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Thermal Bleaching of *F* Centers and Its Correlation to Thermoluminescence in X-Ray Colored KCl Crystals

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A double-Dewar vacuum system, with an effective liquid-air trap close to the crystal inside it, is described. Undisturbed thermal-bleaching curves obtained with this system do not show any restoration of *F* centers when one warms KCl crystals x-irradiated at liquid-air temperature.

The thermal-bleaching curves obtained show steep fall-offs at certain temperatures throughout the examined temperature range of 90–600°K. The temperatures of fall-off in the bleaching curve fit well those of the peaks in the thermoluminescence curves obtained for the same crystal. This implies that *F* electrons are involved in practically all the luminescence peaks appearing in the glow curves of KCl crystals.

INTRODUCTION

It is well known that color centers (e.g., *F* centers), induced in alkali-halide crystals by x-ray irradiation, can be bleached optically as well as thermally.[1]

The bleaching process, however, is not fully understood. Initially, just after the irradiation by x-rays, the *F* centers bleach rapidly, but bleaching becomes later increasingly more difficult. Some investigators[2] suggested that more than one type of *F* center exists and the differences in the rate of bleaching were attributed to the different types of *F* centers. As was already pointed out by Seitz,[1] this suggestion should be discarded for it is difficult to believe that different types of centers will have so many common features as the "soft" and "hard" *F* centers possess. The alternative suggestion was that the different relaxation energies for the thermal bleaching of *F* centers result from differences in the energies needed for the annihilation of electrons in *F* centers by holes in the different *V* centers.

Valuable information about the bleaching process was obtained by thermal-bleaching experiments in which the colored crystals were bleached by uniform heating, absorption measurements being made during warming. Grant[3] used this method for the examination of the thermal bleaching of KCl in the temperature range between room temperature and about 160°C. The shape of the optical density curve measured at the peak of the *F* center as a function of temperature enabled him to calculate two different activation energies for the "soft" and "hard" *F* centers.

The method of thermal-bleaching measurements was discussed at length by Lushchik,[4] who, following the computations by Randall and Wilkins[5] for luminescence glow curves, has similarly calculated the dependence of the optical density at the *F*-band peak on temperature. He has also shown that the thermal-bleaching method has many advantages, compared with the method of luminescence glow curves and photoconductivity for studying traps in crystals. Experimentally Lushchik, like Grant, restricted his measurements to temperatures at and above room temperature.

Difficulties arise if one tries to extend such measurements below room temperature. Hesketh and Schneider[6,7] attempted to measure the thermal bleaching of *F* centers in KCl irradiated at 113°K on heating the colored crystal to room temperature. The bleaching curves showed peaks at about 170°K which they have interpreted as due to restoration of *F* centers. Similar peaks were obtained in measurements of color centers in CdS crystals.[8,9] In this case the authors suggested that the peaks were caused by vapor films which condensed on the surface of the cold crystal. Later this suggestion was shown to be true when the disturbances were successfully eliminated.[10] Measurements of thermal bleaching of color centers could now be taken over a wide range of temperatures. Such measurements of *F* centers in KCl crystals were carried out in the present work starting from liquid-air temperature, up to 600°K. The curves show the existence of, at least, 12 activation energies for the release of electrons from *F* centers. It was further shown that a good correlation exists between thermal bleaching and thermoluminescence of the same crystal.[11]

EXPERIMENTAL

A Beckman DU spectrophotometer was used throughout the work. A few modifications, however, had to be made to adapt the spectrophotometer for the present work.

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[1] For references see the reviews by F. Seitz, Revs. Modern Phys. **18**, 334 (1946); **26**, 7 (1954).

[2] J. J. Oberley and E. Burstein, Phys. Rev. **79**, 217 (1950).

[3] D. F. Grant, thesis, University of Durham, Durham, England, 1950 (unpublished).

