with the temperature dependence of ϵ in accordance with Eq. (8). Similarly, Cowley's[21] neutron-scattering study of this lowest frequency transverse-optic branch shows that $\omega_T{}^2 \propto (T-T_c)$ with $T_c = 32 \pm 5$°K. This is in agreement with the value of $T_c = 35$°K obtained from the measurement of ϵ.

In terms of the present results, and in analogy with Eq. (8), ω_T may vary with pressure as

$$\omega_T{}^2 \propto 1/\epsilon = (p-p_0)/C^*. \tag{9}$$

Unfortunately, there are no available data on the pressure dependence of ω_T to check the validity of Eq. (9). Such measurements would involve surmounting some severe experimental difficulties.

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PHYSICAL REVIEW VOLUME 140, NUMBER 3A 1 NOVEMBER 1965

Evidence of Different Types of F Centers from Thermoluminescence Studies in X-Irradiated Alkali Halides. I. Highly Pure KCl Crystals

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(Received 1 June 1965)

Two thermoluminescence peaks are observed at 135 and 190°C in highly pure KCl crystals (divalent impurity concentration <1 ppm) x-irradiated at room temperature and heated at 40°C/min. Utmost care was taken to avoid exposure of the crystals to light and the concentration of M and other aggregate centers remained negligible in these experiments. The growths of the areas Δ_i and Δ_g under the first and the second peaks, with the time of x irradiation, are found to obey the equations given by Mitchell, Wiegand, and Smoluchowski for the growth of the concentrations f_i and f_g of the first-stage and the second-stage F centers, respectively. From this result and from the observation that the ratio $\Delta_i/f_i = \Delta_g/f_g$ remains constant in a variety of crystals (irradiated for different times or with different x-ray intensities, quenched, slowly cooled, or partially bleached), it is concluded that all the thermoluminescence is due to F centers and that the 135 and 190°C peaks correspond separately to the bleaching of the first-stage and the second-stage F centers, respectively. The values of the parameters in the equations given by Mitchell *et al.* are derived from the observed growths of Δ_i and Δ_g and are found to be in agreement with the values obtained by Mitchell *et al.* The reduction in the area under the thermoluminescence curve on partial optical or thermal bleaching is found to be proportional to the reduction in the F-center density. However, optical bleaching reduces both thermoluminescence peaks, whereas thermal bleaching up to about 100°C reduces mainly the first peak. It is found that complete thermal bleaching does not destroy all the vacancies generated during the irradiation but disperses some of them more uniformly. Both thermoluminescence peaks are found to correspond to a first-order process; therefore, it is concluded that the retrapping of the electrons released from the F centers is negligible. The activation energies of the two peaks are 1.05 ± 0.05 and 1.15 ± 0.05 eV, respectively. This indicates that thermal bleaching of the second-stage F centers at higher temperatures is not due to the retrapping of the electrons by anion vacancies, as concluded by some earlier workers, but to differences in the energies of thermal ionization of the two types of F centers. Possible mechanisms which can give rise to differences in thermal ionization energies are tentatively suggested. These results are not inconsistent with the view that the first-stage F centers are formed by the vacancies present in the crystal prior to irradiation and are distributed uniformly in the crystal, and that the second-stage F centers are formed by the vacancies generated in the crystal during the irradiation process, perhaps near a defect, and are present in small regions of high local concentrations. Results of preliminary experiments indicate that the calcium impurity introduces a new thermoluminescence peak at 85°C, enhances the 135°C peak, and suppresses considerably the 190°C peak. Deformation introduces an additional peak at 270°C and reduces the rate of growth of the second peak at 190°C. The parameter a defining the observed rate of generation of new vacancies varies approximately as the square of the intensity of x irradiation, in agreement with the observation of Mitchell *et al.* and the more recent observation of Abramson and Caspari.

I. INTRODUCTION

SEVERAL authors[1–10] have found it necessary to assume that the F centers in x-irradiated crystals are of two types in order to interpret the results of a variety of their experiments. F centers of the first type are formed by the vacancies present in the crystal prior to the irradiation and are distributed statistically. F centers of the second type are formed by the vacancies generated during the irradiation process. These F

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[3] R. B. Gordon and A. S. Nowick, Phys. Rev. **101**, 977 (1956); A. S. Nowick, *ibid.* **111**, 16 (1958).

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centers are perhaps formed near some defects and are in regions of high local concentrations. Thermoluminescence studies to investigate the nature and properties of these two types of *F* centers in highly pure KCl crystals and perliminary studies of other types of *F* centers generated in deformed and doped KCl crystals have been made. The results of these investigations are presented in this paper.

It is known[11] that the mechanisms of color-center formation at room temperature and at low temperature are quite different. Since the work reported here shows an intimate correlation between color centers and thermoluminescence, this work is confined to room-temperature x irradiation only. The results obtained with crystals irradiated at low temperature will be reported in a separate paper.

II. EXPERIMENTAL

A. Thermal and Mechanical Treatment of the Crystals

Single crystals of zone-refined[12] KCl were kindly supplied by Dr. Srinivasan (the zone-refining method used by Dr. Srinivasan is described in Ref. 12) of Illinois State University, Urbana. Single crystals of spectroscopically pure KCl (material purchased from Johnson Matthey & Co., London), BDH Analar KCl or deliberately doped KCl were grown in our laboratory from the melt by the Kyropoulos method. Thin slices of the crystals were cleaved and were given the desired heat or mechanical treatment. For quenching, the slices were heated to 700°C and cooled rapidly on a large copper plate in front of an electric fan. For slow cooling, the slices were kept in a furnace at 700°C for a few hours and the temperature of the furnace was then lowered at 25°C/h. For deforming the crystal plastically, the slice was held between the two jaws of a micrometer screw and the screw was tightened until the desired amount of deformation occurred.

All calcium-doped crystals were grown from spectroscopically pure KCl. The concentration of calcium in the crystals was taken[13] to be approximately $\frac{1}{10}$ of the concentration added to the melt while growing the crystals. The rate at which the crystals were grown was similar to that used by Kelting and Witt.[13]

The ionic-conductivity measurements made by G. D. Sootha of this laboratory showed that both the zone-refined and the spectroscopically pure crystals contained less than 1 ppm of the divalent impurity and the BDH Analar crystals contained about 30 ppm of the impurity. Thermoluminescence results obtained with zone-refined and spectroscopically pure crystals were identical. No distinction is therefore made in this paper between spectroscopically pure and zone-refined crystals and these crystals are designated as highly pure crystals. The letter S is used to denote these crystals. The letter B denotes crystals grown from BDH Analar KCl. Different numerals placed after the letters S or B indicate the numbers of the batches (grown at different times), from which the samples were cleaved.

B. X Irradiation

The x irradiation was done by a Philips PW 1009 x-ray diffraction unit using a Mo target, working at 35 kV and 2–20 mA. A stabilizer was used to stabilize the input voltage to the x-ray diffraction unit and variation of the x-ray intensity was estimated to be less than 3%.

The x rays from the Mo target at 35 kV consist of an intense K_α doublet near 0.71 Å, and a less intense K_β line at 0.63 Å. The intensity of soft x rays on the long-wavelength side of K_α doublet falls rapidly. After the filtering effect of the mica-beryllium window of the tube, the intensity at 0.8 Å is less than 1% of the intensity at 0.7 Å. Aluminum filters (1 mm thick) were also used in some experiments. It was found that most of the conclusions arrived at in this paper were independent of the filter used. The crystals used were less than 0.5 mm thick and were irradiated on both sides for uniform coloration. Care was taken that no stray light fell on the crystals during the x irradiation or during subsequent measurements.

C. Optical-Absorption and Thermoluminescence Measurements

An ordinary 125-W soldering iron was used for heating the crystals to study the thermoluminescence, for bleaching of color centers or for measuring the optical density between 30 and 300°C. Its soldering tip was removed and a copper plate with two small windows was fixed in its place. For optical-absorption measurements the reference crystal and the colored crystal were mounted, respectively, at the two windows in the copper plate. The plate was so designed that it could be placed in the specimen holder in the Hilger and Watt UVISPEK spectrophotometer.

The bleaching by *F* light and *M* light was done by the UVISPEK spectrophotometer. The slit width was kept at 1 mm and the distance of the crystal from the output slit was about 4 cm.

The thermoluminescence was measured by an RCA 931A or IP21 photomultiplier tube and a Honeywell Brown Electronik type No. 153 millivolt recorder using chart No. 5401-043B, 0–100 Even. Care was taken to place the crystals in exactly the same position in front of the photomultiplier tube in all experiments. When the areas of thermoluminescence curves were compared with the optical density, the thermoluminescence results were reduced to correspond to the

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[11] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962).

[12] T. M. Srinivasan, Air Force Office of Scientific Research, Washington, D. C. Technical Report No. 3 AF-49 (638)-529, 1962 (unpublished).

[13] H. Kelting and H. Witt, Z. Physik **126**, 697 (1949).

recorder sensitivity of 1 mV for full-scale deflection with 100 $k\Omega$-resistance across the plate and the last dynode of the photomultiplier. The sensitivity with this arrangement is designated as "standard" sensitivity.

