. Hence one may assume that $\sigma(F)n_- \gg \sigma(F')n_f$ and that by Eq. (1) $P(F)$ is almost equal to unity; thus the F-band forms and the F'-band is suppressed. On the other hand, rough estimates from Pick's curves, Fig. 1, suggest that $\sigma(F)/\sigma(F')$ decreases by a factor of two in going from 20°K (−250°C) to 90°K (−185°C). To keep $P(F)$ at 90°K, the same as its values at 5°K, n_-/n_f would have to increase by a factor of two. The data indicate that this does not happen and that $P(F)$ decreases with rising temperatures. Perhaps n_-/n_f may also decrease with rising temperature if healing is accelerated.

(2) The difference between the growth curves at low and high temperatures (paragraphs 3, 4, and 5 of Sec. II). If the number of electrons liberated from the filled bands does not change radically with temperature, one may assume from the experiments of Harten and Duerig that many more free electrons are produced than F- or F'-centers. Further, the presence of a strong α-band at 80°K (paragraph 10 of Sec. II) indicates that a larger number of stable negative-ion vacancies are produced at low temperatures than F- and F'-centers.[26] A reasonable assumption is that traps with very large macroscopic cross sections form which capture most of the electrons. One possibility is that a hole center captures an electron, e.g., a center made of two holes and a positive-ion vacancy could trap an electron resulting in a center composed of one hole and a positive-ion vacancy. Thus the rate of F-center formation depends on the fraction of free electrons which can be captured in negative-ion vacancies. One would expect this fraction to be temperature dependent as are the V-bands.[9] This may account for the variations in the growth rate curves.

At high temperatures an additional effect must be considered (see also reference 4). Here the x-rays or the free electrons may bleach the F-centers which have been formed. Probably the bleaching effect during the irradiation accounts for the saturation effects which are observed at high temperatures and accounts for the difference between the high and low temperature growth rate curves. At present the data are too meagre to justify detailed calculations. Przibram[27] has made several suggestions as to how this could be done. The bleaching effect should be small at low temperatures where the excited F-center is stable.

(3) Low density of F-centers produced by excitons (paragraph 9 of Sec. II). The low concentration of F-centers produced by excitons can be explained on the above hypothesis, i.e., there are very few negative-ion vacancies present in the crystal at room temperature and only these vacancies can trap excitons to generate F-centers. This assumption of a small number of virgin vacancies is supported by the absence of the α-band before irradiation. If excitons can produce F-centers by dissociating weakly bound vacancy clusters, the number of such clusters must be small, especially in some pure synthetic crystals (see Schröder, reference 21).

(4) Reproducibility of growth rate curves (paragraph 11 of Sec. II). On the picture presented here, one would assume that the ions which have been displaced by the x-ray find their original position by a relatively simple process. This suggests that the ion vacancies may be refilled by a diffusion of a nearby imperfection.

(5) Belar's experiments:[18] Experiments on natural NaCl indicate that a rather complex process occurs during γ-irradiation. Six samples were exposed to

[26] W. Martienssen (see added note at end) has suggested that fewer free electrons are produced at low temperature. This seems possible since excited ionic states may not dissociate at low temperatures. On the other hand, data taken at this laboratory show that only a very small fraction of the electrons released from F'-centers exposed to light are trapped in negative-ion vacancies at low temperature. This latter fact tends to support the idea that only a small fraction of the free electrons are captured by the α-centers. One would expect the probability for a recombination of an electron and a hole to be small. Although the microscopic cross section may be high, the macroscopic cross section is probably small because of the low concentration of free holes and free electrons since they have a short mean free life.

[27] K. Przibram, Wien. Ber. IIa **135**, 197 (1926).

radium radiation. They were so placed that the radiation per unit time varied from 100 to 1 on a relative scale. The values observed after long exposure (see Fig. 3) showed that the final level is not directly proportional to the rate of irradiation. Colloidal bands of the type predicted by Savostianowa[28] seem to appear after heating the crystals exposed to intense sources for a year, although the bands did not appear in crystals exposed to the weaker sources. Although more work on this effect is needed, these experiments indicate the complexity of the process.

