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X-Ray Expansion and Coloration of Undoped and Impurity-Doped NaCl Crystals*†

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Expansion and coloration measurements of undoped and impurity-doped single crystals of NaCl have been made under x-ray irradiation (43 kvp and 20 ma) for intervals up to three hours. Expansion was measured in a direction normal to the x-ray beam with a sensitive capacitive dilatometer that was designed to compensate automatically for thermal fluctuations. It was found that the initial rate of creation of F centers exceeds the rate of creation of vacancy pairs as computed from the expansion data; however, after continued irradiation the rates of F-center and vacancy-pair production are approximately evenly matched. This suggests that the initial production of F centers results from both vacancies originally contained in the crystal and vacancies created during irradiation, while the later coloration is due essentially to vacancies that are created in the irradiation process. Within the framework of this interpretation it is possible to estimate the initial negative-ion vacancy concentration of a number of crystals. This concentration ranges from $1\times10^{16}/\text{cm}^3$ for a Harshaw crystal to a value larger than $6\times10^{17}/\text{cm}^3$ for a calcium-doped crystal grown at NRL. Although the presence of a large initial concentration of negative-ion vacancies in calcium-doped NaCl explains its enhanced color sensitivity to x-rays without a corresponding enhancement of x-ray-induced expansion, this explanation is not in accord with simple expectations of charge compensation and the law of mass action.

I. INTRODUCTION

FOLLOWING the demonstration of Estermann, Leivo, and Stern[1] that the density of a KCl crystal decreases upon being irradiated with x-rays, the physical expansion that accompanies x-ray irradiation has been measured in the alkali halides by sensitive electronic[2,3] and photoelastic[4,5] methods. In addition Etzel[6] has studied the x-ray generation of negative-ion vacancies by optical methods. As first indicated by Estermann, Leivo, and Stern a general equivalence has been observed between the concentration of F centers as computed from optical measurement and the expected concentration of positive- and negative-ion vacancy pairs as computed from expansion assuming no lattice constant change. The measurement of Estermann, Leivo, and Stern indicated that roughly twice as many vacancy pairs were created as F centers, while Lin,[3] working at a lower coloration range ($<10^{17}/\text{cm}^3$), observed almost perfect correspondence between F centers and vacancy pairs for x-ray-irradiated KCl and NaCl. Wiegand and Smoluchowski,[5] working with x-ray-irradiated LiF at low temperature reported a volume expansion equal to the volume of one negative-ion vacancy per F center.

Because of the interesting correlation between the coloration and expansion that accompanies x-ray irradiation and the variations in this relation that have been observed, it was deemed inviting to investigate further the x-ray expansion of a variety of specimens of the same alkali halide with known differences in sensitivity to x-ray coloration at room temperature. The question to be answered is whether coloration and expansion go hand in hand regardless of the coloration sensitivity of the crystal. The alkali halide system that was chosen was NaCl, and undoped as well as impurity-doped specimens were studied. The reasons for the inclusion of the impurity-doped crystals in this work were twofold. First, a possible connection between the x-ray expansion and the presence of impurities in a crystal has not been previously investigated. Second, the introduction of certain impurities provides a controlled way in which to alter the coloration sensitivity of crystals to x-rays. Etzel,[7] for example, has shown that the addition of calcium to NaCl results in F-band enhancement under x-ray irradiation in proportion to the quantity of calcium introduced, while the addition of cadmium to NaCl does not lead to a similar F-band enhancement. In addition to the impurities of calcium and cadmium which are divalent, the effect of doping with monovalent potassium is also investigated in this study.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Crystals

As listed in Table I four impurity-doped NaCl crystals and one undoped NaCl crystal were grown at NRL. The NaCl from which these crystals were grown was analytical-grade material that was initially purified as a single batch to remove metallic impurities. The crystal growth was performed by the Kyropoulos[8] technique using a platinum crucible. A cylindrical crystal approximately 3 cm in length and 4 cm in diameter was grown in about two and one-half hours. After

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† A preliminary report of this work was given at the March 1958 meeting of the American Physical Society, Bull. Am. Phys. Soc. **3**, 126 (1958).

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

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

[3] L. Lin, Phys. Rev. **102**, 968 (1956).

[4] Primak, Delbecq, and Yuster, Phys. Rev. **98**, 1708 (1955).

[5] D. A. Wiegand and R. Smoluchowski, Phys. Rev. **110**, 991 (1958).

