Radiation Equilibrium of F and M Centers in KCl

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A study of F- and M-center coloration by electron-irradiating single crystals of KCl is made as a function of radiation intensity, electron energy, and crystal preparation. The quadratic relation between M-center and F-center concentration in any particular sample, previously observed for both x-ray and gamma irradiation, is verified for electrons if a constant current is used throughout the irradiation. However, the ratio of M-center concentration to the square of the F-center concentration is dependent upon electron current and sample preparation. Moreover, if a specimen is irradiated at one radiation intensity for a long period and then the intensity is changed for a short time, the relative M- and F-center concentrations are characteristic of the last irradiation intensity. It is concluded from this result that a dynamic equilibrium exists between F centers and M centers during irradiation. Interpretation of the results is proposed in terms of four simultaneous processes producing and destroying F centers and M centers, respectively. The processes for destruction of F centers and creation of M centers are thought to involve a mobile imperfection created by the irradiation. Means by which small concentrations of impurities can affect some of these processes to change the F-M equilibrium and F-center coloring curves are discussed.

INTRODUCTION

A LTHOUGH several processes[1–5] have been proposed to explain the room-temperature coloring of KCl, there is still considerable controversy concerning the dominant mechanisms. Recently, in an effort to broaden the base of experimental results, an investigation of the later stages of coloration and the relationship between F and M centers during gamma irradiation was made.[6] From this research it was concluded that M and F centers are probably in equilibrium with each other during irradiation. This equilibrium (or steady-state condition) is then frozen in when the samples are removed from the radiation source.
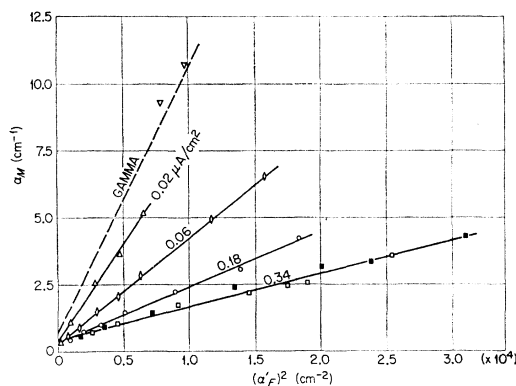

FIG. 1. The effect of radiation intensity on the F-center-M-center relation in Harshaw KCl. The dashed curve is for a sample gamma irradiated in a 4.5×10^6 R source. The solid lines are for samples electron irradiated with 1.5-MeV electrons and current densities shown.

The existence of such an equilibrium would have an important bearing on the ideas of how room-temperature coloring proceeds; e.g., through the implication that F centers are mobile during room-temperature irradiation. The purpose of this investigation was to attempt to confirm the presence of such a F-center-M-center equilibrium and to study this condition in various KCl crystals as a function of the energy and intensity of irradiation.

EXPERIMENTAL PROCEDURE

Most of the irradiations were performed using a Van de Graaff electron accelerator producing 1.5-MeV electrons. The electron current densities at the samples ranged from 0.02 to 0.36 $\mu A/cm^2$. In order to ascertain the amount of sample heating due to the irradiation a thin sandwich of KCl crystals with an imbedded thermocouple was irradiated in a manner identical to the samples. It was found that for the highest flux utilized and a typical irradiation time the sample and holder rose about 8°C above the surrounding 25°C temperature. At the lower irradiation intensities the temperature rise was almost as great, since the irradiations lasted a longer time. Thus, the specimens in all cases attained a temperature of from 30–33°C.

The crystals were prepared by cleaving and the irradiations and optical measurements were performed in light tight holders, as described previously.[6] A 0.002-in. aluminum foil was used during the electron irradiations to permit passage of the electron beam but not light.