(6) Appearance of F'-centers in NaCl and KBr at 5°K (paragraph 6 of Sec. II). Since the growth rate of the F-band does not seem to be directly proportional to the radiation intensity, the number of ion vacancies produced does not seem to be a linear function of the number of quanta absorbed. Belar's experiments and the appearance of F'-centers at 5°K in NaCl and KBr suggest that the production of F'-centers during x-radiation depends on a balance between the number of free electrons, number of F-centers, and the way the irradiation produces vacancies. Under some conditions, perhaps larger intensity of radiation, one would expect F'-centers in KCl at 5°K.

(7) Experiments of Etzel and Maurer[29]: Etzel and Maurer estimate the virgin single vacancies at 550°K to be of the order of 10^{17} per cm^3. This would suggest that the free electrons would initially fill these vacancies and subsequently fill vacancies produced during radiation. The growth rate curves at low temperatures should have a change in slope when the virgin vacancies are filled. Rough estimates, from Fig. 2 of reference 10, suggest the virgin vacancy could be of the order of 10^{17} cm^{-3}, in agreement with Etzel and Maurer's value.

Let us now discuss the diffusion idea. At low temperature one must assume that there is local heating which generates enough energy to cause this diffusion. The author sees the following objection to the diffusion idea:

(a) Smakula's data (paragraph 9 of Sec. II) indicates that inward diffusion does not occur in KBr at 300°K, yet the healing process (paragraph 11 of Sec. II) would require, in contradiction, an outward diffusion at the same temperature.

(b) The pair must break up at liquid helium temperatures in order to keep $P(F)\gg P(F')$. In KI the pair must break up at 80°K, since the α-band appears (paragraph 10 of Sec. II), but not at 300°K; this contradicts the stability ideas.

Several other more complicated possibilities exist. One suggestion is that the pair may diffuse into the crystal because of local heating and the following reactions may take place:

$$(V_+V_-)+e_-\rightarrow(V_+V_-e_-); \quad (3)$$

$$(V_+V_-e_-)\rightarrow V_++F \quad \text{due to diffusion.} \quad (4)$$

A hole in turn may cause the reaction

$$F+e_+\rightarrow V_-. \quad (5)$$

Here the symbols have the following meaning: V_+ = positive-ion vacancy; V_- = negative-ion vacancy; e_- = free electron in the conduction band; e_+ = free hole; F = F-center, i.e., (V_-e_-); (V_+V_-) = vacancy pair; and (V_+V_-e) = complex made of a negative-ion vacancy, a positive-ion vacancy and an electron. If a strong repulsion exists between an F-center and a positive-ion vacancy, reaction (4) may occur at very low temperatures. Reaction (5) will generate free negative-ion vacancies which will account for the α-band. At high temperatures the positive-ion vacancies could diffuse forming vacancy pairs which will suppress the α-band.

There is also the possibility that pairs of vacancies diffuse into the crystal and dissociate. They remain dissociated in the colder crystals because of rapid cooling but not at room temperature where recombination is possible.

These arguments indicate that it is possible that vacancy diffusions account for the coloration of crystals at low temperatures, although these hypotheses require rather complex reactions to explain the observed data. Tentative calculations to be given in Sec. VI indicate that the amount of local heating is small. Further, it is hard to relate this to Smakula's data. This favors the alternative hypothesis of incipient vacancies to be discussed in the next section.

A difficulty with the model proposed is immediately apparent. Estermann, Leivo, and Stern[30] measured a density change during the radiation. An approximate correlation between density and concentration of F-centers was found which suggests a diffusion of vacancy pairs into the crystals. Perhaps the explanation lies in the fact that diffusion of incipient vacancies, as suggested, causes local strains in the crystal which reduce the density. In the next section we shall show that Seitz's suggestion reduces the density of the crystal (see Fig. 4).