[6] H. W. Etzel, Phys. Rev. **100**, 1643 (1955).

[7] H. W. Etzel, Phys. Rev. **87**, 906 (1952).

[8] S. Kyropoulos, Z. anorg. allgem. chem. **154**, 308 (1926).

TABLE I. Crystals investigated with impurity concentrations added to melts specified in mole percent (M%).

NRL	NaCl:0.5 M%	$CaCl_2$
NRL	NaCl:0.5 M%	$CdCl_2$
NRL	NaCl:0.1 M%	$CdCl_2$
NRL	NaCl:1.0 M%	KCl
NRL	NaCl	
Harshaw	NaCl	
Optovac	NaCl	
Natural	NaCl[a]	

[a] The natural crystal was obtained from the Smithsonian Institution through the courtesy of Dr. S. Switzer. It was originally obtained from near Baden-Baden, Germany.

growth, the crystal was cooled by lifting it just above the surface of the residual melt and lowering the oven temperature to 100°C. The molar concentrations of impurity added to the various melts are specified in Table I in mole percent (M%). These impurities were analytical-grade material that were used without added purification. The calcium chloride was used in its hydrated form as it was obtained commercially; the water of hydration presumably boiled out of the melt before the crystal was grown. The concentration of impurity actually built into the crystals was substantially less than the impurity concentration in the melt owing to the purification that occurred during crystallization. For the impurity-doped crystals used in this work the work of McFee,[9] Kelting and Witt,[10] and Etzel and Maurer[11] suggests that a reasonable estimate of the concentration of impurity in the crystal was 10% of the concentration of impurity added to the melt. Table I also lists three undoped crystals used in this investigation that were not grown at NRL; two were obtained commercially (from the Harshaw Chemical Company and the Optovac Company) and the third was a natural crystal.

The requirements of the x-ray expansion measurement, discussed in Sec. B that follows, necessitated the preparation of crystals in rectangular blocks with two opposite faces perfectly plane and parallel; furthermore, it was necessary to prepare these faces in such a way that the distance between them could be reproduced accurately for a number of crystals. It was found that these requirements could not be satisfied by ordinary razor-blade cleaving techniques, and accordingly a grinding technique was developed. The crystal dimension perpendicular to the ground faces was 1.270 cm while the other dimensions were roughly 0.2 cm×1.0 cm as determined by razor blade cleavage. These crystals were irradiated parallel to their smallest dimension and expansion was measured at right angles, parallel to the 1.270-cm dimension. X-ray coloration measurements were performed on crystals approximately 0.040 cm along the x-ray direction that were cleaved from the crystals prepared in the same manner as those used in the expansion measurement. The use of comparatively thin crystals for the x-ray coloration measurement is discussed in Part III.

Prior to irradiation the optical absorption of each crystal was measured over the range of about 2000 A to 7500 A. These observations were made with a Cary Recording Spectrophotometer, the same instrument used for coloration measurements after irradiation. It was found that the crystals listed in Table I were almost perfectly transparent over this range with only two exceptions. First, the 0.5 M% cadmium-doped crystal showed a broad ultraviolet absorption that tailed off into the visible to about 5000 A. A thick section of this crystal showed milky-white when viewed with the naked eye. A method that proved successful in removing this cloudiness was that of heating the crystal at 700°C for approximately 30 minutes and then quenching it in air. Optical examination showed that the previous absorption in the range from 2000 A to 5000 A disappeared. Since the occurrence of turbidity in the 0.5 M% cadmium crystal was an effect that was associated with the presence of the large addition of cadmium impurity, a second cadmium-doped crystal was grown with less cadmium (0.1 M%) in order that it might be initially transparent without further heat treatment after growth. The second instance of an optical absorption in the unirradiated crystal was noted in the region of 2000 A. This absorption which suggested the existence of a band to the short-wavelength side of 2000 A was present in all but the natural and calcium-doped crystals. Measurements verified the existence of this band which peaked near 1850 A. Etzel and Patterson[12] have suggested that this band owes its existence to the presence of the hydroxyl ion.

B. Measurement of X-Ray Expansion and Coloration

A capacitive method was employed for measuring the x-ray-induced expansion in this study. This method

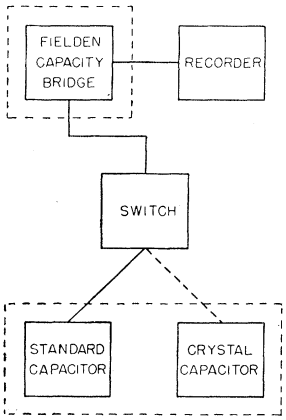

FIG. 1. Block diagram of the electrical circuitry employed in the expansion measurement. The components surrounded in dashed lines are mounted in thermostated enclosures.