EXPERIMENTAL RESULTS

Effect of Radiation Intensity

The fact that the M-center concentration is approximately proportional to the square of the F-center concentration in a given sample of KCl has been demonstrated previously.[6,7] Figure 1 shows clearly that the

* Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.
[1] F. Seitz, Rev. Mod. Phys. **26**, 7 (1954).
[2] J. H. O. Varley, Nature **174**, 886 (1954).
[3] J. H. Crawford, Jr. and C. M. Nelson, Phys. Rev. Letters **5**, 314 (1960).
[4] P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **117**, 442 (1960); **121**, 484 (1962).
[5] C. L. Bauer and R. B. Gordon, Phys. Rev. **126**, 73 (1962).
[6] W. A. Sibley and E. Sonder, Phys. Rev. **128**, 540 (1962).

[7] B. J. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters **7**, 57 (1961).

TABLE I. List of samples and irradiation conditions.

Sample	Source	Electron current density (μA/cm^2)	Gamma-ray dose rate (R/h)	Rate of energy absorption (MeV/sec cm^3)
$H_3{}^a$ $H_{26}{}^b$	Harshaw		4.5×10^6	1.3×10^{11}
$H_{27}{}^b$	Harshaw	0.019		4.9×10^{11}
H_{23}	Harshaw	0.057		1.46×10^{12}
$H_{28}{}^c$ $H_{29}{}^c$	Harshaw	0.153		3.9×10^{12}
H_{21}	Harshaw	0.175		4.5×10^{12}
H_{22} $H_{24}{}^b$	Harshaw	0.35		9×10^{12}
O_{21}	Optovac			
I_{21}	Isomet			
I_{31}	Isomet	0.175		4.5×10^{12}
P_{21}	Cornell			
D_{21}	IBM			
E_{21}	Westinghouse			

ᵃ Sample H_3 of reference 6.
ᵇ Irradiation conditions were changed (see Table II) after lengthy irradiations under the conditions shown here.
ᶜ These samples irradiated with 0.75-MeV electrons. All others with 1.5-MeV electrons or Co^{60} gamma rays.

ratio, or slope of the α_M vs $\alpha_F'^2$ curve, where α_M is the absorption coefficient at the maximum of the M band and α_F' is the corrected absorption[8] at the peak of the F band, is quite strongly dependent upon the intensity of irradiation. Each solid curve in the figure is for one run (a series of absorption measurements performed after successive irradiations with a given electron current). The four samples shown were all from the same ingot of Harshaw KCl. It is quite clear that, as is the case for gamma irradiation, straight lines are obtained; however, the slopes are smaller, the relative M-center concentration is less, for irradiations with higher currents. To compare these results with those on gamma irradiated KCl, a curve for a gamma-irradiated Harshaw KCl sample reported previously[6] is included as a dashed line.

A meaningful comparison between gamma and electron irradiations can be made by calculating the energy absorbed per second for the electron-irradiated and gamma-irradiated samples. In the case of electron irradiation, it was assumed that all the energy lost by the slowing electrons caused ionization in the KCl. In the gamma case a predominance of Compton absorption of the 1.2-MeV Co^{60} gamma rays was assumed so that a simple conversion from the 4.5×10^6 R/h calibration of the source to energy absorbed in the crystal was possible. The rate of energy absorption for the different irradiation conditions are given together with a list of samples used in these experiments in Table I.

It might be noted that, as was also true for the gamma-irradiated KCl, the α_M vs $\alpha_F'^2$ curves do not pass through the origin. It is tempting to attribute the excess M-center concentration observed to early stage processes, since, for the irradiation fluxes used in these experiments, effects due to the early stages of coloring

[8] The total F-center absorption was corrected for the M-center absorption lying under the F band by subtracting $0.8\alpha_M$.
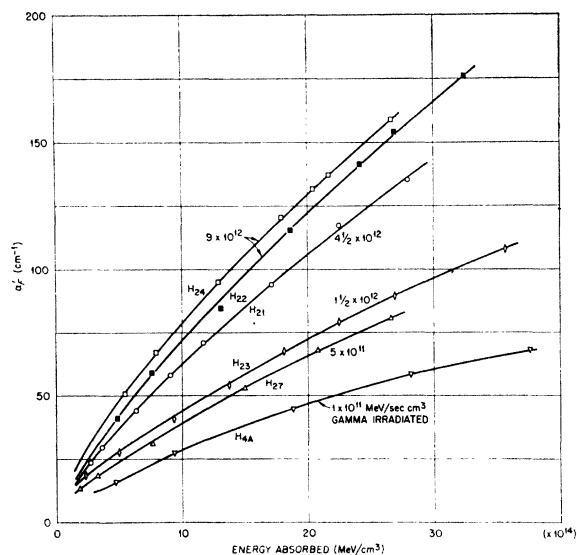