V. THE INTERACTION OF AN X-RAY WITH A DISTORTION

In this section, the author would like to consider how the negative-ion vacancies are produced during x-raying. Calculations to be given in the next section indicate that the local rise in temperature is small so that vacancies do not seem to be produced by local heating which allows diffusion from grain boundaries. Further, recoil energies for 50-kv photons are also too small to produce interstitial ions and vacancies.

Seitz[4] has suggested that the glide plane of a Taylor dislocation may jump from one plane of atoms to another (see Fig. 4). The "extra plane" associated with the edge dislocation has a jog in it, i.e., there is an extra row of ions which does not go along the entire plane.

[28] M. Savostianowa, Z. Physik 64, 262 (1930).

[29] A. W. Etzel and R. J. Maurer, J. Chem. Phys. 18, 1003 (1950).

[30] Estermann, Leivo, and Stern, Phys. Rev. 75, 627 (1949).

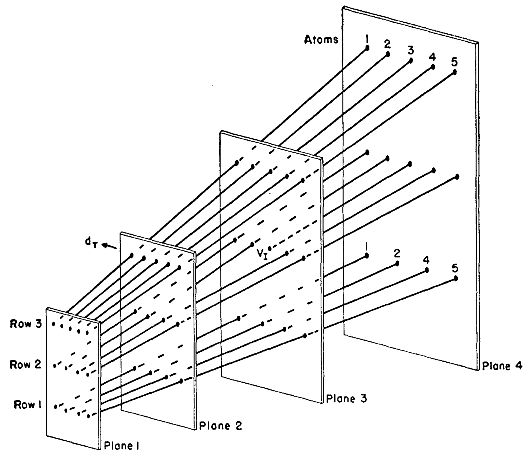

FIG. 4. Schematic drawing of a Seitz jog for a simple cubic crystal. In planes 1 and 2 the extra layer of atoms associated with a Taylor dislocation end in row 3, i.e., atom No. 3 in row 3. In planes 3 and 4 the extra layer reaches row 2, i.e., atoms No. 3 in row 2. Atoms No. 3 are missing in row 1 of all the planes. If atom No. 3 in row 3, plane 2, jumps between atoms No. 2 and No. 4 of row 2 in the same plane, a vacancy will be created in row 3. The jump will cause an expansion of the middle row of atoms in plane 2. This will result in a decrease of the density of the crystal unless row 3 collapses. Note the process considered here causes the dislocation to move at right angles to the Burgers vector, d_T. This should be contrasted to the mechanical problem where the motion occurs along this vector.

It is possible to show that such a jog in an alkali halide has a charge of $\pm\frac{1}{2}e$ associated with it,[31] (e is the charge of an electron). Seitz refers to such a jog as an "incipient vacancy." The term Seitz jog will also be used.

We will now consider a way negative-ion vacancies could be produced in crystals. A slow electron would be attracted to a negative-incipient vacancy and a center (jog center) could be formed at this location. This arrangement is probably not very stable and one of two events may follow:

(1) The center formed at the jog may diffuse away from the dislocation. The diffusion of the center into the lattice causes a negative-ion to jump into the "extra" plane and the Seitz jog moves one lattice distance. Since the charge associated with this jog is half the charge associated with a negative-ion vacancy, one would expect an F-center to be much more stable than a center at the jog. The energy gained by the negative ion which diffuses into the incipient vacancy must also be considered. This will not be attempted here. It is not obvious to the author that energy will be gained by the diffusion of the "jog center"; nevertheless, we shall make this assumption. Some activation energy is probably required to cause the jog center to migrate. This energy probably comes from the electron which is captured at the Seitz jog; or

(2) The jog center, having a negative charge of $\frac{1}{2}e$, may capture a hole, returning the crystal to its original condition. A similarity between the jog center and the F'-center should be noted. Both are charged and tend to attract holes. For this reason one would expect the jog centers which do not migrate to attract holes. This keeps the concentration of jog centers small.

[31] Reference 5, p. 341, footnote 42.