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[9] R. McFee, J. Chem. Phys. **15**, 856 (1947).

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

[11] H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

[12] H. W. Etzel and D. A. Patterson, Phys. Rev. **112**, 1112 (1958).

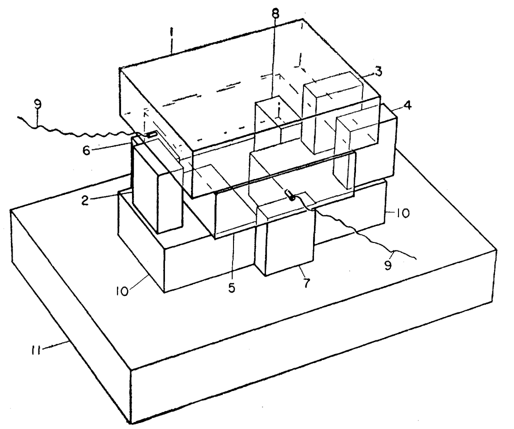

FIG. 2. Temperature "insensitive" crystal capacitor for measuring x-ray expansion. Both the upper capacity plate (1) and the lower capacity plate (5) are mounted on sets of three NaCl crystals, (2, 3, 4) and (6, 7, 8). The expansion of the irradiated crystal (7) causes the gap between the plates to close and the capacity change is measured with the aid of fine copper wires (9). The capacity plates, the support blocks (10) and the base block (11) are precision ground tool steel.

had the advantage that the expansion could be continuously measured during the course of the irradiation, and moreover, directly observed on a recorder. The apparatus is depicted in the block diagram of Fig. 1. The crystal under study was mounted so as to support one plate of a parallel plate capacitor. This capacitor (called the crystal capacitor in the figure) was linked to a capacity bridge through a switch. When the crystal expanded, the change of capacity of the crystal capacitor unbalanced the bridge and the resulting signal was registered on a recorder. The recorder deflections were calibrated in terms of a change in capacity with the use of a variable standard condenser which was switched into the circuit in place of the crystal capacitor. The crystal expansion was then computed from the known capacity change. The capacity bridge was a Fielden Proximity Meter designed for the measurement of small changes in electrical capacity (1×10^{-3} mmf or less). In order to measure expansion continuously over several hours it was found that thermostating the bridge greatly improved its stability. The standard capacitor in addition to being used for calibration was used to correct for drift in the capacity bridge during the course of an expansion measurement. This was accomplished by setting the standard capacitor on some convenient value prior to turning on the x-ray beam. During the course of the expansion the standard capacitor was switched into the circuit periodically in place of the crystal capacitor and deviations that occurred were applied as a correction to the expansion data. In general these corrections were small.

To avoid thermal effects during the course of an expansion measurement the crystal capacitor was designed to compensate automatically for thermal fluctuations. An isometric drawing of this capacitor is shown in Fig. 2. Thermal fluctuation was compensated by supporting both plates of the condenser with NaCl crystals of equal length. The upper plate (1) of dimensions 0.95 cm×2.86 cm×3.81 cm was mounted on three NaCl crystals (2, 3, 4) and the lower plate (5) of dimensions 0.95 cm×2.86 cm×2.86 cm was likewise mounted on three NaCl crystals (6, 7, 8). Thermal fluctuations resulted in both capacity plates moving up and down in unison without a change in the gap spacing and hence without a change in capacity. Only the expansion of the x-irradiated crystal, crystal (7), caused the lower capacity plate to close differentially. The capacity change which resulted from the wedge-shaped closing of the gap was detected by the capacity bridge with the use of fine copper leads (9) which were soldered to the capacitor plates. With all six crystals cut and ground to the same vertical dimension as discussed above, the capacitive gap was established by the difference in thickness between the support blocks (10) and the lower capacitor plate (5). This difference was chosen to give a small gap in order to make the sensitivity sizable. A gap near 0.005 cm was used throughout these measurements.

