

Expansion of Potassium and Sodium Chloride Crystals Due to X-Ray Irradiation of Weak Intensities*†

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Rectangular cleaved samples of potassium and sodium chloride crystals having dimensions of about $12 \times 10 \times 1.5$ mm were irradiated for times up to three hours with x-rays (48 kv at 18 ma) from a molybdenum target tube passing through a beryllium window at room temperature in air and in helium atmospheres. The crystals were placed in a thermostatted enclosure regulated to within 0.01°C . The crystals were about $2\frac{1}{4}$ in. from the x-ray tube beryllium window. The change in length of the largest dimension of the crystal was measured during and after the irradiation by a capacitance-type dilatometer with a sensitivity of 10^{-8} cm. A series of measurements were carried out employing different times of irradiation and it was found that the relation between the relative linear expansion of the crystal and the optically determined average concentration of F -centers was linear with a

constant of proportionality remarkably close to the value of $d^3/12$, where d is the lattice constant of the crystal. There was a time delay of about 20–30 minutes before the expansion could be detected. This time delay was increased by plastic deformation. The results did not depend on the fraction of the crystal volume which was irradiated. The rate of formation of a certain F -center concentration in the irradiated portion of the crystal was directly proportional to the fraction of the volume exposed to the irradiation. In partially irradiated crystals, the rate of formation of F -centers in the nonirradiated portion upon subsequent irradiation was greatly increased by the presence of the adjacent irradiated part. The merits of possible models to explain these results are discussed.

IT is well known that the irradiation of alkali halide crystals with x-rays results in the formation of a large number of F -centers. At the same time a decrease in the density and an increase in the dimensions of the crystal upon x-ray irradiation has been observed by Estermann, Leivo and Stern,¹ Sakaguchi and Suita,² and Witt.³ This change in density or the expansion of the crystal is generally associated with the formation of vacancies upon x-ray irradiation. The aforementioned experiments, however, gave only qualitative and somewhat inconsistent results. It was thought that the inconsistencies may be due to the high x-ray intensities employed in these experiments which resulted in the rapid formation of a very large number of F -centers and vacancies. This paper is concerned with a study of the effect of x-ray irradiations of weak intensities, which cause the slow formation of F -center concentrations of less than $10^{17}/\text{cc}$, on the linear dimensions of KCl and NaCl single crystals. It was hoped that such experiments would yield somewhat more quantitative and consistent results and thus would enhance our knowledge of the mechanism by which alkali halide crystals expand upon x-ray irradiation.

I. LINEAR EXPANSION OF THE CRYSTAL AS A FUNCTION OF TIME OF X-RAY IRRADIATION

Experimental Procedure

The experiments were performed on thin rectangular slabs, cleaved from single crystals of NaCl and KCl obtained from the Harshaw Chemical Company. The direction of the x-ray beam was perpendicular to the largest (100) face, i.e., parallel to the thinnest dimension of the specimen. The dimensions of the samples used were approximately $12 \text{ mm} \times 10 \text{ mm} \times 1.5 \text{ mm}$.

The linear expansion of the crystals was measured by determining the change in capacitance of a parallel plate air capacitor, one plate of which was partly supported by the sample (Fig. 1). The plates P_1 and P_2 of the air capacitor were made of invar; the space between these two plates was about 10^{-2} cm. The diameters of the upper and lower plates P_1 and P_2 were approximately $1\frac{1}{2}$ inches and 1 inch, respectively, and their thickness was $\frac{1}{8}$ inch. The upper and larger plate was supported by three invar legs resting on a "Mykroy" plate. The lower plate P_2 was supported by two invar legs and the crystal specimen S , which were placed on the same "Mykroy" plate. For calibration purposes, the lower plate rested also on an auxiliary leg l which was connected to a screw of 40 threads per inch fastened to the prism table of a spectrometer. With this arrangement, the screw could be turned through very small angles and the angles read to great accuracy on the spectrometer scale. The change of capacity of the air capacitor was detected by an ac capacitance bridge (proximity meter⁴), and recorded on a Brown "Elektronik" recorder. Before each experiment, the apparatus was calibrated mechanically by turning the screw mounted on the spectrometer plate through

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‡ Now at Sylvania Electric Products, Inc., Bayside, Long Island, New York.

¹ Estermann, Leivo, and Stern, *Phys. Rev.* **75**, 627 (1949).

² K. Sakaguchi and T. Suita, *Tech. Repts. Osaka Univ.* **2**, 177 (1952).

³ H. Witt, *Nachr. Akad. Wiss. Gottingen Math.-Phys. Kl. II A*, 17 (1952).