The α-band observed at low temperature during x-radiation seems to be caused by a secondary process. The F-centers form near jogs. Some of these F-centers get bleached by absorbing a hole, thus forming a negative-ion vacancy. These negative-ion vacancies cannot diffuse back to the jog at low temperature and therefore the α-band forms. A period of time may elapse between the formation of the F-center and the formation of the α-center. During this time, the Seitz jog will probably move since more electrons and holes will be captured at the jogs left behind; hence, the α-center need not be near an incipient vacancy although it is near a dislocation.

At low temperatures, about 100°K, the jog center probably does not diffuse very far and remains near the dislocation line. The reason is that the activation energy for diffusion will increase as the center moves away from the jog and the energy the center originally had will be transferred to the lattice. This may account for the difference in the F-centers formed at low and high temperature.[10] The measurements of the width of the F-band formed during x-radiation at low temperature (80°K and below) seem to indicate that it is narrower than when formed at high temperature and cooled to the same low temperature. The change occurs at the long wavelength side of the band. This indicates that the gap between the ground state and excited state of the F-center depends on the position of the centers in the crystal. A possible explanation is that the dislocation affects the frequency spectra of the ionic oscillations which is reflected in the shape of the F-band.

The above hypothesis leads to the following calculations. Assume that next to the surface of a cleaved crystal the density of Taylor dislocations is 10^{10} cm^{-2}. Let us assume the distance between nearest neighbors is $3A$; then the number of vacancies created when a dislocation moves one lattice distance is 3.5×10^7 cm^{-1}. The motion of interest is at right angles to the dislocation line and the slip direction (see Fig. 4). If every dislocation moves 3 atomic distances, then 10^{18} cm^{-3} F-centers could be produced which agrees roughly with experimental values.[10] If the density of dislocations[4] was as low as 10^9 cm^{-2}, then the above explanation seems doubtful since the dislocations would move 50 atomic distances. It seems doubtful that the damping of the oscillations will extend over such large distances.

We may summarize the suggestion made as follows:

$$J_- + e_- \rightarrow (J_-e), \quad \text{(jog centers)} \quad (7)$$

$$(J_-e_-) \text{ plus diffusion} \rightarrow F, \quad (F\text{-centers}) \quad (8)$$

$$F + e_+ \rightarrow V_-, \quad (\alpha\text{-centers}) \quad (9)$$

or

$$(J_-e_-) + e_+ \rightarrow J_-. \quad (10)$$

J_-, J_+ correspond to negative and positive Seitz jogs.

The large number of negative-ion vacancies postulated in the last section seems to be a result of reaction (9).

Two types of negative-ion vacancies may be considered. One is next to the dislocation and another is in a perfect lattice. It would seem probable that the activation energy for diffusion is lower in the first case than in the second. This may explain why diffusion of negative-ion vacancies seems to occur at room temperature during the healing process (paragraph 11 of Sec. II), although one would not expect such diffusion in a perfect lattice.[32] This further suggests that the stability of some centers depends on where they are located within the crystal which may be a function of the way the alkali halide had been treated.

One must assume that an exciton cannot form *F*-centers from Seitz jogs. The reason may be (1) the exciton is not trapped at an incipient vacancy or (2) the jog center which could form by the dissociation of the exciton does not have sufficient energy to migrate.

VI. LOCAL TEMPERATURE DURING X-RADIATION

The question to be considered in this section is "Does the energy transferred to the lattice raise the local temperature sufficiently to permit the creation of vacancies from Seitz jogs by diffusion?" Since we are interested in a process involving the motion of ions, the temperature of interest is that associated with the vibrational energy of the lattice. Seitz estimates that it takes about 1 ev to produce a vacancy from a jog,[33] so that temperatures of the order of 400°K are required.

If the energy of a 50 kv x-ray were distributed over a sphere of radius 50 atomic units and all of it produced thermal vibrations, then the resulting lattice temperature would be approximately 400°K which is sufficient to produce vacancies from jogs and explains how the crystal increases the number of negative-ion vacancies during x-radiation. If the energy were spread out over a much larger area, however, the local temperature would be too low to account for the vacancies.