[4] Ch. B. Lushchik, J. Exptl. Theoret. Phys. (U.S.S.R.) **30**, 488 (1956) [translation: Soviet Phys. JETP **3**, 390 (1956)].

[5] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 347, 366, 390 (1945).

[6] R. V. Hesketh, thesis, University of Durham, Durham, England, 1953 (unpublished).

[7] R. V. Hesketh and E. E. Schneider, Phys. Rev. **94**, 494 (1954).

[8] A. Halperin and G. F. J. Garlick, Proc. Phys. Soc. (London) **B68**, 758 (1955).

[9] A. Halperin and G. F. J. Garlick, Phys. Rev. **95**, 1098 (1954).

[10] A. Halperin and A. A. Braner, Phys. Rev. **98**, 1135 (1955).

[11] The results of the glow-curve experiments are described in the preceding paper [A. Halperin *et al.*, Phys. Rev. **108**, 928 (1957)], which will be further referred to as paper I.

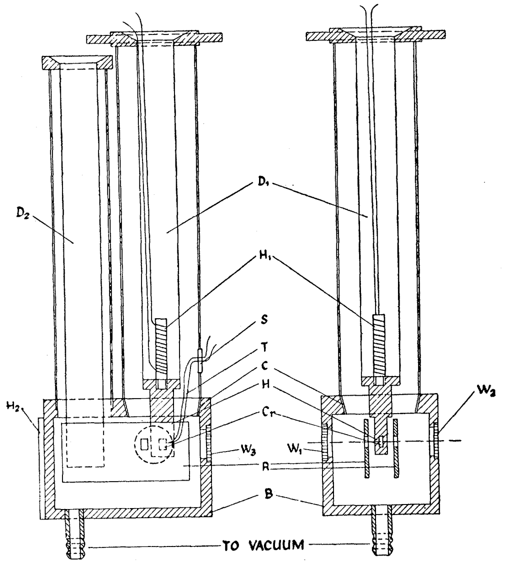

FIG. 1. Schematic diagram of the double-Dewar vacuum cryostat. D_1, D_2—two German-silver Dewars; H_1—crystal heater; H_2—external heater; T—thermocouple; S—insulating seal; C—ground metal cone; H—crystal holder; Cr—crystal; W_1, W_2, W_3—windows; R—radiation shields and vapor trap; B—container.

First, the cell holder was replaced by a special mount to fit the vacuum cryostat, housing the crystal under examination (see below).

At the start of the measurements the dc amplifier in the spectrophotometer was found to possess a temperature sensitivity which caused considerable zero drift. The amplifier was therefore redesigned. The modified amplifier consisted of a pair of electrometer triodes, which served as a differential amplifier, followed by a double triode connected as a balanced cathode follower. A Brown recorder at the output of the amplifier permitted continuous recording of transmission or luminescence. The high stability of the modified apparatus resulted in very accurate records of the thermal-bleaching curves.

Optical densities of the examined crystals were determined by comparing the light intensity transmitted by the crystal, to that transmitted by a reference hole in the crystal holder. For this purpose the cryostat was rocked in its mount between two fixed positions, bringing either the reference hole or the crystal into the optical path.

An RCA 1*P*21 photomultiplier sensitized to ultraviolet by *L* Apiezon grease was used as a radiation detector in most of the measurements.

The vacuum cryostat was a metal double-Dewar system, a diagram of which is given in Fig. 1. The inner walls of the Dewars were made of thin german-silver tubes. One of the Dewars (D_1) had an interchangeable copper crystal holder (H) attached to its lower part. A heating element (H_1) wound on a copper bar was screwed into the base inside the Dewar, thus making it possible to heat the crystal from liquid-air temperature up to about 700°K. Temperatures were measured by a copper-Constantan thermocouple (T). A ground cone fitting (C) permitted the rotation of the crystal out of the optical axis where it could be x-rayed through the window (W_3).