Figure 3 pictures the thermostated enclosure in which the standard capacitor (9) and the crystal capacitor (12) were housed. The temperature was regulated with a mercury thermoregulator (3) which controlled the heating coils (4) at the bottom of the enclosure. Rotating blades (5) were used to circulate the heated air continuously. The thermoregulator was set to maintain a temperature of about 34°C within the enclosure

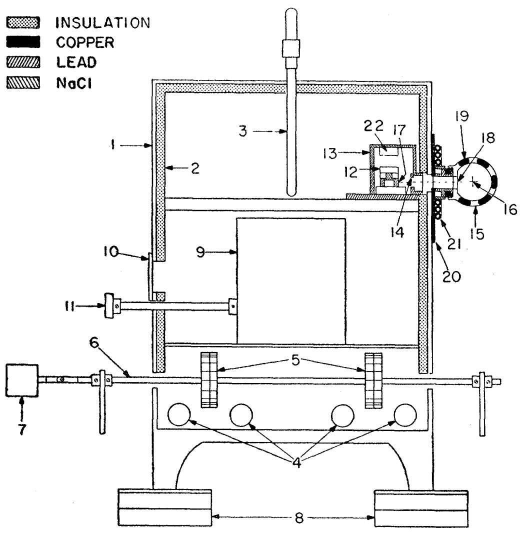

FIG. 3. Crystal capacitor and standard capacitor housing. The following items are numbered in the figure: transite wall (1), glass wool insulation (2), mercury thermoregulator (3), heating coils (4), rotary fan blades (5), fan blade shaft (6), fan blade motor (7), rubber pads (8), standard capacitor (9), viewing window (10), extended knob (11), crystal capacitor (12), lead box (13), x-ray beam aperture (14), x-ray tube (15), x-ray-tube anode (16), x-ray irradiated crystal (17), beryllium exit window of x-ray tube (18), cooling jacket (19), thermostated copper plate (20), copper coils (21), and desiccant box (22).

while room temperature was regulated at about 25°C. The x-ray tube (15), mounted outside the enclosure, was a Machlett OEG-50 tube with a tungsten target; it was used in the self-rectified circuit of a Picker Industrial Generator (not shown in the figure). This tube was operated at 43 kvp and 20 ma for all crystal exposures. Considerable effort was made to avoid the transfer of heat from the anode of the x-ray tube (16) to the irradiated crystal (17), a distance of 12.4 cm. In addition to the anode cooling provided by water coils built into the x-ray tube, the tube was fitted with a jacket of copper tubing (19) that provided for circulation of water. Furthermore, a copper plate (20) was maintained at constant temperature by the circulation of thermostated water through copper coils (21) which were soldered to the plate. One of three beryllium windows (each approximately $\frac{3}{4}$ mm) external to the x-ray tube was soldered to this plate so that a constant temperature barrier separated the x-ray anode and the irradiated crystal.

The results of a large number of measurements to test the thermal stability of the crystal capacitor without x-raying indicated that the effective temperature control was approximately 5×10^{-3}°C over a period of time from two to three hours, the length of the usual x-ray expansion exposure in this study. Furthermore, the expansion measurements indicated that there was negligible crystal heating during the course of the x-ray exposure itself. This was evidenced by the following three observations. First, with only one exception (calcium-doped NaCl) the crystal expansions were stable after the termination of the irradiation. Had the expansions been due wholly or partly to thermal effects one would have expected a contraction of the expanded crystals in all cases. Second, irradiation of a crystal during separated time intervals always resulted in expansions that could be fitted continuously to one another, very much as if the irradiation periods followed each other continuously. After an expansion had been fairly well saturated during the first irradiation interval, the second irradiation interval did not produce additional expansion. Third, the magnitude of expansion of different types of crystals showed consistent but sizeable differences under identical irradiation conditions. This could have resulted from a thermal expansion only in the unaccountable event of sizeable differences in the coefficients of thermal expansion of the various NaCl crystals.

As indicated above, the measurement of the coloration produced by x-ray irradiation was performed in separate exposures. These exposures were carried out under the same irradiation conditions as the expansion measurements in the enclosure of Fig. 3. The procedure adopted was to interrupt the x-ray exposure periodically to make a spectral absorption measurement in order to follow the coloration growth as a function of x-ray time. Experience showed that the few minutes taken to perform the measurement did not appreciably distort the growth curve. Spectral measurements were made over the range from about 2000 A to 7500 A in order that the formation of color centers other than the F center might be observed. The F-center concentration was computed from Smakula's equation as given in a recent paper by Dexter,[13]