⁴ Changes in capacitance as small as $0.001 \mu\text{mf}$ can be detected with this instrument.

known amounts. The calibration was further checked by measuring the known coefficient of thermal expansion of these crystals. The mechanical and thermal calibrations agreed with each other to within about 1%. Expansions down to 4.3×10^{-8} cm could be measured directly with this instrument by estimating the scale of the proximity meter to one-fourth of each division. However, when the meter was replaced by a Brown recorder, expansions of 10^{-8} cm could be detected.

In order to eliminate thermal expansion effects, the sample condenser was surrounded by a furnace, and the temperature in this furnace was regulated to better than 0.01°C by a temperature control unit. The apparatus shown in Fig. 1 and the x-ray tube were placed in a box, which was thermostatically controlled to within 0.1°C . After the crystal was inserted in the apparatus in the proper position and the proximity meter calibrated, the entire unit was stabilized to within 0.01°C at a temperature about 2°C above room temperature, while the cooling water of the x-ray machine was kept running continuously. In the runs reported on in this paper it is believed that the temperature remained constant to within 0.001°C . The x-rays were produced from a molybdenum target tube (48 kv at 18 ma) and entered the unit through the window *W* which was made of a piece of ceramic tube $1\frac{1}{8}$ inches long and 1 inch in outside diameter. Both ends of the tube were closed with beryllium sheets and the crystal was placed $2\frac{1}{4}$ inches from the window of the x-ray tube. The beam was kept on for a period of 2 to 3 hours. After the x-rays were turned off, the recorder was kept in operation for another hour and the cooling water of the x-ray unit kept running, in order to check whether any heating effects had occurred.

The linear expansion was measured as a function of the time of x-ray irradiation along either one of the large dimensions. In our experimental arrangement, irradiation of the order of two hours resulted in a linear expansion Δl of approximately 5×10^{-7} cm and thus in a strain $\Delta l/l$ of 5×10^{-7} .

Most of the experiments were carried out in air, but in order to exclude the possibility of the oxidation of the crystal surfaces in our experiments two KCl crystals were also tested in a helium atmosphere. For these experiments, the whole dilatometer was surrounded with a plastic bag with an inlet and an outlet opening. The bag was kept inflated with helium while a small amount was bled from the outlet. The helium gas was exposed to phosphorous pentoxide before and during the irradiation in order to absorb any water vapor present in the helium gas.

Results

A typical curve for the expansion along one of the large dimensions as a function of the time of x-ray irradiation is shown for NaCl in Fig. 2 and for KCl in Fig. 3. It can be seen from these curves that there was

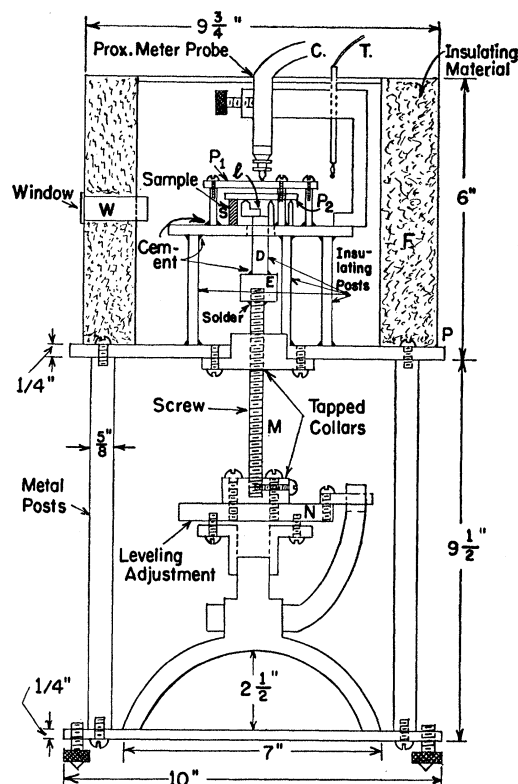


FIG. 1. Diagram of dilatometer.

a time lag of the expansion of about 20 minutes for KCl crystals and one-half hour for NaCl crystals, respectively. When the x-rays were turned off, the expansion was found to continue for about six minutes in both KCl and NaCl crystals. Six minutes after the x-rays were turned off, the crystal did not expand any more. This effect and the time lag in the expansion were independent of the fraction of the crystal volume exposed to the irradiation. Since the intensity of the x-ray beam in the two experiments shown in Figs. 2 and 3 was

