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F- and *M*-Band Absorption in Heavily Gamma-Irradiated KCl

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Measurements of *F*- and *M*-band absorption at room temperature as a function of gamma irradiation are used to study the relation between *F* centers and *M* centers in a number of KCl crystals from a variety of sources. Although the *F*-center coloring curves exhibit a variety of forms, presumably due to different trace impurities and imperfections in the crystals, the *M*-center density seems in all cases to be nearly proportional to the square of the *F*-center concentration. The ratio of the *M*-center concentration to the square of the *F*-center concentration appears to be related to trace impurity content. Zone refining decreases the relative *M*-center introduction, as does deliberate doping with calcium; whereas, plastic deformation has no effect on the ratio. Bleaching increases the *M*-center concentration at the expense of *F* centers; however, short re-irradiation with gamma rays causes the ratio of *M*-center concentration to the square of *F*-center concentration to return to its prebleaching value. The results are thought to indicate that a radiation equilibrium exists between *F* and *M* centers which is frozen in when the crystals are removed from the source.

INTRODUCTION

EVEN though a considerable volume of information has been accumulated on the coloring properties of alkali halides,[1–8] there is much that is not understood. This is particularly true concerning the process or processes by which photons or particles create the defects that are the origin of optical absorption bands. It is now generally assumed that at least two mechanisms[6] must be involved at room temperature. One of these processes, responsible for rapid initial coloration, saturates quickly and can take place even for irradiation with photons of energy less than 10 eV.[9] The later stages of coloration have been attributed to intrinsic properties of the crystal. However, even these later stages are apparently dependent upon past history of the crystals, and are sufficiently complex so that more than one process has been postulated to explain them. The suggested coloring processes fall into two classes. The first involves[10] the creation of negative-ion vacancies at dislocations or vacancy clusters. The second[11] involves double ionization of a halide ion. Several modifications have been proposed[7,12,13] for both of these ideas; however, with the experimental data available to date, it has not been possible to either eliminate or confirm any of the various models.

Within the last few years, a clearer idea of the structure of the *M* center has been obtained through a number of experiments,[14–17] and it is now thought that the *M* center is composed of two adjacent *F* centers. The discovery of a proportionality between the *M* centers introduced by irradiation and the square of the *F*-center concentration[15] is particularly interesting. This relationship is apparently valid even at room temperature, although the proportionality constant is far different from that obtained when a sample is irradiated at liquid nitrogen temperatures or below.

In view of the better understanding of the *M* center and especially since very little emphasis had been placed on observing cluster centers in past investigations of radiation coloring of alkali halides, it was thought that a study of the relation of *F* and *M* centers introduced by gamma rays at room temperature might be helpful in understanding the coloring processes. Moreover, it was felt that since many groups are at present trying to purify alkali halides, a comparison of various "pure"[18] samples might help clarify the role of trace impurities in the coloring process. In the present work the emphasis is on the later stages of coloring where the concentration of color centers is greater than that of the impurities one would expect in "pure" material.

EXPERIMENTAL

In order to obtain growth curves for *F* and *M* centers, cleaved plates of thickness 0.1 cm or less, were placed in light tight sample holders, which were equipped with slides to permit measurement of the absorption spectra of the samples. The irradiations were performed with the samples in the holders, the latter being placed in a

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* Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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[18] When we speak of "pure" material in this paper, we are referring to KCl that has not deliberately been doped. It is thought that Harshaw potassium chloride crystals, as an illustration, contain less than 10^{17} dissolved impurity ions/cm^3.

reproducible position in a 4.5×10^6-r/h Co^{60} gamma source. To obtain absorption spectra, the holders were removed from the gamma source and placed in a Cary Model 14R spectrophotometer, where the slides were withdrawn in total darkness. Repeated spectral measurements showed that no bleaching was caused by the measuring light beam. Usually about three or four short irradiations and measurements were performed during the first 10 min of irradiation, in order to ascertain the approximate shape of the first stage of coloring. Thereafter, irradiations varied between 1/2 and 16 h, to a total, in some cases, of 42 h. The temperature of irradiation was in the neighborhood of 32°C; spectra were measured at room temperature (25°C).