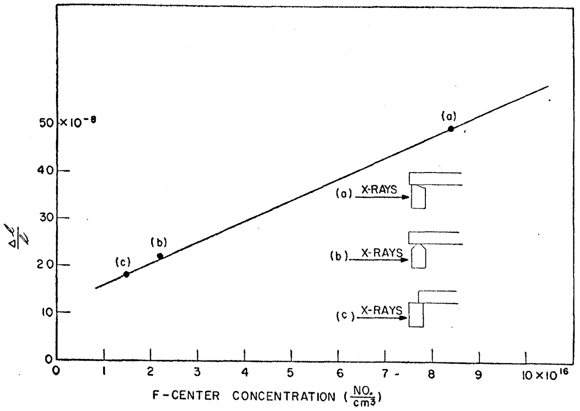

FIG. 4. Relative linear expansion of Optovac NaCl as a function of F-center concentration for three crystal mountings.

$$nf=1.29\times10^{17}[N/(N^2+2)^2]\mu_{\max}W_{\frac{1}{2}}, \tag{1}$$

where n = concentration of F centers (number/cm^3), f = oscillator strength, N = index of refraction, $\mu_{\max}$ = absorption coefficient at the absorption peak (cm^{-1}) and $W_{\frac{1}{2}}$ = width of the absorption at half maximum (electron volts).

III. EXPERIMENTAL RESULTS

It has been pointed out earlier that considerably thinner crystals were used for the coloration measurement (~0.040 cm) than for the expansion measurement (~0.2 cm). This was due to the fact that x-rays were absorbed differentially throughout the body of the irradiated crystals. It was anticipated that owing to the preferential absorption of x-rays near the incident face of an irradiated crystal, it was likely that this face also expanded preferentially in accord with the results of earlier investigations which indicated a correlation between x-ray coloration and x-ray expansion. This expectation was verified in the following manner. Three Optovac NaCl crystals, shown in cross section in Fig. 4, were prepared for an expansion measurement. These crystals were ground so that the front third, the center third, and the back third of the crystals supported the bottom plate of the crystal capacitor as indicated in the sequence (a), (b), and (c), respectively, of Fig. 4. X-ray expansions were determined for each arrangement for an exposure interval of 21 minutes. On the completion of the exposure, each crystal was cleaved and the F-band absorption was determined for the third of the crystal whose expansion was measured. The F-center

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[13] D. L. Dexter, Phys. Rev. **101**, 48 (1956).

concentration and corresponding relative linear expansion are plotted for the three crystal sections. It is clear that the expansion was indeed largest where the coloration was the largest. Since the crystal capacitor of Fig. 2 sensed the maximum expansion (and thus the expansion of the front face of an irradiated crystal), the coloration measurement of comparatively thin crystals gave a more realistic estimate of the *F*-center concentration of the front face of the thicker crystals used in the expansion measurement. An extrapolation to the front surface of the crystal, using the data of Mador, Wallis, Williams, and Herman,[14] for *F*-center concentration *versus* x-ray penetration depth, suggests that this method results in an estimation of *F*-center content to better than 15%.

The expansion as a function of x-ray time for the various crystals listed in Table I is given in Fig. 5. These curves show certain characteristics that were common to all the crystals investigated. In general, the rate of expansion was found to be largest at the onset of the x-ray exposure, followed by a relative decrease in the expansion rate, with the suggestion of an eventual saturation. This behavior of the expansion phenomena was first indicated by the density measurements of Estermann, Leivo, and Stern[1] and later verified by the continuous expansion measurements of Sakaguchi and Suita.[2] Furthermore, the commencement of expansion occurred simultaneously with the commencement of irradiation, contrary to the result reported by Lin[3] in which a delay in expansion was observed at the onset of irradiation. Although the data following the x-ray exposure are not shown in Fig. 5, it was found that the x-ray-induced expansion was stable after the termination of irradiation for all crystals except one, the calcium-doped crystal. This crystal began contracting immediately with the termination of irradiation and the contraction continued at a decreasing rate with over half of the x-ray-induced expansion disappearing in approximately two hours following the exposure. In no case was there observed a continued expansion after the x-ray exposure was terminated as reported by Lin.[3] The data of Fig. 5 indicate a considerable variation in the magnitude of expansion for the various crystals studied. It would be expected that the significance of this variation rests with the fact that the unknown factor or factors giving rise to expansion are different for the different crystals. If "incipient" vacancies at jogs of edge dislocations are the source of vacancies as proposed by Seitz,[15] one is inclined to speculate that the common variable factor from one crystal to another is the dislocation density. Thus, a crystal with a large dislocation density would be expected to have a correspondingly large expansion. Contrary to expectation the crystal with the smallest expansion, the natural crystal, was observed with polarized light to be highly strained, and under etching showed evidence of a dislocation density many times larger than the Optovac crystal, which expanded a considerably larger amount. It is possible, but unlikely, that the highest jog concentration occurred in the crystal with the smallest dislocation density.