FIG. 2. The effect of radiation intensity on the coloring curves of Harshaw KCl. The curves are labeled with the energy absorbed per second from the gamma source in the case of the dashed curve and the electron beam in the case of the solid curves.

are all concentrated very near the origin of the graphs. The implication would be that some of these early stage processes might take place in regions of anomalously high F-center concentrations, for example near impurity clusters or dislocations, where the tendency to form di-F centers would be greater than in the bulk of the KCl.

It is usual in the literature to present irradiation data in the form of coloring curves; i.e., intensity of F band vs amount of irradiation. Therefore, Fig. 2 is included to show the F-center curves of Fig. 1 in the standard form. The data show, as has been observed in the past, that relatively more F centers are introduced for each eV of absorbed energy when higher fluxes are used. Quantitative comparison with results of a study of intensity effects in x-ray coloring[4] was not possible since it is difficult to calculate the energy absorbed in KCl from x rays having a wide energy distribution. Also, the present work was primarily concerned with the late stages of coloration when there was about a factor of ten more centers than was observed in the x-ray work.

Equilibrium between F and M Centers

It has been observed[6,9] that it is possible, with very little re-irradiation, to cause an optically bleached sample to return to its prebleaching relative F- and M-center concentration. Moreover, Fig. 1 indicates that the ratio $\alpha_M/\alpha_F'^2$ is dependent upon radiation intensity. Therefore, it seemed that changing the irradiation rate after a relatively lengthy irradiation might change the ratio, $\alpha_M/\alpha_F'^2$, in a similar way as bleaching or re-

[9] L. E. Silverman and L. I. Grossweiner, Phys. Rev. 121, 1072 (1961).

TABLE II. Change in F- and M-band absorption upon short irradiations.

Sample designation	Type of irradiation	Electron current density $\mu A/cm^2$	Irradiation time	Absorbed energy MeV/cm^3	Corrected absorption at F-band maximum α_F'	Absorption at M-band maximum α_M
H_{24}	e	0.35	5.3 min	26.6×10^{14}	159.4	3.54
H_{24}	e	0.05	10.0 sec	0.1×10^{14}	151.8	6.66
H_{24}	e	0.05	15.0 sec	0.2×10^{14}	147.8	8.51
H_{24}	e	0.35	11.0 sec	1.0×10^{14}	160.1	3.50
H_{26}	γ	$\cdots$	20.5 h	97.0×10^{14}	98.3	10.69
H_{26}	e	0.17	15 sec	0.7×10^{14}	115.4	2.30
H_{26}	e	0.17	10 sec	0.4×10^{14}	117.8	2.08
H_{26}	e	0.02	60 sec	0.4×10^{14}	112.1	5.86
H_{26}	γ	$\cdots$	10 min	0.8×10^{14}	102.7	11.20
H_{27}	e	0.02	90 min	26.2×10^{14}	80.5	5.14
H_{27}	e	0.18	15 sec	0.7×10^{14}	90.3	1.89
H_{27}	e	0.18	10 sec	0.4×10^{14}	92.7	1.99
H_{27}	e	0.02	60 sec	0.3×10^{14}	88.0	4.80
H_{27}	γ	$\cdots$	10 min	0.8×10^{14}	78.4	7.76