A copper-constantan thermocouple was attached to the copper plate and the temperature was recorded by a Philips millivolt and temperature recorder, Model No. PR 2210 A/21. An auxiliary experiment, with two thermocouples attached to the crystal and the plate, respectively, was performed to determine the difference in temperature of the crystal and the plate. The difference was found to be dependent on the heating rate as well as on the actual temperature. For example this difference in the two temperatures was 5, 6, and 8°C at 50, 100, and 150°C, respectively, for a heating rate of 40°C/min. For the heating rate 5°C/min the differences were less than 1°C at all temperatures. Knowing these differences, we corrected temperatures observed with the thermocouple attached to the plate to obtain the temperatures of the crystals.

If the crystals used were thick, the thermoluminescence intensity did not decrease to zero at the end of the thermoluminescence peaks for a considerable further rise of temperature. This occurred perhaps because the interior of the crystal was at a lower temperature than the surface in contact with the metal plate. As mentioned before, the thickness of the samples used was about 0.5 mm or less. Crystals thinner than 0.4 mm warped on cleaving and could not be used.

III. THEORY OF *F*-CENTER GROWTH AND THERMOLUMINESCENCE

In this section we discuss briefly the theory of the growth[3,6,7] of F centers with the time of x irradiation and of thermoluminescence[14,15] and quote the equations which we shall use later to interpret our experimental results.

A. *F*-Center Growth

It is known that F centers are generated in two stages when the crystals are x irradiated.[3,6,7] The F-center concentration f_i in the first stage saturates in a few hours whereas the concentration f_g in the second stage keeps on increasing for longer durations of irradiation. The centers F_i are formed by the vacancies n_i which are present in the crystal before irradiation and are distributed in the crystal statistically. The centers F_g are formed by the vacancies n_g generated during the irradiation process and are in isolated regions of high local concentrations. A certain concentration of the n_g type of vacancies (in regions of high local concentrations) may be present in the crystal prior to irradiation and the F centers formed by these vacancies will be of the F_g type. The differential equations defining the growth of the F_i and F_g centers have been formulated and solved by Mitchell *et al.*[6] and by Fröhlich.[7] The final results are

$$f_i = n(1-e^{-bt}), \tag{1}$$

$$f_g = at - [(a/c) - n'](1-e^{-ct}), \tag{2}$$

and

$$f = f_i + f_g = n(1-e^{-bt}) + at - [(a/c) - n'](1-e^{-ct}), \tag{3}$$

where b and c are the rate constants for the capture of electrons by the vacancies n_i and n_g, respectively, a is the rate of generation of new vacancies of the type n_g, and n and n' are the initial concentrations of the vacancies of n_i and n_g types, respectively. Equation (3) does not take into account the fact that after long times of irradiation, the concentration of the second type of F centers also saturates; thus this equation is applicable only for values of time t which are not large enough so that there are deviations from the linear growth given by the term at. However, the bleaching of the F centers during the irradiation process can be taken into account by Eq. (3) if the constants a, b, c, n and n' are replaced by the new constants[6] involving the bleaching rates also.

B. Thermoluminescence

The theory of thermoluminescence has been discussed by several workers.[14–19] The thermoluminescence intensity L, when retrapping is negligible, is given by[15]

$$L = n_0 s e^{-E/kT} \exp \int_0^T -\frac{s}{\beta} e^{-E/kT} dT, \tag{4}$$

and when retrapping is equally probable to recombination with luminescence centers,

$$L = n_0^2 s e^{-E/kT} \Big/ N \left[1 + \frac{n_0}{N} \int \frac{s}{\beta} e^{-E/kT} dT \right]^2, \tag{5}$$

where N is the concentration of traps (negative-ion vacancies in the present case), n_0 is the number of electrons trapped, E is the trap depth, β is the heating rate and s is the frequency factor.

It has been suggested that during the thermal bleaching of the second type of F centers, retrapping is important.[6] The following features of Eqs. (4) and (5) can be related[15] to the thermoluminescence experiment to find out the relative significance of retrapping:

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[15] G. F. J. Garlick and A. F. Gibson, Proc. Phys. Soc. (London) **60**, 574 (1948).

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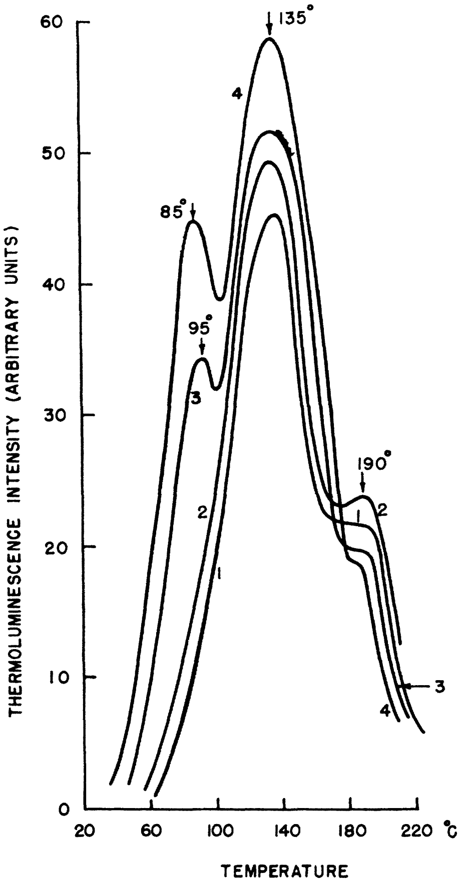

FIG. 1. Effect of impurity on the thermoluminescence of KCl crystals x irradiated at 35 kV and 10 mA for 5 min without filter and heated at 40°C/min. Curve 1—spectroscopically pure crystal S1, background impurity <1 ppm; curve 2—zone-refined KCl crystal S2, background impurity <1 ppm; curve 3—BDH Analar crystal B1, background impurity ~30 ppm; curve 4—KCl crystal S3 grown from spectroscopically pure KCl containing 50 ppm of Ca. 85°C peak in curve 4 is due to the calcium impurity; 95°C peak in curve 3 for crystal B1 is believed to be due to unknown background impurity. The 135 and 190°C peaks are characteristic of the pure KCl crystals.

(i) The position T_g at which the maximum in the L-versus-T curves occurs is independent of the value of n_0/N if retrapping is negligible but depends strongly on the value of n_0/N if retrapping is significant.

(ii) The shape of the curve L-versus-T is independent of the value of n_0/N in the first case but not in the second case.

In both cases, the area under the L-versus-T curve is proportional to n_0, the number of electrons initially trapped.

Garlick and Gibson[15] have described other experiments (e.g., on phosphorescence and on filling the traps by varying the intensity of the exciting radiation) which permit the evaluation of the relative importance of retrapping. Halperin *et al.*[18] and Lushchik[19] have also discussed the methods of finding out the relative importance of retrapping.

IV. RESULTS AND DISCUSSION

A. Influence of Background Impurity on the Thermoluminescence in KCl Crystals

The observed thermoluminescence results obtained with spectroscopically pure samples S1, zone-refined crystals S2, BDH Analar crystals B1, and 50-ppm-calcium-doped crystals S3, are shown by curves 1 to 4, respectively, in Fig. 1. The crystals were quenched from 700°C and were x irradiated (35 kV, 10 mA, without filter) at room temperature for 5 min. The heating rate was 40°C/min. It is seen from curve 3 for the crystal B1 that there are 3 peaks, at 95, 135, and 190°C, respectively. The experiments with different times of x irradiation described later in this paper show that 95°C peak in B1 crystals saturated in about 10 min. The curves 1 and 2 for the S1 and S2 crystals, respectively, show that the 95°C peak is absent in highly pure crystals. It is seen from curve 4 for the crystal S3, spectroscopically pure KCl crystal containing 50 ppm calcium, that the Ca impurity in the highly pure crystals introduces a new peak at 85°C. The preliminary results obtained with other divalent impurities indicate that each impurity has its characteristic thermoluminescence peak, in most cases at temperatures $\lesssim$95°C. The positions of the 135 and 190°C peaks are practically the same in the highly pure, BDH Analar or doped crystals.

The results that the 95°C peak is observed in BDH Analar crystals containing 30 ppm of impurity, that it is absent in the highly pure crystals, that the peak saturates in about 10 min, and that Ca and other divalent impurities give similar peaks at temperatures $\lesssim$95°C, suggest that the 95°C peak is due to the background divalent impurity. We, therefore, conclude that in undeformed KCl crystals, x irradiated at room temperature, there are two thermoluminescence peaks characteristic of the pure KCl. These peaks are at 135 and 190°C respectively, for the heating rate 40°C/min, and at 93 and 165°C for the heating rate 5°C/min.[20] We will discuss the behavior of the two thermoluminescence peaks in the highly pure crystals and their correlation with the two types of F centers in the following section.

B. Growth of Thermoluminescence and F-Center Density with the Time of X Irradiation

(*a*) *Growth of the Total F-Center Density and of the Total Area under the Thermoluminescence Curve*

The results of thermoluminescence measurements on the quenched crystals S6 irradiated with x rays for

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[20] S. C. Jain and P. C. Mehendru, Phys. Letters **5**, 186 (1963). [Further work has shown that the third peak at 230°C reported earlier in spectroscopically pure crystals is in fact related to plastic deformation. The difference in the peak positions reported earlier and those reported here is due to the difference in the heating rates.]