A number of auxiliary experiments were also performed. Among these were qualitative spectrographic analyses, flame photometric determinations of the concentrations of some of the impurities, and optical bleaching experiments. It was also shown that all of the samples luminesce to some extent during gamma irradiation. In addition, the absorption edge of some of the samples was determined with a vacuum ultraviolet spectrometer, and the dislocation densities of the crystals were determined by etching.

RESULTS

A. Introduction of *F* and *M* Centers

A list of the samples used in the experiment is given in Table I. As can be seen, the "pure" crystals were obtained from eight different sources. Figures 1(a) and 1(b) depict the *F*-center growth curves for these various crystals. Shown plotted are the optical absorption coefficient at the peak of the *F* band versus the gamma dose received. A clearer presentation of the data is made possible by using two figures. The dashed line, shown on both graphs, is a composite curve for a number of Harshaw KCl samples. The expanded sections at the left of the curves show the early stages of *F*-center introduction, which have been the subject of much study in the past.[1–8] In some cases a difference was found in the height of the first stage coloring in different samples from the same source. Apparently, the shape of the curves in the later stages of coloration is more characteristic of the whole ingot.

It would seem that perfect KCl crystals should all have the same *F*-center growth curves. The data in Fig. 1, showing large differences between samples both in the early and later stages of coloration, thus indicate that even trace impurities or other imperfections may strongly influence *F*-center formation. There seems to be no obvious correlation between the growth technique or care of preparation[19,20] and the coloring rate, although it seems that the least pure samples (O,*CA*) may have the lowest coloring rates in the late stages.

TABLE I. List of samples.

Crystal designation	Source	Maximum gamma irradiation time (h)	Preparation[a]
AK	Kobayashi[b]	10	P, K
B	IBM[c]	7	G, Z
CB	ORNL	42	K
H_1	Harshaw	4	B
H_2		23	
H_3		25	
I_1	Isomet	4	
I_2		31	
I_3		36	
I_4		36	
O	Optovac[d]	42	
P_1	Cornell[e]	4	G
P_2		7	
W_1	Westinghouse[f]	5	G, Z
W_2		25	
D_1	IBM[g]	10	G, Z
D_2			
CA_1	Cornell[h]	25	D
CA_3		7	

[a] K = pulled from melt. B = solidified in temperature gradient. Z = zone refined. P = purified chemically before growth. G = treated with chlorine gas or HCl. D = doped.
[b] Crystal came from the same boule as sample KCl-*a*K-1 of reference 19.
[c] Kindly supplied by W. E. Bron.
[d] Kindly supplied by H. Rabin.
[e] Kindly supplied by R. Pohl and J. Ashe.
[f] Kindly supplied by J. G. Castle and R. Warren.
[g] Kindly supplied by R. Dreyfus.
[h] Reference 22.

A similar large variation in the shape of the growth curves for *M* centers is shown in Fig. 2. Data is shown for enough of the samples to make clear that both upward and downward curvature is observed and that curves for different samples may cross.

B. The Relationship of *F* and *M* Centers

It has been shown[15] that a plot of the absorption constant for the *M* band vs the square of the *F*-band absorption constant yields a straight line. A plot of this type for most of the crystals used in this investigation is shown in Fig. 3. The slopes obtained are given numerically in Table II. Work of Okamoto,[17] in which dichroic absorption was measured, has indicated that 1/2 to 1 times the *M* absorption at 8250 Å also appears as additional *M*-center absorption under the *F* band. Correction for this was made in the present experiment; 0.8 times the height of the *M* band was subtacted from the measured height of the *F* band.[21]

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[19] K. Kobayashi and T. Tomiki, J. Phys. Soc. Japan **15**, 1982 (1960).

[20] Three crystals obtained from W. E. Bron and R. W. Dreyfus of IBM, as well as one received from R. Warren and J. G. Castle of Westinghouse were also zone refined with great care. The techniques used have not been published.