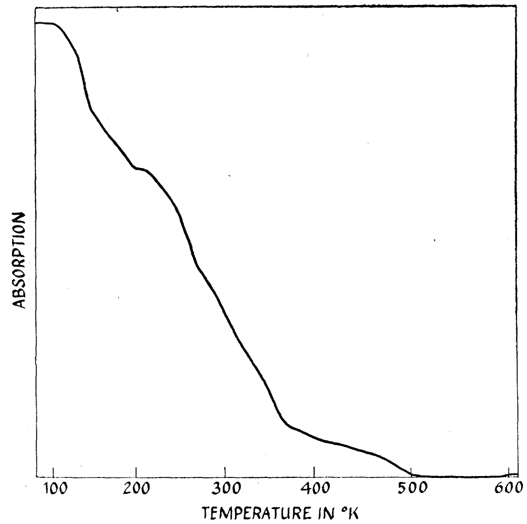

FIG. 2. Recorder tracing of a thermal-bleaching curve of a KCl crystal x-irradiated for 1 hour at liquid-air temperature. (The heating rate was about 30 deg/min.)

The second Dewar (D_2) has its lower end extended by two copper screens (R), shielding both sides of the crystal. This Dewar if kept at liquid-air temperature during the measurement provides an effective trap for vapors which otherwise might condense on the crystal surfaces.[10]

The vacuum system was closed by the container (B) which fitted the mount between the monochromator and the detector compartment of the spectrophotometer. Quartz windows (W_1) and (W_2) allowed optical access through the crystal (Cr). An external heater (H_2) attached to the container prevented atmospheric vapors from condensing on the windows.

Most of the examined crystals were in the form of plates, about 1 mm thick and 5×6 mm in the other dimensions, cleaved from pure KCl single crystals supplied by the Harshaw Chemical Company.

The crystals were colored in the dark, inside the cryostat by putting them at nearest access (3–4 cm) to the window of a General Electric x-ray tube operated at 45 kvp, 14 ma with a copper target or 45 kvp, 20 ma with a molybdenum target.

RESULTS

A typical record of a thermal-bleaching curve is represented in Fig. 2. The crystal was x-rayed (Mo target, 45 kvp, 20 ma) for 1 hour at liquid-air temperature. On measuring thermal bleaching, errors may arise due to shifts in the wavelength of the peak and changes in the width of the *F* band, which take place on warming. Elimination of effects due to the shift in wavelength

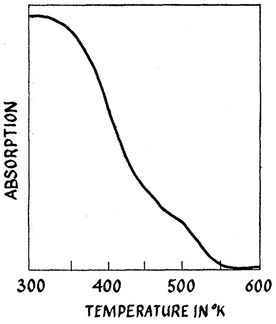

FIG. 3. Thermal-bleaching curve of a KCl crystal x-irradiated for 1.2 hours at room temperature. (The heating rate was about 30 deg/min.)

was secured by measuring the transmission at the wavelength of half peak density to the lower wavelength side of the F band (5170 A for KCl), which was shown by Pohl[12] to be temperature independent. Changes due to temperature broadening are less serious, for the decrease in density caused by broadening is proportional to $T^{-\frac{1}{2}}$, where T is the temperature in °K,[13] and its effects on the bleaching curve can be eliminated easily.

A green filter (Wratten 61) was inserted in the light path between the crystal and the detector to absorb the thermoluminescence which might interfere with the transmission measurements.

The shape of the bleaching curve obtained in Fig. 2 shows that bleaching takes place mainly at several characteristic temperatures. In other words, several activation energies exist for the thermal bleaching of F centers.

Figure 3 shows the bleaching curve obtained after x-irradiation at room temperature. The curve shows in a more pronounced way the bleaching process at higher temperatures.

The characteristic bleaching temperatures (T_b), for release of electrons from F centers can be obtained from these curves. It should be noted that the method is much less sensitive than the glow experiments, for values of T_b are obtained from deviations in the slope of the bleaching curve, which are in some cases quite small. Nevertheless, reproducibility of such variation in many repeated experiments showed that they are not accidental.