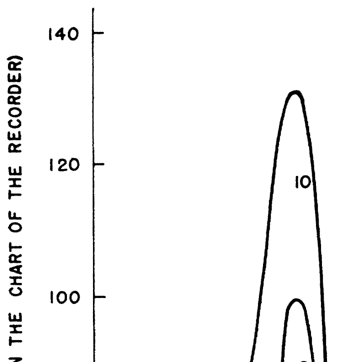

FIG. 2. Growth of the *F* band and the thermoluminescence with the time of irradiation in S6 KCl crystals x irradiated at 35 kV, 10 mA with 1-mm-thick aluminum filter and heated at 40°C/min. Thickness of the crystals was 0.50 mm. All values of the thermoluminescence intensities correspond to "standard" sensitivity (see Sec. II). The times of x irradiation and the corresponding OD_F/cm values are: curve 1—30 min, 2.42; curve 2—1 h, 3.60; curve 3—2 h, 4.50; curve 4—3 h, 4.82; curve 5—5 h, 5.35; curve 6—7 h, 6.10; curve 7—10 h, 7.00; curve 8—14 h, 9.00; curve 9—17 h, 10.40; and curve 10—24 h, 14.40. The fast peak at 135°C saturates in about 7 h and is attributed to the *F* centers formed in the fast first stage by the vacancies already present in the crystal. The slow second peak at 190°C is attributed to the *F* centers formed in the slow second stage by the vacancies created during the irradiation process in regions of high local concentrations.

different times (with 1-mm-thick aluminum filter) are shown in Fig. 2. The values of the optical density OD_F at the maximum of the *F* band, measured in each case before measuring the thermoluminescence, are also shown in the figure. It is seen that for the smallest time of irradiation, i.e., $\frac{1}{2}$ h, only the first peak at 135°C, designated as the fast or the first-stage peak, is observed. For 2-h irradiation, a very weak second peak, designated as the slow or second-stage peak, is observed at 190°C. The fast peak is still considerably larger than the slow peak. As the time of irradiation is gradually increased, both peaks increase in area up to about 7 h, the relative rate of increase of the second peak being larger for the larger irradiation times. If the time of irradiation is increased to more than 10 h, the fast first peak does not increase any more. For higher times of x irradiation, this peak is seen only as a shoulder since it is now saturated and the second peak keeps on increasing and becomes relatively very large for larger times of irradiation. This result is in qualitative agreement with the result obtained by Morehead and Daniels[21] that the fraction of thermoluminescence in LiF obtained at higher temperatures increases with the increase of the time of irradiation.

The areas under the thermoluminescence curves in Fig. 3 were determined by counting the small rectangles on the chart of the recorder under the thermoluminescence curves. The accuracy of the areas determined in this manner was about 4% for small areas (~50 rectangles) and better than 1% for large areas (>200 rectangles). The areas were divided by the thickness of the crystals to obtain the values of Δ/cm and compared with the corresponding values of OD_F observed just before measuring the thermoluminescence. It was found that for any given time of irradiation, the ratio of the values of areas under the two peaks to the values of the corresponding OD_F was always constant and was equal to 425 for the "standard" sensitivity, as defined in Sec. II. This is illustrated in Fig. 3. Curve 1 in the figure gives the OD_F/cm as a function of the time of irradiation for the samples S6. Curve 2 is obtained from curve 1 by multiplying each ordinate by 425. The points on curve 2 are the observed values of the areas Δ/cm of both the thermoluminescence peaks for the corresponding times of irradiation. It is seen that the points lie smoothly on curve 2. This result will be more clearly demonstrated later in Fig. 8 where the plot of thermoluminescence area as a function of OD_F is shown to be the line $\Delta = 425\ OD_F$ for samples S6 and S9. We, therefore, conclude that both thermoluminescence peaks observed in the highly pure crystals are due to bleaching of the *F* centers. In any particular experiment, the total area of both thermoluminescence peaks is thus a measure of the concentration of *F* centers present in the crystal before the crystal is heated to induce thermoluminescence.

The areas of the thermoluminescence curves for crystals which were cleaved from the same block, and which had received identical irradiation and heat treatments, agreed within 4% for very small times of irradiation (OD_F/cm~1) and within 1% for times of irradiation larger than 2 h (OD_F/cm>5, without aluminum filter).

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[21] F. F. Morehead and F. Daniels, J. Chem. Phys. **27**, 1318 (1957).

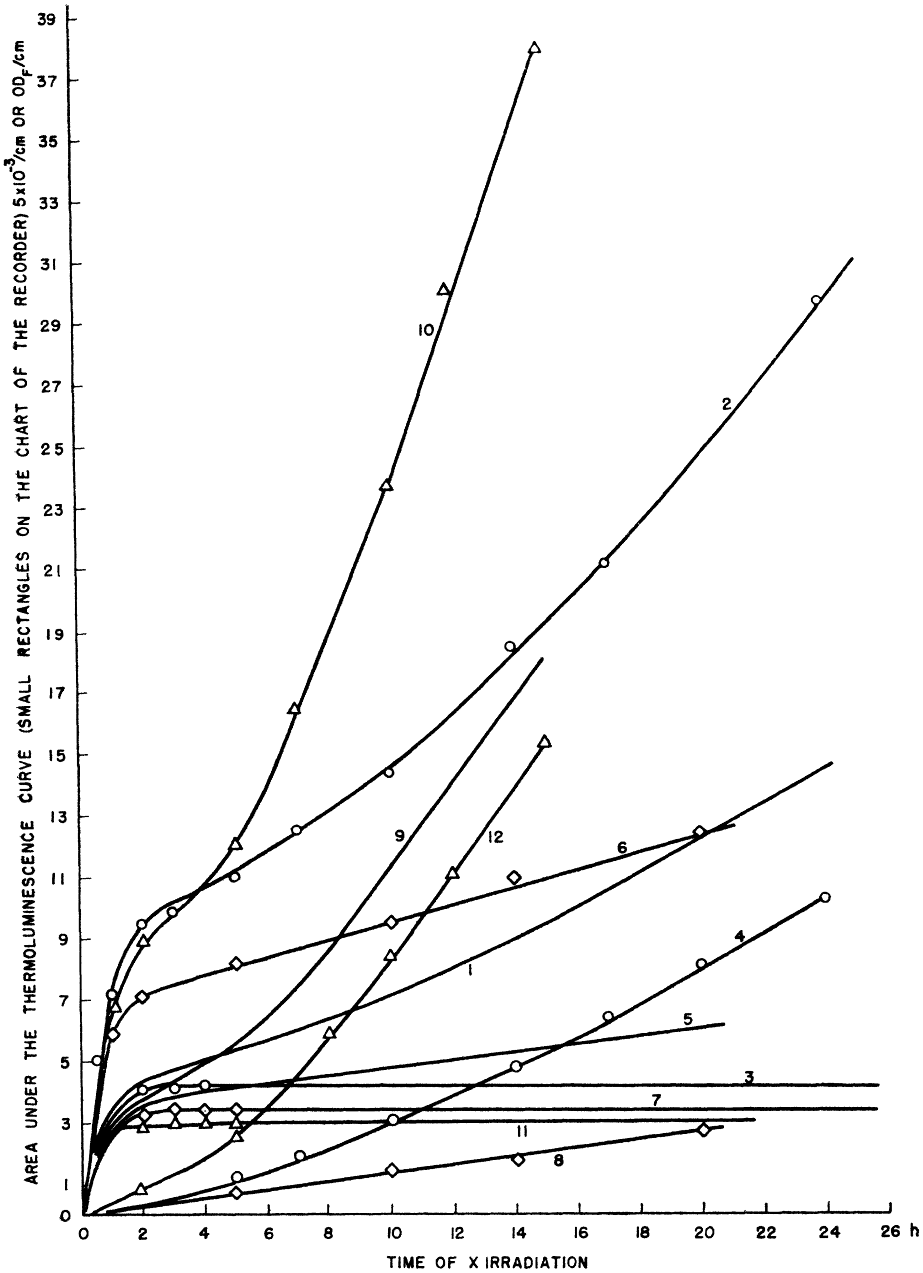

FIG. 3. Comparison of the growths of the thermoluminescence areas Δ_i of the fast first peak and Δ_g of the slow second peak with the numbers f_i and f_g of the F centers generated in the first and second stages, respectively. Curve 1 is the growth of OD$_F$/cm in crystal S6; curve 2 is obtained from curve 1 by multiplying each ordinate by 425. The points on curve 2 are the values of the observed areas $(\Delta_i+\Delta_g)$/cm; curves 3 and 4 are the growths of OD$_{F_i}$ and OD$_{F_g}$ derived from curve 1 using the method of Mitchell *et al.* The points on curves 3 and 4 are 1/425 times the values of the areas Δ_i of the fast peak and Δ_g of the slow peak, respectively. Curves 5, 6, 7, and 8 for crystal S8 and curves 9, 10, 11, and 12 for crystal S9 have the same significance as curves 1, 2, 3, and 4 for crystal S6. All values of the thermoluminescence areas correspond to "standard" sensitivity (see Sec. II). X irradiation was done at 35 kV, 10 mA. For details of heat treatment and filters used, see Table I.

(*b*) *Correlation of the First and Second Types of F Centers with the First and Second Thermoluminescence Peaks, Respectively*

The observation that the 135°C thermoluminescence peak saturates after a few hours of irradiation and that the 190°C peak keeps on increasing in area for larger durations of time is qualitatively similar to the rate of growth of the first stage and the second stage of F centers found by Mitchell *et al.*[6] and by Fröhlich[7] and suggests that these two peaks are related separately to the two types of F centers generated in the first and second stages of x irradiation, respectively. The F_i centers generated in the first stage bleach at lower temperatures giving rise to the 135°C thermoluminescence peak and the F_g centers generated in the second stage bleach at higher temperatures giving rise to the 190°C thermoluminescence peak.