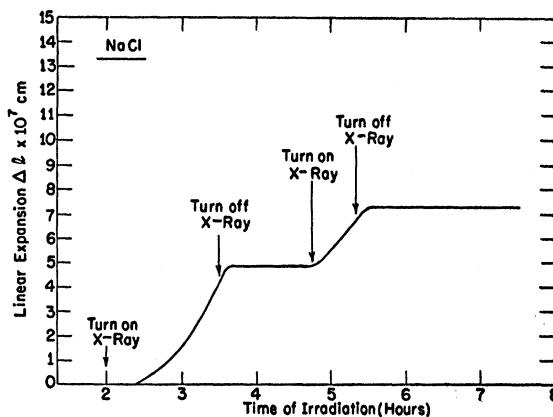


FIG. 2. Linear expansion of a NaCl crystal as a function of the time of x-ray irradiation in air.

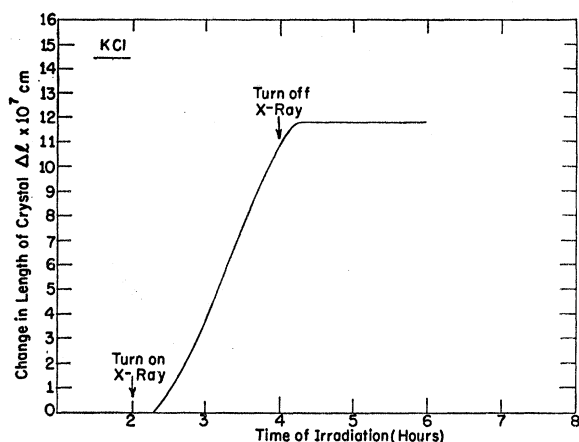


FIG. 3. Linear expansion of a KCl crystal as a function of the time of x-ray irradiation in air.

approximately the same, it is possible to compare the rates of expansion of KCl and NaCl upon x-ray irradiation directly from the curves. The results show clearly that the rate of expansion in KCl is larger than in NaCl. The curve of expansion *vs* time of x-irradiation for a KCl sample in an atmosphere of helium is shown in Fig. 4. Because of the different experimental arrangement in this experiment, the intensity of the x-ray irradiation was not the same as that applied in the experiments in air, and a comparison of the absolute values of the curve shown in Fig. 4 with those in Fig. 3 is no longer possible. It can be seen, however, that the general behavior of the expansion as a function of the time of irradiation is not altered by carrying out the experiment in a helium atmosphere.

II. RELATION BETWEEN THE RELATIVE LINEAR EXPANSION OF THE CRYSTAL AND THE AVERAGE CONCENTRATION OF *F*-CENTERS

Experimental Procedure

It is interesting to compare the relative linear expansion after a certain time of x-ray irradiation with the

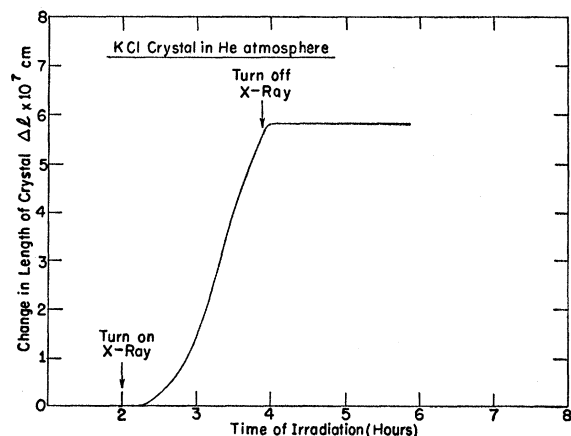


FIG. 4. Linear expansion of a KCl crystal as a function of the time of x-ray irradiation in helium.

F-center concentration present at that time. The average *F*-center concentration was measured with a Beckman spectrophotometer by determining the absorption coefficient due to the *F*-centers. From a measurement of the percentage transmission of the uncolored and colored crystals as a function of the wavelength, the absorption coefficient at the maximum of the *F*-band and the width of the *F*-band at the half-maximum could be determined and the number of *F*-centers per cm³ calculated from Smakula's equation⁵:

$$n_0 f = 1.31 \times 10^{17} \frac{n}{(n^2 + 2)^2} \alpha_m W,$$

where *f* is the oscillator strength of the absorbing centers, *n* is the index of refraction of the crystal, α_m is the absorption at the maximum of the *F*-band, *W* is the width at the half-maximum of the *F*-band, and *n*₀ is the number of *F*-centers per cm³. The oscillator