It was further found that the T_b values obtained in the bleaching experiments fit well the peak temperatures (T_g) of the glow curves obtained for the same crystal (see paper I). These values are compared in Table I. The deviations of the T_b values from the corresponding T_g values are not surprising, as almost the same variations were obtained also when comparing glow curves in different experiments. These variations were attributed to changes in the rate of cooling of the crystal from one experiment to the other, as well as to small variations in the rate of heating of the crystal. In addition, fixing of the peak temperatures was difficult, especially for unresolved peaks, and is in some cases estimated to about ±10 degrees.

The correlation between the processes of thermal bleaching and thermoluminescence is better demonstrated when densities are computed from the transmission values in the bleaching curves and temperature derivatives, dD/dT, are plotted against T. This makes possible direct comparison with the glow curves.

It was shown by other investigators[4] that the additional density D produced in the F band on x-irradiation of a given crystal is proportional to the number of electrons in the F centers—n_F. On the other hand, the luminescence intensity I of a given glow peak should be proportional to the rate of release of electrons from F centers (or for some peaks to the rate of release of holes from trapping states, and subsequent annihilation of F electrons by recombination with these holes). Therefore $I \propto -dn_F/dt$; and on warming at constant rate, I is proportional to dn_F/dT, and therefore also to dD/dT.

Figures 4 and 5 illustrates this correlation, Fig. 4 for a crystal irradiated at liquid-air temperature, and Fig. 5 for one irradiated at room temperature. It seems that practically all the peaks in the glow curve should in some way be related to the relaxation of F centers.

Relative intensities of the glow peaks, with the exception of two (at 250 and 280°K), fit fairly well the corresponding dD/dT values. Even more, good correspondence was obtained also for the peaks at 250 and 280°K for unaged crystals for which the intensities of these peaks were still normal. After aging of the crystal (by many repeated cycles of cooling, x-irradiating, and heating), however, these peaks have increased in intensities by a factor of hundred or more (see paper I), while the bleaching curves did not change appreciably. The increase in glow intensity by aging should, therefore, be attributed to an increase in the luminescence efficiency of the concerned transitions, and not to a change in the number of F electrons released during the glow.

DISCUSSION

The thermal bleaching of the F centers in colored KCl crystals was shown in the present work to take place mainly at certain characteristic temperatures and a good correlation was found to exist between these

TABLE I. The characteristic bleaching temperatures (T_b), for the release of electrons from F centers, compared with glow-peak temperatures (T_g) for the same crystal.

T_b	T_g	T_b	T_g
120	125	310	315
140	145	360	360
170	170	370	390
230	250	430	420
265	280	515	520

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[12] R. W. Pohl, Proc. Phys. Soc. (London) 49, (extra part), 3 (1937).

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temperatures and the peak temperatures in the glow curves of the same crystal. This seems to imply that the activation energies for the relaxation of *F* centers are to be identified with the thermal activation energies obtained from the glow curve. This view is supported by the results obtained by Lushchik,[4] who, working independently, has examined the thermal bleaching of KCl crystals. On warming the crystal up to 380°K and subsequent cooling to room temperature, Lushchik was able to obtain "crystals in which there were practically only traps of a single depth." The glow curve obtained contained practically only one peak at 410°K. This seems to correspond to the peak obtained in our work at 415°K, the difference being attributed to difference in rate of heating which was about 0.5 degree/sec in our work compared to 0.15 degree/sec in Lushchik's work. On measuring the thermal bleaching under the same conditions, Lushchik obtained a curve with a single rapid fall-off from which the corresponding activation energy was calculated. The value of 0.97 ev given by Lushchik (or 1.02 ev obtained by him by another method) fits well the value of 1 ev obtained in our glow experiments for the glow peak at 415°K (see paper I). The bleaching curves in our experiments, though complex, allow in some cases a rough estimation of activation energies,[14] which fit the results obtained from our glow curves.