The growth of concentration f_i of the F_i centers and f_g of F_g centers were found separately using the methods of Mitchell *et al.*[6] and Fröhlich.[7] Equation (3) was fitted with curve 1 of Fig. 3 and the values of the parameters a, b, c, n and n' were determined. The

TABLE I. The values of the parameters in Eqs. (3) and (4) describing the growth of the *F* centers and of the thermoluminescence *x* irradiation with Mo target operating at 35 kV, 10 mA.

Sample number	Treatment	*a* (OD cm^{-1} hr^{-1})	*b* (hr^{-1})	*c* (hr^{-1})	*n* (OD cm^{-1})	*n'* (OD cm^{-1})
S6	Quenched (1-mm Al filter)	0.55	1.5	0.16	4.2	1.35
S7	Quenched (1-mm Al filter)	0.69	1.6	0.16	5.2	1.65
S8	Slowly cooled (1-mm Al filter)	0.15	1.5	0.07	3.4	2.00
S9	Quenched (without filter)	1.40	2.5	0.27	3.0	1.57
S10	Quenched (without filter)	1.42	2.0	0.28	2.0	1.00

growths of f_i and f_g were then calculated separately with the help of Eqs. (1) and (2) and are shown by curves 3 and 4, respectively, in Fig. 3.

The separate areas Δ_i and Δ_g of the first and the second peaks, respectively, for different irradiation times, were determined by resolving the peaks of the curves in Fig. 2 in the following manner: The thermoluminescence equation (4) (see Sec. IIIB) was fitted with the rising part of the first peak and the values of E and s were determined. The falling part of the first peak was then found using Eq. (4) and the known values of E and s. The earlier part of the second peak was found by subtracting the ordinates of the first peak from the composite curve. In several cases the thermoluminescence experiments were performed with 5°C/min heating rate when the two peaks appeared separately. It was found that the two areas obtained separately from the experiments with slow heating rates were equal to the areas, respectively, of the two peaks obtained in the manner described above, provided that the crystals were identical and the irradiation times were the same.

The values of the areas Δ_i and Δ_g determined in this manner and multiplied by the ratio 1/425 of the initial OD_F to the corresponding total thermoluminescence areas, found earlier, are shown by the points on curves 3 and 4. It is seen that the points lie smoothly on the curves. This shows that the areas of the two thermoluminescence peaks are proportional to the concentrations of the two types of *F* centers separately. The constant of proportionality is a function only of the geometry and the sensitivity of the measuring equipment. The areas Δ_i and Δ_g are thus measures, respectively, of the concentrations f_i and f_g of the two types of *F* centers.

This result is of great practical value since it shows that thermoluminescence provides an experimental method of finding separately the concentrations of the two types of *F* centers. The values of the constant parameters in Eqs. (1) and (2) can now be determined more conveniently as these two equations can be separately fitted with the growth rates of two areas of the thermoluminescence peaks. On the other hand, the *F*-center growth has to be fitted with Eq. (3), and it is only after the values of constants have been determined in (3) that the two stages of *F* centers can be separated mathematically[6,7] with the help of Eqs. (1) and (2).

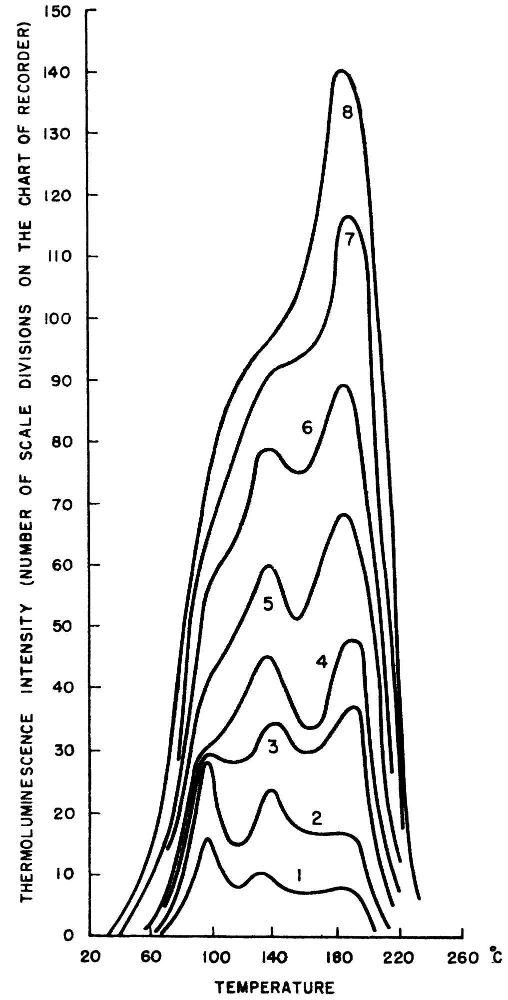

FIG. 4. Growths of the *F* band and thermoluminescence in BDH Analar KCl crystals B2, x irradiated without filter at 35 kV, 10 mA and heated at 40°C/min. Thickness of the samples used was 0.76 mm. All values of the thermoluminescence intensities correspond to "standard" sensitivity. The times of x irradiation and the corresponding value of OD_F/cm are: curve 1—5 min, 0.72; curve 2—10 min, 1.40; curve 3—15 min, 1.81; curve 4—25 min, 2.40; curve 5—40 min, 4.20; curve 6—60 min, 6.26; curve 7—90 min, 7.40; and curve 8—180 min, 9.45. The 95°C peak saturates in about 10 min and is due to the unknown background impurity in B crystals. For larger irradiation times, the 135°C peak also saturates.

The growth rates of OD_F and of Δ_i and Δ_g were also measured in samples cleaved from S7, S8, S9 and S10. The results for S8 and S9 are included in Fig. 3. The values of the constant parameters in Eqs. (1) and (2) for all samples are given in Table I. No filter was used while irradiating samples S9 and S10.

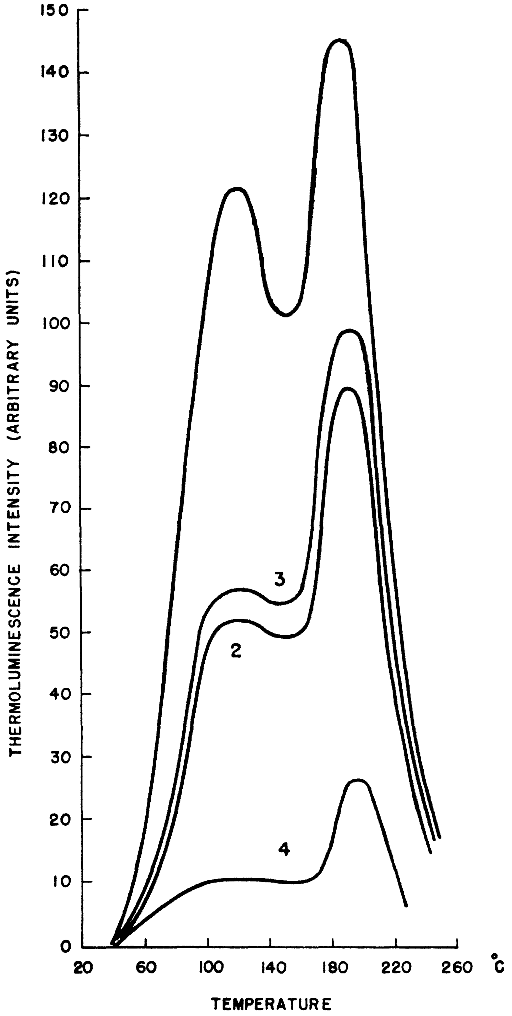

FIG. 5. Effect of optical bleaching with F and M lights on the thermoluminescence of crystal S11 x irradiated at 35 kV, 10 mA, without filter for 30 min and heated at 40°C/min. Curve 1—no optical bleaching; curve 2—after 6 min of bleaching with F light; curve 3—6-min bleaching with F light followed by 5 min of bleaching with M light; curve 4—after 10 min of bleaching with F light.

We observed points of inflection in curves 1, 5, and 9 for all specimens and the values of n' are, therefore, small as compared to the values of a/c, even in the quenched crystals.[6]

(c) *Crystals with Background Impurity*

The growth rates of OD_F and of thermoluminescence were also measured in slowly cooled, quenched and deformed BDH Analar crystals which contain about 30 ppm of divalent impurity. Typical results for crystal B2, quenched from 700°C, are shown in Fig. 4. It is seen that the 95°C impurity peak is fastest to grow and saturates in about 10 min. The behavior of 135 and 190°C peaks is not much affected. For larger irradiation times, the 190°C peak increases so much that the 95°C peak apparently disappears and the 135°C peak can be seen only as a shoulder. Equations (1) and (2) were fitted with the growth of Δ_i, the area of the 135°C peak and Δ_g, the area of the 190°C peak for the samples B. It was found that Eq. (3) could also be fitted to the growth of the total areas of the 95°C peak due to impurity and of the 135°C peak taken together, giving different values of the parameters b and n.

The typical values of the constant parameters a, b, c, n and n' for a few S crystals are given in Table I. From these and from the values for B samples, not included in the table, the following conclusions can be drawn:

(i) Values of c are an order of magnitude smaller than the values of b, in agreement with the results of Mitchell *et al.*[6] The values of b are less sensitive to heat treatment but are strongly dependent on the background impurity.