[21] Okamoto's work was done at liquid nitrogen temperature, while the present measurements were made at room temperature. Nevertheless, it was felt that relative shifting of the bands with temperature would make only small differences in the amount of *M*-center absorption at the *F*-band peak wavelength.

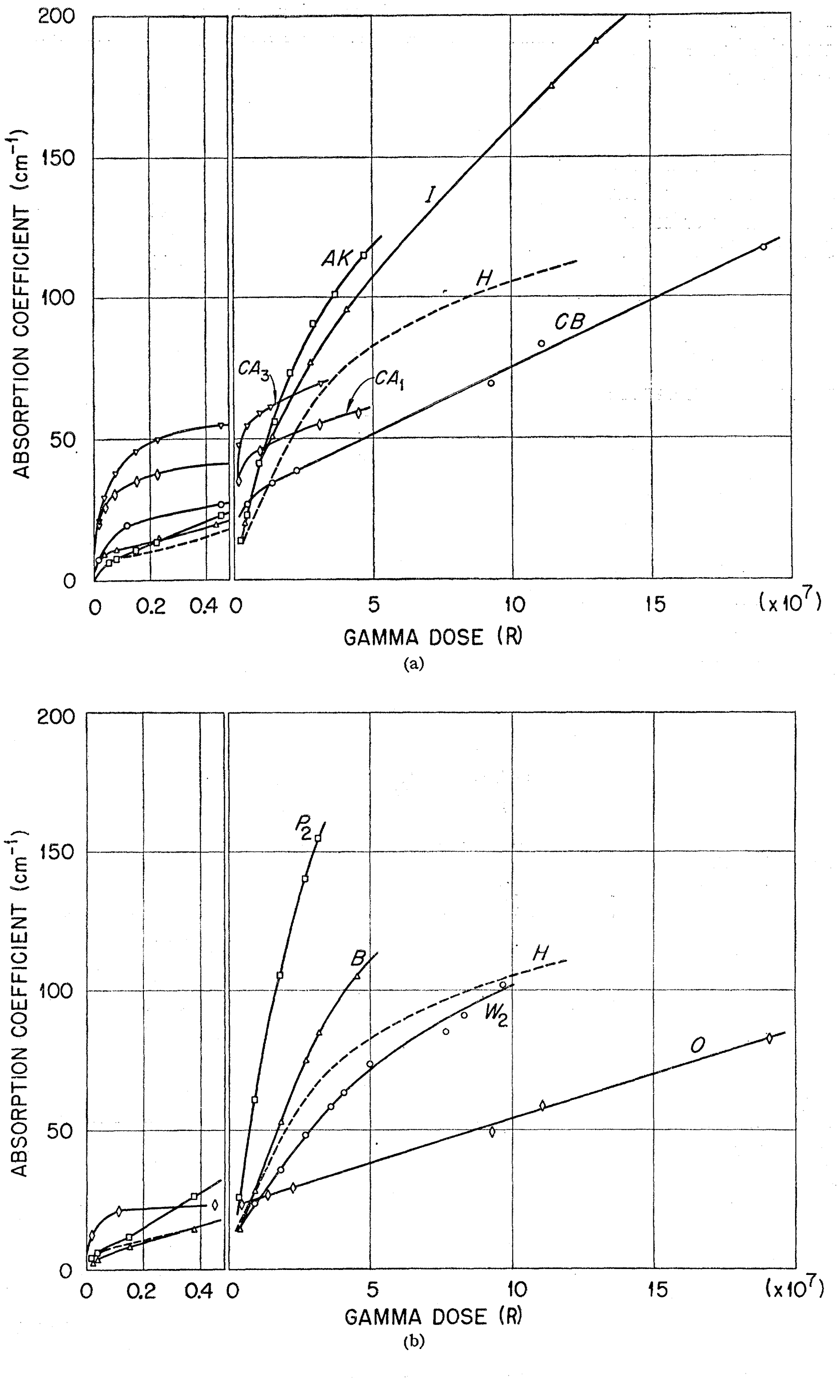

FIG. 1. *F*-center coloring curves for KCl prepared in different laboratories. The source and preparation techniques for the various samples are summarized in Table I. A composite curve for a number of Harshaw samples is shown dashed on both figures. An expanded scale is used for the results of light irradiations to permit comparison of first and second stage coloring properties with previous measurements. Symbols used to identify the points of the various samples are as follows: In Fig. 1(a), □—*AK*, △—*I*, ○—*CB*, ◇—CA_1, ▽—CA_3. In Fig. 1(b), □—P_2, △—*B*, ○—W_2, ◇—*O*.

