

FORMATION AND OPTICAL BLEACHING OF COLOR CENTERS  
IN X-RAYED POTASSIUM CHLORIDE CRYSTALS

by

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A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of  
the requirements for the  
degree of

DOCTOR OF PHILOSOPHY

June 1961

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Date thesis is presented November 28, 1960 -----

Typed by Lilah N. Potter

## ACKNOWLEDGMENTS

In completion of this work, the author wishes to express his indebtedness to Dr. Allen B. Scott for many valuable discussions and numerous suggestions, and to the National Science Foundation for material support.

The author also wishes to thank Dr. M. B. Williams for extensive use of the x-ray unit, Dr. P. M. Gruzensky for furnishing some of the melt-grown crystals, and Mr. R. E. Woodley for his friendly cooperation and useful discussion.

The author is indebted to the Fulbright Commission for a travel grant and to the Institute of International Education for encouragement throughout this work.

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## FORMATION AND OPTICAL BLEACHING OF COLOR CENTERS IN X-RAYED POTASSIUM CHLORIDE CRYSTALS

### I. GENERAL INTRODUCTION

Potassium chloride crystals are transparent to light over a wide range of wavelengths. Light in the infrared region is absorbed when the wavelength of the light becomes so long that vibration of the ions is excited by the incident light. For crystals a few millimeters thick, the absorption is clearly apparent at about  $20\mu$  (41, p. 187). The electronic fundamental absorption starts in the ultraviolet at about  $180\text{ m}\mu$  (27, p. 816). The crystal is transparent to light having wavelengths between these limits. If a potassium chloride crystal is irradiated with ionizing radiation, such as x-rays,  $\gamma$ -rays, cathode rays, or alpha particles, the crystal takes on a violet color. Several other absorption bands appear in its spectrum, which depends on the temperature at which the irradiation is performed. As a result of room temperature irradiation, the so-called "F-band" appears at  $560\text{ m}\mu$  and is responsible for the violet coloration.  $V_2$  and  $V_3$  bands also appear at  $230\text{ m}\mu$  and  $215\text{ m}\mu$ , respectively (4, p. 1564; 8, p. 168; and 9, p. 321). When the colored crystal is exposed to light absorbed by the F band (F-light) at room temperature, the F band decreases. At the same time, the V bands decrease

in the lightly x-rayed crystals (60, p. 34-36 and p. 68-71), whereas in the heavily x-rayed crystals a number of new absorption bands which are called  $R_1$ ,  $R_2$ , M, and N bands develop on the long wavelength side of the F band (2, p. 1853-1863; 38, p. 622).

de Boer (6, p. 301-309) proposed that an F center is an electron trapped at a negative-ion vacancy. This model was further developed by Gurney and Mott (20, p. 506-511), and is generally accepted in accordance with other experimental evidence (30, p. 493-494). The models of the V centers are not well established but are considered as a certain number of holes trapped at a positive-ion vacancy or at a vacancy cluster (60, p. 57).

A real crystal is in some respects imperfect, that is, there exist some deviations from a perfect regular lattice or structure, which are considered to furnish the vacancies necessary to form color centers upon irradiation by ionizing radiation. The simplest type of lattice imperfection in potassium chloride or other alkali halide crystals is the so-called Schottky defect (44, p. 26-29), which is a vacant lattice site, or in other words, a lattice site from which the corresponding ion is missing. A certain number of the Schottky defects always exist in a real crystal in thermodynamic equilibrium above 0°K. In addition to the Schottky

defects present in thermodynamic equilibrium, additional single vacancies, pairs of vacancies, or larger aggregates of vacancies, and dislocations are introduced into the crystal during crystal growth, by quenching from high temperature, by mechanical strain or through incorporation of impurities.

The mechanism of the formation and the optical bleaching of color centers is considered to be as follows: Negative-ion vacancies introduce new localized energy levels just below the conduction band. When the crystal is irradiated with ionizing radiation, some electrons are excited into the conduction band, leaving behind an equal number of holes in the valence band. The excited electrons and holes can move through the crystal and the electrons may drop into these new levels and so become trapped to form F centers. Holes may become trapped by the new localized levels originating at the positive-ion vacancies to form V-type centers. Irradiation of a crystal containing F centers with F-light results in the excitation of the trapped electrons back into the conduction band. Some of the freed electrons will be re-trapped and others will recombine with holes associated with V-type centers. In addition to these processes, some electrons are trapped at other imperfections, such as a cluster of vacancies, forming secondary centers,

such as the  $R_1$ ,  $R_2$ , M, and N centers. Although models for these secondary centers have been proposed by Seitz (60, p. 9), they are not well established and extensive researches are in progress at present, especially on the dichroic properties and the excited states of these centers in connection with their proposed models and symmetries (29; 31; 32; 36; 46; 47; 65; 70; 71; 72).

It has been known for a long time that the rate of coloration by irradiation with ionizing radiation (darkenability or colorability) and the rate of bleaching of F centers by irradiation with F-light depend greatly on the preparation and the history of the crystal. The major imperfections in alkali halide crystals are lattice vacancies, impurities, and dislocations. These imperfections are associated with each other in varying degrees depending on the preparation and the history of the crystal. A number of important properties of the crystal, such as ionic conductivity, optical absorption, luminescence, and diffusion as well as color center phenomena are controlled by the imperfections. A trace of impurities, even when present in concentrations below the limit of chemical analysis, changes these properties of the crystal.

Schulman (55, p. 749-752) has summarized the influence of impurities on darkenability and suggested that

the ideally pure crystal may not darken under the action of ionizing radiation since the impurities are essential catalysts for the process. Seitz (60, p. 63), on the other hand, put more emphasis on the role of the dislocations on darkenability and proposed that dislocations alone should be adequate catalysts for coloration.

The alkali halide single crystals for optical and electrical work are usually grown from the melt by Kyropoulos' (34, p. 308-313; 35, p. 849-852) or Stockbarger's (63, p. 133-136; 64, p. 299-306) method. Since the salts are held at high temperatures for a long time, there are several possibilities that impurities are incorporated into the crystal during its growth. In addition to the impurities present in the starting material, it is recently recognized that the atmospheric oxygen and moisture which are in contact with the melt during crystal growth have a great influence on the ultraviolet absorption and the darkenability of the crystal (14, p. 1112-1116; 53, p. 56-57). Such atmospheric contamination can be largely eliminated by growing the crystal under a controlled atmosphere, e.g., an argon atmosphere (19). A serious difficulty, however, comes from the container in which the molten salt is held during crystal growth. Either platinum, porcelain, quartz, or graphite is most widely used as a container.

Although some of them are not corroded appreciably by the molten salt, crystals grown in such containers are expected to contain traces of impurities originating in the container material or in the impurities present in the container material. In fact, the optical absorption spectrum of such a crystal sometimes shows absorption in the wavelength range where the pure crystal should be perfectly transparent. Since the impurities, even if they are present only as a trace, affect the observed optical and electrical properties, it is most desirable to prepare crystals of higher purity than any now available. If single crystals of sufficient size for optical work could be grown from aqueous solution, all the contaminations which arise from crystal growth at high temperature would be eliminated although there might be some inclusion of water or growing solution in such crystals (3, p. 433-443).

The present investigation, in connection with other investigations on the purity of potassium chloride crystals in progress in this laboratory, was undertaken with the purpose of preparing highly pure potassium chloride single crystals from aqueous solution and of studying their properties, such as x-ray darkenability and optical bleaching rate in comparison with those of various melt-grown and water-grown crystals containing



impurities. In order to account for the difference of the properties observed among various crystals, analyses were attempted for the coloration and bleaching processes in terms of the crystal quality. The present investigation was limited entirely to room temperature coloration and bleaching processes since the process involved in the coloration at low temperatures is different from the room temperature process and the structure-sensitivity of the crystal disappears at these temperatures (51, p. 1007).

## II. PREPARATION OF SINGLE CRYSTALS FROM AQUEOUS SOLUTION

### A. Introduction

There are two common methods of growing crystals from aqueous solution, i.e., (1) spontaneous evaporation at constant temperature, and (2) gradual cooling of the saturated solution. In each case, crystals can be grown with or without a seed crystal. Although these methods are applicable in principle for the case of potassium chloride, preliminary experiments have shown a great difficulty in growing transparent crystals of sufficient size for optical work by either method. Usually small polycrystals grew on the seed crystal. Without a seed crystal, the crystals grown were transparent and cubic until the cube edges became 2 mm, but the larger crystals were opaque. When a shallow container was used for spontaneous evaporation, very thin crystals of about 1 cm square grew on the bottom of the container, but the crystals were so thin that they were easily bent by handling. Crystal growth was tried in the temperature range from room temperature to 80°C, but no improvement was obtained.

It is known that if a sodium chloride solution contains a trace of lead ions, transparent single

crystals can be grown fairly easily by spontaneous evaporation (17, p. 492-493). Therefore, trials were made for the growth of potassium chloride in the presence of the trace of lead ions. Transparent crystals up to 5 mm cube edge were obtained without difficulty by either method mentioned above, and it was found that the best crystals were grown with a reasonable rate at slightly above room temperature. The crystal grown in the presence of lead ions was of cubic shape in the beginning of the growth, but as the crystal grew it showed predominant  $\{111\}$  planes and finally the cubic habit of the crystal was changed to octahedral (52, p. 309; 57, p. 980-981).

Now, let us consider the nature of the saturated and supersaturated solutions (3, p. 7-10). The solubility of a salt is defined as the equilibrium concentration of the salt in contact with solvent at a specified temperature. Crystals, therefore, do not develop in a just-saturated solution. Theoretically any cooling below the saturation temperature or evaporation of solvent ought to result in the separation of solid, i.e., crystallization, but this does not occur although growth will take place on crystals already in the solution. Further cooling or evaporation brings the solution to a point of supersolubility where spontaneous crystallization

occurs suddenly by slight shock or disturbance. The supersolubility, however, depends on the experimental conditions as well as the kind of solution. The solution in the concentration range between the equilibrium solubility and the supersolubility is metastable and is called the supersaturated solution.

It is a preliminary requirement for the growth of a good crystal that the crystallization is carried out in the metastable region if other factors are favorable for the crystal growth. The simplest way to keep a solution in the metastable state is to lower the temperature of the solution or to evaporate the solution very slowly as a crystal grows. The conditions, however, are not easily achieved experimentally.

With these considerations, another method of crystal growth was tried, in which the solution was kept at a constant temperature gradient and the density convection current was utilized. In this way the difficulties arising from the control of temperature lowering or of evaporation rate were eliminated and transparent crystals of sufficient size were obtained. The details of the method are described in the next section.

## B. Procedure

Water used for recrystallization and crystal

growth was triply distilled using pyrex glassware. The warm solution of potassium chloride was always kept in a polyethylene container and never brought in contact with any glassware since the ordinary pyrex glass was extremely etched by boiling with a saturated solution of potassium chloride.

Reagent grade potassium chloride (Baker's analyzed quality) was recrystallized three times in a polyethylene container. At first, a saturated solution was prepared at about 60°C and cooled to near room temperature. The crystals formed were filtered and discarded since it is known that most of the heavy metal impurities are carried down in the first part of the crystallization (48, p. 133). Four crops of crystals were then recovered by evaporating the solution to the saturation point at about 60°C and cooling to 0°C. Crystals formed were filtered on a sintered glass filter and the solution remaining after the fourth crop was discarded. The crystals were partially dried in the air at room temperature and submitted to further recrystallization by an identical process. After the third recrystallization, the crystals were dried in the oven at 110°C and used for the following crystal growth.

Approximately 240 ml of potassium chloride solution saturated at 60°C was placed in each polyethylene

bottle (5 cm diameter and 15 cm height) and sealed with a polyethylene stopper. The bottom of the bottle was kept at 50°C, the surrounding room temperature being kept at 25°C. In this way, a temperature difference of 25°C was held between the top and the bottom of the bottle. After two weeks when thermal equilibrium was reached and excess salts crystallized out on the bottom of the bottle,  $10^{-4}$  mole of  $\text{PbCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{KOH}$  dissolved in 20 ml of warm water were added to the solutions, respectively, except for a solution in which a pure crystal was to be grown. From the average temperature of the solution at equilibrium, it was estimated that each bottle contains approximately 1 mole of dissolved potassium chloride. Accordingly, the nominal concentration of the impurities in each solution was about  $10^{-2}$  mole % in the beginning of the crystal growth. After four day standing, four seed crystals were suspended in each solution using nylon string. The seed crystal whose dimensions were about 1 x 1 x 2 mm was cleaved from a pure  $\text{KCl}$  single crystal obtained from the Harshaw Chemical Company. Except in the solution containing lead ions, crystals grown were not single. Usually a crystal grown on a seed crystal was composed of several smaller single crystals grown on each other, and water inclusion was observed in the region where two crystals grew in

contact. After two months of crystal growth several transparent single crystal sections up to 8 x 8 x 5 mm were obtained. In the case of the solution containing lead ions, the crystals grown were transparent throughout the crystal volume and no water inclusion was observed. Crystals larger than 10 mm in cube edge were easily grown. Although the presence of lead ions favors the octahedral crystal habit, as previously mentioned, these crystals exhibited good cleavage on {100} planes.

The crystals thus obtained were used in the coloration and bleaching experiments.

The processes of crystal growth occurring in the solution are considered as follows. A density convection current due to the temperature gradient brings warm saturated solution from the bottom to the cooler upper portion of the bottle. Thereby the warm saturated solution becomes supersaturated. As seed crystals grow, the cool solution at the top of the bottle becomes less saturated and is brought down to the bottom, where the solution is warmed again and dissolves more salts present on the bottom. Thus the solution is again saturated at high temperature and then the identical processes will follow for a continuous growth of the crystal.

### III. X-RAY COLORATION AND OPTICAL BLEACHING

#### A. Introduction

A typical room temperature growth curve of F centers by the irradiation with ionizing radiation shows an early rapid rise to  $10^{16} - 10^{17}$  centers per  $\text{cm}^3$ , followed by a relatively slow rise until saturation at about  $10^{18} - 10^{19}$  centers per  $\text{cm}^3$ . It has been observed recently that the growth of F centers again becomes rapid after prolonged irradiation with high intensity ionizing radiation (15, p. 453; 43, p. 443). In the present investigation, interest was limited to the initial two stages since the later stage of coloration is not structure-sensitive (15, p. 454). Gordon and Nowick (18, p. 977-983; 45, p. 16-25) have proposed a two stage coloration process: (1) The rapid part of the growth curve (first stage) is due to the capture of electrons by the vacancies which are present initially in the crystal, and (2) the slow part of the growth curve (second stage) is due to the capture of electrons by vacancies newly created during x-ray irradiation. The primary necessity of the creation of vacancies during x-ray irradiation arises from the facts that F-center concentrations of the order of  $10^{18} - 10^{19}$  per  $\text{cm}^3$  can be attained by x-ray irradiation whereas comparison of the mass density



of a crystal with that calculated from x-ray data shows that the concentration of vacancies present in an annealed crystal probably does not exceed about  $10^{17}$  per  $\text{cm}^3$  (58, p. 405-406). The facts that x-ray irradiation decreases the density (11, p. 627-633) and increases the length of the crystal (54, p. 177-183), support the supposition of creation of vacancies during x-ray irradiation. Furthermore, Rabin (50, p. 1386-1387) has recently shown that the expansion of the crystal during the first stage of coloration is much less than that expected from the concentration of F centers produced. This result supports the proposal that during the first stage of coloration, a large fraction of F centers are formed from vacancies present initially in the crystal. Since the x-rays which produce the F centers do not have sufficient energy to cause atomic displacements, the vacancies responsible for the second stage of coloration must be created in some indirect way. The process is not well understood at present. Varley (68, p. 886-887; 69, p. 134-135) has suggested that the negative-ion vacancies are produced through the multiple ionization of halogen ions. Discussions on the Varley's mechanism are not settled (7, p. 934-935; 28, p. 314-315; 43, p. 443). On the other hand, Seitz (59, p. 239-241) and Markham (39, p. 505-507) have proposed that defects are

produced by the interaction of radiation with dislocations. Gordon and Nowick (18, p. 977-983; 45, p. 16-25) have demonstrated that during the second stage of coloration plastically deformed crystals which contain many dislocations are colored to a much greater extent than undeformed crystals containing fewer dislocations. This fact suggests an important role of dislocations for the second stage of coloration. There are several experiments which show the effect of impurities on the darkenability of the crystal (12, p. 906-907; 49, p. 36; 60, p. 63). It has been known that a trace of  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ , or KOH enhances the darkenability of sodium and potassium chloride crystals at room temperature, especially for the first stage of coloration. Etzel and Allard (15, p. 453) and Rolf (53, p. 56-57) have recently demonstrated that the darkenability of a crystal is proportional to the amount of hydroxyl impurities which are introduced inadvertently into the crystal during crystal growth under ordinary atmosphere.

A qualitative feature of bleaching of F centers when irradiated with F-light at room temperature is that the bleaching occurs rapidly at first and then becomes increasingly difficult (67, p. 1591-1595). The existence of the fast and the slow bleaching rates has been ascribed to the different environments of the two groups

of F centers, one localized near dislocations and one distributed through the crystal, on the basis of the two stage process of x-ray coloration (43, p. 443). Bron (2, p. 1853-1863) has recently demonstrated the interrelation between the two stages which are observed in coloration and bleaching. The rate of the bleaching is strongly structure-sensitive and, therefore, dependent upon the particular specimen under observation. It has been known (2, p. 1855-1859; 49, p. 39 and p. 42; 66, p. 1390; 67, p. 1591) that the F centers in deformed or impure crystals are less stable and tend to bleach optically and thermally more rapidly than those in undeformed or pure crystals. A quantitative treatment for the bleaching rate is not available yet except for a few special cases (23, p. 435-442; 24, p. 114-125; 38, p. 623-626) since the bleaching process involves several possibilities for the fate of the electrons released from F centers into the conduction band by F-light: (1) They may be trapped by negative-ion vacancies to reform F centers, (2) they may recombine with holes in V-type centers, and (3) they may be trapped by crystal imperfections other than negative-ion vacancies, such as pairs of vacancies, larger clusters of vacancies or the vacancies associated with impurities, to form secondary centers.

## B. Experimental Procedure

The single crystals of potassium chloride used in this investigation are tabulated below:

crystal	additive	crucible	atmos- phere	designation
melt-grown KCl	none (Harshaw)	----	----	H-KCl
	none	graphite	argon	M-KCl(G20)*
	none	graphite	argon	M-KCl(G23)*
	Ca (0.001mole%)	platinum	air	M-KCl (0.001Ca)
	Ca (0.1mole%)	platinum	air	M-KCl(0.1Ca)
water-grown KCl	none	----	----	W-KCl
	OH(0.01mole%)	----	----	W-KCl(OH)
	Cu(0.01mole%)	----	----	W-KCl(Cu)
	Pb(0.01mole%)	----	----	W-KCl(Pb)

\*grown by Gruzensky (19)

Crystals were usually cleaved into specimens 7 mm x 8 mm x 0.40-0.42 mm thick with a single edge razor blade. The crystal holders were designed to fit the cell holders of Beckman DU and DK1 Spectrophotometers and the x-ray unit. All crystals were irradiated with the same incident x-ray flux from a copper target operated at 35 KVp and 15 ma through a beryllium window and a thin black paper which forms a part of a light-tight container. During x-ray

irradiation the crystal was mounted at a distance of about 4.5 cm from the beryllium window.

Optical absorption measurements were made in a Beckman model DK1 recording spectrophotometer over the wavelength range from 200  $m\mu$  to 1500  $m\mu$ . For most of the F band peak height measurements, a Beckman model DU spectrophotometer was used with the wavelength set at 560  $m\mu$  and the slit set at 0.04 mm. Optical bleaching of the x-ray colored crystals was performed in the Beckman DU spectrophotometer with the wavelength set at 560  $m\mu$  and the slit set at 2.0 mm, the light being incident on the crystal face opposite to that of x-ray irradiation.

The experimental data were taken successively in the following order: (1) F-center growth curve for initial x-ray irradiation, (2) F-center bleaching curve for F-light irradiation, and (3) F-center growth curve for re-x-ray irradiation, followed by experiments (2) and (3) repeatedly in some cases. X-ray irradiation, optical bleaching and optical absorption measurements were carried out at room temperature. In order to obtain the F-center growth or bleaching curve as a function of irradiation time, the irradiation by x-rays or F-light was interrupted periodically for optical absorption measurements. The transfer of the crystals from the x-ray unit to the spectrophotometer was performed in

total darkness.

The concentration of F centers was calculated by using Smakula's equation (62, p. 603-614) which reduces to (58, p. 386)

$$n_F f = 1.06 \times 10^{16} \alpha_m H$$

where  $n_F$  is the concentration of F centers per  $\text{cm}^3$ ,  $f$  is the oscillator strength for the F center,  $\alpha_m$  is the absorption coefficient per cm at the peak of F band, and  $H$  is the half-width of the F band expressed in eV. Using 0.35 eV for  $H$  at room temperature (32, p. 850) and since  $\alpha_m$  is equal to the optical density per cm at the maximum of the F band multiplied by 2.303, the equation reduces further to

$$n_F f = 8.5 \times 10^{15} \cdot \left( \frac{OD}{\text{cm}} \right)$$

where  $\left( \frac{OD}{\text{cm}} \right)$  is the optical density per cm at the maximum of the F band. The actual value of the oscillator strength is not well established. The experimental value ranges from 0.66 to 1.17 (10, p. 1077). If the oscillator strength is assumed to be equal to 0.85 for simplicity, the concentration of F centers per  $\text{cm}^3$  at room temperature can be expressed conveniently as follows:

$$n_F \approx 10^{16} \cdot \left( \frac{OD}{\text{cm}} \right)$$

Since the incident x-rays are attenuated more on the front part of the crystal and accordingly coloration of the crystal is not uniform, the front surface being colored most heavily, the F-center concentrations calculated using the above equation are averages over the crystal thickness of 0.40-0.42 mm. Problems arising from nonuniformity of the coloration will be discussed in a later section.

### C. Experimental Results and Discussion

As mentioned in the previous sections, the darkening and the bleaching rate of potassium chloride crystals are strongly structure-sensitive and differ from crystal to crystal depending on the preparation and the history of the crystal. In the present investigation, pure potassium chloride crystals obtained from the Harshaw Chemical Company were used as a standard because of their comparatively good quality and fairly uniform properties as have been recognized by other investigators. The experimental results obtained for a variety of other crystals were compared with the results obtained for Harshaw KCl.

## 1. Harshaw KCl

### Experimental results

A typical experimental result obtained for a Harshaw KCl (H-KCl-11) is shown in Figure 1, in which OA is the F-center growth curve for initial x-ray irradiation, B'C and D'E are the F-center growth curves for re-x-ray irradiation after the corresponding optical bleaching, and AB, CD, and EF are the F-center bleaching curves for F-light irradiation.