TABLE I. Relative linear expansion and average *F*-center concentration in NaCl crystals after x-ray irradiation for a certain length of time. In experiments in which only part of the crystal was irradiated, the *F*-center concentration applies to the irradiated part only. Volume of unit cell = $d^3 = 178 \times 10^{-24}$ cm³; $d^3/12 = 14.8 \times 10^{-24}$ cm³.

| Dimension of crystal (<i>l</i> ₁ × <i>l</i> ₂ × <i>l</i> ₃) cm ³ | Percentage of area irradiated | Linear strain ($\Delta l/l$) _t | Av. <i>F</i> -center concentration <i>n</i> ₀ (cm ⁻³) | ($\Delta l/l$) _t / <i>n</i> ₀ cm ³ |
|--|-------------------------------|---|--|---|
| 1.200 × 0.950 × 0.162 | 70 | 8.3 × 10 ⁻⁷ | 5.2 × 10 ¹⁶ ^a | 15.9 × 10 ⁻²⁴ |
| 1.195 × 0.975 × 0.250 | 70 | 5.8 × 10 ⁻⁷ | 3.8 × 10 ¹⁶ | 15.3 × 10 ⁻²⁴ |
| 1.200 × 0.950 × 0.170 | 70 | 6.1 × 10 ⁻⁷ | 3.9 × 10 ¹⁶ | 15.5 × 10 ⁻²⁴ |
| 0.745 × 0.910 × 0.175 | 100 | 8.5 × 10 ⁻⁷ | 5.5 × 10 ¹⁶ ^b | 15.4 × 10 ⁻²⁴ |

^a Spectrophotometer measurement was made about 20 days after the irradiation and expansion measurement; hence *n*₀ is probably too small.

^b This crystal was supplied by J. H. Schulman of the Naval Research Laboratory. All other crystals were supplied by the Harshaw Chemical Company.

strength *f* was taken as 0.81⁶ and 0.77 for KCl and NaCl, respectively.

The average *F*-center concentration was measured as soon as possible after the x-ray beam was turned off and the linear strain determined. Care was taken to avoid bleaching during the transfer of the sample from the dilatometer to the Beckman spectrophotometer. In some of these experiments the whole area of the largest (100) face of the crystal was uniformly irradiated; in other experiments part of the area was shielded by a lead sheet so that only 70% to 40% of the area was irradiated. When only part of the area was irradiated, the irradiated part of the crystal was closest to the capacitor plate of the dilatometer.

Results

The results for NaCl are shown in Table I and for KCl in Table II. In these tables, ($\Delta l/l$)_t at a certain

⁵ A. Smakula, Z. Physik 59, 603 (1930).

⁶ F. A. Kleinschrod, Ann. Physik 27, 97 (1936).

⁷ F. Seitz, Revs. Modern Phys. 18, 384 (1946).

time t is the linear strain along one of the largest dimensions after a certain time of x-ray irradiation, while n_0 is the concentration of F -centers in the *colored portion* of the crystal, (i.e., in the part of the area exposed to the x-ray beam) which was determined immediately after the irradiation in the expansion measurement. The concentration of F -centers was found to be uniformly distributed throughout the whole colored area. In order to obtain reproducible results, it was necessary to employ rather thin specimens since in thicker samples the distribution of F -centers produced by the irradiation was very nonuniform throughout the thickness of the crystal.

The degree of uniformity of the concentration of the F -centers through the thickness of the crystals could be tested by cleaving a 2-mm thick irradiated crystal, perpendicular to the thickness dimension, into two pieces, each having a thickness of approximately 1 mm, and measuring the average F -center concentration in

TABLE II. Relative linear expansion and average F -center concentration in KCl crystals after x-ray irradiation for a certain length of time. In experiments in which only part of the crystal was irradiated, the F -center concentration applies to the irradiated part only. Volume of unit cell = $d^3 = 247 \times 10^{-24}$ cm³; $d^3/12 = 2.06 \times 10^{-23}$ cm³.