The slopes seem to be near 10^{-3} cm for the case of the commercially obtained crystals (*H*,*I*,*O*) and for those simply pulled from Baker reagent (*CB*). Significant suppression of *M*-center introduction is observed both in samples that have been purified chemically or by zone refining and in those that have been doped with calcium.[22]

Even though the curves in Fig. 3 seem to be good straight lines, it might be noted that they do not extrapolate to the origin. In the case of three Isomet samples, for which irradiations were continued for a longer time, it became evident as illustrated in Fig. 4, that the straight lines observed may actually be tangents to a slowly saturating curve. [It should be pointed

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[22] The doped crystals used were kindly supplied by R. L. Sproull. The details of their preparation and the technique of determining the calcium content by radioactive tracer technique have been described by G. A. Slack, Phys. Rev. **105**, 832 (1957). Analysis by flame photometry at this laboratory agreed with the values given by Slack within 25%.

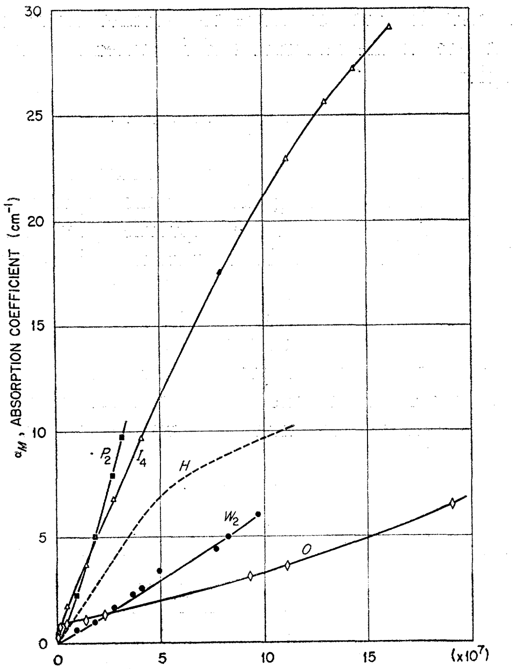

FIG. 2. Introduction of M centers as a function of Co^{60} gamma ray dose. Data for only a few of the samples are shown.

out that the measuring error in the upper half of Fig. 4 may be quite appreciable due to the high optical density (OD) of the samples—$OD \cong 4$ to 6.]

A further note should be added concerning the ratio of M- and F-center concentration. Long standing in the dark seemed to cause a small decrease of the F-band absorption and an increase in the M-band absorption. The points in Fig. 3 which are connected by curved lines are those for which optical absorption was measured immediately after removal from the gamma source, and then ~18 to 36 h later. The irradiations that followed the storage in the dark seemed (at least in the case of the Harshaw sample, where the change due to standing was larger than the general scatter) to cause the samples to continue along the original curve.

TABLE II. Summary of results. Asterisks following numbers indicate that the results were obtained on the same sample as was used for the irradiations.

Sample	Dislocation density (cm^{-2})	Ultraviolet absorption edge[a] (eV)	Slope of $(M)/(F)^2$ plot (cm)
AK	1.5×10^6	7.14	8.12×10^{-4}
B	2.2×10^6*	NM[b]	4.7×10^{-4}
CB	2.8×10^6	NM	10.0×10^{-4}
H	1.5×10^6	6.83	10.0×10^{-4}
I	1.7×10^6	7.04	10.8×10^{-4}
O	1.2×10^6	6.97	10×10^{-4}
P	1.9×10^6*	7.14	3.9×10^{-4}
W_1	3.7×10^6	7.08	4.0×10^{-4}
W_2			6.2×10^{-4}
D_1	NM[b]	NM	3.9×10^{-4}
D_2			3.9×10^{-4}
CA_1	1.8×10^6	7.06	6.2×10^{-4}
CA_3	1.4×10^6	7.03	3.9×10^{-4}

[a] The absorption edge has arbitrarily been defined as the energy at which the absorption coefficient reaches 30.
[b] NM indicates that no measurement was performed.