The x-rays are attenuated by two processes: scattering from ions and absorption by ions. The second process is followed by the ejection of a photoelectron. The photoelectron further excites secondary electrons into the conduction band. Since the ions have a finite mass, they gain some recoil energy during these processes. This energy is very small and is usually neglected.[34]

The collision between a photon and an ion or between a photoelectron and an ion is a very complex process and a rigorous treatment will not be attempted. It is hoped that the crude approximations made here will give an insight into the problem. We first calculated the recoil energy for various processes occurring within the crystal and then interpreted these results in terms of a temperature. The calculations are based on a 50-kv photon since 50- or 60-kv x-ray tubes have been used to color crystals at low temperatures.[9,10]

(a) Photon and Ion

This situation corresponds to the Compton effect with the electron replaced by an ion. Using the mass of sodium, one finds that the maximum recoil energy is 0.23 ev while the recoil energy averaged over all angles is 0.12 ev.[35] The corresponding values for lithium are 0.76 ev and 0.4 ev.

(b) Electron and Ion

The x-ray may produce photoelectrons of energies equal to the x-ray photon.[36,37] These electrons, 50 kv, will have about ten times the momentum of the photons so that the recoil energies of the ions will be much larger. For a head-on collision the energy transferred to the sodium ion from a 50 kv electron is 4.7 ev. If, however, the electron is deflected 30°, only 0.3 ev are transferred.[38] This value would not be affected if one considers inelastic collisions, provided the ejected electron has a much lower energy than the photoelectron.[39,40]

Seitz[41] estimates that it takes about 25 ev to eject an atom from its normal site; hence, the recoil energy does not create vacancies in a perfect lattice.

Let us now attempt to estimate the rise in temperature due to the scattering of an x-ray by ions. If it is assumed that every ion in a region received 0.12 ev from the photon, the crystal temperature in this region would rise from 5°K to 450°K and various high temperature processes could occur. A highly simplified example will indicate that this assumption is incorrect. Let us assume that the photon is in the middle of a highly condensed gas (i.e., the ions are arranged at random), say at *P*, and that the scattering is isotropic.[42] Further, we shall assume that the x-ray is not absorbed by an ion before

[32] Reference 2, p. 401.

[33] Reference 6, p. 52.

[34] P. A. Ross and P. Kirkpatrick, Phys. Rev. **45**, 223 (1934) have considered a case when the ion has a finite mass.

[35] H. Semat, *Atomic Physics* (Rineheart & Company, New York, 1946), p. 141.

[36] We neglect the binding energy to the ion which for Na is small compared to 50 kv. See for example reference 37, p. 796.

[37] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935), second edition.

[38] See H. Soodak and E. C. Campbell, *Elementary Pile Theory* (John Wiley & Sons, Inc., New York, 1950), p. 4.

[39] Mott and Massey (reference 40, p. 227 ff) have considered the inelastic scattering from hydrogen atoms. If the incoming electron has the energy of 300 ev, the most probable value of the ejected electron is 2.5 ev. One might suspect this to be true in our case and that the ejected electrons are of much lower energy. Further the maximum cross section occurs when there is a conservation of momentum between the bombarding electron and the ejected electron, i.e., no recoil ionic momentum.

[40] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, New York, 1949).

[41] F. Seitz, Disc. Faraday Soc. **5**, 271 (1949).

[42] The distinction between modified and unmodified scattering need not be made if the energy absorbed by electrons bound to the ions is small compared to the energy of the x-ray; hence, we are interested in the total cross section for scattering. Although it is not isotropic, (see reference 37, p. 140 ff), a sizable fraction is scattered through 180°.

it makes n_T collisions. This is the random walk problem. The probability that after n collisions the photon is in unit volume at a distance R from P is

$$W(R, n)=\left(\frac{3}{2\pi}\right)^{\frac{3}{2}}\frac{1}{l^3}\frac{1}{n^{\frac{3}{2}}}\exp(-3R^2/2nl^2), \quad (11)$$

where l is the mean free path.[43]

The total number of times the photon is at R during the n_T collisions is

$$N=\int_1^{n_T} W(R, n)dn.$$

Replacing the upper limit by ∞ and making the substitution $3R^2/2nl^2=z^2$, we obtain

$$N=\frac{3}{\pi^{\frac{3}{2}}}\frac{1}{Rl^2}\int_0^{(R/l)\surd(3/2)}\exp(-z^2)dz.$$