(ii) The parameter a is found to be strongly dependent on the background impurity and on the heat treatment. The values for the quenched crystals are larger than for the slowly cooled crystals. In B crystals, a is smaller than in S crystals indicating that the generation of second stage F centers is suppressed by the background impurity.

(iii) It is not possible to establish any correlation between the values of n and n' and the heat treatment. However, the value of n for the B crystals containing background divalent impurity is certainly large as compared to the values for the highly pure S crystals.

(iv) The results of the preliminary experiments with different x-ray intensities, with plastically deformed crystals and with highly pure crystals doped with Ca are given later in this paper. The results of these experiments (not shown in Table I) show that a varies approximately as I^2 in agreement with the results of earlier workers.[6,22] The values of the constants b and c also decreased with the decrease in x-ray intensity. The decrease in the values of a, b and c for the quenched crystals when x irradiation is done through an Al filter is due to the reduction in the intensity of x irradiation by the filter.

It is not possible to compare the values of the parameters a, b and c in Table I with those obtained by earlier workers[6,7] since the values of a, b and c are functions of the intensity of x irradiation and sensitive to the background impurity. The crystals used by the earlier workers[6,7,22] contained unknown amounts of background impurity[23–25] and the absolute value of the intensity of x irradiation is not known in our experiments. However, the relative magnitude of the param-

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[22] E. Abramson and M. E. Caspari, Phys. Rev. **129**, 536 (1963).

[23] A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.

[24] S. Anderson, J. S. Wiley, and L. J. Hendricks, J. Chem. Phys. **32**, 949 (1960).

[25] C. T. Butler, W. A. Sibley, and E. Sonder, J. Chem. Phys. **39**, 242 (1963).

eters and their dependence on the intensity of x irradiation are in general agreement with the results obtained by Mitchell *et al.*[6] and by Abramson and Caspari.[22]

Mitchell *et al.*[6] have mentioned that Eqs. (1), (2) and (3) are based on the assumption that the concentration of M and other aggregate color centers is small as compared to the F concentration. After x irradiation, the maximum value of $\mathrm{OD}_M/\mathrm{OD}_F$ obtained in our experiment was 0.06; hence the concentration of M centers was small initially. It will be shown in the next section that the concentration of M centers remained negligibly small during the thermoluminescence process also.

C. Influence of Optical and Thermal Bleaching on F-Center Density and Thermoluminescence

(*a*) *Optical Bleaching*

The effect of bleaching the color with F and M lights on the thermoluminescence in 4 samples cleaved from crystal S11 and x irradiated for 2 h (without aluminum filter) is shown in Fig. 5. Curve 1 is for sample 1, in which no optical bleaching was done; curve 2 is for sample 2 in which the color was bleached with F light for 6 min; curve 3 is for sample 3 in which the color was bleached for 6 min with F light and then for 5 minutes with M light; and curve 4 is for sample 4 in which the color was bleached with F light for 10 min. The values of OD at the peak of F, M and other F-aggregate bands were measured at one-minute intervals during the bleaching with F or M light. The effect of F-light bleaching on the relative concentrations of different color centers was qualitatively the same as that obtained by earlier workers.[5,26] After x irradiation, the ratio $\mathrm{OD}_M/\mathrm{OD}_F$ was 0.058 in sample 1 and 0.18 and 0.83 in samples 2 and 4 after 6 and 10 min of F light bleaching, respectively. The corresponding values of $\mathrm{OD}_F/\mathrm{cm}$ were 6.03, 3.40 and 0.92. The values of OD_F and $\mathrm{OD}_M/\mathrm{OD}_F$ in the third sample were 6.03 and 0.058 after x irradiation, 3.40 and 0.18 after 6 min of bleaching with F light and 3.40 and almost 0 after further bleaching with M light for 5 min. Curves 2 and 4 of Fig. 5 show that bleaching the color with F light suppresses both the thermoluminescence peaks. This result is in qualitative agreement with the observation of Halperin *et al.*[27] that all the thermoluminescence peaks are suppressed by bleaching the color with F light. The more interesting observation is, however, that the fractional decrease in the areas of both peaks is equal to the fractional decrease of the F centers for both curve 2 and curve 4. This is demonstrated more clearly in Fig. 8 by plotting the areas under the thermoluminescence curves versus OD_F for another crystal S12 before and after partial optical bleaching with F light. It is seen that all points lie, within experimental error, on the straight line passing through the origin and having a slope 425.

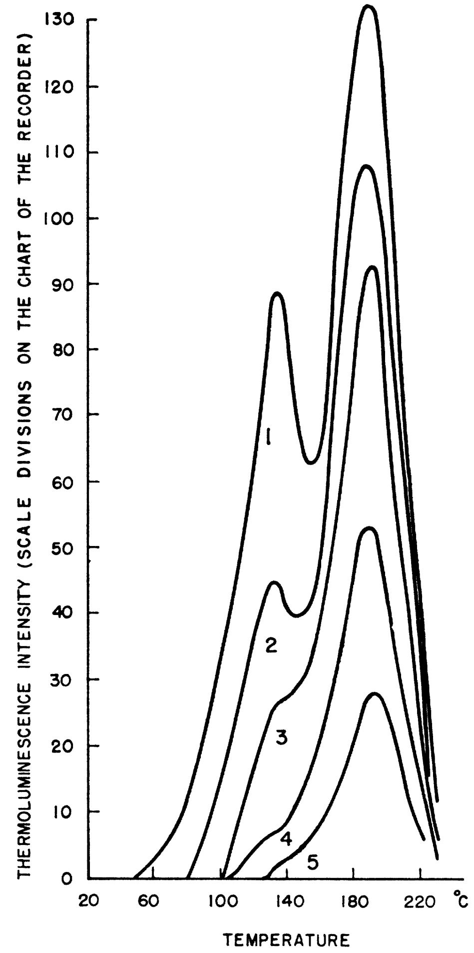

FIG. 6. Effect of partial thermal bleaching on the F centers and thermoluminescence of crystals S13, x irradiated at 35 kV, 10 mA for 2 h without filter. The thickness of the crystals used was 0.45 mm. The thermal treatment given to these crystals before making the thermoluminescence measurements was as follows: curve 1—no thermal bleaching; curve 2—heated at the rate 40°C/min to 125°C, kept at this temperature for $1\frac{1}{2}$ min and cooled to room temperature; curves 3, 4, and 5—crystals were similarly heated to and kept at 140°C for $1\frac{1}{2}$ min, 160°C for $1\frac{1}{2}$ min, and 160°C for $2\frac{1}{2}$ min, respectively, and then cooled to room temperature.

We now discuss thermoluminescence curve 3 of Fig. 5 obtained after bleaching with F light and then with M light. Since the F-band absorption overlaps with the excited-state absorption of the M center and since $\mathrm{OD}_M/\mathrm{OD}_F$ was ~0.18 after 6-min bleaching with F light, the observed value of OD_F was corrected by using the following equation[28]:

$$\mathrm{OD}_F(\text{corrected}) = \mathrm{OD}_F(\text{observed}) - 0.65\ \mathrm{OD}_M. \quad (6)$$

Equation (6) shows that a substantial decrease in the M band should be accompanied by a decrease in

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

[27] A. Halperin, A. A. Braner, and E. Alexander, Phys. Rev. **108**, 928 (1957).

[28] S. Schnatterly and W. D. Compton, Phys. Rev. **135**, A227 (1964).

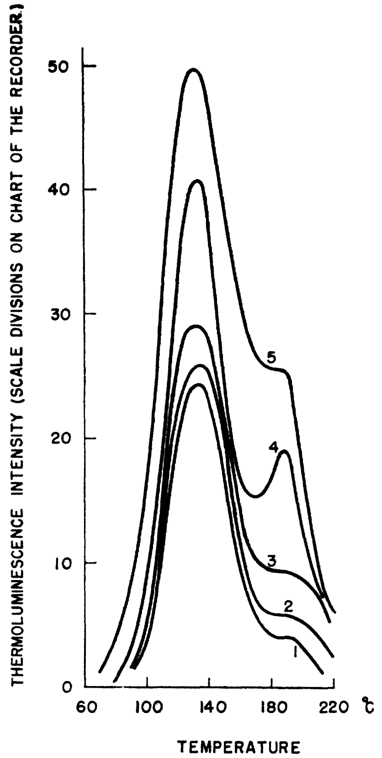

FIG. 7. Effect of repeated thermal bleaching and x irradiation with 1-mm Al filter at 35 kV, 10 mA on the *F* centers and thermoluminescence in crystals S6. All values of thermoluminescence intensities correspond to "standard" sensitivity. Curve 1—the crystal irradiated for 1 h; curve 2—after measuring the thermoluminescence given by curve 1, the same crystal was again irradiated for 1 hr; curve 3—after measuring thermoluminescence given by curve 2, the same crystal irradiated again for 1 h; curve 4—after measuring thermoluminescence given by curve 3, the same crystal again irradiated for 2 h; curve 5—another crystal from the sample S6, irradiated for 5 h.

the *F* band. The fact that OD_F remained unaltered in sample 3 by a subsequent bleaching with *M* light suggests an increase in the *F* band compensated by a decrease in the absorption of the excited *M* centers. This effective increase in the *F*-center concentration on bleaching the *M* band is found to be about 10% by using Eq. (6). This is in good agreement with the 8% increase of the area under curve 3 as compared to that under curve 2.