The F band was the most prominent of the various absorption bands which were observed in the crystals irradiated with x-rays. In the ultraviolet region, the  $V_3$  band appeared with a maximum at  $215 \text{ m}\mu$ . The  $V_2$  band was not resolved from the nearby large  $V_3$  band. On the long wavelength side of the F band, the  $R_1$ ,  $R_2$ , M, and N bands were formed in a later stage of the x-ray irradiation although these bands were very small compared with the F band. As seen in curve OA in Figure 1, the F-center growth curve for the initial x-ray irradiation shows an initial rapid increase followed by a slow linear growth. There have been a number of attempts to fit the experimental growth curve of F centers into a theoretical expression (49, p. 93-98). Etzel and Allard (15, p. 453) have shown for a variety of sodium chloride crystals that



for the early stage of coloration the F-center growth curve at room temperature is represented by the following equation (using the notation adopted in the present paper),

$$n_F = \left( \frac{1}{n_H^0} + \frac{E^0}{W} \right)^{-1} \quad (1)$$

where  $n_F$  is the F-center concentration per  $\text{cm}^3$ ,  $W$  is the total energy absorbed per  $\text{cm}^3$ ,  $E^0$  is the energy required to form an initial F center, and  $n_H^0$  is a constant whose value depends on the individual crystal. It should be noted that in the case of the calcium-doped NaCl the equation is applicable to an F-center concentration greater than  $2 \times 10^{18} \text{ cm}^{-3}$ . In general the applicable range is smaller for the pure crystal. The growth curve for natural rock salt, for example, cannot be fitted to equation (1) over the entire range of F-center concentration. These facts suggest that equation (1) might be applicable only for the first stage of coloration where impurities are most effective for the darkenability of the crystal. In order to test the applicability of equation (1) for the F-center growth for pure Harshaw KCl, the equation was expressed conveniently in the following form,

$$t/n_F = t/n_H^0 + E^0/\gamma J \quad (2)$$

where the substitution  $W = \gamma Jt$  has been made. Here  $J$  is the intensity of x-rays per  $\text{cm}^2$  per sec,  $\gamma$  is the linear x-ray absorption coefficient per cm,  $t$  is the x-ray irradiation time, and  $\gamma J$  is the efficiency of x-ray energy absorption by crystal per  $\text{cm}^3$ . For the moment, uniform x-ray absorption, and accordingly uniform coloration throughout crystal volume, will be assumed. As shown in Figure 2, the plot,  $t/n_F$  versus  $t$ , does not give the straight line which is expected from equation (2). The curvature was concave downwards similar to those observed by Etzel and Allard (15, p. 453) for natural rock salt and Harshaw NaCl. If the F-center growth consists of two processes corresponding to the so-called first and second stages and the second stage growth is assumed to be linear with irradiation time as seen in Figure 1, the growth curve for the first stage can be obtained by the subtraction of the second stage growth. The F-center concentrations thus obtained for the first and the second stages of coloration will be designated as  $n_F^I$  and  $n_F^{II}$ , respectively,  $n_F$  being the total F-center concentration, i.e.,  $n_F = n_F^I + n_F^{II}$  or  $n_F^I + a t$  where  $a$  is the slope of the second stage growth curve. As shown in Figure 2, the plot,  $t/n_F^I$  versus  $t$ ,

gives a straight line except at the very beginning of the irradiation. From this result, it may be concluded that equation (2) is applicable only for the first stage of coloration. If the first stage growth is fairly large relative to the second stage growth as observed for calcium-doped NaCl, however,  $n_F$  may be used instead of  $n_F^I$  without any appreciable error.

The general features of the absorption spectrum during the bleaching of F centers corresponding to the bleaching curves, AB, CD, and EF in Figure 1 were essentially the same in each case. During the bleaching of F centers the absorption at the short wavelength tail of the F band, which is called the K band, increased continuously. M band grew during the early stage of F-light irradiation and decreased after reaching a maximum.  $R_1$ ,  $R_2$ , and N bands grew continuously, approaching saturation values. The absorption in the region of the  $V_2$  and  $V_3$  bands remained constant or decreased very slightly. As a whole, the bleaching process observed in the present experiment is very similar to those of additively colored crystals. This kind of bleaching process is usually observed in heavily x-rayed crystals (2, p. 1855; 38, p. 622). In analogy to the F-center growth curve,  $t/(n_F^0 - n_F)$  was plotted as a function of the F-light irradiation time for the bleaching curves, where  $n_F^0$  is the initial

F-center concentration. As shown in Figures 3 and 4, a straight line was obtained over the entire range of the bleaching curve for each of the three cases. The difference in the slopes of the three lines will be discussed in a later section.

As shown in curves B'C and D'E in Figure 1, the concentration of F centers increased very rapidly at the beginning of the re-x-ray irradiation, followed by slow linear growth with the same slope as the linear part of the F-center growth curve for the initial x-ray irradiation. During the re-x-ray irradiation, the  $R_1$ ,  $R_2$ , N and K bands decreased very rapidly whereas the M band grew slightly during the very early stage of the irradiation and then decreased after reaching a maximum. When the F-center growth curve resumed the slow linear growth, the  $R_1$ ,  $R_2$ , M, N, and K bands attained their pre-bleaching magnitude and then started to grow with the same rates as those observed in the initial x-ray irradiation. The  $V_3$  band continued its growth without any observable decrease at the beginning of the irradiation. From these results, it may be concluded that in the early stage of the re-x-ray irradiation F centers are converted from secondary centers by x-rays, and the linear part of the growth curve is due to the same process as the second stage for the initial x-ray irradiation. The two stages

will be called the first and the second stages, respectively, as before. It is interesting to note that the F-center formation in the first stage is similar to the conversion of U centers to F centers by the x-ray irradiation observed by Martienssen and Pick (40, p. 309-317), which will be discussed in the following section. In analogy to the F-center growth curve for the initial x-ray irradiation,  $t/n_F$  as well as  $t/n_F^I$  were plotted as a function of the re-x-ray irradiation time, where  $n_F$  and  $n_F^I$  are the actual increments of the F-center concentration due to the re-x-ray irradiation. As shown in Figure 5, only the plot,  $t/n_F^I$  versus  $t$ , gives a straight line.

#### Discussion of the x-ray coloration

From the results obtained for Harshaw pure KCl, the F-center growth curves for both initial and re-x-ray irradiations are well represented by the following equation,

$$n_F = n_F^I + n_F^{II} \quad (3)$$

where

$$n_F^I = \frac{t}{\frac{t}{n_H^0} + \frac{E^0}{\gamma J}} \quad (4)$$

$$\text{and} \quad n_F^{II} = a \cdot t \quad (5)$$

The differential form of equation (4) takes the form

$$\frac{d n_F^I}{d t} = \frac{\gamma J}{E^0 n_H^{02}} (n_H^0 - n_F^I)^2 \quad (6)$$

Now let us consider the significance of the unknown constant,  $n_H^0$ , whose value is equal to the reciprocal of the slope in the plot,  $t/n_F^I$  versus  $t$ . For the initial x-ray irradiation,  $n_H^0$  for Harshaw KCl (H-KCl-11) was found to be  $2.5 \times 10^{16} \text{ cm}^{-3}$  from Figure 2. The results obtained by Etzel and Allard (15, p. 453) for NaCl crystals show that the value of  $n_H^0$  is larger for the less pure crystal. This is also true for the case of KCl crystals as seen in the later section. For example,  $n_H^0$  for the KCl crystal doped with 0.1 mole % of calcium ions is  $1.7 \times 10^{17} \text{ cm}^{-3}$ . Rabin (50, p. 1387) has estimated the initial concentration of negative-ion vacancies in NaCl crystals from the expansion of the crystal during x-ray irradiation and shown that the concentration is  $1 \times 10^{16} \text{ cm}^{-3}$  for Harshaw pure NaCl and  $6 \times 10^{17} \text{ cm}^{-3}$  for NaCl doped with 0.5 mole % calcium ions. From this evidence, it is plausible to correlate  $n_H^0$  to the initial concentration of negative-ion vacancies.

On the other hand, the values of  $n_H^0$  were found to

be  $4.2 \times 10^{16}$  and  $4.5 \times 10^{16} \text{ cm}^{-3}$  for the first and the second re-x-ray irradiations shown in Figure 5. These values are closely related to the concentration of F centers destroyed during the preceding optical bleaching,  $\Delta n_F^0$ , that is, the corresponding values are  $4.1 \times 10^{16}$  and  $4.6 \times 10^{16} \text{ cm}^{-3}$ , respectively (see H-KCl-11 in Table II). If the negative-ion vacancies created by the preceding optical bleaching remain and act as traps for electrons released by the subsequent x-ray irradiation to reform F centers (5, p. 353; 13, p. 1643-1645; 16, p. 885-887),  $n_H^0$  will be the concentration of negative-ion vacancies readily available to form F centers at the beginning of the re-x-ray irradiation. Thus the significance of  $n_H^0$  is just the same as expected previously, i.e., the initial concentration of negative-ion vacancies.

It is interesting to compare the experiment on F-center growth by re-x-ray irradiation in the optically bleached crystals with the experiment on the conversion of U centers to F centers by x-ray irradiation in KBr crystals. Martienssen and Pick (40, p. 314) have found the following relation to hold:

$$E_U = \frac{dW}{dn_F} = E_U^0 e^{\varepsilon \frac{n_F}{n_U^0}} \quad (7)$$

where  $E_U$  is the energy required to convert a U center to an F center,  $E_U^0$  is the initial value of  $E_U$ ,  $W$  is the total absorbed x-ray energy per  $\text{cm}^3$ ,  $n_U^0$  is the initial concentration of U centers and  $\epsilon$  is a constant which is equal to 4.6.  $E_U^0$  was found to be about 35 eV for all crystals independent of the magnitude of  $n_U^0$ . Although there are several possibilities for the mechanism of the conversion of U to F centers (60, p. 90), the negative-ion vacancies used to form F centers are considered to be furnished by U centers from which hydrogen atoms diffused away while the U centers were excited or ionized by excitons or x-rays. Therefore,  $n_U^0$  can be regarded as the initial concentration of negative-ion vacancies available to form F centers as well as the initial concentration of electrons readily ionizable. On the other hand, in the case of F-center formation during re-x-ray irradiation in an optically bleached crystal, the electrons to form F centers are substantially furnished by the secondary centers which were formed during the preceding optical bleaching of F centers. Therefore, this process may be called the conversion of secondary centers to F centers by x-ray irradiation. Electrons released from F centers to form secondary centers during optical bleaching leave the same number of negative-ion vacancies behind if the formed vacancies do not diffuse away, and



the concentration of the negative-ion vacancies thus formed will be equal to the concentration of the bleached F centers,  $\Delta n_F^0$ . Therefore it is expected that  $n_H^0$  plays a role similar to  $n_U^0$ , in the respective experiments. First compare the expression for the energy required to form an F center in both cases. From equation (6), the energy,  $E$ , for the conversion of a secondary center to an F center will be given as

$$E = \frac{dW}{dn_F^I} = \frac{E^0}{\left(1 - \frac{n_F^I}{n_H^0}\right)^2} \quad (8)$$

where the substitution  $W = \gamma Jt$  has been made. If  $E$  is plotted as a function of  $n_F^I/n_H^0$ , all curves for different  $n_H^0$  can be brought into coincidence just as found by Martienssen and Pick in plotting  $E_U$  as a function of  $n_F/n_U^0$  as seen in equation (7). Further, the integrated form of equation (7),

$$\frac{n_F}{n_U^0} = \frac{1}{\varepsilon} \ln \left( 1 + \frac{\varepsilon \gamma J}{E_U^0} \cdot \frac{t}{n_U^0} \right) \quad (9)$$

indicates that the plot,  $n_F/n_U^0$  versus  $t/n_U^0$ , can be brought into coincidence for different  $n_U^0$ . The same kind of coincidence can be obtained by plotting  $n_F^I/n_H^0$  as a

function of  $t/n_H^0$  as seen in equation (4) for the conversion of secondary centers to F centers. It is also interesting to compare equation (8) with (7) or (4) with (9) for small  $t$  where  $n_F^I/n_H^0$  and  $n_F/n_U^0$  are small compared with one. We obtain the following equations for small  $t$ ;

$$E \cong E^0 \left( 1 + 2 \frac{n_F^I}{n_H^0} \right)$$

and

$$n_F^I \cong \frac{\gamma J t}{E^0} \left( 1 - \frac{\gamma J t}{E^0 n_H^0} \right)$$

for the conversion of secondary centers to F centers, and

$$E_U \cong E_U^0 \left( 1 + \varepsilon \frac{n_F}{n_U^0} \right)$$

and

$$n_F \cong \frac{\gamma J t}{E_U^0} \left( 1 - \frac{\varepsilon}{2} \cdot \frac{\gamma J t}{E_U^0 n_U^0} \right)$$

for the conversion of U centers to F centers. From a comparison of these equations, the correspondance of  $n_H^0$  to  $n_U^0$  is obviously seen except for a constant factor.

From this evidence and that found in the experiments on the initial and re-x-ray irradiation, it seems reasonable to assume that  $n_H^0$  is the initial concentration of negative-ion vacancies or vacancy clusters which can form F centers upon trapping the electrons released by x-rays.

Mitchell et al. (42, p. 5-20; 43, p. 442) have proposed the following rate expression for the first and

the second stages of coloration;

$$\frac{dn_F^I}{dt} = k_1 (n_H^0 - n_F^I) \quad (10)$$

and 
$$\frac{dn_F^{II}}{dt} = k_2 (at - n_F^{II}) \quad (11)$$

where  $k_1$  and  $k_2$  are the rate parameters for the capture of electrons in the first and the second stages of coloration, respectively,  $n_H^0$  is the initial concentration of vacancies, and  $a$  is the rate constant for generation of new vacancies by x-rays. Equation (10) is of a form similar to equation (6) except for the order of the reaction. If the initial vacancies and those generated by irradiation are indistinguishable from each other (42, p. 5),  $k_1$  is equal to  $k_2$  and equations (10) and (11) can be combined in the following form;

$$\frac{dn_F}{dt} = k (n_H^0 + at - n_F) \quad (12)$$

where  $n_F = n_F^I + n_F^{II}$  and  $k = k_1 = k_2$ . On the basis of the empirical equation, equation (6), the concentration term of equation (12) should enter as the second power and  $k$  is expected to be equal to  $\gamma J / E^0 n_H^{02}$ . Therefore, the rate expression for the F-center growth can

be expressed in the following form:

$$\frac{d\eta_F}{dt} = \frac{\gamma J}{E^0 \eta_H^2} (\eta_H^0 + at - \eta_F)^2 \quad (13)$$

with the solution,

$$\eta_F = \eta_H^0 \frac{\left( \frac{\gamma J}{E^0} - a \right) \left( e^{-\frac{2}{\eta_H^0} \sqrt{\frac{\gamma J a}{E^0}} \cdot t} - 1 \right)}{\frac{\gamma J}{E^0} \left( e^{-\frac{2}{\eta_H^0} \sqrt{\frac{\gamma J a}{E^0}} \cdot t} - 1 \right) - \sqrt{\frac{\gamma J a}{E^0}} \left( e^{-\frac{2}{\eta_H^0} \sqrt{\frac{\gamma J a}{E^0}} \cdot t} + 1 \right)} + at \quad (14)$$

The solution (14) reduces to

$$\eta_F \cong \eta_H^0 + at \quad (15)$$

for large  $t$ , and

$$\eta_F \cong \frac{t}{\frac{t}{\eta_H^0} + \frac{E^0}{\gamma J}} + at \quad (16)$$

for small  $t$ , if  $E^0 a / \gamma J \ll 1$ . The experimental values of  $E^0 a / \gamma J$  are of the order of  $10^{-2}$  for re-x-ray irradiation and a little larger for initial x-ray irradiation. Equation (16) is of exactly the same form as the combined form of equations (4) and (5). Furthermore, equation (15)

is included in equation (16) since the latter equation reduces to equation (15) for large  $t$ . In conclusion, therefore, equation (13) is considered as a rate expression for F-center formation by x-rays, both for initial and re-x-ray irradiations, with approximate solution (16), assuming that the second stage coloration is linear with irradiation time. It is seen in equation (16) that the first and the second terms correspond to the so-called first and second stage coloration, respectively, as expected in equations (4) and (5), and the rate of the second stage coloration is equal to the rate of generation of vacancies by x-rays.

F-center growth curves obtained by other investigators (2, p. 1856; 42, p. 46 and 48) were also well fitted to equation (16) as shown in Figures 6 and 7. The ratio of the reciprocals of the intercepts on the axis for crystals I4 and I7 in Figure 6 is roughly equal to the ratio of the x-ray intensities as expected from equation (16).

Now let us consider the problem arising from non-uniform coloration. In equation (16),  $\gamma$  is dependent on the wavelength of x-rays, and  $J$  and  $a$  are functions of the wavelength of x-rays and the position in the crystal along the direction of the x-ray beam.  $E^0$  and  $n_H^0$  are constant throughout the crystal volume assuming

uniformity of the crystal before x-ray irradiation. If a crystal is composed of  $m$  thin sections perpendicular to the direction of x-ray beam in which the coloration is uniform and equation (16) is applicable, the average concentration of color centers over the crystal thickness will be given as

$$\bar{n}_F = \frac{1}{m} \sum_i^m \left[ \frac{t}{\frac{t}{n_H^0} + \frac{E^0}{\gamma_i J_i}} + a_i t \right]$$

where  $\bar{\quad}$  indicates the average value. This equation can be reduced to

$$\bar{n}_F = \frac{t}{\frac{t}{n_H^0} + E^0 \left( \frac{1}{\gamma J} \right)} + \bar{a} t$$

if  $E^0 n_H^0 / \gamma_i J_i t \ll 1$ . Since the individual values of  $E^0 / \gamma_i J_i$  were not obtained in the present experiment, the validity of the above restriction for the approximation is unknown. It is expected, however, from the linear relation in the plot,  $t/n_F^I$  versus  $t$ , that for re-x-ray irradiation the relation,  $E^0 n_H^0 / \gamma_i J_i t \ll 1$ , holds for an irradiation time less than one minute for most crystals including impurity doped and water-grown crystals. For initial x-ray irradiation, the restriction seems to be valid for an irradiation time a little larger than those in the case of re-x-ray irradiation, at least for Harshaw KCl. The values

of  $n_H^0$  obtained for the same crystal should be independent of the crystal thickness used although the average F-center concentration,  $\bar{n}_F$ , is smaller for the thick crystal since the front portions of the crystal are colored more heavily. To confirm the expectation, two specimens of different thickness cleaved from the same single crystal block were colored with x-rays. They are designated as H-KCl-9 and -7 in Table I. Values of  $n_H^0$  found in the plot,  $t/n_F^I$  versus  $t$ , agreed with each other within experimental error. Furthermore, the growth curve obtained by subtracting the growth curve for the thinner crystal from the thicker crystal gave approximately the same value of  $n_H^0$  as the original crystal, which is designated as H-KCl-7(9) in Table I (see also Figure 19a). The growth curve obtained by the above subtraction corresponds to that for the back portion of the thick crystal. Since in this portion the second stage coloration is expected to be small,  $t/n_F$  instead of  $t/n_F^I$  was plotted as a function of  $t$ .

Mador et al. (38, p. 621) obtained a set of F-center growth curves for Harshaw NaCl which were measured from the direction perpendicular to the x-ray beam with a narrow slit setting. In this way, the growth curves were obtained as a function of the depth from the irradiated surface. Their data were plotted according

to equation (16) and it was found that the values of  $n_H^0$  obtained from the different depths were approximately the same in each case as expected on the basis of the uniformity of the crystal before x-ray irradiation. In Figure 8,  $t/n_F$  instead of  $t/n_F^I$  was plotted as a function of  $t$  since the second stage coloration is expected to be small in these sections of the crystal.

#### Discussion of optical bleaching of F centers

As shown in Figures 3 and 4, the plot,  $t/(n_F^0 - n_F)$  versus  $t$ , gives a straight line over the entire range of the bleaching curve studied. In analogy to the case of x-ray coloration, it might be expected that the reciprocal of the slope in this plot is the initial concentration of traps for electrons released from F centers by F-light. Thus, the rate expression for the optical bleaching of F centers may be written in the following form:

$$-\frac{dn_F}{dt} = \frac{K}{n_T^0} [n_T^0 - (n_F^0 - n_F)]^2 \quad (17)$$

with the solution,

$$\frac{t}{n_F^0 - n_F} = \frac{t}{n_T^0} + \frac{1}{K} \quad (18)$$



where  $n_F^0$  and  $n_T^0$  are the initial concentration of F centers and electron traps, respectively, and K is a constant. In equation (17),  $(n_F^0 - n_F)$  means the concentration of F centers bleached and  $[n_T^0 - (n_F^0 - n_F)]$  the concentration of electron traps present in the crystal at time t. Two kinds of electron traps must be considered in equation (17); one is the holes associated with the V-type centers which annihilate electrons, and one is the vacancy clusters which form secondary centers upon trapping electrons.

Mador et al. (38, p. 623-626) have derived theoretically the following rate expression for the optical bleaching of F centers, assuming that the bleaching of F centers occurs only through the recombination of electrons and holes;

$$-\frac{dn_F}{dt} = \frac{\sigma_F I}{N} n_F^2 \quad (19)$$

with the solution,

$$\frac{n_F^0}{n_F} = 1 + \frac{n_F^0}{N} \sigma_F I t \quad (20)$$

where I is the intensity of the bleaching F-light,  $\sigma_F$  is the cross section for the optical decomposition of F centers and N is the sum of the initial concentrations of the negative-ion vacancies and the F centers, i.e.,  $N = n_H^0 + n_F^0$ . They used equation (20)

to test the validity of their rate expression (19), and found that  $n_F^0/n_F$  is linear with  $t$  only for the initial part of the bleaching. They ascribed the deviation from linearity for large  $t$  to the nonuniform bleaching of F centers along the light path due to the attenuation of the incident F-light (23, p. 435-442).

If holes are the only electron traps for the bleaching of F centers as assumed by Mador et al., the initial concentration of electron traps will be equal to that of holes, and the latter is also equal to that of F centers since x-rays produce the same number of electrons and holes in the crystal. Thus the rate expression (17) reduces to

$$-\frac{dn_F}{dt} = \frac{K}{n_F^0} n_F^2 \quad (21)$$

This equation is equivalent to equation (19) proposed by Mador et al., if

$$K = \frac{\sigma_F I n_F^0}{N} \quad (22)$$

The solution of equation (21) can be expressed in the following two forms,

$$\frac{n_F^0}{n_F} = 1 + \frac{K}{n_F^0} t \quad (23)$$

and

$$\frac{t}{n_F^0 - n_F} = \frac{t}{n_F^0} + \frac{1}{K} \quad (24)$$

Since equation (20) can also be expressed in the form of equation (24), the reciprocal of the slope in the plot,  $t/(n_F^0 - n_F)$  versus  $t$ , should be equal to the initial concentration of F centers if the assumption made by Mador et al. is correct. Figures 9 to 12 show their results (23, p. 435-442) plotted according to equation (24). Although their data give straight lines for the entire range of the bleaching curve, the reciprocal of the slopes is slightly different from  $n_F^0$  as given in Tables III and IV. This means that either all holes are not readily available for trapping electrons or some vacancy clusters also act as electron traps. In other words, it is not correct to assume that the bleaching of F centers occurs only through the recombination of electrons and holes or that  $n_T^0$  is equal to  $n_F^0$  in equation (17). If  $n_T^0$  is different from  $n_F^0$  by  $\Delta n_T^0$ , equation (18) will take the following form,

$$\frac{n_F^0}{n_F} = \frac{(n_F^0 + \Delta n_T^0) + Kt}{(n_F^0 + \Delta n_T^0) - \frac{\Delta n_T^0}{n_F^0} Kt} \quad (25)$$

where  $\Delta n_T^0 = n_T^0 - n_F^0$ . If  $\Delta n_T^0$  is zero, equation (25)

reduces to equation (23) and the linear relation between  $n_F^0/n_F$  and  $t$  will be obtained. The observed curvature in the plot,  $n_F^0/n_F$  versus  $t$  (23, p. 438-439), is consistent with the sign of  $\Delta n_T^0$  given in Tables III and IV. For small  $t$ , however, equation (25) can be approximated by

$$\frac{n_F^0}{n_F} \cong 1 + \frac{K}{(n_F^0 + \Delta n_T^0)} \cdot t$$

Thus, the plot,  $n_F^0/n_F$  versus  $t$ , will give a straight line as observed by Mador et al.