irradiation after bleaching. Three such experiments were performed. Table II gives the history of these runs, one in which the sample was first colored in the gamma source and two others where the primary coloring was done using the electron accelerator, with 0.02 and 0.35 $\mu A/cm^2$, respectively. The results are illustrated in Fig. 3. In this figure the curves of Fig. 1 are reproduced lightly and the dashed lines and arrows show the changes in F- and M-center concentration induced by the short irradiations. The irradiation time and energy absorbed per second for each step is also shown. It is clear from the figure that short irradiations at changed intensity will cause the ratio $\alpha_M/\alpha_F'^2$ to shift. Increased radiation flux causes a decrease in M-center and an increase in F-center concentrations, and a lowering of the flux
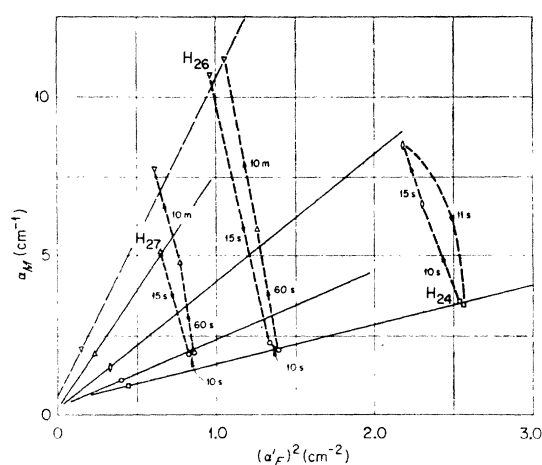

FIG. 3. Radiation equilibrium between F and M centers. The points connected by the heavy dashed curves show changes in F-center and M-center concentrations upon irradiation with different intensities of electrons and with gamma rays. The different symbols indicate the following irradiation intensities: □, electrons 0.34 $\mu A/cm^2$; ◇, electrons 0.06 $\mu A/cm^2$; ○, electrons 0.18 $\mu A/cm^2$; △, electrons 0.02 $\mu A/cm^2$; ▽, gamma rays 4.5×10^6 R.

causes the converse to take place. There is a definite tendency, after short irradiation at a given flux, for the ratio $\alpha_M/\alpha_F'^2$ to approach the value it would have reached if the sample had been irradiated at the given flux all the time. This would seem to confirm that a steady state exists under irradiation conditions, and that except for the slow introduction of additional F and M centers, the dynamic equilibrium is reversible. The time to reach equilibrium, as shown for instance by the 10- and 15-sec irradiation of sample H_{24}, seems to be of the same order as the time necessary to go through the first stage of coloration in these samples.

Similar measurements were performed on a number of samples from an ingot of chlorine treated KCl.[10] Although the relative M-center concentration in all of these samples was lower, the same variation of $\alpha_M/\alpha_F'^2$ with intensity and reversibility with short irradiation at changed intensity was found.

The possibility of the ratio of $\alpha_M/\alpha_F'^2$ being strongly energy dependent was checked by irradiating two Harshaw KCl specimens, H_{29} and H_{28}, with an intensity comparable to that used previously, but with the electron energy reduced from 1.5 to 0.8 MeV. Within the uncertainty of measuring the electron flux at different energies ($\sim$20%), no effect of changed energy on the ratio was found.

Comparison of Different KCl Samples

Another purpose of the electron irradiations was to determine whether there was any essential difference between coloring by electrons or gamma rays. In Figs. 4 and 5 are presented coloring curves and α_M vs $\alpha_F'^2$ curves for a number of differently prepared samples of KCl, all irradiated at the same electron current density. The curves are meant to be compared with Figs. 1 and 3 of reference 6. The shapes of the curves are similar for

[10] Kindly supplied by R. Pohl and J. Ashe of Cornell University.
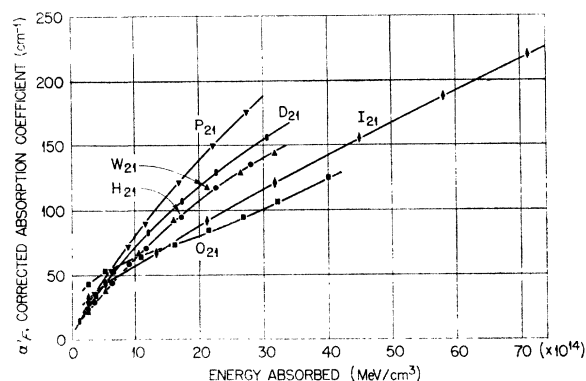
FIG. 4. Introduction of *F* centers by 1.5-MeV electrons (0.18 μA/cm^2) in differently prepared samples of KCl. Samples H_{21}, I_{21}, and O_{21} were obtained commercially, from Harshaw, Isomet, and Optovac, respectively. Sample P_{21} was pulled from the melt after chlorine treatment and samples W_{21} and D_{21} were zone refined. Except for I_{21}, the samples came from the same ingots as samples with similar letters in reference 6.