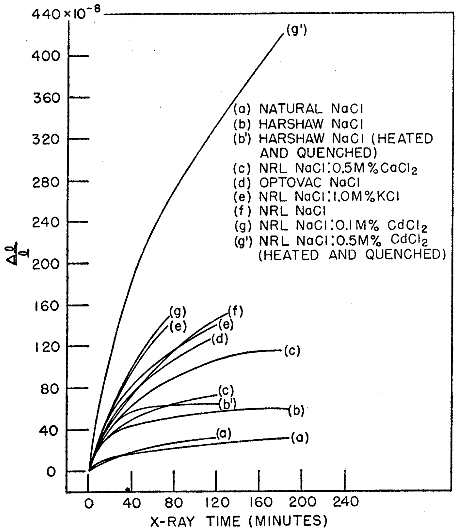

Fig. 5. Relative linear expansion as a function of x-ray exposure time.

The expansion results indicate that the presence of impurity atoms did not alter the x-ray-induced expansion of crystals in a consistent manner. Excluding the heavily doped cadmium crystal, Fig. 5 shows that the lightly doped cadmium crystal expanded more than the undoped NRL crystal, the calcium-doped crystals expanded less, and the potassium-doped crystals showed very nearly the same expansion. The very large comparative expansion of the heavily doped cadmium crystal that was heated and quenched to remove initial turbidity was possibly related to the state of dispersal of the cadmium in the crystal in accord with the work of Zückler[16] who associated the turbidity of cadmium-doped KCl with the formation of colloidal cadmium chloride. Apparently the heat treatment used in this study resulted in the production of a transparent crystal by dispersing these colloids. It is interesting to speculate that the action of the x-rays was to cause a re-precipitation of the cadmium chloride out of the lattice with an accompanying lattice expansion, however, insufficient information limits an interpretation of this type. It was confirmed, however, that the large expansion was not simply associated with the heating and quenching process since a similar treatment given to one of the Harshaw crystals resulted in essentially the same expansion as an untreated Harshaw crystal as seen in Fig. 5. Furthermore, the lightly doped cadmium crystal that was initially free of cloudiness with-

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[14] Mador, Wallis, Williams, and Herman, Phys. Rev. **96**, 617 (1954).

[15] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

[16] Z. Zückler, thesis, Göttingen University, 1949 (unpublished). See reference 15 for a discussion.

out heat treatment showed a considerably smaller expansion, comparable with the expansions of the other crystals in this study.

The results of the x-ray coloration measurements are summarized in Fig. 6, in which the *F*-center concentration is plotted as a function of x-ray time. These concentrations were computed from Eq. (1) using an oscillator strength of 0.7.[17] As expected, the calcium-doped NaCl crystal showed the greatest sensitivity to coloration. Notable are the relatively low coloration sensitivities of the Harshaw and natural crystals, roughly an order of magnitude below that of the calcium-doped crystal. The coloration of the other crystals is observed to fall somewhere between these extremes. Undoubtedly one of the most interesting results of this investigation was the fact that the large enhancement of *F*-band coloration in calcium-doped NaCl over the undoped NRL crystal (Fig. 6) was not accompanied by a proportionate enhancement of x-ray expansion (Fig. 5). The consequences of this result are discussed in the section which follows.