The explicit form of the constant  $K$  is unknown from the present experiment. In the crystals which were cleaved from the same large single crystal block and colored to the same initial F-center concentration, the values of  $n_T^0$  are expected to be same in each and  $K$  in equation (17) will be only a function of the intensity of the bleaching F-light. The values of  $n_T^0$  and  $K$  for such crystals were obtained by plotting  $t/(n_F^0 - n_F)$  as a function of  $t$  using the data taken from Herman and Wallis' paper (23, p. 438-439). As seen in Table IV, a rough constancy of  $n_T^0$  and the approximate proportionality between the intensity of the bleaching F-light and  $K$  were obtained (see also Figures 11 and 12).

Next, consider the case in which electrons released from F centers are trapped by vacancy clusters to

form secondary centers. This process is the one observed in the present experiment as described previously and is usually found for heavily x-rayed crystals as well as for additively colored crystals. Thus,  $n_T^0$  in equations (17) and (18) is expected to be the initial concentration of vacancy clusters if the secondary centers are formed by the capture of electrons by pre-existing vacancy clusters in the crystal. Although it is necessary to consider that the different kinds of vacancy clusters have different cross sections for electron capture, these were regarded as the same in the present argument (21, p. 545). The values of  $n_T^0$  for Harshaw KCl (H-KCl-11) obtained from Figures 3 and 4 are given in Table V together with the corresponding values of  $n_F^0$ . Data obtained by other investigators (2, p. 1856 and 1859; 23, p. 440; 67, p. 1591) were also plotted according to equation (18). As seen in Figures 13 to 16, the experimental results are well represented by the equation. If  $n_T^0$  is the initial concentration of electron traps in the crystal, the values of  $n_T^0$  obtained for the same crystal should be independent of the initial concentration of F centers. Contrary to expectation,  $n_T^0$  was dependent on  $n_F^0$  as shown in Table V. In general, for the same crystal  $n_T^0$  was larger for large  $n_F^0$  but the ratio  $n_T^0/n_F^0$  was smaller for large  $n_F^0$ .

Since the initial concentration of F centers is not uniform throughout the crystal volume, the initial concentration of electron traps is also nonuniform if  $n_T^0$  is dependent on  $n_F^0$  as shown above. Furthermore, because the intensity of the bleaching F-light decreases along the light path due to the attenuation of the light by the F centers present in the crystal, it is necessary to consider the nonuniform bleaching process for the crystal which has a nonuniform initial concentration of electron traps. As considered in the case of nonuniform coloration of crystals by x-rays, the average concentration of F centers bleached is expressed by the following equation if  $n_{Ti}^0/K_i t \ll 1$ ;

$$\overline{(n_F^0 - n_F)} = \frac{t}{\frac{t}{n_T^0} + \frac{1}{(n_T^0)^2} \overline{\left(\frac{n_T^{02}}{K}\right)}}$$

Therefore the reciprocal of the slope in the plot,  $t/(\overline{n_F^0} - n_F)$  versus  $t$ , will be the average value of  $n_T^0$  in the crystal. If  $n_T^0$  is uniform throughout the crystal, the equation reduces to

$$\overline{(n_F^0 - n_F)} = \frac{t}{\frac{t}{n_T^0} + \left(\frac{1}{K}\right)}$$

Because there are several possibilities for the optical bleaching process (38, p. 623-626; 58, p. 406-407; 60, p. 34-36 and 69-71; 67, p. 1591-1595), and because the nature of the secondary centers is not well understood, further information on  $n_T^0$  cannot be obtained from the present experiment. Among many difficulties, the possibility of the overlapping of the absorption due to excited states of the secondary centers with F band absorption must be taken into consideration as mentioned previously. If the excited states of the secondary centers absorb in the same wavelength range as the F band, the F-light bleaches the secondary centers as well as F centers, especially during the later stage of bleaching when the absorption due to secondary centers is large, and finally an equilibrium state will be reached between F centers and the secondary centers. Another difficulty which has to be taken into consideration is the interaction of various centers during bleaching (29, p. 1063-1068; 36, p. 684-693). In spite of the ambiguity of the significance of  $n_T^0$ , some correlations between the magnitude of  $n_T^0$  and crystal quality will be discussed in the next section.

## 2. Comparison of the results obtained for various kinds of crystals

Optical absorption spectra were measured before

x-ray irradiation in the wavelength range from  $200\text{ m}\mu$  to  $1500\text{ m}\mu$ . All crystals except those grown from aqueous solution in the presence of lead ions were transparent to light having a wavelength larger than  $210\text{ m}\mu$ . The optical absorption increased from about  $210\text{ m}\mu$  towards  $200\text{ m}\mu$ . The absorption in this region was small for the crystals  $0.04\text{ cm}$  thick used in this experiment so that quantitative comparison of the absorptions was not made. Potassium chloride crystals grown from aqueous solution in the presence of  $\text{Pb}^{++}$  ions showed two prominent absorption bands in the ultraviolet region. Both absorptions were so strong that the band maxima were well beyond 2.0 in absorbance for a crystal  $0.04\text{ cm}$  thick. The location of the band maxima agreed with those observed in melt-grown crystals containing  $\text{Pb}^{++}$  ions (25, p. 868-869; 26, p. 42; 56, p. 855). The fact that the crystals grown from aqueous solution in the presence of  $\text{Cu}^{++}$  or  $\text{OH}^-$  ions showed no optical absorption in the ultraviolet region indicates that the incorporation of these ions in the lattice is probably very slight, since it is known that melt-grown KCl crystals containing these ions show absorptions in this region (1, p. 433; 14, p. 1113; 26, p. 42; 37, p. 336-341; 53, p. 56-58; 61, p. 1-12).

F-center growth curves for initial and re-x-ray



irradiation are shown in Figures 17a and b. Figure 18 shows initial stages of the F-center growth in various crystals for the initial x-ray irradiation. The energy required to form an F center is defined as  $dW/dn_F$ , where  $W$  is the total energy absorbed per  $\text{cm}^3$ . Under the given x-ray intensity and crystal thickness,  $W$  will be proportional to the total irradiation time if the linear absorption coefficient for x-rays is not affected by the small amount of impurities present in the crystal. Therefore, the reciprocal of the slope of F-center growth curve at  $t = 0$  will be proportional to the energy required to form an initial F center, i.e.,

$$E^0 = \left( \frac{dW}{dn_F} \right)_{t=0} \propto \left( \frac{dt}{dn_F} \right)_{t=0}$$

The experimental results show that  $E^0$  for various crystals decreases in the following order:

- (1) W-KCl, W-KCl(OH), W-KCl(Cu), and W-KCl(Pb)
- (2) M-KCl(G20) and M-KCl(G23)
- (3) H-KCl
- (4) M-KCl(0.001Ca)
- (5) M-KCl (0.1Ca)

Second stage growth curves for M-KCl (G20) and (G23) and for water-grown crystals were not linear with irradiation time in the range of the irradiation time studied, and

the rates of growth in this stage were higher than those for Harshaw KCl and melt-grown KCl containing calcium ions. In order to estimate  $n_F^I$  for a crystal which showed nonlinear second stage growth, a linear second stage growth was approximated from the observed growth curve at large  $t$ . In analogy to the Harshaw KCl,  $t/n_F^I$  was plotted as a function of  $t$ . Melt-grown KCl containing calcium ions gave a straight line whereas M-KCl(G20) and (G23) and water-grown crystals showed deviation for small  $t$  from the expected linear relation as shown in Figures 19a and b. The deviation from the linear relation between  $t/n_F^I$  and  $t$  might be partly due to the characteristics of these crystals and partly due to the improper selection of the second stage growth curve. The F-center growth in the second stage might not be linear with irradiation time. For further understanding of F-center growth, especially in the second stage, it must be taken into consideration that x-rays produce bleaching as well as coloration and that the F-center growth is determined by these two effects (22, p. 624-631). The values,  $a$  and  $n_H^0$ , obtained from the above plots for Harshaw and calcium-doped crystals are given in Table I.

F-center growth curves for re-x-ray irradiation in the crystals containing secondary centers are shown in Figures 17a and b. In Figures 20a and b,  $t/n_F^I$  was

plotted as a function of  $t$ . The figures show a linear relation with the exception of water-grown KCl containing  $Pb^{++}$  ions. The reciprocal of the slope in the plots is  $n_H^0$  as expected from equation (4). The values of  $n_H^0$  obtained are given in Table II together with the concentration of F-centers bleached,  $\Delta n_F^0$ , during the preceding F-light irradiation. The values of  $n_H^0$  for Harshaw KCl and melt-grown KCl containing calcium ions with an exception of M-KCl(0.1Ca)-I were nearly equal to the corresponding values of  $\Delta n_F^0$ . This means as mentioned previously that the vacancies created during the preceding optical bleaching of F centers remained and were refilled with the electrons released during subsequent re-x-ray irradiation. In the case of M-KCl(0.1Ca)-I, the concentration of F centers produced by the initial x-ray irradiation ( $11.08 \times 10^{16} \text{ cm}^{-3}$ ) was less than that of vacancies present in the original crystal ( $17.24 \times 10^{16} \text{ cm}^{-3}$ ). Accordingly, the concentration of available vacancies upon re-x-ray irradiation,  $n_H^0$ , will be much higher than that of F centers bleached,  $\Delta n_F^0$ , during the preceding F-light irradiation. This is consistent with the experimental result as seen in Table II. On the other hand, in the case of water-grown crystals,  $n_H^0$  was always smaller than  $\Delta n_F^0$  and the growth curve for the re-x-ray irradiation failed to resume the extrapolation

of the growth curve for the initial x-ray irradiation as seen in Figures 17a and b. This might indicate that some of the vacancies created by the ionization of F centers during the preceding optical bleaching do not remain and diffuse away before they are refilled with electrons. The intercept of the plot on the  $t/n_F^I$  axis is  $E^0/\gamma J$  according to equation (4), and therefore, is a measure of the energy required to form an initial F center by re-x-ray irradiation if the x-ray intensity and the crystal thickness are kept constant. As given in Table II, the values are about  $0.3 \times 10^{-16}$  for all crystals studied. This means that the mechanism of F-center formation due to re-x-ray irradiation is the same for all crystals and is independent of the impurity content of the crystal.

In the case of optical bleaching of F centers by F-light, the plot,  $t/(n_F^0 - n_F)$  versus  $t$ , gave a straight line over the entire range of bleaching in accordance with equation (18). Some of the results are shown in Figures 21a to h. In the case of water-grown KCl, a slight deviation from the linear relation was observed for an irradiation time less than 2 minutes (see Figures 21d and e). The direction of the deviation indicates that the initial bleaching rate is too small to fit the equation. The values,  $n_T^0$  and  $K$ , obtained in the plots are given in Table V.  $n_T^0$  was not constant for a given

kind of crystal but depended on the initial concentration of F centers similar to the case of Harshaw KCl. In general,  $n_T^0$  was larger for the crystals which contain large  $n_F^0$ . The ratios,  $n_T^0/n_F^0$ , were approximately constant for a given kind of crystal, however. On the average, the ratio was largest for calcium-doped crystals and smallest for water-grown crystals except those containing  $Pb^{++}$  ions. This means that if the crystals which contain the same initial F-center concentration are compared,  $n_T^0$  for the calcium-doped crystal is larger than that for the water-grown crystal. The value of K also depended on the kind of crystals and the initial concentration of F centers. In general, K was larger for impure crystals, such as calcium-doped crystals. In a given kind of crystal, K was larger for the crystal containing large  $n_F^0$ . Therefore if crystals contain the same initial concentration of F centers, the bleaching rate is higher for impure crystals. It is interesting to note that  $K/n_F^0$  is approximately constant for a given kind of crystal and largest for the calcium-doped crystals. From the above arguments, the magnitude of  $n_T^0/n_F^0$  and  $K/n_F^0$  may be used as a measure of crystal quality. From the values given in Table V, the following order will be assigned for crystal quality:

- (1) W-KCl, W-KCl(OH), and W-KCl(Cu)
- (2) M-KCl(G20) and M-KCl(G23)
- (3) H-KCl
- (4) W-KCl(Pb)
- (5) M-KCl(0.001Ca)
- (6) M-KCl(0.1Ca)

The above order of crystal quality agrees with that obtained on the basis of the energy required to form an initial F center except in the case of W-KCl(Pb). The properties of W-KCl(OH) and W-KCl(Cu) observed in the experiments on x-ray coloration and optical bleaching of F centers were very similar to those of W-KCl. This fact and the optical absorption in ultraviolet region indicate that  $\text{Cu}^{++}$  and  $\text{OH}^-$  ions are not incorporated appreciably into the potassium chloride lattice when the crystals are grown from aqueous solution.

#### IV. SUMMARY OF CONCLUSIONS

The following conclusions can be made from the results of the present investigation:

1. Potassium chloride crystals of sufficient size for optical work can be grown from aqueous solution by utilizing the density convection current due to a temperature gradient.

2.  $\text{Pb}^{++}$  ions not only promote the growth of potassium chloride crystals from aqueous solution but also modify the crystal habit due to the incorporation of  $\text{Pb}^{++}$  ions in the lattice.  $\text{OH}^-$  and  $\text{Cu}^{++}$  ions do not affect appreciably the growth and the habit of potassium chloride crystal. The incorporation of these ions into the lattice is expected to be negligible, as shown by optical absorption and the x-ray coloring and optical bleaching rates.

3. F-center growth curves for x-ray irradiation consist of two stages as proposed by Nowick. The initial rapid part of the growth curve (the first stage) is due to the capture of electrons by vacancies which are present initially in the crystals. The slow part of the growth curve (the second stage) is due to the capture of electrons by vacancies newly created during x-ray irradiation.

4. The second stage growth is approximately linear with irradiation time for Harshaw KCl and melt-grown KCl containing calcium ions, but not for M-KCl(G20) and M-KCl(G23) and water-grown crystals.

5. The energy required to form an initial F center is largest for water-grown crystals and smallest for melt-grown crystals containing calcium ions.

6. The rate expression for F-center growth by x-ray irradiation in crystals which show a linear second stage growth is given in the following form:

$$\frac{dn_F}{dt} = \frac{\gamma J}{E^0 n_H^0} (n_H^0 + at - n_F)^2$$

with the approximate solution,

$$n_F \cong \frac{t}{\frac{t}{n_H^0} + \frac{E^0}{\gamma J}} + at$$

in which the first and the second terms correspond to  $n_F^I$  and  $n_F^{II}$ , respectively. For crystals which show nonlinear second stage growth, the above equations are not applicable.

7. When crystals containing secondary centers produced during the preceding optical bleaching of F centers are irradiated with x-rays, that is re-x-ray irradiation, the secondary centers disappear and F



centers are reformed. The process may conveniently be called the conversion of secondary centers to F centers by x-rays and forms a system analogous to the conversion of U centers to F centers by x-rays.

8. The same rate expression as that given for the initial x-ray irradiation is applicable to F-center growth by re-x-ray irradiation.

9. The energy required to form an initial F center in a crystal which contains secondary centers is independent from the impurity content of the crystal.

10. Most of the vacancies produced by the ionization of F centers seem to remain in the crystal and to act as traps for electrons released by subsequent x-ray irradiation.

11. The F-center bleaching curve for F-light irradiation can be represented by the following equation over the entire range of bleaching studied:

$$-\frac{dn_F}{dt} = \frac{K}{n_T^{o2}} \left[ n_T^o - (n_F^o - n_F) \right]^2$$

with the solution

$$\frac{t}{n_F^o - n_F} = \frac{t}{n_T^o} + \frac{1}{K}$$

For lightly x-rayed crystals,  $n_T^0$  is nearly equal to  $n_F^0$  and for heavily x-rayed crystals,  $n_T^0$  and  $K$  are dependent on the magnitude of  $n_F^0$ .  $n_T^0/n_F^0$  and  $K/n_F^0$ , however, are approximately constant for a given kind of crystal and can be used as a measure of crystal quality.

12. The results of the present investigation permit the following conclusion on crystal quality: The crystal quality decreases in the following order:

- (1) W-KCl, W-KCl(OH), and W-KCl(Cu)
- (2) M-KCl(G20) and M-KCl(G23)
- (3) H-KCl
- (4) W-KCl(Pb)
- (5) M-KCl(0.001Ca)
- (6) M-KCl(0.1Ca)

## V. SUGGESTIONS FOR FURTHER WORK

In reviewing the course of the present investigation, some modifications in experimental technique as well as new experiments are suggested.

1. In order to eliminate nonuniform coloration by x-rays and nonuniform bleaching of F centers by F-light, it is desirable to measure the absorption spectrum of a thin section of the crystal from the direction perpendicular to that of irradiation. Another approach to the problem is the use of  $\gamma$ -rays which are more penetrating than x-rays.

2. Although heavily x-rayed crystals behave like additively colored crystals under F-light irradiation, it is recommended that additively colored crystals be used for experiments on the optical bleaching of F centers and on the conversion of secondary centers to F-centers by x-rays since this eliminates the factor which arises from the recombination of electrons and holes.

3. Before any further work is done on the kinetics of the optical bleaching of F centers, it is highly desirable to examine the properties of the secondary centers which are formed during the optical bleaching of F centers, especially on the models, the mechanism of formation, and the optical absorptions arising from excited

states of the secondary centers. If the optical absorptions due to excited states overlap with the F band absorption as expected from experiments on the dichroic properties of the secondary centers, the so-called F band will not be a true F band when secondary centers are present in the crystal, and will be composed of the F band and the absorption bands due to the excited states of various secondary centers.

TABLE I. Values of  $a$ ,  $n_H^0$ , and  $E^0/\gamma J$  for F-center growth during initial x-ray irradiation in Harshaw and calcium-doped KCl crystals.

Crystal	Thickness (cm)	$a \times 10^{-16}$ ( $\text{cm}^{-3} \text{ min}^{-1}$ )	$n_H^0 \times 10^{-16}$ ( $\text{cm}^{-3}$ )	$\frac{E^0}{\gamma J} \times 10^{16}$ ( $\text{cm}^3 \text{ min}$ )
H-KCl-9	0.040	0.032	2.64	< 0.5
H-KCl-11	0.040	0.031	2.49	< 0.5
H-KCl-7	0.058	0.025	2.39	< 0.5
H-KCl-7(9)	0.018	$\sim 0$	2.42	< 0.5
H-KCl-9a	0.040	0.033	1.85	< 0.5
M-KCl(0.001Ca)	0.040	0.033	5.53	< 0.5
M-KCl(0.1Ca)	0.040	0.016	17.24	< 0.5

TABLE II. Values of  $a$ ,  $\Delta n_F^0$ ,  $n_H^0$ , and  $E^0/\gamma J$  for F-center growth during re-x-ray irradiation in various KCl crystals.

Crystal	Exptl. order	Thickness (cm)	$a \times 10^{-16}$ (cm <sup>-3</sup> min <sup>-1</sup> )	$\Delta n_F^0 \times 10^{-16}$ (cm <sup>-3</sup> )	$n_H^0 \times 10^{-16}$ (cm <sup>-3</sup> )	$\frac{E^0}{\gamma J} \times 10^{16}$ (cm <sup>3</sup> min)
H-KCl-11	I	0.040	0.031	4.05	4.20	0.35
	II	0.040	0.031	4.60	4.47	0.26
H-KCl-9a	I	0.040	0.033	3.58	3.83	0.29
	II	0.040	0.033	4.20	4.35	0.24
M-KCl (0.001Ca)	II	0.040	0.033	6.57	6.88	0.34
M-KCl (0.1Ca)	I	0.040	0.016	10.35	18.80	~0.3
	II	0.040	0.016	17.85	19.09	~0.3
W-KCl-2	I	0.040	0.040	4.35	3.32	0.31
	II	0.040	0.028	4.48	4.21	0.24
W-KCl-3	I	0.042	0.045	4.16	3.54	0.31
W-KCl(OH)	I	0.040	0.049	4.53	2.95	0.22
W-KCl(Cu)	I	0.040	0.048	4.38	3.30	0.28
W-KCl(Pb)	I	0.046	~0.061	6.11	----	~0.3

TABLE III. Values of  $n_F^0$ ,  $n_T^0$ ,  $\Delta n_T^0$ ,  $K$ , and  $K/n_F^0$  for optical bleaching of F centers in lightly x-rayed Harshaw NaCl crystals for initial F-center concentrations in the ranges  $\sim 10^{15} - \sim 10^{16}$  and  $\sim 10^{16} - \sim 10^{17} \text{ cm}^{-3}$ . Data from Figures 6 and 7 in reference 23 (pages 438 and 439). Bleaching light intensity =  $0.87 \times 10^{14} \text{ quanta/cm}^2 \text{ sec}$ .