These results suggest that the area under the thermoluminescence curves is a unique function of the *F*-center density initially present in the crystal and that the thermoluminescence results are not affected by the presence of *M* centers. Further, it appears that by optically bleaching the *M* band by *M* light, at least some of the *M* centers are converted into *F* centers. The increase in the area of both the thermoluminescence peaks indicates that both types of *F* centers were involved in the formation of *M* centers, in agreement with a recent result of Thommen.[8] The relative concentrations of *R* and *N* centers remained negligible in all these experiments.

(*b*) *Thermal Bleaching*

The effect of heating on the relative concentration of different color centers was investigated. It was found that if utmost care is taken to avoid exposure of the crystals to stray light, the *M* band decreased monotomically on heating. However, if the crystal received some exposure to stray light, the *M* band increased up to about 90°C and then decreased with further rise in temperature. Since utmost care was taken to avoid exposure of the crystals to light and since the initial value of $\mathrm{OD}_M/\mathrm{OD}_F$ never exceeded 0.06, *M*-center concentration remained small in all crystals except in those cases where *F* bleaching was used.

The effect of partial thermal bleaching on the *F*-center density and on the thermoluminescence is shown in Fig. 6. Five slices, approximately 0.45 mm thick, were cleaved from the crystal S13 and each x irradiated for 2 h (without filter). Curve 1 is for the sample without any bleaching; curve 2 is for the sample partially bleached by heating at the rate 40°C/min to 125°C, kept at this temperature for $1\frac{1}{2}$ min and cooled to room temperature before thermoluminescence was measured. Curves 3, 4, and 5 are for the samples similarly heated and kept at 140°C for $1\frac{1}{2}$ min, at 160°C for $1\frac{1}{2}$ min, and at 160°C for $2\frac{1}{2}$ min, respectively. The values of OD_F/cm after partial thermal bleaching and before thermoluminescence measurements were 7.30 (no bleaching), 5.22, 3.60, 2.34, and 1.58, corresponding to the curves 1, 2, 3, 4, and 5, respectively. In all cases the areas of the thermoluminescence curves decrease in proportion to the decrease in *F* centers by partial thermal bleaching. Similar results have been obtained by Morehead and Daniels[21] for γ-irradiated LiF.

Another experiment was performed in which a sample cleaved from crystal S6 was x irradiated for 1h. Its OD_F/cm was 2.00, and its thermoluminescence is shown by curve 1 of Fig. 7. After the measurement of thermoluminescence, OD_F/cm became zero. The same sample was again irradiated for 1h, giving OD_F/cm as 2.44 and thermoluminescence by curve 2. This process of complete thermal bleaching and x irradiation was repeated two more times and the x irradiation was now done for 1 and 2h, respectively. The OD_F/cm values obtained were 2.96 and 4.00. The thermoluminescence results are shown by curves 3 and 4, respectively. Curve 5 is for another virgin sample from crystal S6 x irradiated for 5 h.

A comparison of the various curves in Fig. 7 shows interesting features. The area under the 190°C peak increases very fast from curves 1 to 4. Curves 4 and 5 show that the area of the 190°C peak in the crystal corresponding to curve 4 is comparable and slightly less than the area of curve 5, even though the color centers generated in crystal 4 were due to the final 2h of irradiation only. This result indicates that the vacancies of the n_0 type created during the previous irradiations did not anneal out completely in the thermal bleaching. A more detailed analysis of the growth rate of the two peaks in these crystals shows that the observation, that the second peak of curve 4 is slightly less than the second peak of curve 5, is due to the fact that during the heating process some of the vacancies of the n_g type dispersed[29] in the crystal, increasing the concentration of n_i type of the vacancies, in agreement with the results obtained by Fröhlich.[7]

The values of the area under the thermoluminescence curves as functions of the corresponding values of OD_F/cm (which are proportional to the concentrations of the *F* centers present in the crystal prior to thermoluminescence measurements) are plotted in Fig. 8 for a variety of crystals. It is seen that in all experiments the areas are proportional to the initial *F*-center density, irrespective of the type of sample used, the heat treatment given or the amount by which the color is partially bleached optically or thermally.

D. The Two Types of *F* Centers in Highly Pure Crystals

For fitting Eq. (4) or (5) with the thermoluminescence results, the two thermoluminescence peaks were resolved by using a slow rate of heating. Alternatively, a relatively pure first peak was obtained by using small times of x irradiation and high recorder sensitivity, and a relatively pure second peak was obtained by using large irradiation times and removing the first peak by partial thermal bleaching. Equation (4), based on first-order process (neglecting the retrapping), could be fitted rather accurately with $E_1 = 1.05 \pm 0.05$ eV and $s_1 = 4.5 \times 10^{11}$ sec^{-1} with the first peak, and with $E_2 = 1.15 \pm 0.05$ eV and $s_2 = 5 \times 10^{11}$ sec^{-1} with the second peak, respectively. The comparison of the theoretical curve calculated from Eq. (4) with these values of E_1, s_1, E_2 and s_2 with the experimental results is shown in Fig. 9. The experimental results are for a sample cleaved from crystal S1 irradiated for 7 min without filter and heated at 40°C/min. The thermoluminescence was measured with a high recorder sensitivity. It is seen that the agreement between the theory, assuming no retrapping, and the experimental results is good. The values of E and s are evaluated for several experimental curves obtained with different times of x irradiation. The values of E_1 and E_2 varied within ± 0.05 eV in different experiments but the value of $(E_2 - E_1)$ was always ~ 0.10 eV.

The methods described by Garlick and Gibson[15] to investigate the importance of retrapping was discussed earlier. In the first-order process described by Eq. (4) the peak position and shape of the curve are independent of the value of n_0/N (N is the concentration of both the anion vacancies and F centers and n_0 is the concentration of F centers) whereas both the position and the shape depend on the value of n_0/N if the process is second order, given by Eq. (5). A sample from crystal

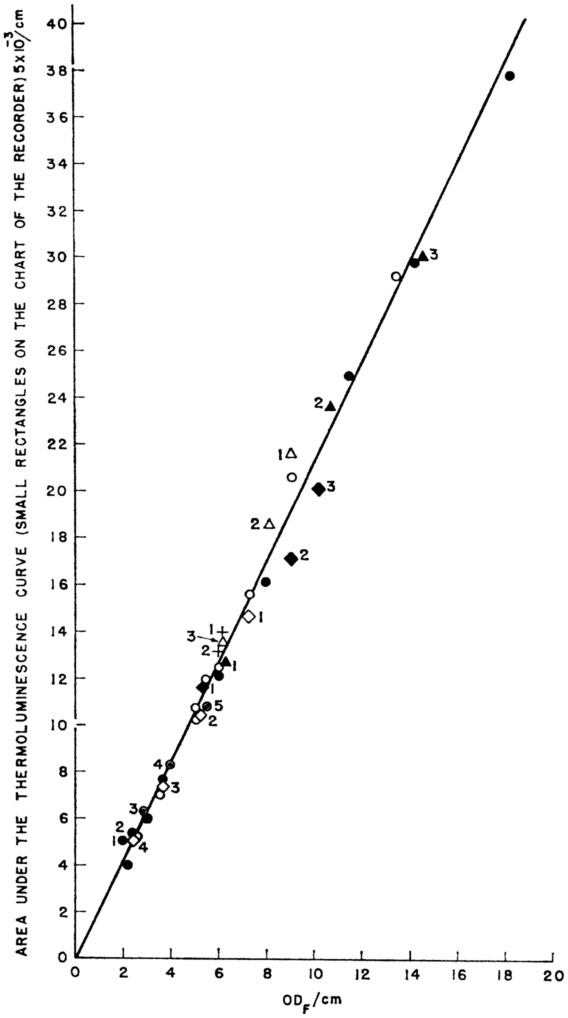

FIG. 8. The plot of areas under the thermoluminescence curves versus the initial values of corresponding OD_F for a variety of crystals x irradiated at 35 kV, 10 mA, unless otherwise stated. ○ and ●—crystals S6 and S9 each x irradiated for several different values of times. △—optically bleached crystals S12, x irradiated for 30 min; the numbers 1, 2, and 3 indicate no bleaching, 6-min bleaching with *F* light, and 14-min bleaching with *F* light, respectively. ◇—thermally bleached crystals S13, x irradiated for 2 h without filter; the numbers 1, 2, 3, and 4 indicate no thermal bleaching, heated at 40°C/min to 125°C and kept at this temperature for 1½ min, heated at 40°C/min to 140°C and kept at this temperature for 1½ min, heated at 40°C/min to 160°C and kept at this temperature for 1½ min, respectively. ⊙—crystals S6 with repeated thermal bleaching and x irradiated with filter; the numbers 1 to 5 indicate treatment corresponding to curves 1 to 5 of Fig. 7, respectively. ▲—calcium-doped crystals S16, S17, and S18 each x irradiated for 45 min with Al filter; ▲1—Crystal S16 containing 50 ppm of Ca; ▲2—crystal S17 containing 200 ppm of Ca; ▲3—S18 crystal containing 500 ppm of Ca. +—crystal S14 irradiated with x rays of different intensities; the numbers 1 and 2 indicate irradiation with 2-mA x rays for 45 min and x irradiation with 10-mA x rays for 12 min, respectively. ◆—Plastically deformed crystals S19; the numbers 1 to 3 indicate no deformation, 8% deformation, and 13% deformation, respectively.

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[29] A part of the increase of the two peaks may be due to enhanced colorability because of the diffusion of oxygen from air into the crystal on heating. See W. A. Sibley, Phys. Rev. **133**, A1176 (1964).