If the further assumption is made that a collision takes place every time the photon is at a distance a from the center of an ion, we have

total number of collisions

$$=\frac{2}{R_0 l_0{}^2}\frac{2}{\sqrt{\pi}}\int_0^{(R_0/l_0)\surd(3/2)}\exp(-z^2)dz, \quad (12)$$

where R_0 and l_0 are in units of a. Setting $R_0=l_0=2$ and assuming that the energy transferred per collision is 0.12 ev, we see that the total number of collisions is 0.23, or an ion will receive on the average 0.027 ev of energy corresponding to a rise in temperature of 100°K. Consideration of the nonclassical behavior of the oscillator at low temperature would only raise the temperature slightly.

The large value of the energy transferred when an electron is deflected 180° suggests that the mechanism might account for local heating. Collisions of this type are, however, very rare. Calculations of Mott and Massey[44] based on the Born Approximation and a Fermi-Thomas model of an atom show that the cross section for a deflection through 30° is very small compared to the cross section for a deflection of zero degrees. If $I(\theta)$ is the differential cross section, then for $Z=11$ and a 50-kev electron $I(0)/I(30)$ is about 1.5×10^{-6}; further, if the density of ions is 4×10^{22} per cm^3, the mean free path for scattering through a steradium at 30° is 1.5×10^5 angstroms. Comparison of the tables in reference 44 indicates that consideration of inelastic collision would only decrease the mean path slightly. Evidently the electron occasionally does give some energy to the lattice, but this is not a common occurrence. Since the recoil energy must be shared by many atoms, the actual local heating must be small for a 30° deflection. It would seem that these improbable processes could not explain the darkening at low temperatures.

When an electron is captured by a trapping center or by a hole, some energy must be transferred to the lattice. This energy may be of the order of 5 ev and it would create a local rise in temperature right around the lattice point where the electron was absorbed. This is too localized to cause pair diffusion. It could, however, assist in the evaporation of ion vacancies from a Seitz jog if the trapping was sufficiently near. Trapping at a center resulting from reaction (9) might cause an evaporation of an incipient vacancy. Probably the trapping at the Seitz jog creates the activation energy for the diffusion of the jog centers.

Unquestionably, the above calculations are only approximate and many refinements are possible. The conclusion that the transfer of energy from a 50-kv x-ray to the lattice takes place over many lattice ions, however, seems justified. One would not expect that the local temperatures (over 1000 lattice sites) would vary by several hundred degrees from the macroscopic temperatures.[45] The above arguments do not consider the diffusion of the recoil energy which would tend to lower the local temperature.

VII. CONCLUSIONS AND ACKNOWLEDGMENTS

It has been suggested in this paper that x-radiation and radium radiation produce three effects on the crystals: generation of electrons, generation of holes, and generation of single-ion vacancies by a local perturbation of the lattice rather than by a diffusion of pairs. These vacancies account for the presence of the α-band at low temperature and the very small F'-band at 5°K. This idea seems to explain in a qualitative way the observations on color centers at low temperature. Since the experimental data were gathered from many sources and since these were not designed to test this hypothesis, more experimental work is needed to establish the validity of these suggestions. Theoretical exploration of this idea would be helpful.

The author would like to thank Professor F. Seitz and Professor R. Maurer for a helpful discussion of the paper; Dr. W. H. Duerig for the use of his data; Dr. K. Elder and Miss A. Fogelgren for editorial assistance; and

[43] See S. Chandrasekhar, Revs. Modern Phys. 15, 1 (1943) especially Eqs. (62), (87), and (93). We assume that our Eq. (11) holds for $n=1$ which is true for Chandrasekhar's Eq. (62). We shall replace a finite sum by an integral which is an approximation.

[44] Reference 40, p. 187, especially Table III, and p. 240, especially Table II.