Curve	Thickness (cm)	$n_F^0$ ( $\text{cm}^{-3}$ )	$n_T^0$ ( $\text{cm}^{-3}$ )	$\Delta n_T^0$ ( $\text{cm}^{-3}$ )	$K$ ( $\text{cm}^{-3} \text{ min}^{-1}$ )	$K/n_F^0$ ( $\text{min}^{-1}$ )
I	0.635	$0.34 \times 10^{16}$	$0.35 \times 10^{16}$	$+0.01 \times 10^{16}$	$0.08 \times 10^{16}$	0.24
II	0.635	0.63	0.62	-0.01	0.13	0.21
III	0.635	1.42	1.39	-0.03	0.22	0.15
I	0.064	$0.32 \times 10^{17}$	$0.33 \times 10^{17}$	$+0.01 \times 10^{17}$	$0.06 \times 10^{17}$	0.19
II	0.064	0.67	0.69	+0.02	0.13	0.19
III	0.064	1.44	1.48	+0.04	0.38	0.26

TABLE IV. Values of  $n_F^0$ ,  $n_T^0$ ,  $\Delta n_T^0$ , and K for optical bleaching of F centers in lightly x-rayed Harshaw NaCl crystals for various bleaching light intensities at initial F-center concentrations of  $3.1 \times 10^{16}$  and  $1.4 \times 10^{17} \text{ cm}^{-3}$ . Data from Figures 8 and 9 in reference 23 (page 439).  $I_0 = 0.87 \times 10^{14} \text{ quanta/cm}^2 \text{ sec.}$

Curve	Thickness (cm)	Bleaching light intensity	$n_F^0$ ( $\text{cm}^{-3}$ )	$n_T^0$ ( $\text{cm}^{-3}$ )	$\Delta n_T^0$ ( $\text{cm}^{-3}$ )	K ( $\text{cm}^{-3} \text{ min}^{-1}$ )	Relative value of K
I	0.064	1.00 $I_0$	$3.1 \times 10^{16}$	$3.24 \times 10^{16}$	$+0.14 \times 10^{16}$	$0.56 \times 10^{16}$	1.00
II	0.064	0.734 $I_0$	3.1	3.37	+0.27	0.37	0.66
III	0.064	0.305 $I_0$	3.1	3.05	-0.05	0.23	0.41
I	0.064	1.00 $I_0$	$1.4 \times 10^{17}$	$1.45 \times 10^{17}$	$+0.05 \times 10^{17}$	$0.33 \times 10^{17}$	1.00
II	0.064	0.734 $I_0$	1.4	1.60	+0.20	0.20	0.61
III	0.064	0.305 $I_0$	1.4	1.61	+0.21	0.12	0.36



TABLE V. Values of  $n_F^0$ ,  $n_T^0$ ,  $K$ ,  $K/n_F^0$ , and  $n_T^0/n_F^0$  for optical bleaching of F centers in various x-rayed KCl crystals

Crystal	Exptl. order	Thickness (cm)	$n_F^0 \times 10^{-16}$ (cm <sup>-3</sup> )	$n_T^0 \times 10^{-16}$ (cm <sup>-3</sup> )	$K \times 10^{-16}$ (cm <sup>-3</sup> min <sup>-1</sup> )	$K/n_F^0$ (min <sup>-1</sup> )	$n_T^0/n_F^0$
H-KCl-11	I	0.040	4.68	3.75	9.3	1.98	0.80
	II	0.040	6.50	4.61	11.1	1.71	0.71
	III	0.040	8.00	5.13	13.9	1.74	0.64
H-KCl-9a	I	0.040	4.25	3.40	7.5	1.77	0.80
	II	0.040	6.23	4.10	13.3	2.14	0.66
	III	0.040	8.23	4.98	15.2	1.84	0.61
M-KCl (0.001Ca)	I	0.040	7.68	6.41	24.4	3.18	0.84
	II	0.040	4.10	3.22	12.5	3.05	0.79
	III	0.040	9.55	7.51	27.0	2.83	0.79
M-KCl (0.1Ca)	I	0.040	10.55	9.21	~100	~9.5	0.87
	II	0.040	18.58	16.34	~100	~5.4	0.88
	III	0.040	20.25	16.78	~100	~4.9	0.83
M-KCl(G20)	I	0.042	6.67	4.81	5.2	0.77	0.72
M-KCl(G23)	I	0.040	7.83	5.15	5.0	0.64	0.66

Table V - Continued

Crystal	Exptl. order	Thickness (cm)	$n_F^0 \times 10^{-16}$ ( $\text{cm}^{-3}$ )	$n_T^0 \times 10^{-16}$ ( $\text{cm}^{-3}$ )	$K \times 10^{-16}$ ( $\text{cm}^{-3} \text{min}^{-1}$ )	$K/n_F^0$ ( $\text{min}^{-1}$ )	$n_T^0/n_F^0$
W-KCl-2	I	0.040	6.80	4.08	$\sim 2.5$	$\sim 0.37$	0.60
	II	0.040	8.05	4.52	$\sim 2.5$	$\sim 0.31$	0.56
	III	0.040	9.40	4.77	$\sim 2.5$	$\sim 0.27$	0.51
W-KCl-3	I	0.042	7.10	4.35	$\sim 2.7$	$\sim 0.38$	0.61
	II	0.042	9.12	4.95	$\sim 3.3$	$\sim 0.36$	0.54
W-KCl(OH)	I	0.040	6.75	4.20	2.9	0.43	0.62
	II	0.040	8.08	4.56	3.4	0.42	0.56
W-KCl(Cu)	I	0.040	7.08	4.38	3.3	0.47	0.62
	II	0.040	8.15	4.62	4.0	0.49	0.57
W-KCl(Pb)	I	0.046	8.02	5.79	17	2.1	0.72
	II	0.046	8.98	5.84	17	1.9	0.65

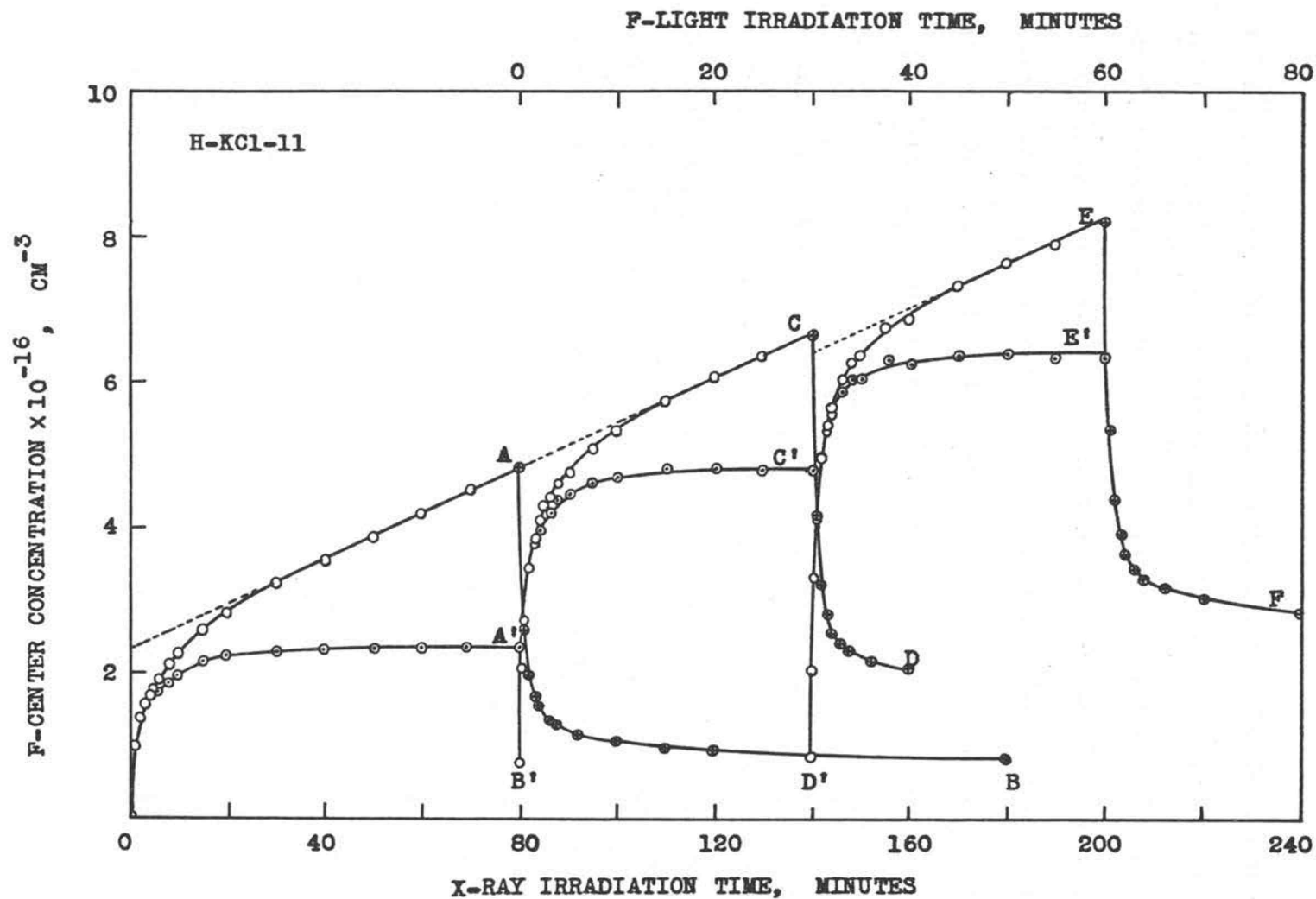


FIGURE 1. F-CENTER GROWTH CURVES FOR INITIAL AND RE-X-RAY IRRADIATIONS AND OPTICAL BLEACHING CURVES OF F CENTERS FOR F-LIGHT IRRADIATION IN HARSHAW KCl (H-KCl-11).

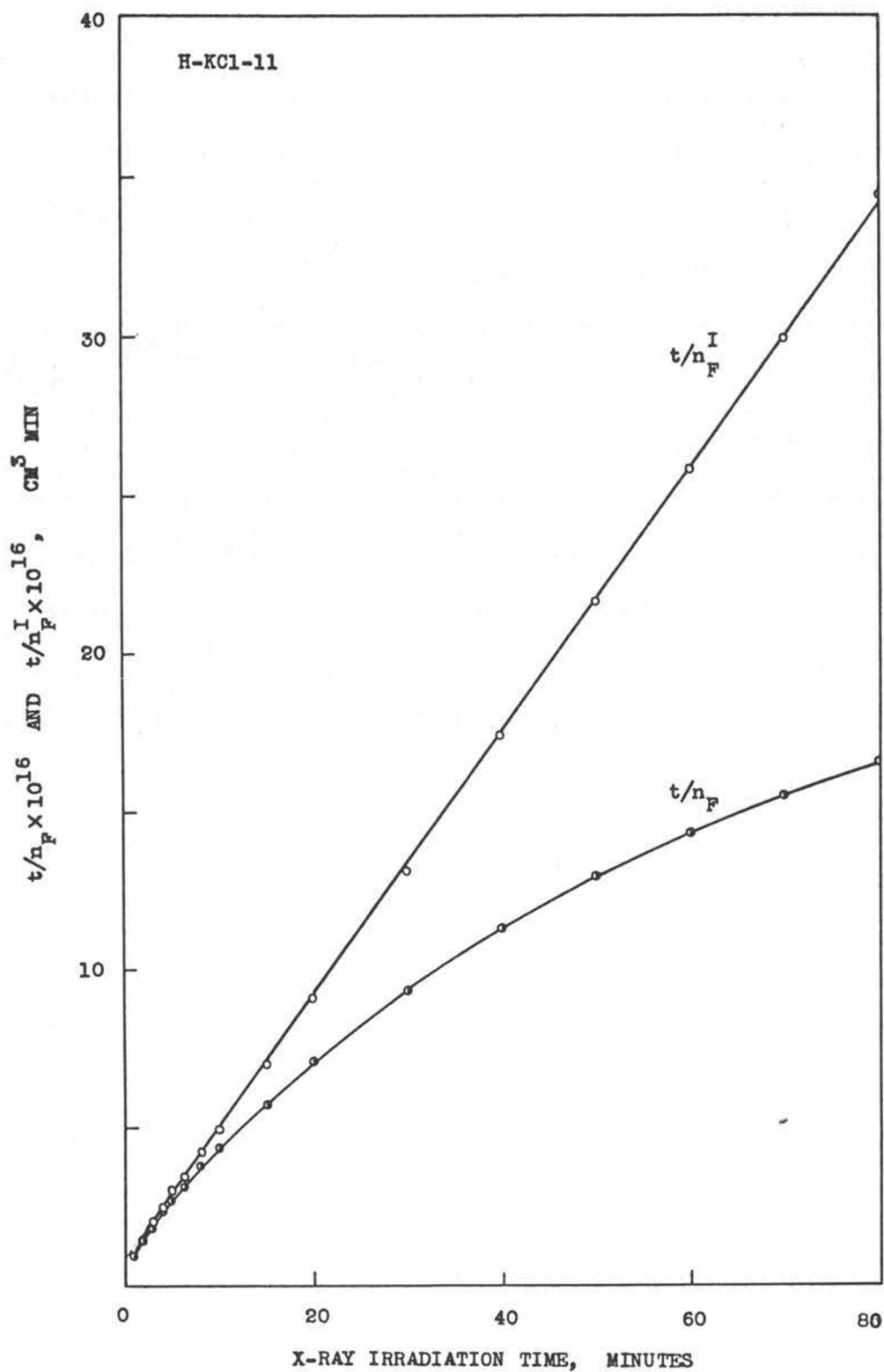


FIGURE 2.  $t/n_F$  AND  $t/n_F^I$  AS FUNCTIONS OF  $t$  FOR F-CENTER GROWTH DURING INITIAL X-RAY IRRADIATION CORRESPONDING TO CURVES OA AND OA' IN FIGURE 1, RESPECTIVELY.

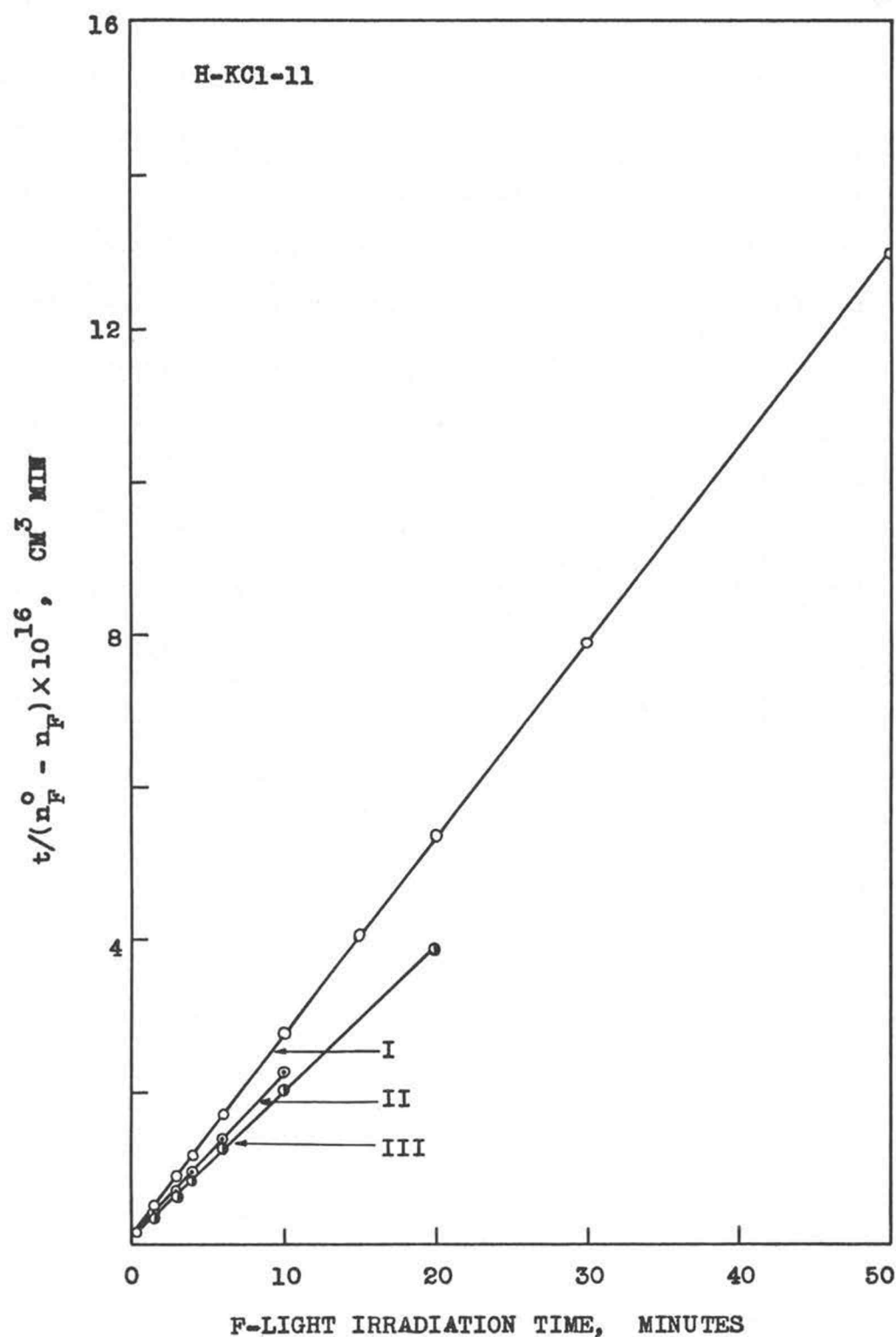


FIGURE 3.  $t/(n_F^0 - n_F)$  AS A FUNCTION OF  $t$  FOR OPTICAL BLEACHING OF F CENTERS CORRESPONDING TO CURVES AB, CD, AND EF IN FIGURE 1.

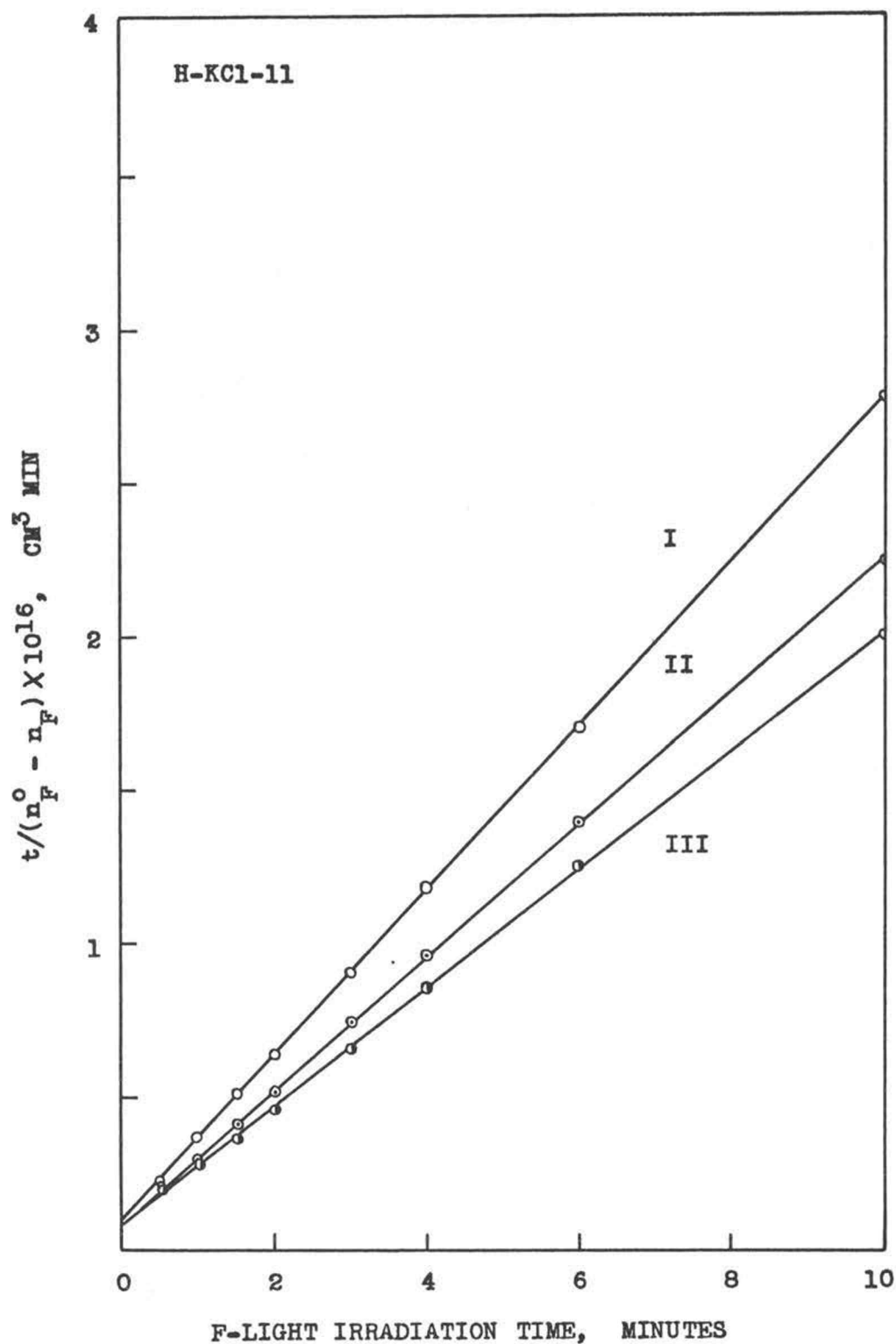


FIGURE 4.  $t/(n_F^0 - n_F)$  AS A FUNCTION OF  $t$  FOR INITIAL STAGES OF OPTICAL BLEACHING OF F CENTERS SHOWN IN FIGURE 3.

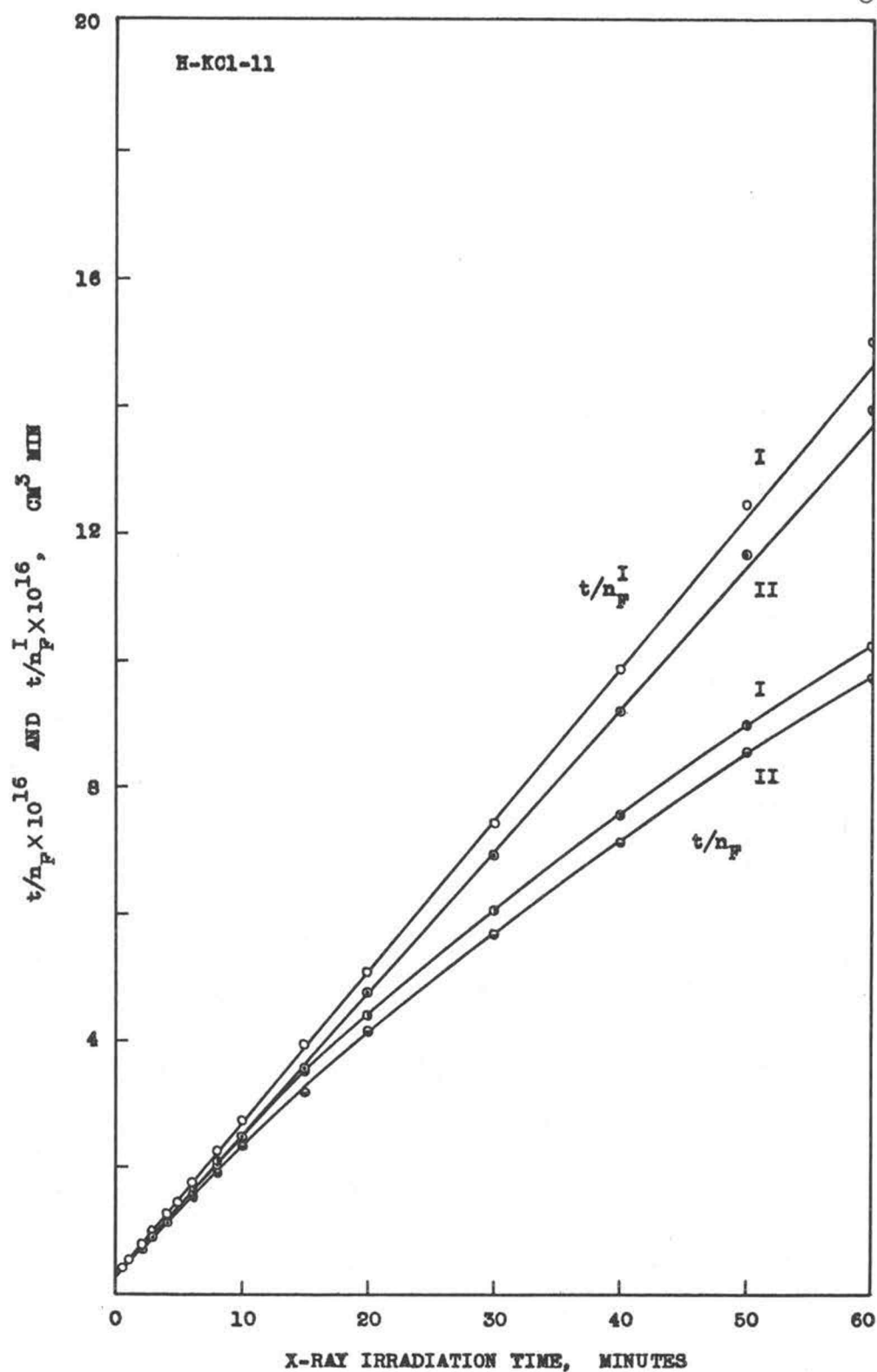


FIGURE 5.  $t/n_F$  AND  $t/n_F^I$  AS FUNCTIONS OF  $t$  FOR F-CENTER GROWTH DURING RE-X-RAY IRRADIATION CORRESPONDING TO CURVES B'C, B'C', D'E, AND D'E' IN FIGURE 1.