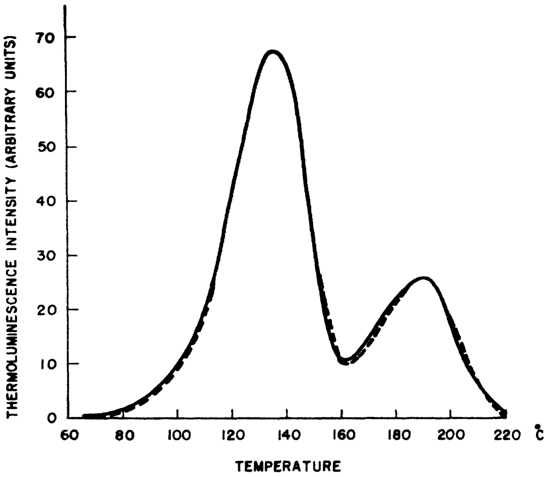

FIG. 9. Comparison of the experimental thermoluminescence curve with theoretical equation (4) valid when retrapping is negligible. Dotted curve—experimental; continuous curve—theoretical, calculated from Eq. (4) with $s_1=4.5\times10^{11}$/sec, $E_1=1.05$ eV for the first peak, and $s_2=4.9\times10^{11}$/sec and $E_2=1.20$ eV for the second peak, respectively.

S1 was irradiated for 3 h to create a large number N of n_g type of anion vacancies and was heated at 280°C to bleach it completely. Since the density N of anion vacancies generated during the initial 3 h of x irradiation decreases only slightly on thermal bleaching (Sec. IV C), the value of n_0/N will depend on subsequent x irradiation times. The crystal was then irradiated for 2 min and its thermoluminescence was measured. It was then irradiated for 5 min and the thermoluminescence was again measured. The experiment was repeated with the same crystal three more times, the irradiation times being 15, 25, and 45 min, respectively. It was found that though the values of n_0/N varied by a factor of about 15 in these experiments, the peak position remained constant within experimental error. The plot of thermoluminescence intensities L at any fixed temperature taken from these five experiments, as a function of the corresponding area Δ_i or Δ_g was found to be a straight line, indicating that the shape of both peaks is independent of the value n_0/N and retrapping is negligible[15] in the thermoluminescence process in KCl crystals. The analysis of the symmetry and shape of the peaks by the methods discussed by Halperin and Braner[18] also show that the thermoluminescence in alkali halides corresponds to first-order process, in agreement with the results obtained by Halperin *et al.*[18] and by Lushchik.[19]

Thus the thermal bleaching of F band in pure KCl crystals x irradiated at room temperature takes place in two stages, and each stage has a separate well-defined thermoluminescence peak. The numbers of F centers generated in the first and second stages are equal separately to the number of F centers annihilated during the first and second thermoluminescence peaks, respectively. The reason that the F centers generated in the slow second-stage bleach at higher temperature is not the dominant retrapping as suggested by earlier authors (see, for example, Ref. 6) but because of the higher thermal-activation energy of the second-stage F centers.

In addition to the growth of F-center experiments[6,7] and growth of thermoluminescence experiments described here, the other experiments which indicate that the F centers are of different types are (1) thermal bleaching[30] [also work of E. E. Schneider and coworkers[31]], (2) photoconductivity,[2] (3) expansion on x irradiation,[4] (4) growth of M centers,[8] (5) EPR studies of F centers[9] and (6) thermal-conductivity measurements of colored crystals at low temperatures.[10] The present work shows that the close proximity of other F centers or of defects with an F center changes its thermal ionization energy, leaving the optical-absorption energy practically unaltered. We tentatively suggest the following possible mechanisms for this difference in the thermal-ionization energies of the two types of F centers which have the same optical-absorption band. (1) Since the radius of the first excited state is much smaller than the radii of the higher excited states, the energy of transition from the ground state to the first excited state may remain unaltered, but the energy of excitation to higher states may be modified due to the close proximity of the F centers or defects. (2) It is well known[32] that the optical-excitation energy is larger than the thermal-excitation energy since in thermal excitation a large part of the energy is regained by readjustment of surrounding ions. This readjustment of the ions and the consequent gain in energy may be modified due to close proximity of other F centers or defects.

If the lifetime of the electrons in the conduction band is not sufficiently large, the ionized and un-ionized F centers will not be in equilibrium. In this case the number of F centers ionized per second will be mainly determined by the largest energy of transition between any two consecutive levels and not by the total energy of ionization. The large thermal ionization energy (1.95 eV) for the F centers in additively colored KCl crystals obtained in Pohl's laboratory[33] may indicate that the electrons in the conduction band have a large life time in additively colored crystals than in the irradiated crystals. Further work is necessary to clarify these points.

In passing we observe that since all the F centers are found to have the same optical absorption, the shift in the peak position or the change in half-width of the F band observed by earlier workers[34,35] must be due to

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[30] A. A. Braner and A. Halperin, Phys. Rev. **108**, 932 (1957).

[31] Discussed in Ref. 1, p. 69.

[32] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, England, 1940), p. 160.

[33] Reference 31, p. 143.

[34] S. Petroff, Z. Physik **127**, 443 (1950).

[35] J. D. Konitzer and J. J. Markham, Phys. Rev. **107**, 685 (1957).

the absorption[36] to the higher excited states of *M* and other aggregate centers formed on bleaching the *F* band optically.

E. Influence of X-Ray Intensity, Calcium Impurity and Deformation on the Thermoluminescence and the *F*-Center Density

(*a*) *Influence of the X-Ray Intensity*

Curve 1 in Fig. 10 shows the thermoluminescence peaks for samples S14 x irradiated for 45 min at 35 kV and 2 mA. The value of OD_F/cm was 6.0. Another sample from the same crystal S14 developed OD/cm $=5.8$ in 12 min when irradiated with the x-ray machine working at 10 mA; the thermoluminescence results for this sample are shown by curve 2 in Fig. 10. It is seen from the figure that the total area under both the peaks is nearly the same in each case but in the case of low-intensity irradiation the first peak is enhanced at the cost of the second peak. The areas Δ under the curves 1 and 2 of Fig. 10 are plotted versus the corresponding OD_F/cm in Fig. 8.

Thermoluminescence was measured in samples S15 (not shown in the figure), x irradiated with 5, 10, 15, and 20 mA for times from 5 min to 25 h for each intensity. No filter was used in these experiments. The values of a and other constant parameters in Eqs. (1) and (2) were determined for intensity of x irradiation corresponding to plate currents of 5, 10, 15, and 20 mA. The values of a varied approximately as I^2, in agreement with the observation of Mitchell *et al.*[6] and of Abramson and Caspari.[22]

(*b*) *Influence of the Calcium Impurity*

Thermoluminescence results for crystals containing 50, 200, and 500 ppm of calcium and x irradiated for 45 min with Al filter are shown by curves 1, 2, and 3 in Fig. 11. Curves for other concentrations of the impurity are not shown for the sake of clarity of the diagram. The following conclusions can be drawn from these curves:

(1) The area of the 85°C peak, characteristic of the calcium impurity, increases with the concentration of the calcium impurity for a given time of x irradiation. The color corresponding to this peak is much less stable than the first-stage *F* centers in S crystals. It is not clear whether this peak is due to the pure Z_1 centers obtained in Ca-coped x irradiated alkali halide crystals.[37]

Since the growth rate of the thermoluminescence areas of the 135°C peak and the 85°C calcium peak taken together can be fitted with Eq. (3) and since Z_1 band overlaps with *F* band, experiments such as those of Fröhlich[7] cannot distinguish between the first-stage *F* centers and the centers due to the Ca impurity giving the thermoluminescence peak at 85°C.

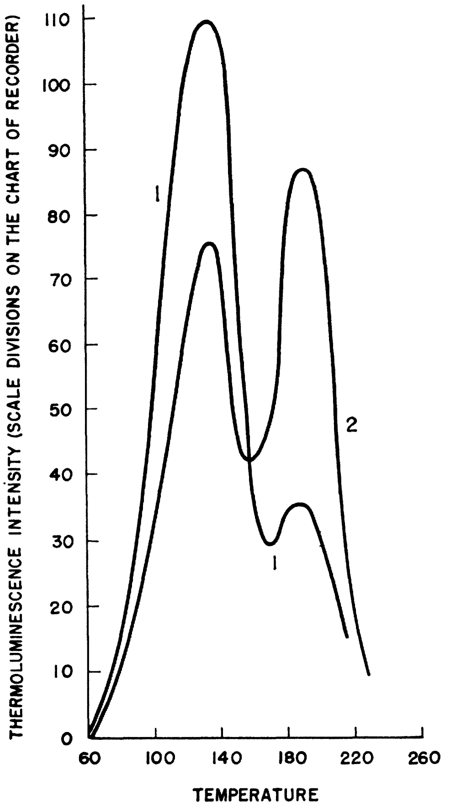

FIG. 10. Effect of x-ray intensity on the *F*-center density and the thermoluminescence of highly pure KCl samples cleaved from crystal S14. Curve 1—x irradiated at 2 mA for 45 min and curve 2—x irradiated at 10 mA for 12 min. After x irradiation OD_F/cm was the same in both samples. Total area under both the peaks (at 135 and 190°C), is the same under both curves 1 and 2. However, x irradiation at 2 mA enhances the 135°C peak at the cost of 190°C peak.