Although the temperatures (T_g) of the peaks in the glow curves fit well those of the peaks in the dD/dT curve (T_b), the heights of the peaks do not. This misfit is especially striking for the glow peaks at 250 and 280°K which increased enormously in intensity on aging the crystal, the bleaching curve remaining practically the same (see Fig. 4). We may infer from this fact that the increase in intensity on aging the crystal is mainly due to an increase in the luminescence efficiency of the transitions involved, while the number of *F* electrons does not change considerably.

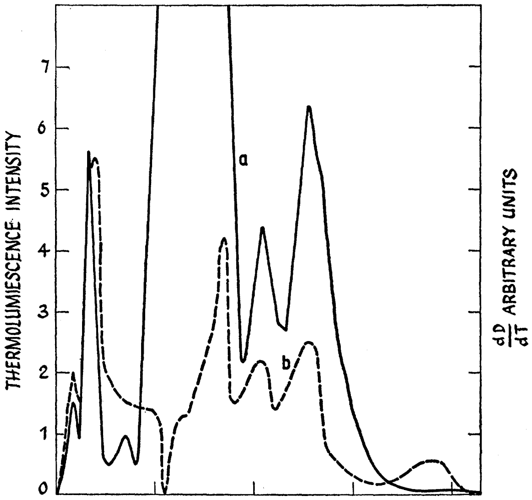

FIG. 4. Correlation between glow curves and thermal-bleaching curves obtained after x-irradiation (1 hour) at liquid-air temperature: *a*—glow curve; *b*—temperature derivative of the thermal-bleaching curve for the same crystal.

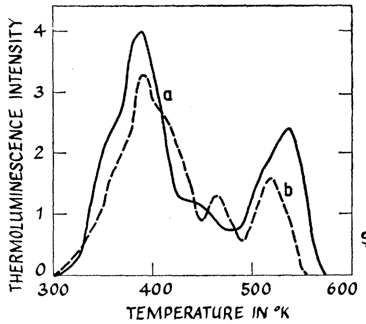

FIG. 5. Correlation between glow curves and thermal-bleaching curves obtained after x-irradiation (1 hour) at room temperature: *a*—glow curve: *b*—temperature derivative of the thermal-bleaching curve for the same crystal.

Mention should also be made of the "shelf" above 200°K appearing in the bleaching curves (Fig. 2). As mentioned before, the curve should show a downward slope on warming the crystal, owing to the temperature broadening of the *F* band. This slope can easily be obtained by cooling to liquid-air temperature a crystal x-irradiated at some higher temperature. On rewarming, one gets then the pure broadening effect up to the temperature at which the crystal was x-irradiated. The origin of the anomalous shelf is yet uncertain. It might be attributed to traces of vapor which the liquid-air trap in the cryostat fails to condense, and which therefore reach the crystal surfaces,[7,10] leading to a small scale "Hesketh effect." It seems, however, very improbable that such an effect would just compensate the drop in the curve due to the temperature broadening of the *F* band.

It should be stressed again that no restoration of *F* centers takes place on warming the crystal. We have repeatedly x-irradiated our crystals and then partially bleached them by *F* light. It seems that *F* irradiation changes the bleaching curve to some extent. It is, however, certain that with the effective trap inside the cryostat in action, no rise is obtained in the bleaching curve.

This conclusion is in opposition also to results reported by Katz,[15] according to which the concentration of *F* centers was observed to rise on heating the crystal to the temperature of the first visible luminescence burst. There are no details in the paper by Katz as to the exact conditions for which this effect was observed. We suppose that it should also be attributed to disturbances by vapors condensing on the crystal surfaces.

Katz has also suggested a model to explain his ob-

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[14] The formula $E_T = kT_b^2/\delta_b \ln 2$ used by Lushchik was also the basis for our estimations.