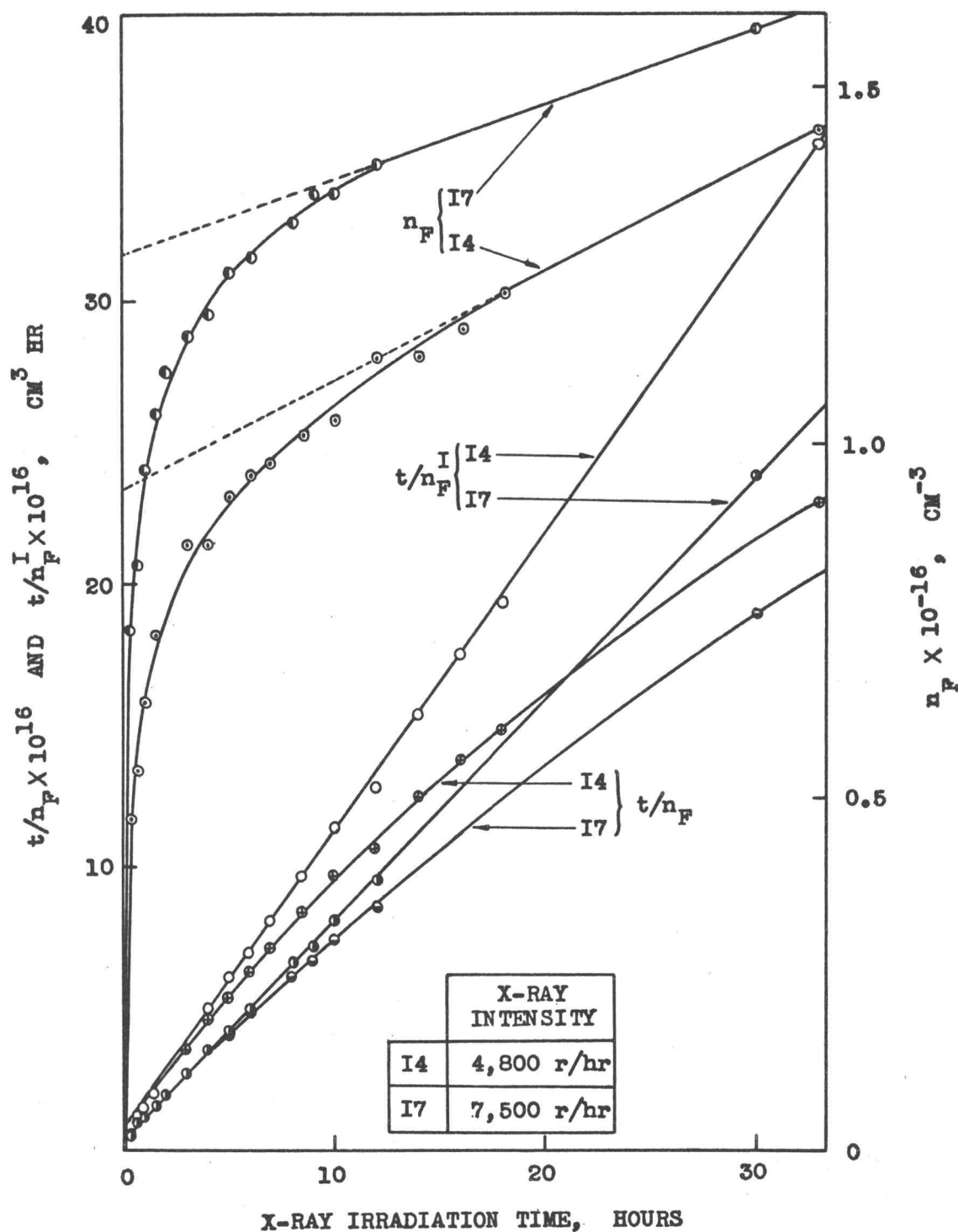


FIGURE 6. F-CENTER GROWTH CURVES AND TESTS OF EQUATION (16) FOR HARSHAW KCl. DATA FROM CURVES I4 AND I7 IN REFERENCE 42 (PAGES 46 AND 48).



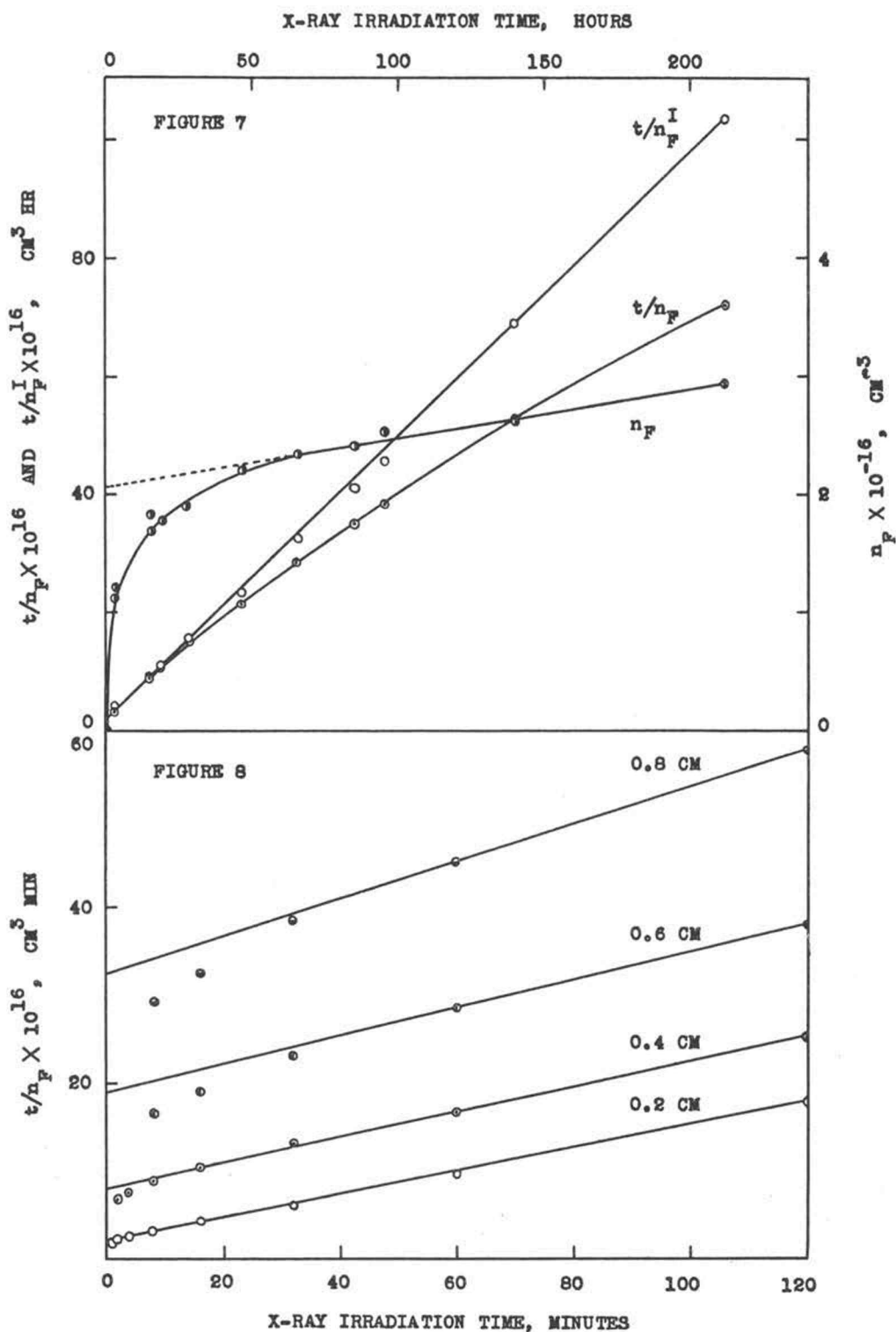
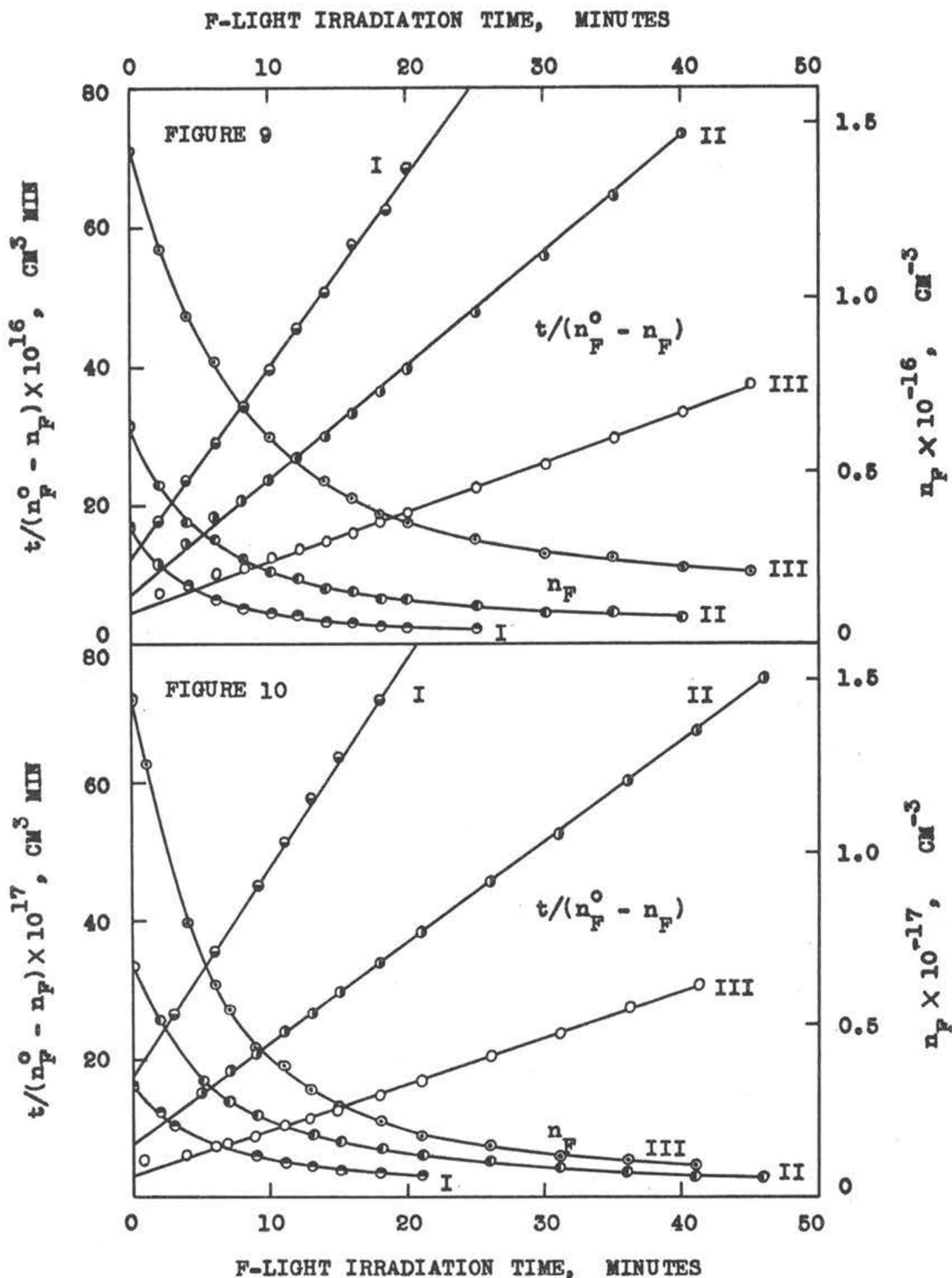
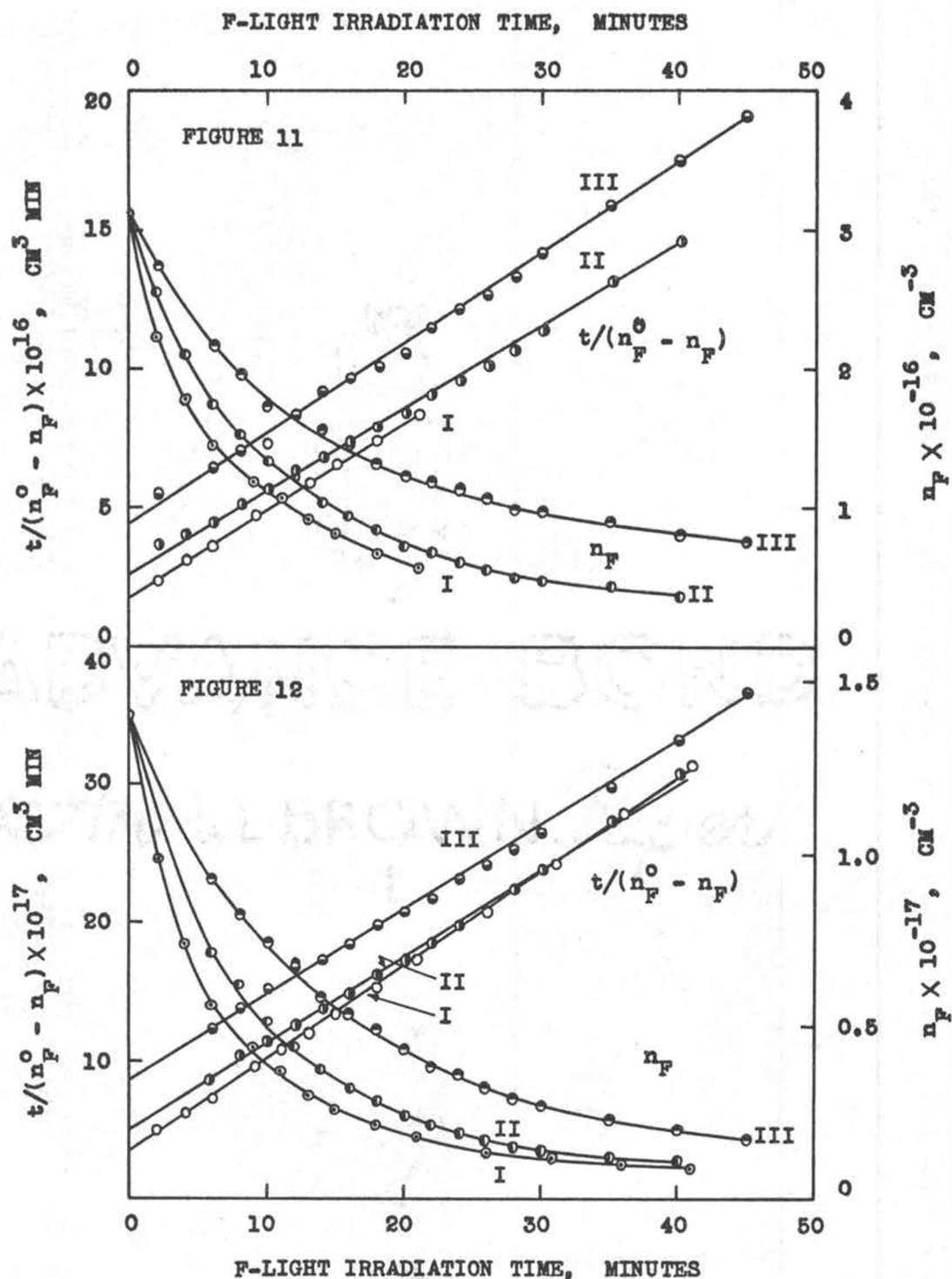


FIGURE 7. F-CENTER GROWTH CURVE AND TEST OF EQUATION (16) FOR HARSHAW KCl. DATA FROM FIGURE 3 IN REFERENCE 2 (PAGE 1856).

FIGURE 8. TEST OF EQUATION (16) FOR F-CENTER GROWTH CURVES OBTAINED AT SEVERAL DEPTHS IN HARSHAW NaCl. DATA FROM FIGURE 5 IN REFERENCE 38 (PAGE 621).



FIGURES 9 AND 10. OPTICAL BLEACHING CURVES OF F-CENTERS AND TESTS OF EQUATION (18) FOR LIGHTLY X-RAYED NaCl FOR INITIAL F-CENTER CONCENTRATIONS IN THE RANGES  $\sim 10^{15}$ – $\sim 10^{16}$  AND  $\sim 10^{16}$ – $\sim 10^{17}$   $\text{CM}^{-3}$ , RESPECTIVELY. DATA FROM FIGURES 6 AND 7 IN REFERENCE 23 (PAGES 438 AND 439).



FIGURES 11 AND 12. OPTICAL BLEACHING CURVES OF F-CENTERS FOR VARIOUS BLEACHING LIGHT INTENSITIES AND TESTS OF EQUATION (18) FOR LIGHTLY X-RAYED NaCl AT INITIAL F-CENTER CONCENTRATIONS OF  $3.1 \times 10^{16}$  AND  $1.4 \times 10^{17} \text{ cm}^{-3}$ , RESPECTIVELY. DATA FROM FIGURES 8 AND 9 IN REFERENCE 23 (PAGE 439).

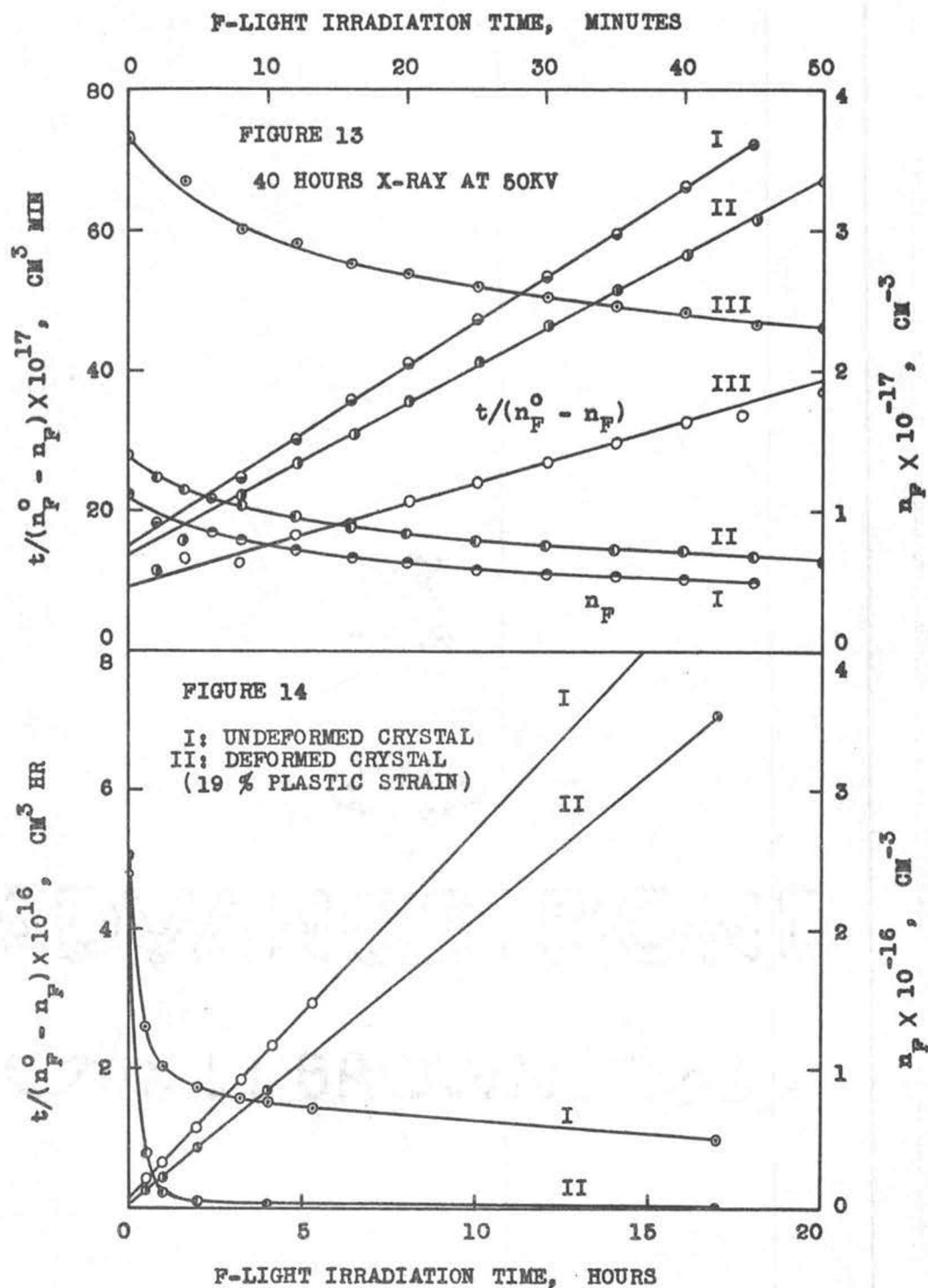
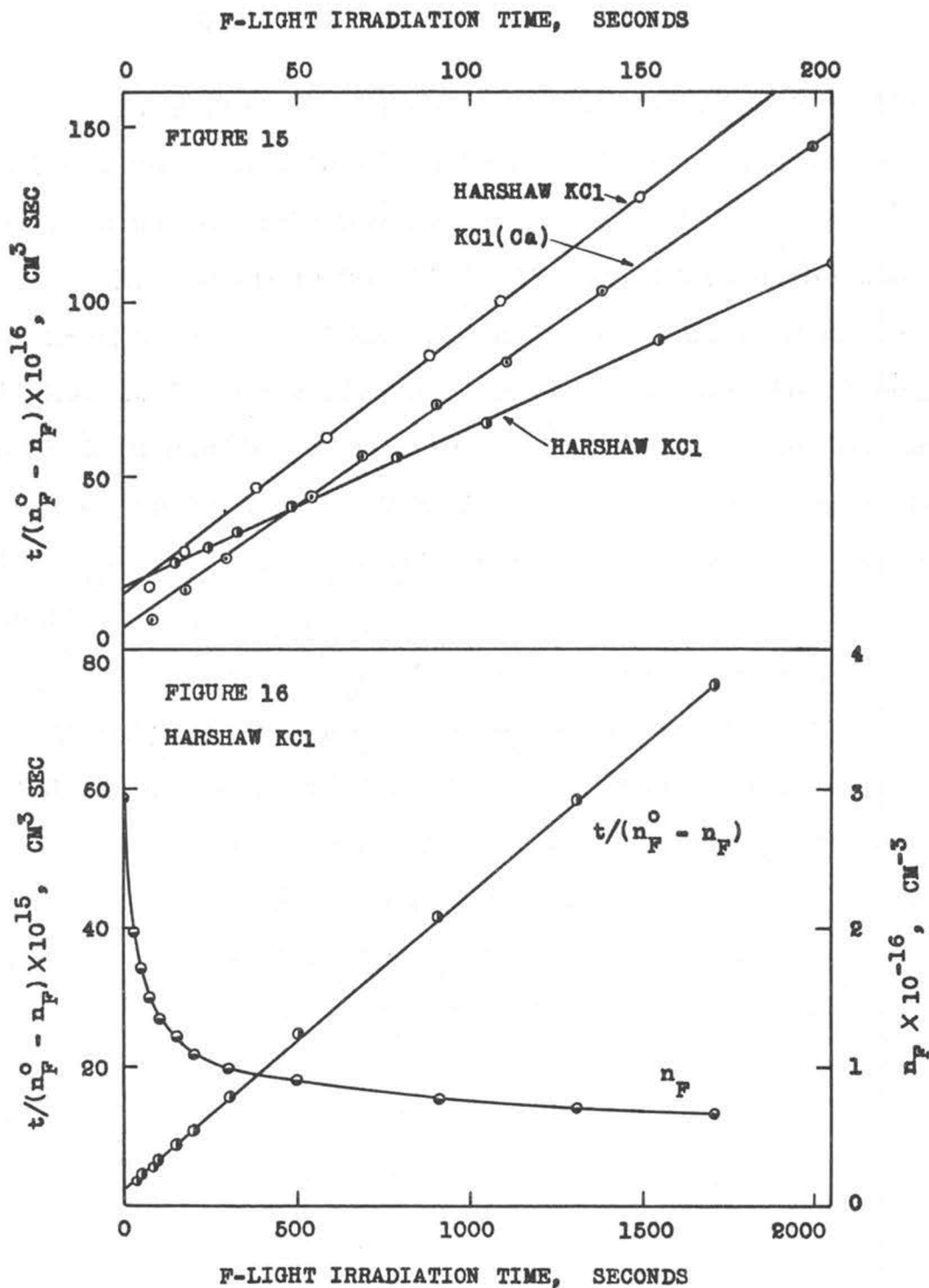
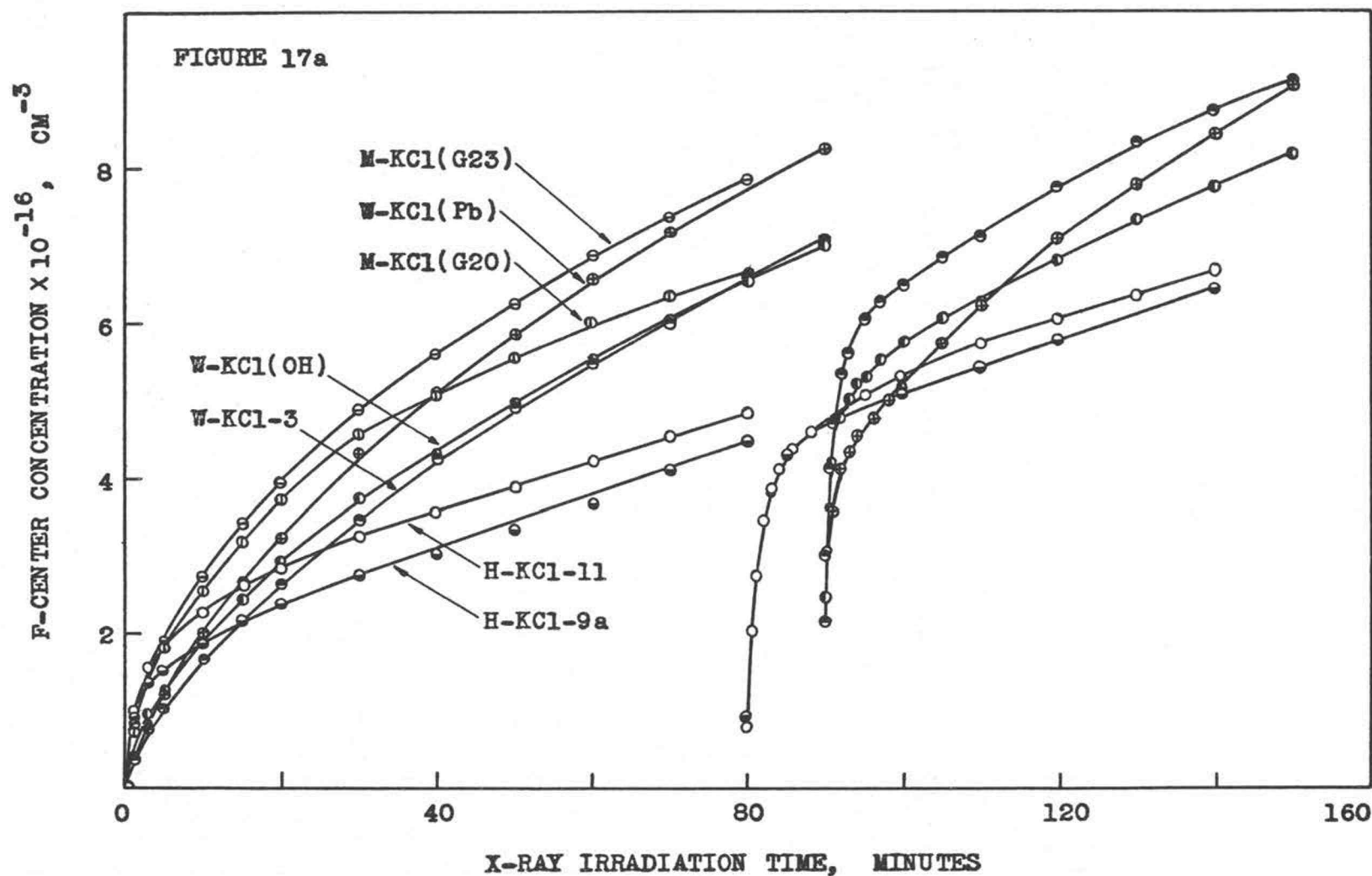