IV. DISCUSSION

A. Two-Stage Coloration Model

It was pointed out that the comparison of expansion and coloration in the alkali halides in earlier work was made on the basis of a model which assumed a match between the number of *F* centers observed optically and the number of vacancy pairs computed from the expansion with no account taken of lattice constant changes. In order that the expansion be correlated with the *F*-center concentration, the model tacitly assumes that the negative-ion vacancies produced by the irradiation are exclusively converted to *F* centers.[18] The exclusive production of *F* centers was very closely approximated in the irradiation conditions of this experiment. The only other color center observed was the *M* center, and its absorption peak height amounted to at most 2% that of the *F* center at the termination of irradiation. The composite results of relative linear expansion *versus* *F*-center concentration are given in Fig. 7. Also given in the figure is the line of slope $a^3/12$ (a is the lattice constant) which serves to indicate perfect agreement with the theoretical model of a vacancy pair per *F* center as given by Lin.[3] As noted in curves (*d*), (*e*), (*f*), and (*g*) of Fig. 7 the data are observed to pass through two stages with respect to agreement or disagreement with the theoretical model. The initial or first stage at low coloration is marked by disagreement with the theoretical slope, whereas after further expansion and coloration, a second stage is reached in which approximate agreement is obtained with the theoretical slope. In the Harshaw crystal, curve (*b*), the first stage occurs quite rapidly so that essentially only the second stage appears in Fig. 7, while in the calcium-doped crystals, curves (*c*), it is presumed that the measurements were not carried out long enough to observe the second stage and only the first stage is observed. It is thought that the natural crystals, curves (*a*), like the Harshaw crystal, are in their second stage throughout the major portion of the measurements and the disagreement with the theoretical slope is due to the uncertainty in the small expansion that was obtained for these crystals. The natural crystals are shown as dashed lines in Fig. 7 so as to be more easily distinguished from other curves which are bunched near the origin.

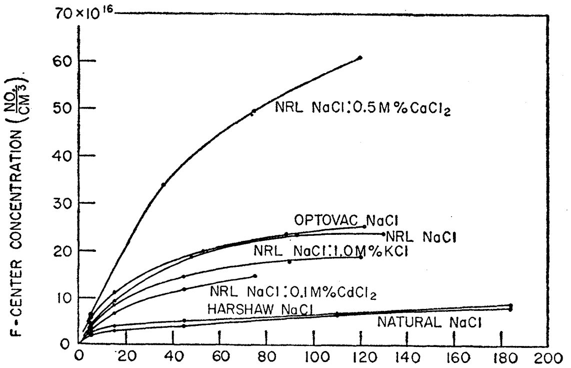

FIG. 6. *F*-center concentration as a function of x-ray exposure time.

The fact that the initial slopes of the curves of Fig. 7 are lower than the theoretical slope suggests that an insufficient number of vacancies were produced during the initial expansion to account for the *F*-center concentrations observed. This divergence is interpreted as resulting from the production of *F* centers from vacancies originally in the crystal prior to irradiation. Thus the first stage coloration results from the production of *F* centers from both vacancies originally within the crystal as well as vacancies produced by the x-rays. The second stage expansion and coloration, however, in which agreement with the theoretical slope is approximated, indicates that the production of *F* centers is very closely matched by the production of an equivalent number of vacancies. In this case each *F* center results from a negative-ion vacancy created by the x-rays. The initial rapid rise of *F*-center growth (Fig. 6) is associated with the first stage, while the gently increasing portion of the coloration growth curve that follows is associated with the second stage. The fact that different crystals reach the second stage at different *F*-center concentrations suggests that the initial concentration of negative-ion vacancies varies from crystal to crystal. This interpretation is supported by the fact that the crystals with the most rapid coloration growth

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[17] F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

[18] It is also assumed that the expansion measured in this study corresponds to the uniform, unrestrained motion of the front surface of the irradiated crystal. The validity of this assumption is limited by the degree of irregularity of the expanded surface [see T. Hibi and K. Ishikawa, J. Phys. Soc. Japan **13**, 709 (1958)] and the extent of strain in the crystal owing to the expansion gradient through the body of the crystal as evidenced by photoelastic studies.[4,5]