| Dimensions of crystals ($l_1 \times l_2 \times l_3$) cm ³ | Percentage of area irradiated | Linear strain ($\Delta l/l$) _t | Av. F -center concentration n_0 (cm ⁻³) | ($\Delta l/l$) n_0 cm ³ |
|---|-------------------------------------|---|---|---|
| 1.200 × 0.960 × 0.145 | 70 | 1.36×10^{-6} | 6.7×10^{16} | 2.03×10^{-23} |
| 1.200 × 0.965 × 0.145 | 70 | 8.8×10^{-7} | 4.3×10^{16} | 2.05×10^{-23} |
| 1.190 × 0.980 × 0.145 | 70 | 8.3×10^{-7} | 4.0×10^{16} | 2.07×10^{-23} |
| 0.745 × 0.900 × 0.145 | 100 | 4.3×10^{-7} | 2.0×10^{16} | 2.15×10^{-23} |
| 0.780 × 0.900 × 0.145 | 100 | 2.4×10^{-7} | 1.1×10^{16} | 2.14×10^{-23} |
| 1.225 × 0.930 × 0.140 | 39 | 3.4×10^{-7} | 1.6×10^{16} | 2.12×10^{-23} |
| 1.217 × 0.940 × 0.188 | 73 | 4.2×10^{-7} | 2.0×10^{16} | 2.10×10^{-23} |
| 1.225 × 1.50 × 0.190 | 70 | 4.8×10^{-7} | 2.2×10^{16} a | 2.16×10^{-23} |
| 1.211 × 0.755 × 0.205 | 70 | 6.3×10^{-7} | 3.0×10^{16} a | 2.10×10^{-23} |

a These experiments were performed in an atmosphere of helium.

each of the two slabs. The average concentration of F -centers in the slab closest to the x-ray source was 5.56×10^{16} cm⁻³, while in the piece further from the x-ray source it was 5.53×10^{16} cm⁻³. It can, therefore, be safely concluded that in our experiments with thin samples (less than 2 mm in thickness) the distribution of F -centers throughout the whole crystal was not far from uniform.

In all our experiments, the intensity and the time of irradiation was so low that the F -center concentration produced by the irradiation never exceeded 10^{17} cm⁻³. For larger concentrations the results described below were found to be no longer valid.

It can be seen from these tables that the average concentration of the F -centers in the colored portion is directly proportional to the relative linear expansion for both NaCl and KCl crystals (Figs. 5 and 6). The constant of proportionality does not appear to depend on the percentage of the area of the crystal which was irradiated, if n_0 is taken as the average F -center con-

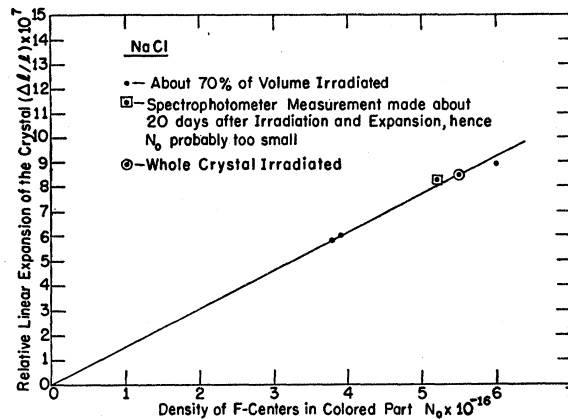


FIG. 5. Relative linear expansion of NaCl crystals as a function of the average F -center concentration.

centration of the colored part only. From Fig. 5, the slope of the straight line [i.e., the average value of $(\Delta l/l)/n_0$] is 15.5×10^{-24} cm³ for NaCl and from Fig. 6, 2.10×10^{-23} cm³ for KCl. These two values agree to within 5% with the values of $d^3/12$, where d is the lattice constant of the crystals. The significance of this result will be discussed below. The results did not depend on whether the experiments were carried out in air or in helium.

III. INFLUENCE OF BLEACHING ON THE CRYSTAL DIMENSIONS

Experimental Procedure

The bleaching experiments were carried out with light in the F -band (560 m μ for KCl and 450 m μ for NaCl). The apparatus was set up as for the expansion experiments except that a crystal previously colored by x-rays was used instead of a virgin piece. The sample was kept in the dark until the thermal steady state was reached. The shutter was then opened and the light was turned on. In order to test whether any heating effects had occurred during the illumination, the light

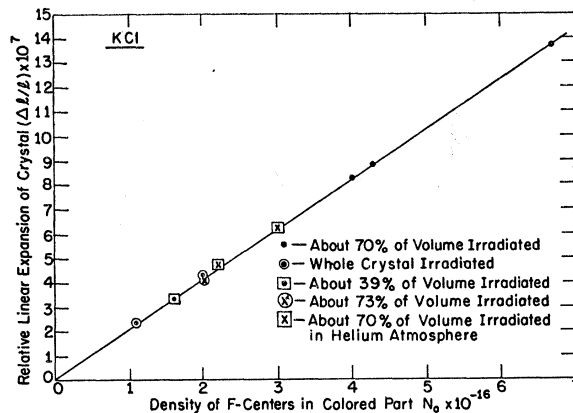


FIG. 6. Relative linear expansion of KCl crystals as a function of the average F -center concentration.

was turned off after fifteen minutes and the crystal was kept in the dark for fifteen minutes before the light was turned on again. After another fifteen minutes of illumination, the light was finally turned off and the Brown recorder was kept running for another hour to observe whether any heating effect had occurred in the crystal.