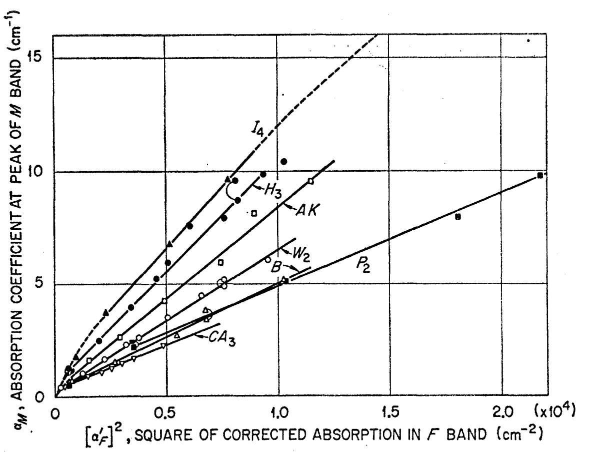

FIG. 3. Relation between M centers and F centers. Shown plotted is α_M, the optical absorption coefficient at the peak of the M band, versus $\alpha_F'^2$, the square of the absorption coefficient at the peak of the F band, corrected for M-center absorption under the F band. The letters refer to samples listed in Table I.

C. The Effect of Plastic Deformation on F and M Centers

Several Isomet samples were deformed before coloration experiments were performed. A jeweler's vise was used to compress samples 4-6%. In Fig. 5 the F-center growth curves for two deformed samples, and one deformed and heat treated sample are compared with that of an undeformed specimen. Notice that, as has been previously observed,[2,3,6] the rate of F-center formation increases with deformation. However, for gamma doses, above 2×10^7 r, the growth curves ap-

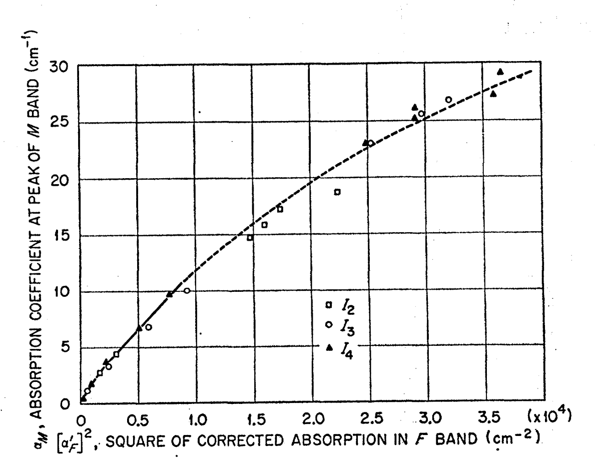

FIG. 4. Relation between M and F centers in heavily colored Isomet KCl. The solid portion of the curve is the straight line shown for Isomet in Fig. 3.

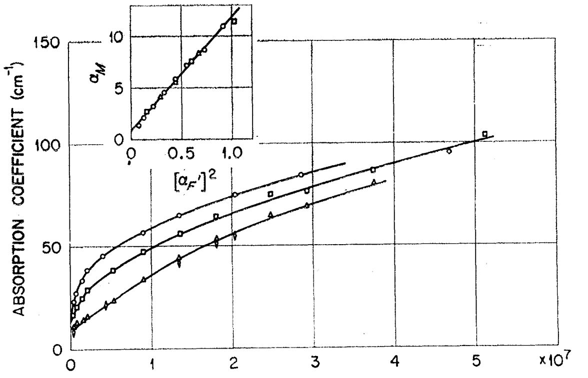

Fig. 5. The effect of plastic deformation on the coloring properties of Isomet KCl. The inset shows absence of any effect of deformation on the M-center to F-center relationship. ◇—Undeformed; □—4% deformed; ○—5-1/2% deformed; △—4% deformed and annealed.