[15] M. L. Katz, J. Exptl. Theoret. Phys. (U.S.S.R.) **18**, 501 (1948).

servations, including an explanation of the "restoration" of F centers. Although this explanation should be discarded according to our views, there is a part of his model that might be taken into consideration. This concerns his assumption that defect levels near the valence band are responsible for some of the peaks in the thermoluminescence curve. By thermal agitation, holes trapped in these levels are freed into the valence band and combine with electrons from F centers. The luminescence emitted at the same time is due to one of the transitions involved in the process of annihilation.

It is of interest to point out that the thermal activation energy of 0.29 ev found by us for the glow peak at 125°K fits well the gap between the valence band and the β band which was calculated by Bassani and Inchauspé[16] to be 0.28 ev for KCl. Similarly, the value of 0.53 ev found by the same authors for the gap between the α band and the valence band seems to fit the thermal activation energy of the glow peak at 250°K.

However, before any model is given to account for the thermal bleaching and thermoluminescence phenomena, it seems profitable to measure the thermal bleaching curves for all the F-type, V-type, and α- and β-type centers, which is in our program now.

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[16] F. Bassani and N. Inchauspé, Phys. Rev. **105**, 819 (1957).

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Thermal Breakdown in Silicon *p-n* Junctions

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It is shown that the normal avalanche breakdown of well-etched silicon *p-n* junctions can pass at higher temperatures into a kind of thermal breakdown at which most of the current flows through a small hot hole in the potential barrier.

It is known that the breakdown in broad silicon *p-n* junctions is caused by an avalanche process[1,2] and that the passage of a reverse-bias breakdown current is usually accompanied by the emission of visible light.[3,4] In some well-etched grown silicon *p-n* junctions, we have observed that on increasing the breakdown current we finally reach a point a (Fig. 1) where the current-voltage characteristic $U\approx U_b=\text{const}$ suddenly changes. The change can be described as a fast jumping from a state a to another a' followed by a characteristic which can be at least approximately described as $U=\text{const}/J$. The current J_a at a is smaller if the temperature of the junction is higher. The characteristic given in the figure assumes its normal form $U\approx\text{const}=U_b'$ (where $|U_b'|<|U_b|$) when the maximum of the external sinusoidal voltage is passed.

The process occurring at the point a is accompanied by a sudden change in the aspect of the light emitted. In the avalanche breakdown region for $|J|<|J_a|$ the junction usually appears as a sequence of more or less intense bright white spots forming eventually an almost continuous line; simultaneously with the jump $a\to a'$ all these white spots disappear and a single red spot appears. When measuring with direct current we can maintain this red spot once generated even with a current intensity smaller than J_a. With increasing current its dimensions increase and its color darkens and finally its outlines become diffuse. Its position is not stable; it often shows a tendency to dwell at the corners of the sample. Its temperature is considerably higher than the temperature of the rest of the junction or the temperature of the mentioned white spots; e.g., a cigarette paper catches fire at the red spot. The recently observed external electron emission from silicon *p-n* junctions[5] is very much smaller from this red spot than from white spots.

We suggest that the observed effect is caused by a temperature rise in a certain small part of the junction in which the potential barrier ceases then to present a resistance to the flow of the current. Through this glowing spot the major part of the current passes producing the necessary heat to maintain its high temperature. We assume that the normal avalanche breakdown can pass into this kind of breakdown if it is energetically more economical. If we consider McKay's breakdown as a solid state analog to the glow discharge in gases, this breakdown would correspond to a kind of arc discharge.

We could make a rough theoretical estimate of this process by assuming that the whole current passes through a circular hole in the barrier with a radius r_0. This hole has a uniform temperature T_m which is higher than the temperature T_0 at the contacts. To calculate

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[2] K. G. McKay, Phys. Rev. **94**, 877 (1954).
[3] R. Newman, Phys. Rev. **100**, 700 (1955).
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