Results

No change in dimensions was observed when an x-irradiated crystal was subsequently bleached with light in the F -band, although the F -center concentration was thus reduced from about 10^{17} cm^{-3} to less than 10^{15} cm^{-3} .

IV. FORMATION OF F -CENTERS AS A FUNCTION OF THE TIME OF X-RAY IRRADIATION

A single crystal of KCl ($12 \times 8 \times 1.5$ mm) was placed in the dilatometer and the average density of F -centers in the colored portion was determined as a function of the time of irradiation. The F -center concentration was determined for times of irradiation of 20, 40, 65, and 90 minutes, with a fresh piece of KCl crystal being used for each experiment in order to reduce bleaching effects. The result is shown in Fig. 7. It can be seen that the rate of formation of F -centers increases steadily with the time of irradiation, until after about 40 minutes of irradiation an approximately linear dependence of the average concentration of F -centers on the time of irradiation is reached, corresponding to a maximum rate of formation of F -centers.

V. RATE OF FORMATION OF F -CENTERS IN PARTIALLY IRRADIATED CRYSTALS

As will be discussed later, the fact that the relative linear expansion, in experiments in which only part of the crystal was irradiated, was proportional to the average density of F -centers in the colored portion of the crystal but not to the concentration of F -centers averaged over the entire crystal, suggests that a large

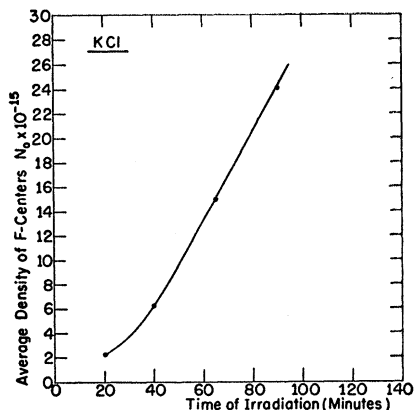


FIG. 7. F -center concentration as a function of the time of x-ray irradiation.

number of vacancies were also present in the nonirradiated portion during the x-ray irradiation, although F -centers were formed only in the irradiated part.

This fact could be qualitatively verified by an experiment in which a KCl crystal of the same dimensions as that employed in the previous experiments was placed 10 cm away from the x-ray source and irradiated for 30 minutes with half of the exposed surface area shielded by a lead sheet. The average F -center density within the colored portion was then measured to be $1.18 \times 10^{16}/\text{cc}$. Using a fresh KCl crystal of the same dimensions, half of the crystal was again irradiated for 30 minutes, but the irradiated half was then covered with a lead sheet, while the other half was irradiated with x-rays for 30 minutes under identical conditions. The average F -center concentration over this portion of the crystal was then determined and found to be $2.1 \times 10^{16}/\text{cc}$, showing an increase of about 75% which was apparently caused by the preirradiation of the adjacent portion.

The rate of formation of F -centers in the irradiated part was also studied as a function of the percentage of the surface exposed to the x-irradiation. Three pieces of KCl crystal, of approximately the same dimensions as the other crystals, were irradiated with the same intensity of x-rays for the same lengths of time. In this experiment the crystal was placed only about 3 cm from the x-ray source and quantitative comparisons between this and the previous experiments are thus impossible. The time of irradiation was of the order of 30 minutes. In one crystal 70% of the largest face was irradiated, while on the other two crystals, the percentage area irradiated was 52% and 32%, respectively. The x-ray beam was again perpendicular to the largest face, and the average F -center concentration was determined immediately after irradiation. The results are shown in Fig. 8. This demonstrates clearly that the average F -center concentration in the colored part is directly proportional to the percentage of the area which was irradiated and hence that the rate of formation per unit volume of the F -centers increases linearly as the irradiated area is increased.

VI. EFFECT OF PLASTIC DEFORMATION ON THE TIME LAG OF THE EXPANSION

It is shown in Figs. 2 and 3 that the expansion upon x-ray irradiation does not start until a certain time after the irradiation has been applied. The effect of plastic deformation on this time lag has been investigated by experiments with deformed crystals. Crystals of KCl of approximately the same dimensions were compressed in a vise to produce a uniform linear plastic deformation of from 3 to 7%. The time lag of the expansion in these deformed crystals was then investigated under identical conditions. The results are shown in Table III. This shows very clearly that the time lag is greatly increased by plastic deformation.