[45] An insulator heats up during the x-radiation because the material is unable to conduct the heat away. If a 50-kv x-ray tube is run at 50 ma, 600 calories are produced per second. Probably no more than 1 percent fall on the crystal, however. At 5°K alkali halides are good heat conductors so that large macroscopic temperatures would not be expected. See W. J. de Haas and T. Biermasz, Physica 4, 752 (1937).

Miss D. Rubenfeld for designing Fig. 4. Finally, the author would like to thank his wife for her encouragement.

Note added after completion of the paper: The content of this paper was presented at the Columbus meeting of the American Physical Society, March 22, before which time the details of the paper were worked out. At that meeting, the author obtained a copy of an unpublished paper by W. Martienssen, "Photochemische Vorgänge in Alkalihalogenidkristallen" [see Z. Physik **131**, 488 (1952)]. The suggestion is made in this paper that **x**-rays generate vacancies. Martienssen does not, however, examine in detail the consequences of this idea, nor does he suggest any detail regarding the mechanism of vacancy formation. The production of a strong α-band at 20°K in KBr reported in this paper (see also W. Martienssen, Naturwiss. **38**, 482 (1951)) has caused a slight revision of Sec. **IV**.

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Photoproduction of Mesons in Deuterium*

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The production of positive mesons by photons incident on deuterium is calculated in terms of an effective Hamiltonian containing one term which is independent of and another which depends upon the nucleon spin. The meson spectrum at a given angle to the incident photon beam is evaluated at high photon energies by the closure approximation. At low and intermediate energies the closure approximation is not made, but the neutron-neutron force in the final nucleon state is neglected. These spectra have been integrated over a bremsstrahlung spectrum. The total cross section is found at high photon energies and near the threshold for meson production. It is found that the meson spectrum for small angles is sensitive to the relative size of the spin dependent and spin independent terms.

I. INTRODUCTION

THE production of mesons by photons on deuterium is particularly sensitive to the details of the effective Hamiltonian describing the coupling among the photon, meson and nucleon fields. Its charge dependence is revealed by comparing the production of negative and positive mesons. Its spin dependence affects the variation of the total cross section as a function of the energy of the incident photons, the angular distribution and the energy spectrum of the mesons produced at a given angle. These last effects are a consequence of the Pauli exclusion principle[1] and are thus particularly important at small angles where the recoil neutrons have small relative momenta.

On the other hand, the deuteron is the simplest example of a target with structure. It may therefore be employed to test some of the approximate results given earlier for photo-meson production in nuclei.[2] There are, however, some significant differences from the case of heavy nuclei inasmuch as the mass of the residual nucleus is comparable to that of the particle absorbing the photon.

In the present paper we shall employ the same phenomonological treatment as that employed in reference 2, wherein it is assumed that the meson-photon interaction with a nucleus may be treated as a sum of the interactions with the individual nucleons. This clearly neglects cooperative higher order effects such as those given by exchange currents, and the scattering and absorption of the meson produced by one nucleon by another. These should be small in deuterium because of its relatively large structure and the relatively small nucleon scattering amplitude.[3] Once these assumptions are made, it is possible to affect all spin sums and reduce the calculation to quadratures. Further progress requires some statement on (1) the dependence of the effective Hamiltonian on nucleon momenta and (2) on the nature of the interaction of the two residual neutrons. We have omitted both possibilities for reasons of simplicity. The omission of the first of these may be of importance in computing the negative to positive meson production ratio. The second omission is invalid for final states in which the relative kinetic energy of the nucleons is small, i.e., near threshold, at the high energy end of the meson spectrum, or for mesons produced at small angles. A more precise calculation is now in progress.[4]

A similar treatment of this problem has been simul-

* This paper was presented to the American Physical Society. See Phys. Rev. **82**, 324 (1951).

[1] H. Feshbach and M. Lax, Phys. Rev. **76**, 134, 689 (1949).

[2] M. Lax and H. Feshbach, Phys. Rev. **81**, 761 (1951).

[3] G. Chew and H. Lewis, Phys. Rev. **84**, 779 (1951).

[4] Feshbach, Goldberger, and Villars, private communication.