(2) The area of the 135°C peak due to the first-stage coloration in pure crystals also increases with the increasing concentration of calcium impurity.

(3) The 190°C peak due to the second-stage coloration is considerably suppressed by calcium impurity. It can be seen from curve 2 of Fig. 10 that second peak is larger than the first peak after 12 min of x irradiation of the highly pure crystal. Curves 1 and 2 of Fig. 11 show that in spite of larger x irradiation of 45 min, it becomes very weak in the crystals containing 50 and 200 ppm of the impurity and disappears completely in curve 3 for the crystal S18 containing 500 ppm of Ca. Curve 4 in Fig. 11 for the sample S18 x irradiated for $5\frac{1}{2}$ hours shows that the 190°C peak just appears after $5\frac{1}{2}$ hours of irradiation in the heavily doped crystal.

It appears that the easy formation[11] of *F* centers and the rapid thermal bleaching[20] of the centers in calcium-doped crystals is due to the fact that the formation of the "hard" second-stage *F* centers is considerably

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[36] W. E. Bron, Phys. Rev. **125**, 509 (1962).

[37] J. E. Caffyn and B. K. Ridley, Proc. Phys. Soc. **77**, 153 (1961).

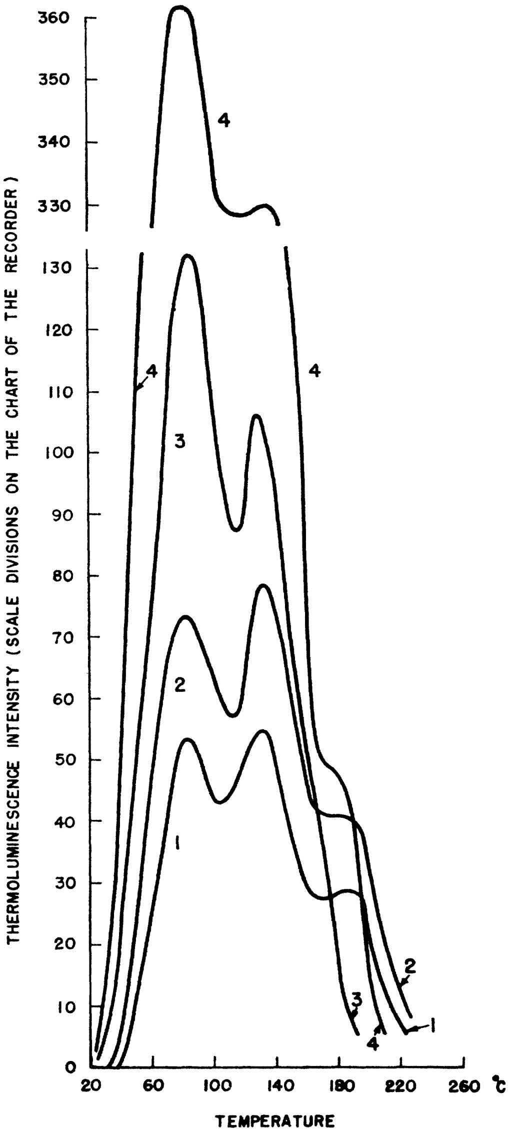

FIG. 11. Effect of the Ca impurity on the F-center density and the thermoluminescence in crystals S16, S17, and S18, x irradiated at 35 kV, 10 mA with Al filter. All thermoluminescence intensities correspond to "standard" sensitivity. Curve 1—crystal S16 containing 50 ppm of Ca, x irradiated for 45 min; Curve 2—crystal S17 containing 200 ppm of Ca, x irradiated for 45 min; Curve 3—crystal S18 containing 500 ppm of Ca, x irradiated for 45 min; Curve 4—crystal S18, x irradiated for 5¼ h. For 45-min x irradiation, the 190°C peak is weak in crystals S16 and S17 and completely disappears in 500-ppm Ca-doped crystal S18. This 190°C peak appears in heavily doped crystal S18 after 5¼ h of x irradiation.

suppressed and the number of soft first-stage F centers is enhanced due to the calcium impurity. The result that the calcium impurity suppresses the second-stage coloration is in agreement with the recent observation of Sibley, Sonder and Butler.[38]

(4) The proportionality $\Delta/\mathrm{OD}_F=425$ found earlier for pure crystals, holds for the doped crystals also. This is demonstrated by plotting OD_F and Δ values in Fig. 8 for the doped crystals also.

(*c*) *Influence of Plastic Deformation*

The influence of plastic deformation on thermoluminescence in crystals S19 is shown in Fig. 12. Curve 1 is for an undeformed crystal, curves 2 and 3 are for crystals deformed plastically by 8 and 13%, respectively. The following conclusions can be drawn from these and other results not quoted in this figure:

(1) Plastic deformation introduces a new peak at 270°C. The growths of 135 and 190°C peaks are suppressed by plastic deformation. A peak at 250°C (at a lower heating rate), sensitive to plastic deformation has also been observed by Ueta, Sugimoto and Nagasawa.[39]

(2) The total area Δ under the thermoluminescence curve is 425 times the OD_F for plastically deformed crystals also. This is illustrated by plotting the values of Δ under curves of Fig. 12 versus corresponding values of OD_F in Fig. 8. This indicates that the trapped electron centers responsible for the 270°C peak have absorption under the F band.

(3) More detailed investigations show that the value of a determined from the observed growth of the 190°C peak is smaller in plastically deformed crystals in agreement with the conclusion of Mitchell *et al.*[6] The growth rate of the 270°C peak is somewhat similar to that of the 135°C peak and Eq. (1) can be fitted to the growth rate of the area of these two peaks taken together. It seems that the enhancement of colorability in the deformed crystals is due to vacancies produced during the deformation itself rather than during the irradiation after the deformation. This is in agreement with the findings of Ueta and Känzig[40] and more recent results of Sibley.[29]

Thermoluminescence in crystals quenched to liquid-air temperature also showed the 270°C peak and was perhaps due to the plastic flow which might have occurred due to this very rapid cooling.

The results obtained with the crystals deformed after irradiation (not shown in the figure) show that the second peak is reduced and the 270°C peak appears in these crystals. This indicates that on deformation some of the second-state F centers are converted into the F centers giving rise to the 270°C peak. It is possible that because of the heat generated or other unknown factors the second-stage F centers bleach and the electrons liberated from the F centers are trapped in the new vacancies generated during the deformation process, to form the centers giving rise to the 270°C peak and optical absorption under the F band.

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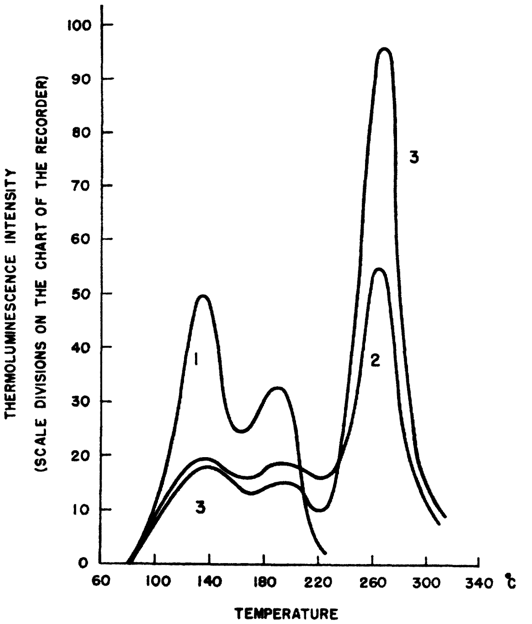

FIG. 12. Influence of plastic deformation on the thermoluminescence and *F*-center density in crystals S19, x irradiated at 35 kV, 10 mA without filter for 15 min. Curve 1—no deformation; curve 2—8% deformation and curve 3—13% deformation. In addition to the peaks at 135 and 190°C, a new thermoluminescence peak is observed at 270°C in deformed crystals. The height of this peak depends upon the amount of deformation. Growths of the 135 and 190°C peaks are suppressed by plastic deformation. All thermoluminescence intensities correspond to "standard" sensitivity.

There has been considerable interest in recent years on the mechanism of formation of color centers,[6,11,22] the enhancement in colorability on deformation,[30] on doping with calcium,[7,11] and on the effect of x-ray intensity[6,22] on color-center growth. Since the results of this section show that the effect of deformation and calcium impurity is to introduce centers which have absorption under the *F* band but give separate well-defined thermoluminescence peaks, the results indicate that the systematic thermoluminescence investigations with doped and deformed crystals and with different intensities of x irradiation may throw some light on these obscure mechanisms. The results of this section are only of preliminary experiments and a more detailed report will be published later.

Finally, the results described in this paper indicate that the number, height and positions of the observed thermoluminescence peaks are very sensitive to the background or deliberately introduced impurity, thermal and mechanical treatment, and time and intensity of x irradiation. For example the 95°C peak found in B crystals is absent in S crystals, the 135°C peak apparently disappears for large times of irradiations and the 190°C peak is suppressed by Ca impurity, by low-intensity x irradiation, and by plastic deformation. Plastic deformation introduces a new peak at 270°C. It seems that the second-stage coloration giving rise to the thermoluminescence peak at 190°C is the intrinsic property of good KCl crystals and any perturbation such as deformation or impurity suppresses this coloration.

ACKNOWLEDGMENTS

The authors are deeply indebted to Professor F. Seitz for advice and for the interest he took in this work. The benefit of discussions with Professor H. Curien is also gratefully acknowledged.