FIGURE 13. OPTICAL BLEACHING CURVES OF F CENTERS AND TESTS OF EQUATION (18) FOR HEAVILY X-RAYED NaCl. DATA FROM FIGURE 11 IN REFERENCE 23 (PAGE 440).

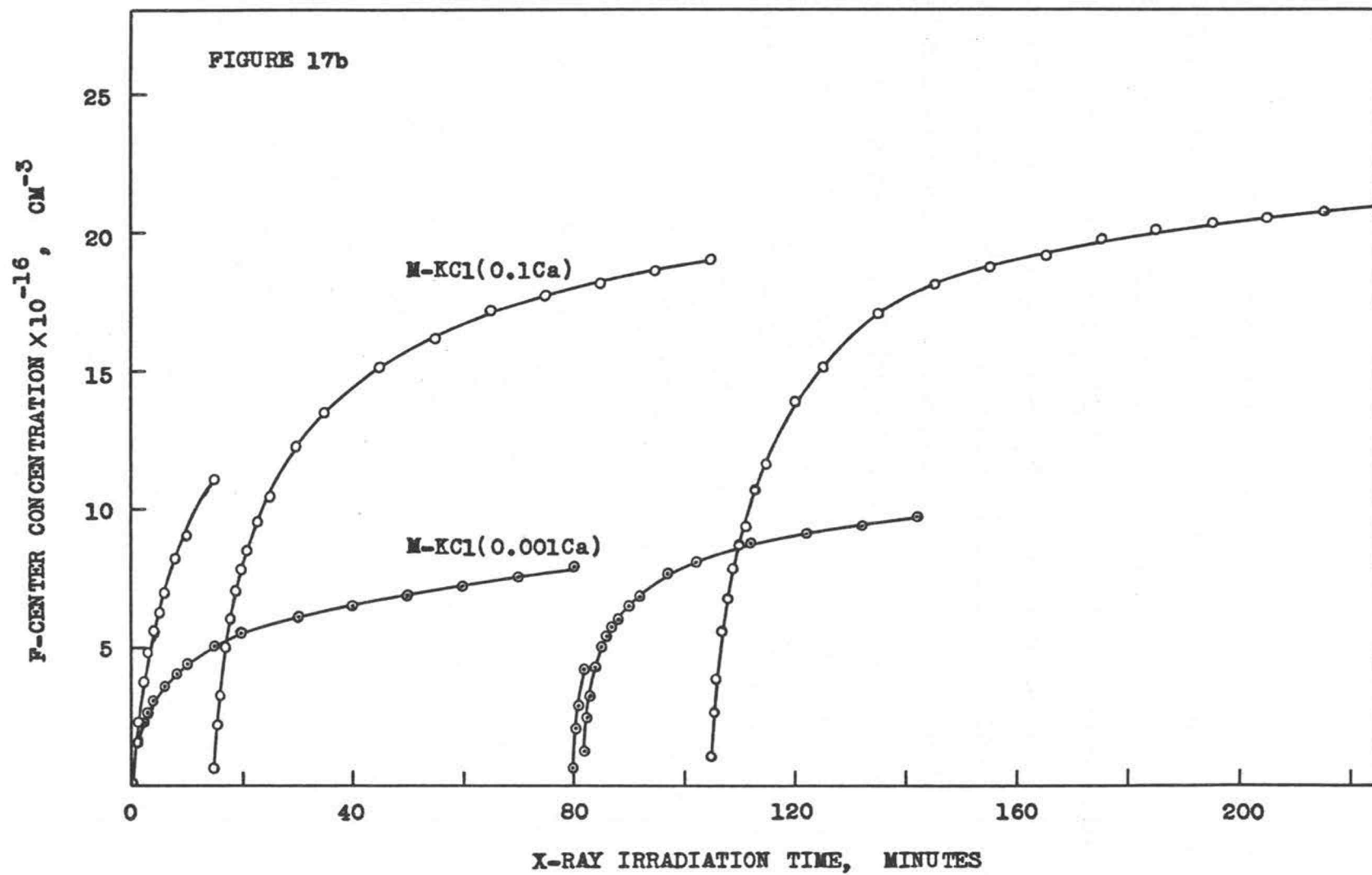
FIGURE 14. OPTICAL BLEACHING CURVES OF F CENTERS AND TESTS OF EQUATION (18) FOR ADDITIVELY COLORED KCl. DATA FROM FIGURE 1 IN REFERENCE 67 (PAGE 1591)



FIGURES 15 AND 16. TESTS OF EQUATION (18) FOR OPTICAL BLEACHING OF F CENTERS IN HARSHAW KCl AND CALCIUM-DOPED KCl. DATA FROM FIGURES 3 AND 5 IN REFERENCE 2 (PAGE 1856)



FIGURES 17a and b. F-CENTER GROWTH CURVES FOR INITIAL AND RE-X-RAY IRRADIATIONS IN VARIOUS KCl CRYSTALS.



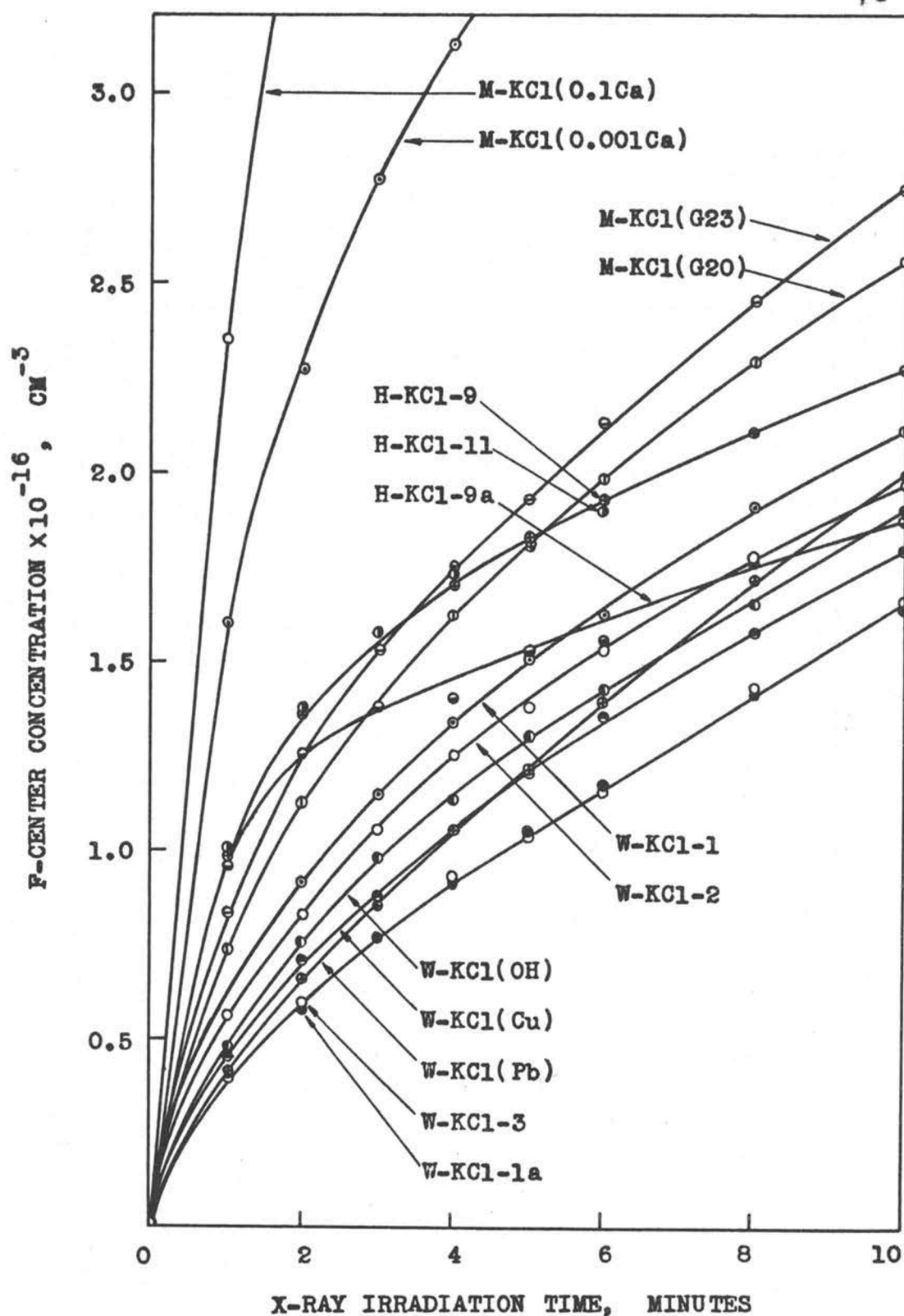
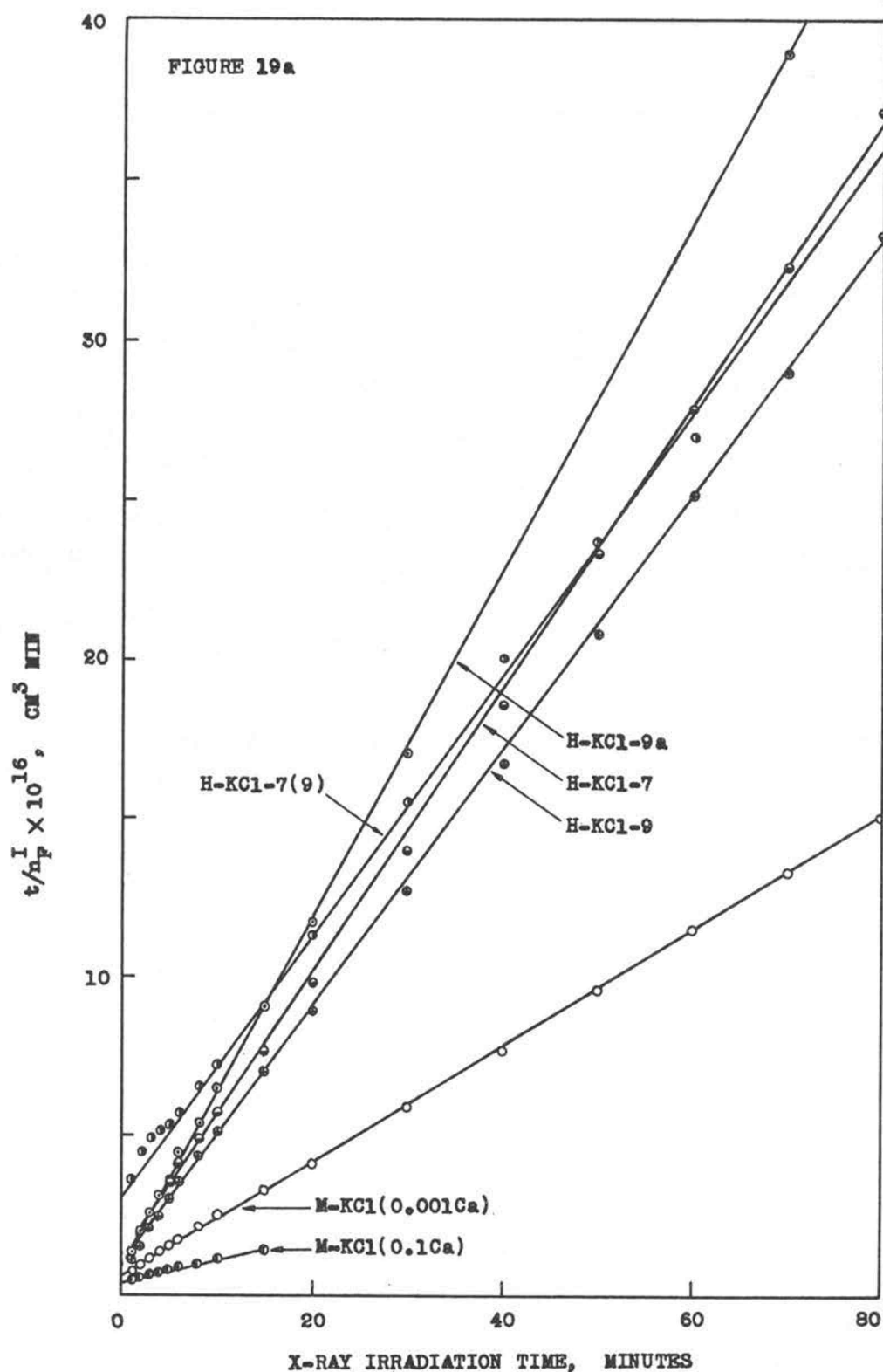
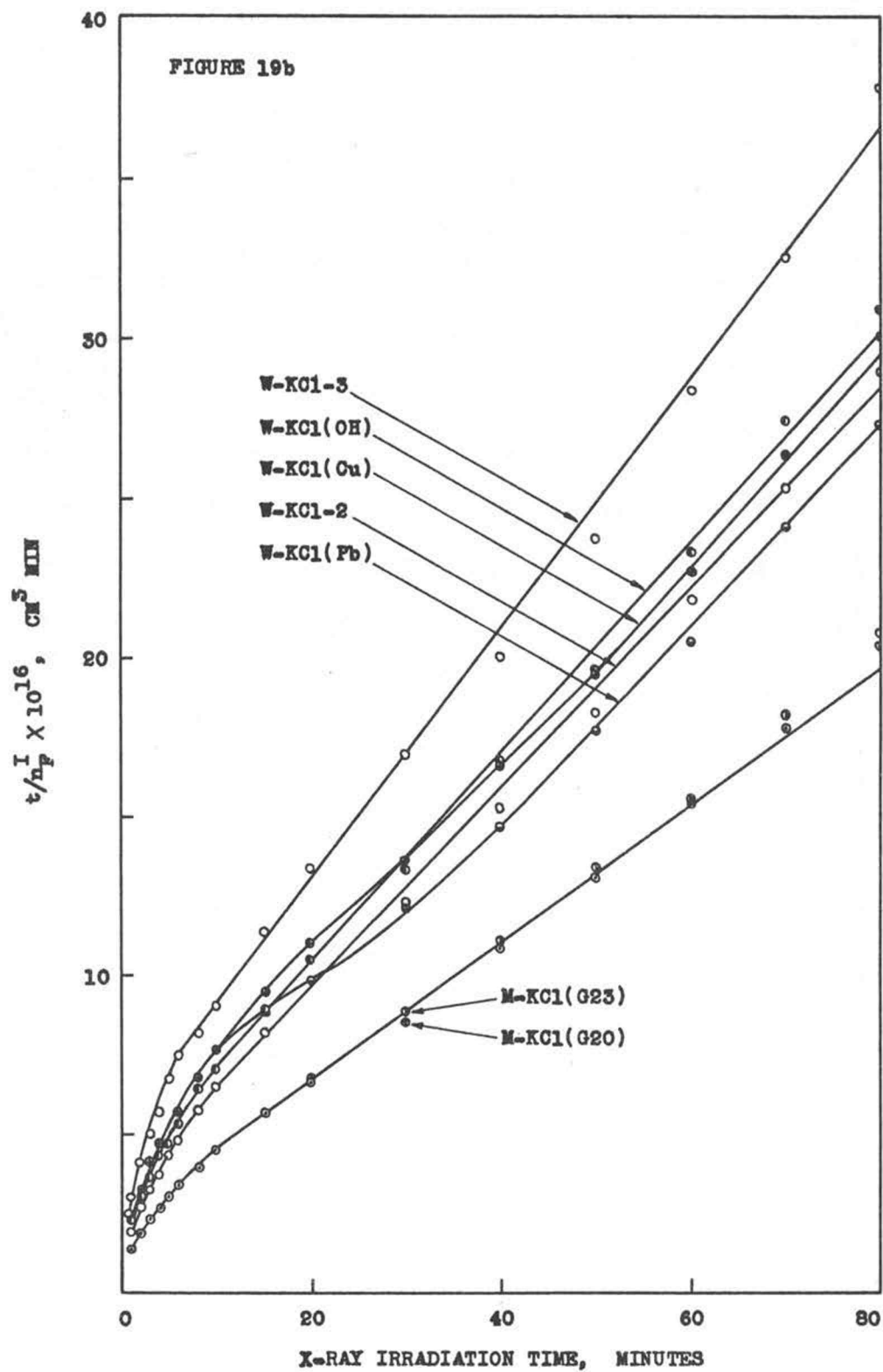


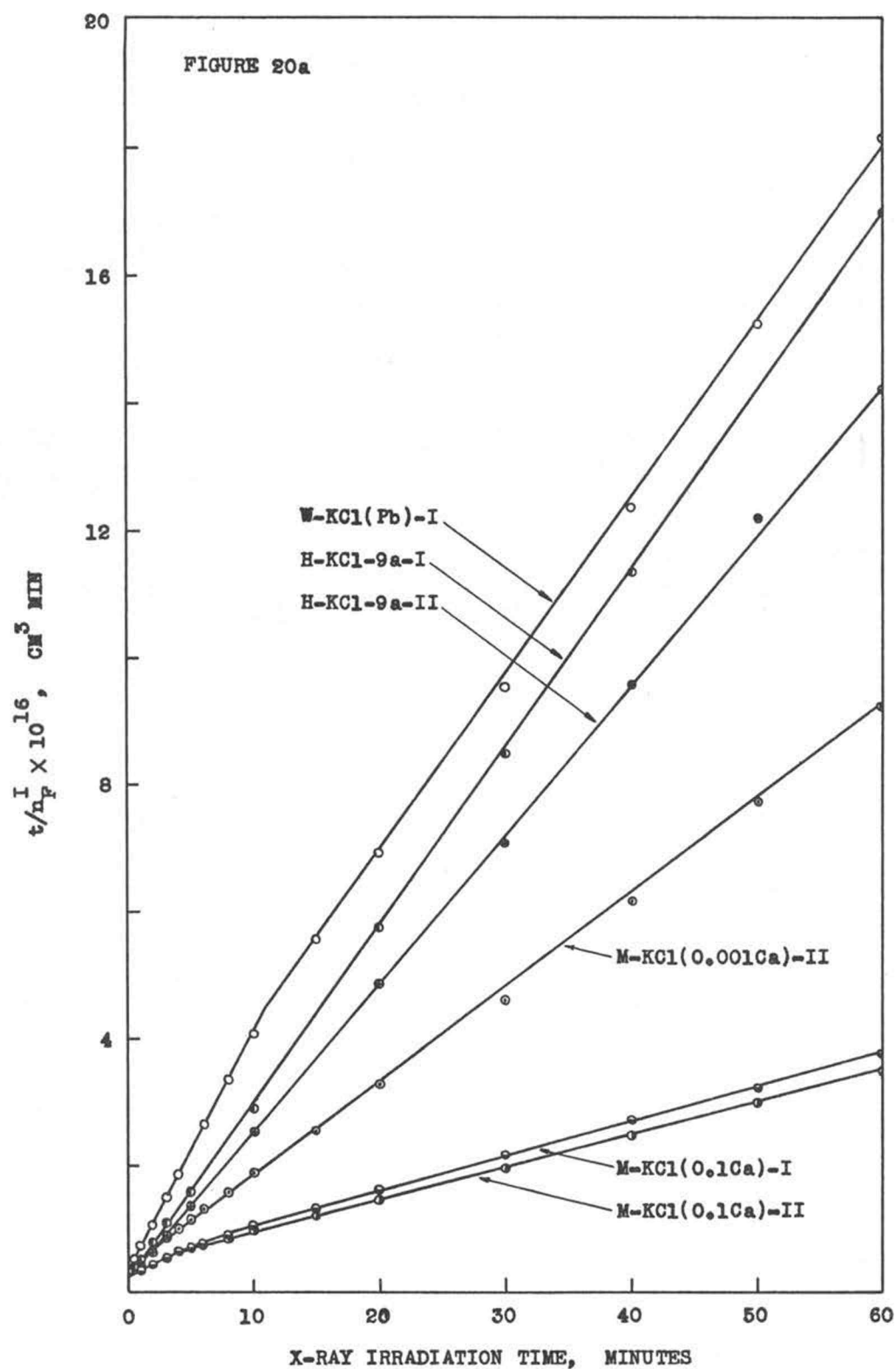
FIGURE 18. INITIAL STAGES OF F-CENTER GROWTH FOR INITIAL X-RAY IRRADIATION SHOWN IN FIGURES 17a AND b.