parently begin to approach that characteristic of the "as received" crystals. Annealing of a 4% deformed sample for 2 h at 575°C causes the growth curve to return to that typical of an undeformed sample. Since contamination of the sample is possible if it is heated in air, the following precautions were taken. An ingot 5 cm long was deformed 4% and an irradiation sample was cleaved from a position one-third of the distance from the ingot face. The remaining two-thirds of the crystal was then heated in air to a temperature of 575°C and kept at that temperature for 2 h. After cooling, the center part of this section of the ingot was cleaved out and used as the deformed and heat treated specimen. It should be mentioned in this connection that, if an ingot is annealed at 575°C for several hours, a sample cleaved from the face of the ingot has a much higher first-stage F-center growth curve than a sample cut from the center, even when the ingot is slowly cooled to room temperature.

The inset of Fig. 5 reveals that the deformation, as well as the annealing had no effect on the slope of the $\alpha_M/\alpha_F'^2$ curve of the Isomet crystals. The solid line in the inset is that for untreated Isomet samples; the points are for the deformed and deformed and annealed samples.

D. Other Measurements

An unsuccessful attempt was made to correlate difference in the coloring curves or the slopes of curves shown in Fig. 3, with trace impurities present in the KCl samples. In Table III are summarized most of the results of trace impurity analysis. The values obtained by flame photometry are probably accurate to 25%. However, it was felt that the values obtained from semiquantitative spectrographic analyses are less reliable; therefore, for the case of the latter, only the indication of the presence of impurities is shown by the letter P.

It has been suggested[19] that bromine can be detected by its effect upon the absorption edge. In order to investigate the possible effect of bromine on the coloring properties, the ultraviolet absorption edge of the various samples was measured. The results are reproduced in Fig. 6. It is evident that not only does the absorption edge differ in the various samples, but there are indications of a number of unresolved peaks very close to or superimposed upon the edge. This would tend to indicate that other impurities besides bromine may affect the far ultraviolet absorption of KCl. The photon energy at which the absorption coefficient reaches 30 cm^{-1} is given in Table II. Variation of the position of the absorption edge yielded no correlation with the different coloring behavior shown in Figs. 1–3. The results for sample AK agree quite well with those obtained earlier on a different instrument by Kobayashi.[19] However, the Harshaw material utilized (at least two different ingots were measured) has an absorption edge much nearer the visible than the Harshaw sample, HA-1 measured by Kobayashi.

To check for large differences in dislocation content of the various undeformed samples measured, the dislocation density was determined by an acetic-acid etching technique.[23] The results of counting etch pits

Table III. Trace impurities. Numbers in the table indicate parts per million of impurity ions per ion of K, as obtained from flame photometry measurements. The letter P indicates that the impurity was detected by spectrochemical means. Dots indicate that the amount of impurity present is less than the limit of detection.

	Limit of detection	Sample									
Element	(μg/g)	B	CB	H	I	O	P	W	D	CA_1	CA_3
Al	2	...	...	P	P	P	...	P	P	...	...
Bi	20	...	...	P	...	...	...	...	P	...	...
Ca	5[a]	...	...	...	...	10	...	...	...	110	280
Cu	2	...	...	...	...	P	...	...	...	...	...
Fe	20	...	P	P	P	...	...	P	...	...	...
Mg	5	...	P	P	...	P	...	...	P	...	...
Na	15[a]	...	90	...	25	750	100	...	...	45	95
Si	1	P	...	P	P	...	...	...	...	...	...

[a] Calcium and sodium obtained by flame photometry. Spectroscopic analysis showed the presence of small traces of Ca in all samples.

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[23] M. Sakamote and S. Kobayashi, J. Phys. Soc. Japan **13**, 800 (1958).

on either the actual colored specimens (results shown starred) or specimens cleaved from the same ingot and to the same size as the experimental samples are given in Table II. The dislocation densities of the various samples appear to be enough alike to indicate that the results observed on undeformed samples are not primarily due to dislocations.