the gamma irradiation and electron irradiation. This evidence, together with the fact noted earlier, that when the actual energy absorbed per second is calculated the rate of coloration under gamma rays is consistent with coloring rate for electrons, makes it probable that displacement, or so-called knock-on type damage is negligible as compared with photolytic processes during electron irradiation of KCl.[2] However, closer comparison of the two sets of curves, recalling that samples labeled with the same letter are from the same ingots, shows that the total spread in late stage coloring rate between samples is less for the case of electron irradiation than it was for the case of gamma irradiation. Moreover, the order in which one would list the samples according to the magnitude of their slopes differs in the two cases, i.e., Isomet KCl colors more rapidly than Harshaw in the gamma source but more slowly in the accelerator. These quantitative differences seem to be due to the fact that the energy absorbed per second is a factor of 40 greater in the case of the electron irradiation than for the case of gamma irradiation.

DISCUSSION AND SUMMARY

The experimental observations that so many factors; e.g., impurities, radiation intensities,[11] etc., affect the coloring curves of the alkali halides imply that a complex set of processes is involved in room-temperature coloring. This complexity is implicit also in the five parameter equation used to fit first and second stage coloring in a previous study.[4] Thus, it would seem that no one model can be proposed to explain the coloring, but that a number of processes go on simultaneously. Therefore, we shall only summarize the results and rela-

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[11] K. Thommen (private communication) has shown recently that the ratio $\alpha_M/\alpha_F{}^2$ is a strong function of temperature in the vicinity of room temperature, and that it can be decreased by lowering the irradiation temperature in a way similar to our lowering it by increasing the irradiation intensity.

tions observed in this and the previous study[6] and indicate what type of processes are necessary to account for these. Only the late stages of coloring will be considered.

1. The *F*-center coloration in a given type of KCl is intensity dependent, i.e., the mathematical relation between coloration rate and intensity is of a power greater than linear. There seems to be no qualitative difference between electron and gamma-ray coloring.

2. The *F*-center coloring curves appear to have a saturation character in the late stages, especially if a relatively low intensity of irradiation is used. The saturation character becomes lessened with higher fluxes.

3. The coloring rate varies, depending upon the preparation of material. The difference is presumed to be due to impurities. There are indications that this variation is smaller when higher irradiation intensities are employed.

4. Except for a small rapid introduction of a few excess *M* centers during early coloration, the concentration of *M* centers is proportional to the square of the *F*-center concentration. No breaks in the curves of α_M vs $\alpha_F{}'^2$ are visible for any of the samples over the range of measurements.

5. The proportionality constant for the *M*-center–(*F*-center)^2 relationship is strongly affected by the same factors that affect the coloring curves; i.e., intensity of ionization and source of material.

6. It is possible to cycle the ratio of *F* and *M* centers by short irradiations of different intensities. This indicates that these centers are in dynamic equilibrium during irradiation.

The saturation behavior (2) could be explained by exhaustion of sites or necessary constituents for forming *F* centers. However, the fact that the saturation behavior becomes less obvious at higher radiation intensity makes an explanation in terms of two processes, one for forming, and one for destroying *F* centers more plausible. Since the rate of *F*-center introduction is proportional to a power higher than one of the rate of energy absorption (1) (also reference 4), an assumption of a simple proportionality between *F*-center destruction
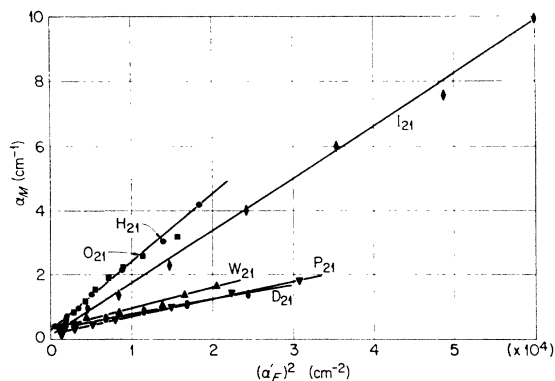