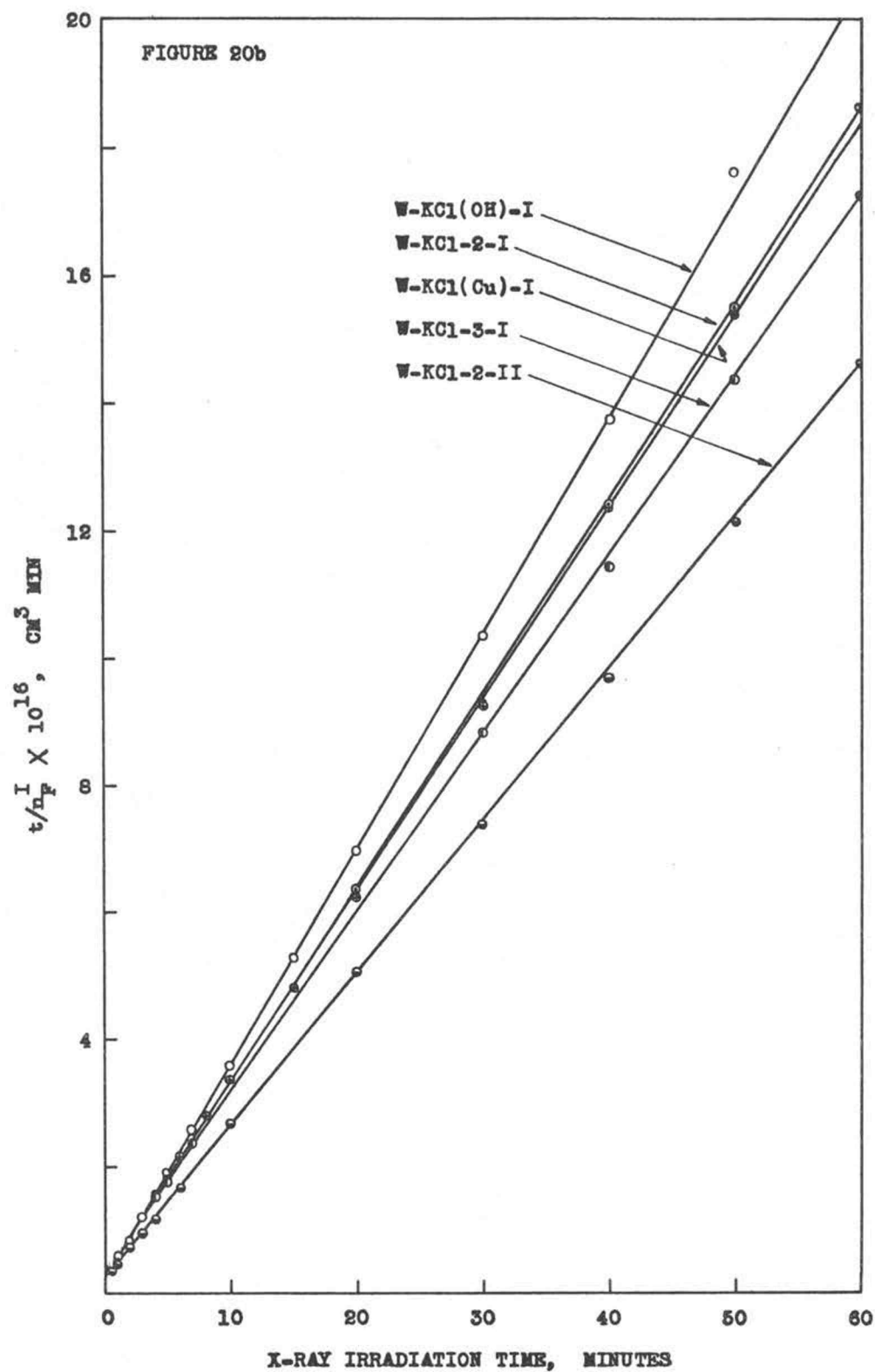


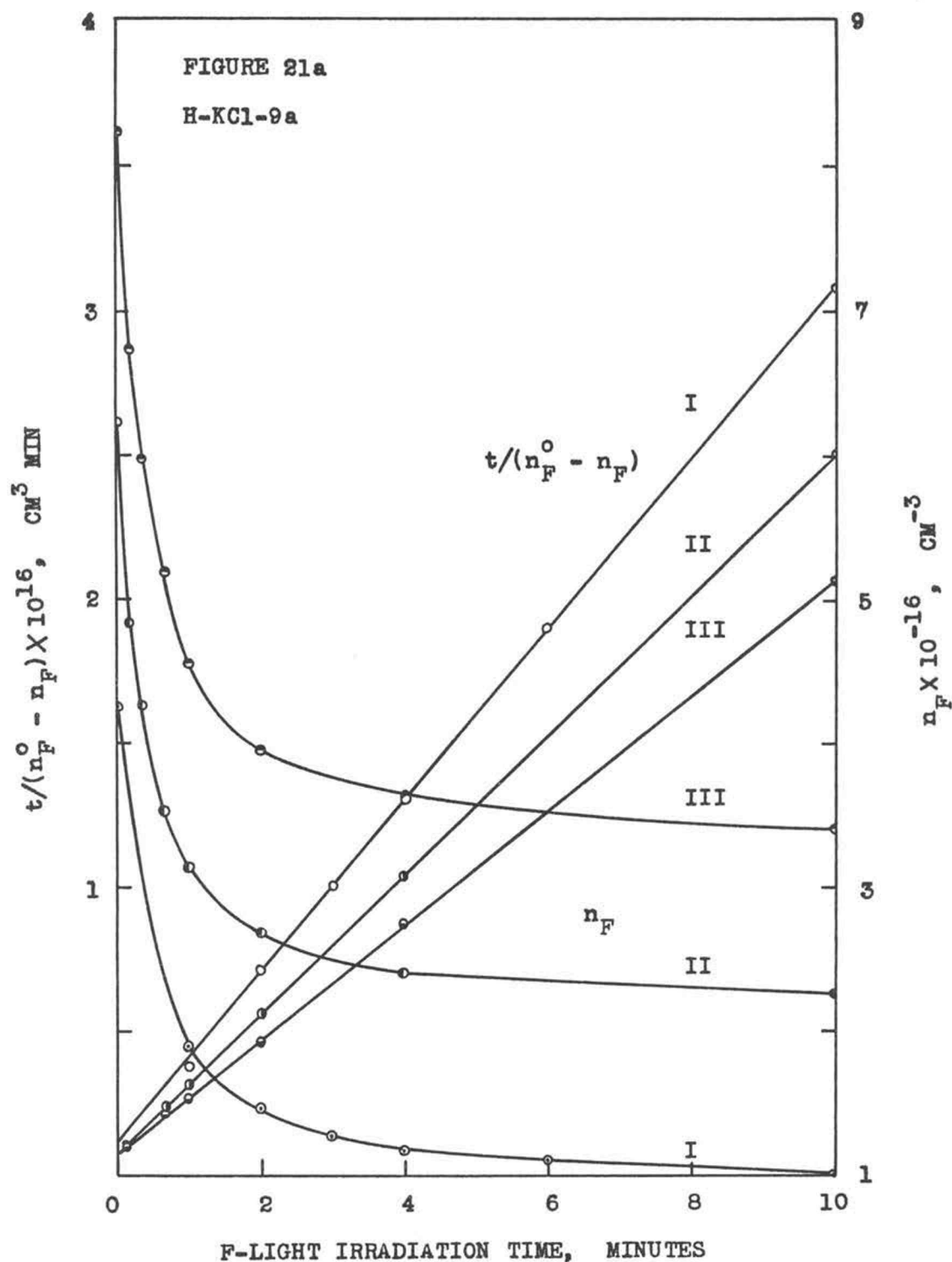
FIGURES 19a AND b. TESTS OF EQUATION (16) FOR F-CENTER GROWTH DURING INITIAL X-RAY IRRADIATION IN VARIOUS KCl CRYSTALS.



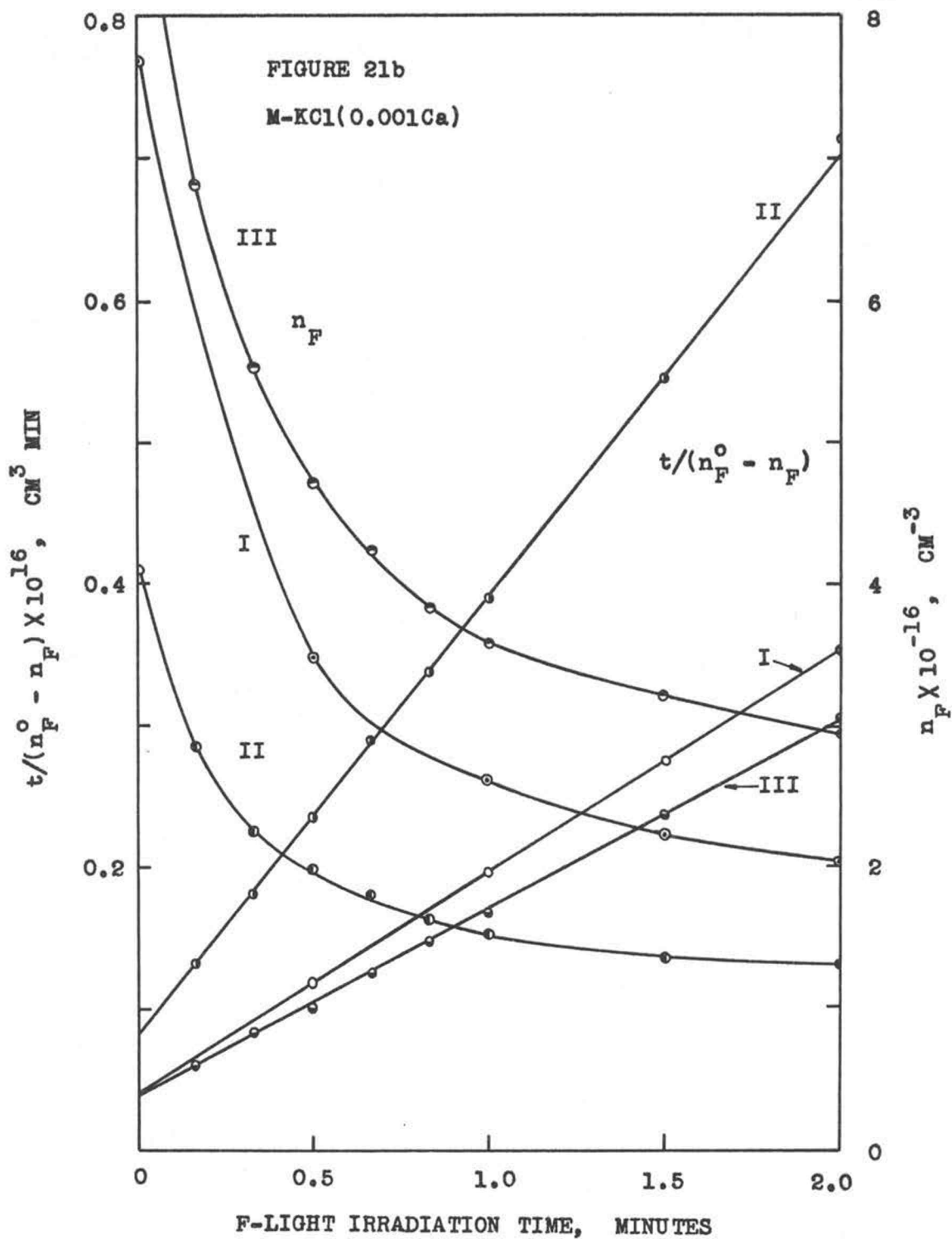


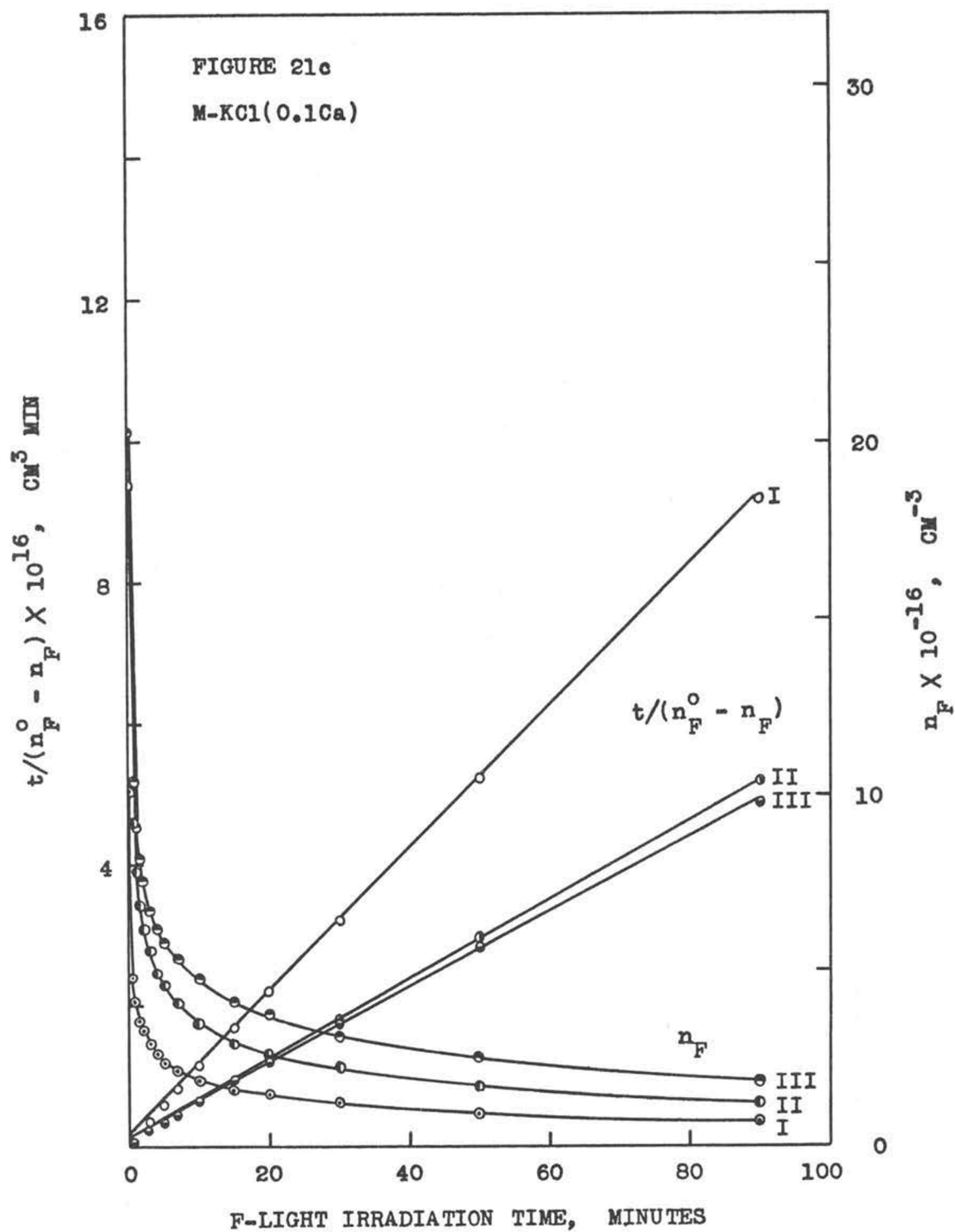
FIGURES 20a AND b. TESTS OF EQUATION(16) FOR F-CENTER GROWTH DURING RE-X-RAY IRRADIATION IN VARIOUS KCl CRYSTALS.

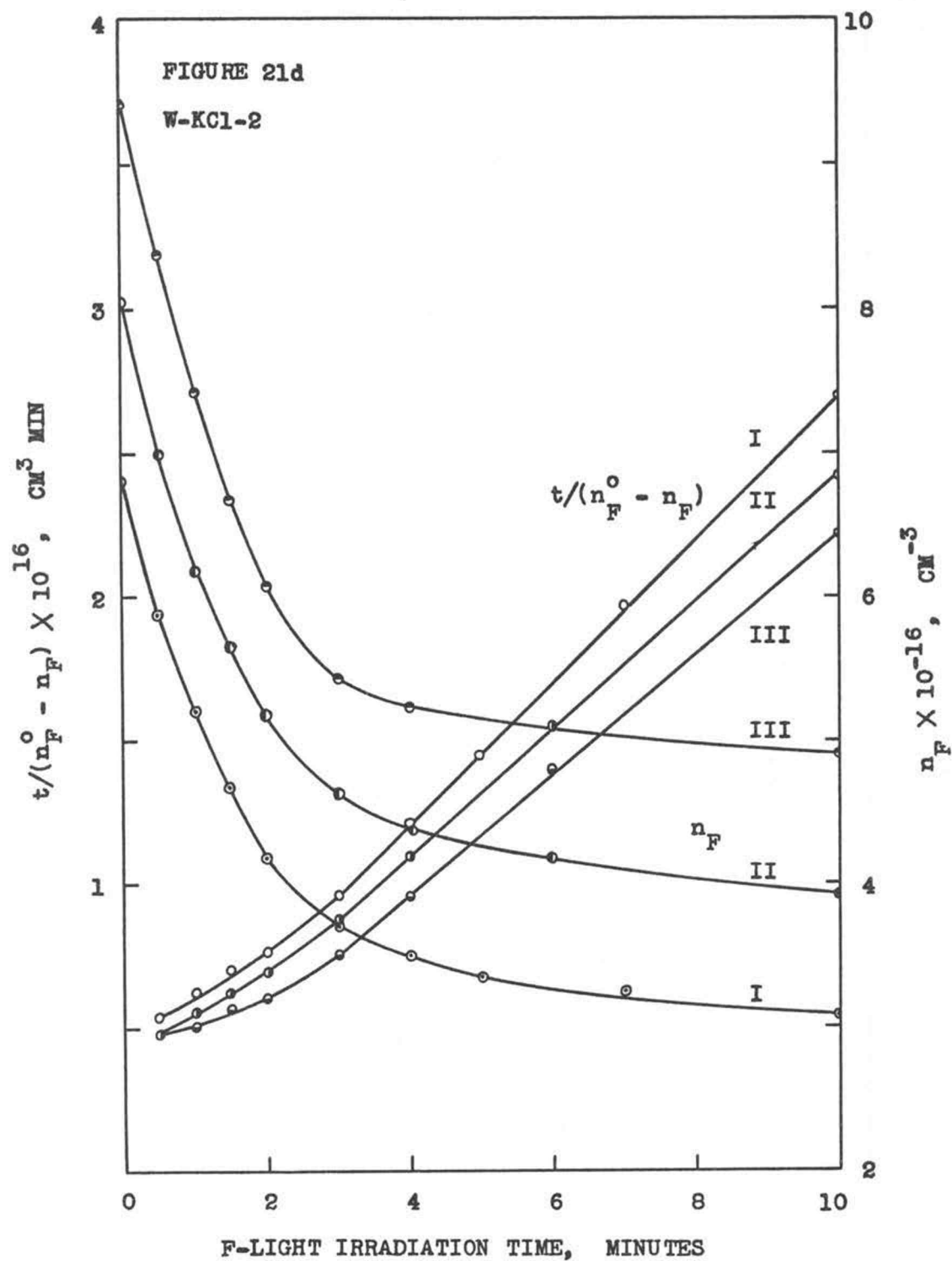




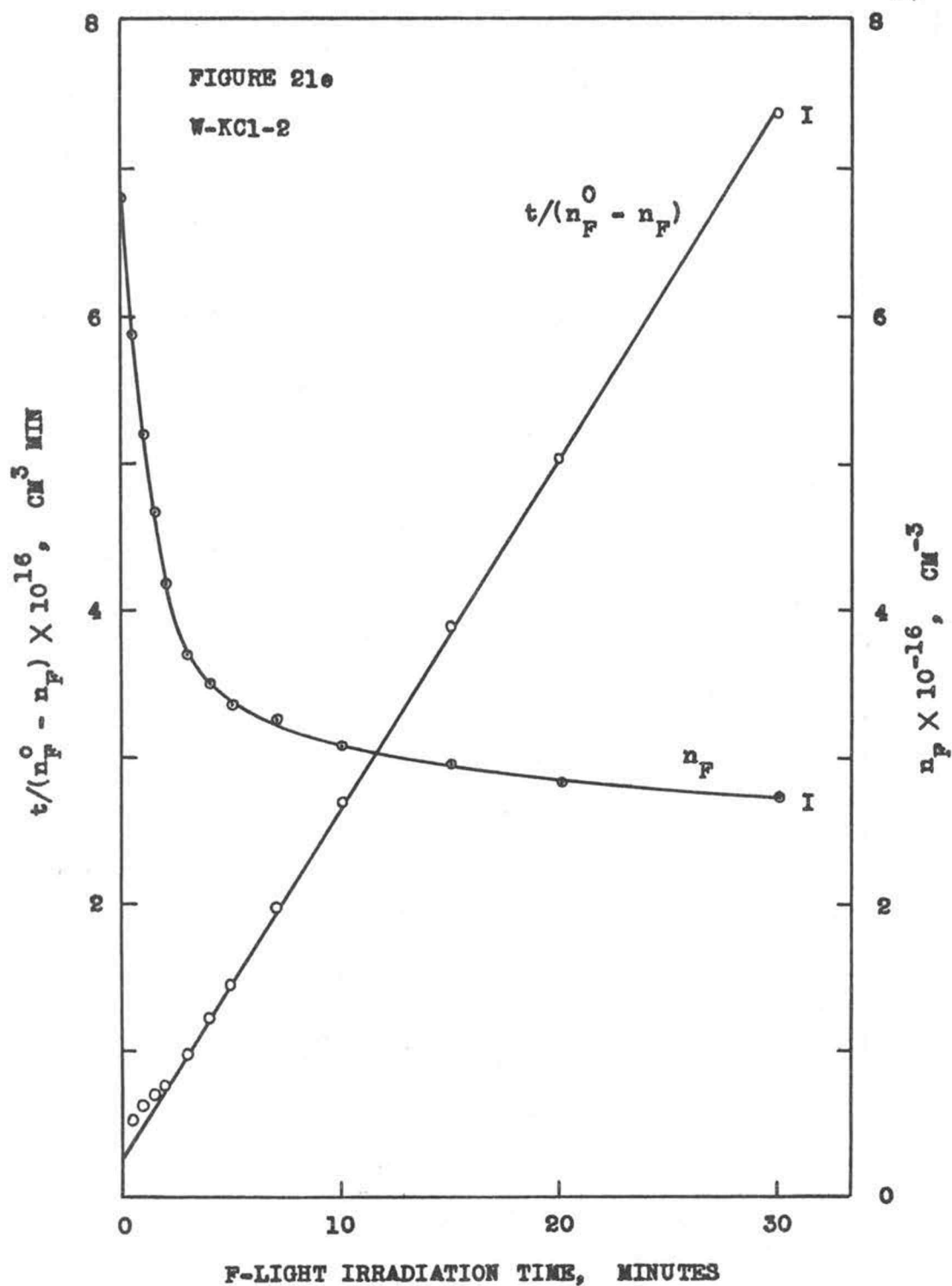
FIGURES 21a TO h. OPTICAL BLEACHING CURVES OF F CENTERS AND TESTS OF EQUATION (18) FOR VARIOUS X-RAYED KCl CRYSTALS.