DISCUSSION

The almost quadratic relation between M and F centers in KCl and the absence of any well-defined break in the curves of Fig. 3 place some restrictions on previous concepts of color-center formation. Two possibilities will lead to the square law dependence observed. In the first, which has been shown to be valid at low temperatures,[15] an M center forms when two F centers are created in close proximity to each other. Secondly, an equilibrium between F and M centers could exist.

The first model suggests that there exists a region of interaction about each F center within which all adjacent F centers would be attracted by some short-range force. However, at room temperature the interaction radius would have to be some six to ten lattice spaces for agreement with experiment unless special regions existed in the crystal which had a very high concentration of F centers. Since no breaks are observed in Fig. 3, it must be assumed that, over the range of F centers investigated, either all the coloring occurs in special regions or it all occurs in the normal crystal. Moreover, on the basis of the above ideas, it would appear that the M centers formed in this manner would be rather stable; however, we observed that after an excess number of M centers had been created by optical bleaching, it was possible to cause the ratio of $\alpha_M/\alpha_F'^2$ to return to its prebleaching value by a very short re-irradiation[24] (15 min in the gamma source utilized).

The second possibility is that equilibrium obtains between F and M centers. On the basis of considerable experimental results, a thermodynamic equilibrium can be eliminated.[25] However, the possibility that a steady state is established under irradiation conditions and is frozen in when the sample is removed from the gamma source cannot be ruled out. The detailed processes involved in such an equilibrium may involve a redistribution of electrons on negative-ion vacancies and divacancies or they may involve ionic motion. The former idea is not consistent with the observation that the rate of M-center formation by optical bleaching is temperature dependent[26] and is related to the bleaching intensity in a complicated way.[27] The latter concept, that of radiation enhanced mobility is consistent with the results reported herein, as well as with bleaching experiments. It is not unreasonable to propose that trace impurities by acting as sources or traps of photons that would cause preferential bleaching of the M or F band, or by acting as recombination centers for electrons and holes, could cause a shift in the equilibrium during irradiation. In this connection it is of interest to report some preliminary qualitative results concerning luminescence of KCl while under gamma irradiation. All samples investigated were observed to luminesce,[28] and pictures taken of a number of crystals while they were in the gamma source revealed that both the intensity and the spectral distribution of the luminescent light differs in the various specimens.

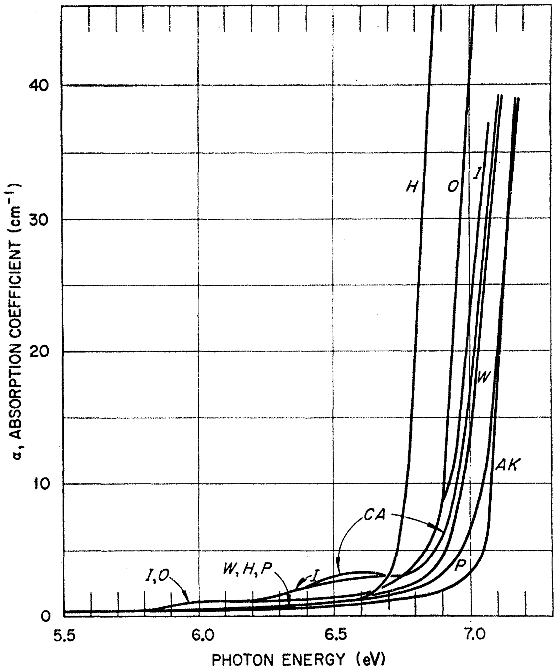

FIG. 6. Absorption spectra of a number of KCl samples near the ultraviolet.

SUMMARY

(1) No obvious correlation was found between the details of the late stages of the F- and M-center growth curves and either the concentration of detectable impurities or the ultraviolet absorption edge.

(2) The M-center concentration and the square of the F-center concentration were observed to be nearly proportional in all samples. No breaks were observed in any of the curves of M-center concentration versus the square of F-center concentration, although the slopes were different, depending upon the source of the

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[24] The recovery of the pre-bleaching conditions have also been reported for x-rayed KCl by L. E. Silverman and L. I. Grossweiner, Phys. Rev. **121**, 1072 (1961).