FIG. 5. The effect of sample preparation on the *F*-center–*M*-center relationship.

and energy absorption would be consistent with the observed saturation properties.

The radiation equilibrium observed between F centers and M centers (6) also requires at least two processes for its explanation, one creating M centers from F centers, and one in the reverse direction. In this case the reaction $M \rightarrow 2F$ must be the one with the higher power law dependence upon absorbed energy (as compared with the $2F \rightarrow M$ process) in order to have the relative M-center density decrease when a higher flux of radiation is used.

Thus, there are four processes (a) creation of F centers, (b) destruction of F centers, (c) agglomeration of two F centers, and (d) breaking up of M centers. Processes (b) and (c) might be the same, but since the large change in saturation level with intensity (Fig. 2) is difficult to explain by the small percentage of M centers (with respect to F centers) introduced, it would seem more likely that M centers are formed (c) by only a fraction of the F centers that are destroyed (b).

We should like to propose that under irradiation at room temperature there exists a mobile entity (perhaps the negative ion vacancy or the excited F center) that is involved in processes (b) and (c), and that either the concentration of this entity in a given sample or its ease of motion is proportional to the ionization density, but may differ in different samples due to different impurity content. The mechanism by which specific impurities may act upon this mobile entity is not known but at least two possibilities can be considered. Impurity atoms or ions may act as electron-hole recombination centers, thereby decreasing the steady-state electron (or hole) concentration in the conduction (or valence) band. This could easily affect the steady-state concentration or mobility of the mobile entity. The other possible mechanism involves luminescent light that might be given off by excited impurity ions. Self-absorption of this luminescence in the crystal could cause a different equilibrium concentration or mobility of the unknown entity.[12]

Whatever the mechanism is by which certain impurities act upon the mobile entity, it is logical that an increase of the irradiation rate can cause saturation of the mechanism. This would account for the smaller variation in coloring curves seen in the electron irradiation of various samples of KCl (3), as compared to the gamma-ray coloring curves.[6] It would also contribute to the lessening of the saturation character of the late stage coloring curves (Fig. 2) when higher fluxes are used.

The square dependence between M centers and F centers (4), the variation of the proportionality constant with intensity (5), and the fact that the proportionality constant can be changed in a reversible manner by changing radiation intensity (6) do not necessarily require any of the above-mentioned mechanisms. They are purely the result of having processes (c) and (d) going on simultaneously under irradiation conditions, with the latter process varying more rapidly (higher power) with the radiation intensity than the former.

We have deliberately refrained from proposing specific models (except as an example in reference 12) for the processes and centers involved. It is felt that too many possibilities exist, especially when considering the effect of impurities. We feel that first the relationship between the properties described here and *specific* impurities must be demonstrated and a real "intrinsic" coloring curve must be found.

ACKNOWLEDGMENTS

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[12] One possible specific example is indicated by the results of gamma irradiations of KCl (reference 6) where it seemed that Ca doping caused the ratio $\alpha_M/\alpha_F'^2$ to be similar to that found for zone-refined KCl; whereas in commercial material which presumably contains OH and oxygen impurity (which is easily observed by its visible fluorescence upon uv excitation), a higher value was found. Presumably, in commercial KCl, oxygen in one of its dissolved forms, luminescing in the F-band region would ionize an excess of F centers (over and above the number normally ionized by the gamma rays) causing more mobile negative-ion vacancies to be present; thus, increasing processes (b) and (c). Added calcium would, by chemically combining with the oxygen [for example, to form $Ca(OH)_2$], effectively remove the latter impurity from solution.