VII. DISCUSSION

The observed results were very sensitive to the intensity of the x-ray irradiation which in all experiments, with one exception (see Fig. 8 and Sec. V), was very low. For reasons as yet not completely understood, the linear relation between the relative linear expansion and the average concentration of F -centers could only be observed when this condition was fulfilled, and when the total concentration of F -centers was kept below $10^{17}/\text{cc}$. For this reason it is impossible to compare our results quantitatively with those of other workers¹⁻³ who measured the expansion or the change in density with x-ray irradiation of high intensities accompanied by the formation of large F -center concentrations. In particular, the expansion experiments of Sakaguchi and Suita² were carried out with thick crystals (leading to a much larger concentration of F -centers near the surface than within the volume of the crystal) and extremely high x-ray intensities. The relative linear expansions measured by Sakaguchi and Suita were of the order of 10^{-5} , while the maximum relative linear expansion in the experiments described in this paper was only 10^{-6} .

TABLE III. Effect of plastic deformation on the initial time delay in the expansion of x-ray irradiated KCl crystals.

| Deformation (percent) | Initial time delay (minutes) |
|-----------------------|------------------------------|
| 0 | 20 |
| 3 | 60 |
| 5 | 75 |
| 7 | 120 |

It is generally accepted that the formation of F -centers in alkali halide crystals upon x-ray irradiation is due to the trapping of excited electrons at negative-ion vacancy sites.¹⁻³ However, the formation of F -center concentrations of more than $10^{16}/\text{cc}$ after irradiation, even at liquid air temperature, which is much larger than the equilibrium concentration of vacancies at such temperatures, strongly indicates that vacancies are created during the irradiation through some secondary process probably in the form of positive- and negative-ion vacancy pairs which subsequently disassociate when an electron is trapped at a negative-ion vacancy site. It has been suggested that the sources of these vacancies could be the surface of the crystal,¹ voids,⁸ the surfaces of small cubes responsible for the small-angle mosaic structure,⁹ or dislocations,¹⁰ which may also be associated with the small-angle mosaic structure.^{10,11} It seems most reasonable to attribute the expansion of the crystal upon x-ray irradiation to these vacancies.

⁸ M. E. Straumanis, *Am. Mineralogist* **38**, 662 (1953).

⁹ R. Furth and S. P. E. Humphreys Owen, *Nature* **167**, 715 (1951).

¹⁰ F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

¹¹ C. R. Berry, *Phys. Rev.* **97**, 676 (1955).

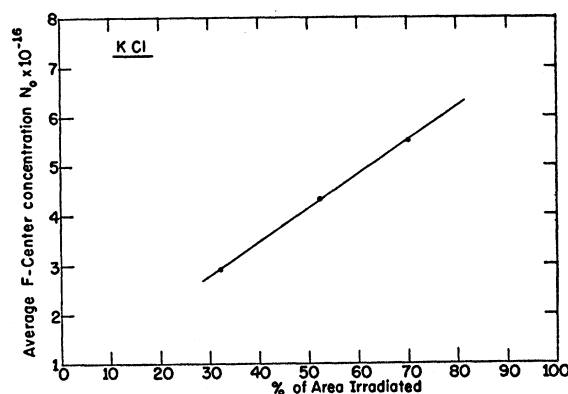


FIG. 8. Average concentration of F -centers in the colored portion of a KCl crystal as a function of the percentage of the volume irradiated.

It is easy to show that the linear relationship between the average F -center concentration and the resulting strain with the experimentally observed proportionality constant can be expected, if it is assumed that each vacancy pair created by the x-irradiation produces a volume increase equal to its own volume (or that of the ion pair which it has replaced) uniformly distributed over all the crystal faces, thus leading to an isotropic linear strain. If the vacancies initially present are only a small fraction of the vacancies created by the x-rays, each F -center formed during the irradiation should correspond, to a first order of approximation, to the formation of one vacancy pair. Thus the increase in volume ΔV is given by the relation

$$\Delta V = n_0 V v,$$

where n_0 is the average F -center concentration, V the volume of the crystal, and v the volume of each ion pair, which is approximately $d^3/4$ if the lattice constant d does not change greatly during the x-ray irradiation. In a rectangular sample of dimensions $l_1 \times l_2 \times l_3$ we then obtain for the increase in length Δl_1 , using the assumption that the volume increase is distributed uniformly over all the crystal faces, the result

$$\Delta l_1 \times l_2 \times l_3 = \frac{n_0 V d^3}{3} = n_0 \times l_1 \times l_2 \times l_3 \times \frac{d^3}{12}$$

or,

$$\frac{\Delta l_1}{l_1} = \frac{d^3}{12} n_0$$

as observed in our experiments.