[25] For example, an increase in the M-center concentration by bleaching does not disappear upon removal of the light. Moreover, van Doorn (reference 14) had no difficulty freezing F and M centers which were at equilibrium at elevated temperatures.

[26] W. E. Bron and A. S. Nowick, Phys. Rev. **119**, 114 (1960).

[27] N. Itoh and T. Suita, J. Phys. Soc. Japan **17**, 348 (1962).

[28] Part of the visible and ultraviolet light given off by the samples may be due to Čerenkoff radiation.

KCl. Commercial material had the highest slope. In zone-purified material, the slope was lower. It was also suppressed in material doped with calcium.

(3) The increase of coloring rate due to deformation that had been observed previously was confirmed. However, there were indications that as the samples were irradiated more and more heavily, the coloring curves tended to approach each other again. Deformation had no effect whatsoever on the F- to M-center relationship.

(4) It was determined that changes in the ratio of M and F centers brought about by bleaching could be reversed by short re-irradiation. Moreover, luminescence was observed in the crystals under gamma irradiation, the spectral distribution and intensity of which was observed to differ in various samples. It is thought possible that the square relation between the M- and F-center concentration is due to an equilibrium under irradiation conditions.

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Hartree Calculations for the Ground State of Solid He and other Noble Gas Crystals*

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A single-particle model in which the wave functions are spherically symmetric about each lattice site was used to calculate the ground-state energy E_0 of solid He. The self-consistent Hartree equations (which yielded the best such wave functions) were solved numerically to an accuracy of better than 1%. The results were worse than could have been expected *a priori:* At the observed densities, the calculated values of E_0 were approximately +34 and +14 cal/mole for He^3 and He^4, respectively, as compared with experimental values of −4.5 and −12 cal/mole. Previous calculations are discussed in the light of our results. In addition, we calculated E_0 for the crystals of the other noble gas elements. The results for Ar, Kr, and Xe are within experimental error whereas E_0 for Ne is definitely outside this error (being about 5% higher than experiment).

I. INTRODUCTION

IN the last few years the properties of solid He^3 have received considerable attention both theoretically and experimentally.[1] The fact that He^3 has a nuclear spin of $\frac{1}{2}$ makes it possible to do a variety of experiments on it (e.g., measurements of the magnetic susceptibility, longitudinal and transverse relaxation times, and self-diffusion coefficient) which are not possible with He^4. The crucial point in understanding these phenomena theoretically is the calculation of the effect of Fermi-Dirac statistics and exchange forces on the properties of solid He^3. Such a calculation requires a detailed knowledge of the wave function of solid He^3. The object of this note is to present our recent computer calculations of the ground-state energy and wave function of solid He^3 and to discuss previous calculations[2–4] in the light of our results. In addition, we will also present calculations of the ground-state properties of crystals of the other noble gas elements.

The difficulty of computing the low-temperature properties of solid He^3 arises from the fact that its kinetic energy is of the same order of magnitude as its potential energy; this is due to the low mass of He^3 and the weakness of the attraction between two He atoms. Because of the relatively large kinetic energy, an external pressure of about 30 atmospheres is necessary to solidify He^3. Under these conditions He^3 has a body-centered cubic structure which is to be contrasted with the close packed structures of He^4 and the other noble gas elements.[5] In addition, the average deviation of a He^3 atom from its equilibrium position is certainly of the order of 30–40% of the nearest-neighbor distance;

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[1] *Helium Three*, edited by J. G. Daunt, (Ohio State University Press, Columbus, Ohio, 1960).

[2] N. Bernardes and H. Primakoff, Phys. Rev. Letters **2**, 290 (1959); **3**, 144 (1959); Phys. Rev. **119**, 968 (1960).

[3] N. Bernardes, Phys. Rev. **120**, 1927 (1960).

[4] E. M. Saunders, Phys. Rev. **126**, 1724 (1962).

[5] J. Vignos and H. Fairbank, Phys. Rev. Letters **6**, 265 (1961), have recently found a new ("high" temperature) phase of He^4 which almost certainly has the bcc structure.