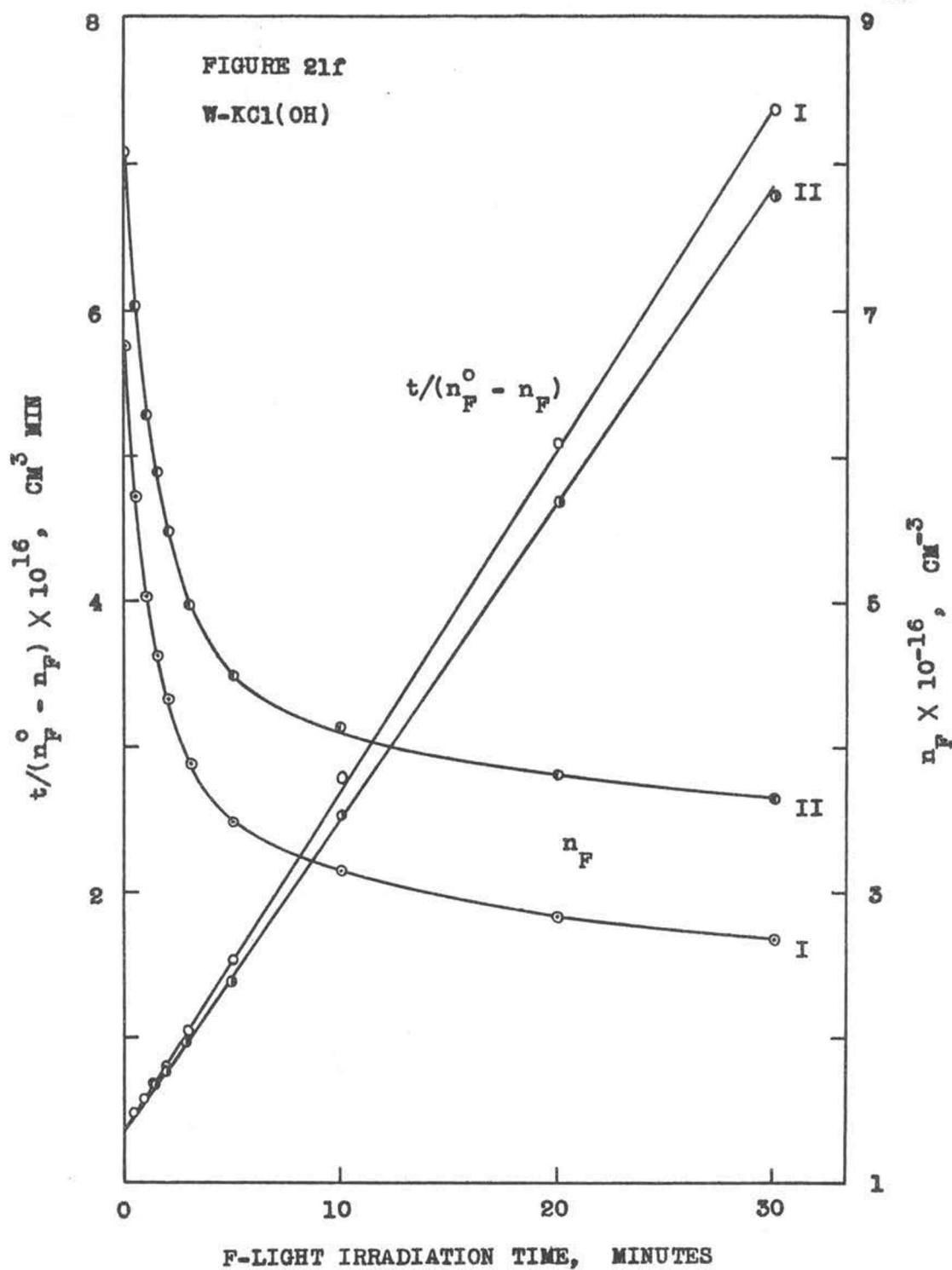


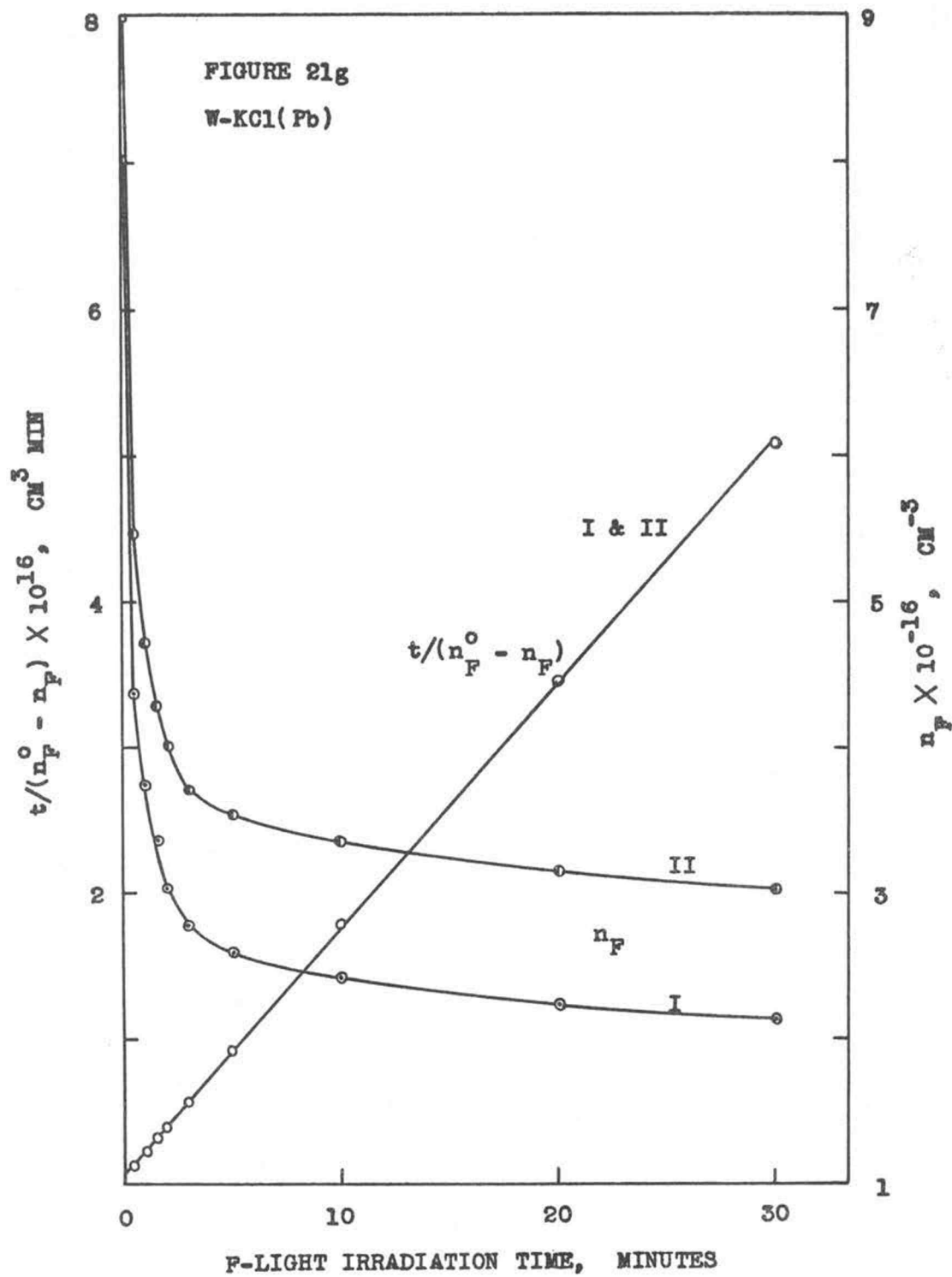


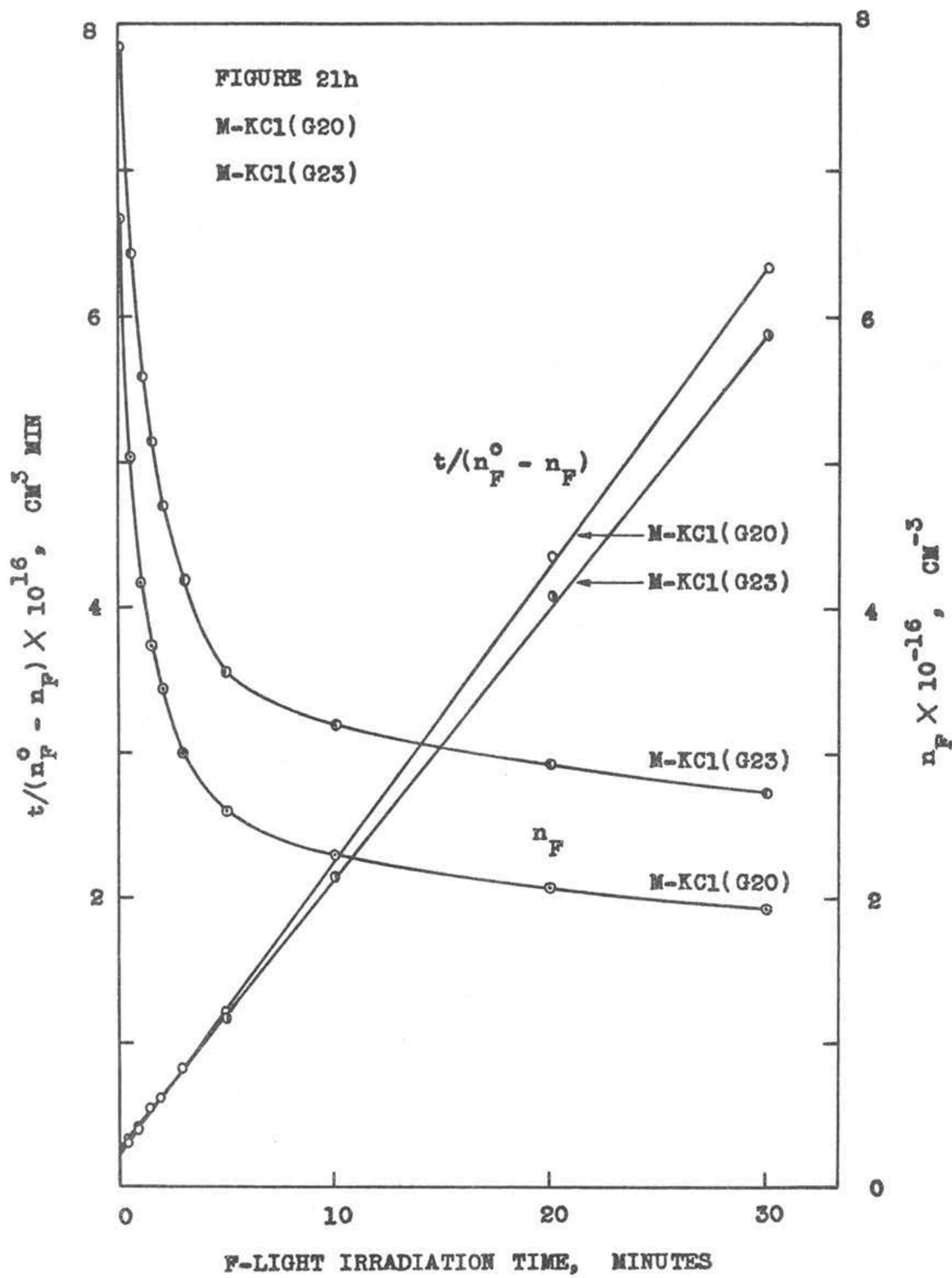












## BIBLIOGRAPHY

1. Akpınar, Sait. Über den Einbauchemisch definierter Zusätze in Alkalihalogenidkristallen. *Annalen der Physik* 37:429-441. 1940.
2. Bron, W. E. Relation between x-ray coloration and optical bleaching of KCl crystals. *The Physical Review* 119:1853-1863. 1960.
3. Buckley, H. E. *Crystal growth*. New York, Wiley, 1951. 571 p.
4. Casler, Ruth, Peter Fringsheim, and Philip Yuster. V-centers in alkali halides. *The Journal of Chemical Physics* 18:1564-1571. 1950.
5. Compton, W. Dale, and Clifford C. Klick. Symmetry of the H centers in KCl and KBr. *The Physical Review* 110:349-353. 1958.
6. de Boer, J. H. The nature of color centers in alkali halide crystals. *Recueil des Travaux Chimiques des Pays-Bas* 56:301-309. 1937. (Abstracted in *Chemical Abstracts* 31:5236-9. 1937)
7. Dexter, D. L. Varley mechanism for defect formation in alkali halides. *The Physical Review* 118:934-935. 1960.
8. Dorendorf, Heinz and H. Pick. Verfärbung von Alkalihalogenidkristallen durch energiereiche Strahlung. *Zeitschrift für Physik* 128:166-171. 1950.
9. Dorendorf, Heinz. Ultraviolette Absorptionsbanden an photochemisch veränderten KCl- und KBr-Kristallen. *Zeitschrift für Physik* 129:317-326. 1951.
10. Doyle, William T. Optical absorption by F centers in alkali halides. *The Physical Review* 111:1072-1077. 1958.
11. Esterman, I., W. J. Leivo and O. Stern. Change in density of potassium chloride crystals upon irradiation with x-rays. *The Physical Review* 75:627-633. 1949.

12. Etzel, H. W. Enhancement of the F- and V-bands in sodium chloride containing calcium. The Physical Review 87:906-907. 1952.
13. \_\_\_\_\_. Detection of vacancies created by x-rays in sodium chloride. The Physical Review 100:1643-1645. 1955.
14. Etzel, H. W. and D. A. Patterson. Optical properties of alkali halides containing hydroxyl ions. The Physical Review 112:1112-1116. 1958.
15. Etzel, H. W. and J. G. Allard. Color center formation in sodium chloride. Physical Review Letters 2:452-454. 1959.
16. \_\_\_\_\_. Optical detection of vacancies created by high-energy radiation in sodium chloride. The Physical Review 116:885-887. 1959.
17. Gibbs, W. E. and W. Clayton. The production of large, clear, cubical crystals of sodium chloride. Nature 113:492-493. 1924.
18. Gordon, R. B. and A. S. Nowick. Structure sensitivity of the x-ray coloration of NaCl crystals. The Physical Review 101:977-983. 1956.
19. Gruzensky, Paul Milnore. Electrical conductivity and ultraviolet absorption spectra of high-purity potassium chloride single crystals. Ph.D. thesis. Corvallis, Oregon State College, 1960. 100 numb. leaves.
20. Gurney, R. W. and N. F. Mott. Conduction in polar crystals. III. On the colour centres in alkali-halide crystals. Transactions of the Faraday Society 34:506-511. 1938.
21. Hardtke, Fred C., Allen B. Scott and Robert E. Woodley. Decrease of F-center photoconductivity upon bleaching. The Physical Review 119:544-549. 1960.
22. Harten, H. U. Zur Wirkung von Röntgenlicht auf KCl-Kristalle. Zeitschrift für Physik 126:619-631. 1949.

23. Herman, Robert and Richard F. Wallis. Optical bleaching of F centers in x-rayed alkali halide crystals. *The Physical Review* 99:435-442. 1955.
24. Hesketh, R. V. The photo creation and destruction of F centers. *The Philosophical Magazine* 4:114-125. 1959.
25. Hilsch, Rudolf. Die Absorptionsspektren einiger Alkali-Halogenid-Phosphore mit Tl- und Pb-Zusatz. *Zeitschrift für Physik* 44:860-870. 1927.
26.                     . Alkali-halide phosphors containing heavy metals. *The proceedings of the Physical Society* 49, Extra Part:40-45. 1937.
27. Hilsch, R. and R. W. Pohl. Einige Dispersionsfrequenzen der Alkalihalogenidkristalle im Schumanngebiet. *Zeitschrift für Physik* 59:812-819. 1930.
28. Howard, R. E. and R. Smoluchowski. Formation of interstitials in alkali halides by ionizing radiation. *The Physical Review* 116:314-315. 1959.
29. Kanzaki, Hiroshi. Dichroism of the F and M bands in KCl. *The Physical Review* 110:1063-1068. 1958.
30. Kittel, Charles. *Introduction to solid state physics*. 2d ed. New York, Wiley, 1956. 617 p.
31. Knox, R. S. Inversion symmetry of the M center. *Physical Review Letters* 2:87-88. 1959.
32. Konitzer, John D. and Jordan J. Markham. Experimental study of the shape of the F-band absorption in KCl. *The Journal of Chemical Physics* 32:843-856. 1960.
33. Kuwabara, Goro and Akira Misu. Luminescence and dichroism of F and M centers in potassium chloride. *Journal of the Physical Society of Japan* 13:1038-1047. 1958.
34. Kyropoulos, S. Ein Verfahren zur Herstellung grosser Kristalle. *Zeitschrift für anorganische und allgemeine Chemie* 154:308-313. 1926.

35.                     . Dielectrizitätskonstanten regulärer Kristalle. Zeitschrift für Physik 63: 849-854. 1930.
36. Lamb, John and W. Dale Compton. Luminescence and symmetry properties of color centers. The Physical Review 106:684-693. 1957.
37. MacMahon, Andrew M. Zur Kenntnis der Alkali-halogenidphosphore mit Kupferzusatz. Zeitschrift für Physik 52:336-341. 1928.
38. Mador, I. L. et al. Production and bleaching of color centers in x-rayed alkali halide crystals. The Physical Review 96:617-628. 1954.
39. Markham, Jordan J. Speculation on the formation of F-centers during irradiation. The Physical Review 88:500-509. 1952.
40. Martienssen, W. and H. Pick. Quantitatives zur Röntgenverfärbung sensibilisierter KBr-Kristalle. Zeitschrift für Physik 135:309-317. 1953.
41. Mentzel, A. Untersuchung des Absorptionsverlaufes von KCl und KBr auf der kurzwelligen Seite ihrer ultraroten Eigenschwingung. Zeitschrift für Physik 88:178-196. 1934.
42. Mitchell, Phillip Vickers. F-center growth in KCl. Ph.D. thesis. Pittsburgh, Pennsylvania, Carnegie Institute of Technology, 1960. 96 numb. leaves. (AT(30-1)-1828 Radiation effects in solids. NYO-2515-unclassified)
43. Mitchell, P. V., D. A. Wiegand and R. Smoluchowski. F-center growth curves. The Physical Review 117: 442-443. 1960.
44. Mott, N. F. and R. W. Gurney. Electronic processes in ionic crystals. 2d ed. London, Oxford University Press, 1953. 275 p.
45. Nowick, A. S. Effect of plastic deformation on the  $\gamma$ -ray coloration. The Physical Review 111:16-25. 1958.
46. Okamoto, Fumio. Symmetry of the M center in KCl. To be published.



47. Pick, H. Farbzentren-Assoziata in Alkalihalogeniden. Zeitschrift für Physik 159:69-76. 1960.
48. Pringsheim, Peter. Fluorescence and phosphorescence of thallium-activated potassium-halide phosphors. Reviews of Modern Physics 14:132-138. 1942.
49. Przibram, Karl. Irradiation colours and luminescence. London, Pergamon, 1956. 332 p. (Tr. by John Espenett Caffyn)
50. Rabin, Herbert. X-ray expansion and coloration of undoped and impurity-doped NaCl crystals. The Physical Review 116:1381-1389. 1959.
51. Rabin, Herbert and Clifford C. Klick. Formation of F centers at low and room temperatures. The Physical Review 117:1005-1010. 1960.
52. Retgers, J. W. Beiträge zur Kenntnis des Isomorphismus. V. XIII. Über den Einfluss fremder Substanzen in der Lösung auf die Form, die Reinheit und die Grösse der ausgeschiedenen Kristalle. Zeitschrift für Physikalische Chemie 9:267-322. 1892.
53. Rolfe, J. Hydroxide absorption band in alkali halide crystals. Physical Review Letters 1:56-58. 1958.
54. Sakaguchi, Kiyokazu and Tokuo Suita. Electrical measurement of numbers of lattice defects produced by x-rays in alkali halide crystals. Technological Reports of Osaka University 2:177-182. 1952. (Abstracted in Chemical Abstracts 47:8448f. 1953)
55. Schulman, James H. Effects of impurities on the coloration of solids by ionizing radiations. The Journal of Physical Chemistry 57:749-752. 1953.
56. Schulman, James H., Robert Ginther and Clifford C. Klick. Some optical properties of lead-activated sodium chloride phosphors. Journal of the Optical Society of America 40:854-862. 1950.
57. Sears, Gerald W. Growth of potassium chloride crystals from aqueous solution. The Journal of Chemical Physics 29:979-983. 1958.

58. Seitz, Frederick. Color centers in alkali halide crystals. Reviews of Modern Physics 18:384-408. 1946.
59. \_\_\_\_\_. Influence of plastic flow on the electrical and photographic properties of the alkali halide crystals. The Physical Review 80: 239-243. 1950.
60. \_\_\_\_\_. Color centers in alkali halide crystals. II. Review of Modern Physics 26:7-94. 1954.
61. Smakula, Alexander. Einige Absorptionsspektren von Alkalihalogenidphosphoren mit Silber und Kupfer als wirksamen Metallen. Zeitschrift für Physik 45:1-12. 1927.
62. \_\_\_\_\_. Über Erregung und Entfärbung lichtelektrisch leitender Alkalihalogenide. Zeitschrift für Physik 59:603-614. 1930.
63. Stockbarger, Donald C. The production of large single crystals of lithium fluoride. Review of Scientific Instruments 7:133-136. 1936.
64. \_\_\_\_\_. Improved crystallization of lithium fluoride of optical quality. Discussions of the Faraday Society no. 5:299-306. 1949.
65. Ueta, Masayasu. On the bleaching of color centers (M-center) in KCl crystal with polarized light. Journal of the Physical Society of Japan 7:107-109. 1952.
66. Ueta, M. and W. Kanzig. Effect of plastic flow upon color centers in alkali halide crystals. The Physical Review 94:1390. 1954.
67. \_\_\_\_\_. Generation of electron traps by plastic flow in alkali halides. The Physical Review 97:1591-1595. 1955.
68. Varley, J. H. O. A mechanism for the displacement of ions in an ionic lattice. Nature 174:886-887. 1954.
69. \_\_\_\_\_. A new interpretation of irradiation-induced phenomena in alkali halides. Journal of Nuclear Energy 1:130-143. 1954.

70. van Doorn C. Z. and Y. Haven. Dichroism of the F and M absorption bands in KCl. The Physical Review 100:753. 1955.
71. \_\_\_\_\_. Absorption and luminescence of colour centres in KCl and NaCl. Philips Research Reports 11:479-488. 1956.
72. van Doorn, C. Z. Anisotropy of colour centres in alkali halides. Philips Research Reports 12:309-323. 1957.