Although it is possible in this manner to obtain agreement with the experimental results, we are, as yet, unable to justify the assumptions made in this model. It is possible, however, to make a few remarks concerning the type of model for which these assumptions might be expected to hold. The fact that the F -center concentration is proportional to the relative linear expansion (strain $\Delta l/l$) and not simply to the linear

expansion (Δl) indicates that the vacancy sources must be uniformly distributed centers throughout the volume of the crystal, such as the small cubes responsible for the mosaic structure or dislocations, and not the surfaces of the crystal itself. The expansion may then be due to the ion pairs deposited at these centers in such a way as to lead to an increase in volume which is uniformly distributed over the crystal faces. This increase in volume must be equal to the volume of the ions deposited in order to agree with the experimental findings. This state of affairs might be expected to hold if the ions were deposited along the surfaces of small cubes (mosaic structure) with weak forces between them or possibly at uniformly distributed edge dislocations or clusters of dislocations.¹² The experimental fact that there was no detectable change in the crystal dimensions upon bleaching of the F -centers subsequent to the irradiation (see Sec. III) suggests that the elastic effects of the vacancies on the volume of the crystal are not very large. The elastic strains observed in the irradiation experiments of Primak, Delbecq, and Yuster¹³ are not necessarily in disagreement with our results. In their experiments the vacancies causing the observed elastic strain were present in much larger concentrations and were formed much more rapidly than in our experiments. Under such circumstances, as stated above, the linear relationship between the relative linear expansion and the average F -center concentration, as well as most of the other results described in this paper, did no longer hold.

The fact that if only part of the crystal was irradiated, the over-all linear expansion was proportional to the F -center concentration in the colored part alone, suggests strongly that a uniform distribution of vacancies had been established throughout the crystal by this partial irradiation. The presence of a large number of vacancies in the nonirradiated portion of the crystal is also indicated by the slower rate of formation of F -centers in the colored portion of partially irradiated crystals, and by the fact that the F -center concentration after a certain period of irradiation in a previously uncolored part appears to be greatly increased by first irradiating an adjacent part (see Sec. V). The

¹² The extension of an extra half-plane of ion pairs in an edge dislocation in an alkali halide crystal completely through the crystal would lead, on the average, to a volume increase equivalent to the volume of the ion pairs responsible for the growth of the extra half-plane through the crystal. If the edge dislocations are uniformly distributed throughout the volume, the increase in the volume will, on the average, be equally distributed among each one of the crystal faces. In this process, some of the dislocations may, of course, disappear.

¹³ Primak, Delbecq, and Yuster, *Phys. Rev.* **98**, 1708 (1955).

rate of diffusion of vacancy pairs in alkali halide crystals, is certainly not large enough to account for the migration of vacancies over distances of several millimeters in relatively short periods of time. It can only be concluded that some other, still unknown, mechanism, such as possibly the migration of dislocations (i.e., slip) from the irradiated to the nonirradiated portion of the crystal must be responsible for the appearance of a large number of vacancies in the nonirradiated region. Recently, Smith, Leivo and Smoluchowski¹⁴ investigated the surfaces of x-ray irradiated alkali halide crystals by interferometric methods. Although the authors were unable to find any evidence for the diffusion of ions or vacancies to and from the surfaces, which is also in agreement with our results, they were able to detect definite slip lines on the crystal surfaces. It may be that such slip processes, which were activated by the x-rays in the irradiated region of the crystal, may lead to the rapid generation of vacancies in other nonirradiated portions of the crystal and may also be responsible for at least part of the expansion of the crystal upon x-ray irradiation.

The initial time lag of the expansion (see Figs. 2, 3, 4, and 7) and the effect of plastic deformation on this time lag (see Sec. 6) may be due to the fact that the crystal before irradiation contains a number of vacancies or other trapping centers, which are increased by plastic deformation, so that at least part of the excited electrons may be trapped at sites already present with the possible formation of F -centers but without the formation of additional vacancies. On the other hand, this behavior may also depend on the details of the time-dependent processes involved in the expansion of the crystal upon x-ray irradiation. The details of these processes may also account for the short time delay in the cessation of the expansion after the x-rays are turned off.

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¹⁴ Smith, Leivo, and Smoluchowski, *Phys. Rev.* **101**, 37 (1956).