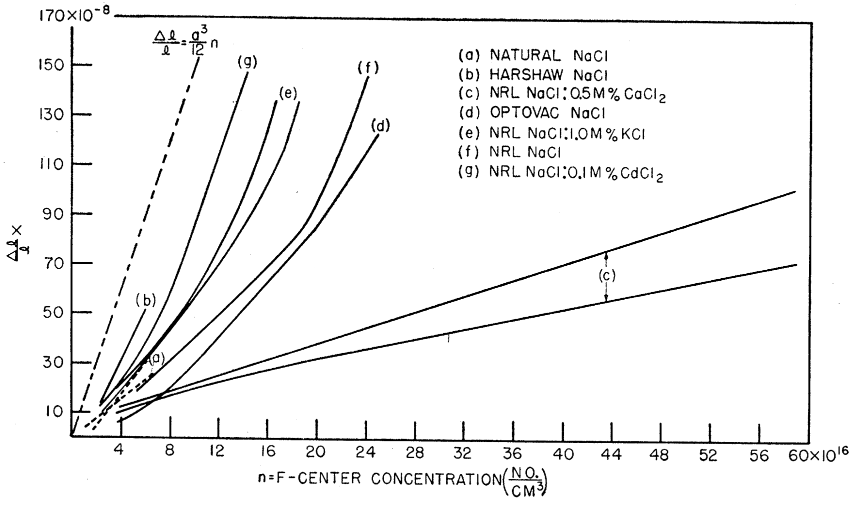

FIG. 7. Relative linear expansion as a function of F-center concentration. The long dashed line gives the locus of points for which there is a one to one relationship between vacancy pairs and F centers. This line has slope $a^3/12$ where a is the lattice constant.

(Fig. 6), owing presumably to vacancies originally in the crystal, are the crystals that reach their second stage at the largest F-center concentration. This two-stage model for F-center coloration in the alkali halides is identical to the model first proposed by Gordon and Nowick[19] on the basis of x-ray coloration work on deformed NaCl which was later strengthened by the gamma-ray work of Nowick.[20] This model, however, is at variance with the results reported by Lin[3] in which the initial production of F centers is evenly matched by the production of vacancy pairs. Lin's result implies that it is unnecessary to assume the presence of vacancies in the crystal prior to irradiation to account for the F-center concentrations observed.

B. Estimate of Negative Ion Vacancy Content

Within the framework of the two stage model discussed above, the data of Fig. 7 can be used to obtain an estimate of the initial negative ion vacancy concentration of a number of the crystals investigated. A simple, linear extrapolation of the second stage (to the abscissa) gives an estimate of the F-center concentration that cannot be ascribed to vacancy production during irradiation. These values are given in Table II. They not only apply to free negative ion vacancies, but also to other negative ion vacancies originally in the crystal that become F centers on irradiation without contributing appreciably to the expansion, for example, negative ion vacancies contained in vacancy clusters. Because the calcium-doped crystal was observed presumably only during the first stage, its initial negative ion vacancy content is larger than the maximum F-center concentration observed; it is estimated at roughly $6\times10^{17}/\text{cm}^3$. Furthermore, the uncertainty in the absolute expansion of the natural crystal owing to its small expansion, does not allow for an extrapolation. The second stage slopes of a number of the curves of Fig. 7 are not perfectly defined, so that the concentrations in Table II must be considered approximate. It might be pointed out in connection with the estimates of Table II that Straumanis[21] has found, on the basis of density and lattice constant measurements of NaCl, that the porosity can account for a minimum of 3×10^{18} negative ion vacancies per cm³ and perhaps as many as $9\times10^{18}/\text{cm}^3$ at room temperature. The void volume indicated by Straumanis is not necessarily associated only with vacancies and vacancy clusters, but can also be associated with other flaws in the perfect structure such as submicroscopic cavities and cracks. Straumanis's result indicates, however, enough porosity to account for the negative ion vacancy concentrations given in Table II.

It is informative to consider the estimates of negative ion vacancy content in the crystals listed in Table II in light of ionic conductivity measurements. Under conditions of thermodynamic equilibrium the concentrations of positive and negative ion vacancies are given by the mass action law, which states that the product of the positive ion and negative ion vacancy concentrations within a crystal is a constant at a given temperature. The conductivity in the intrinsic range, i.e., at temperatures of the knee of the conductivity curve and above, is dominated by thermally generated Schottky defects so that the positive and negative ion vacancy

TABLE II. Estimate of initial concentrations of negative ion vacancies.

Harshaw	NaCl		$1\times10^{16}/\text{cm}^3$
NRL	NaCl:0.1 M%	$CdCl_2$	4×10^{16}
NRL	NaCl:1.0 M%	KCl	$7-9\times10^{16}$
NRL	NaCl		14×10^{16}
Optovac	NaCl		16×10^{16}
NRL	NaCl:0.5 M%	$CaCl_2$	60×10^{16}

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[19] R. B. Gordon and A. S. Nowick, Phys. Rev. **101**, 977 (1956).

[20] A. S. Nowick, Phys. Rev. **111**, 16 (1958).

[21] M. E. Straumanis, Am. Mineralogist **38**, 662 (1953).

concentrations in this range are approximately equal. This concentration can be computed for NaCl from the expression given by Etzel and Maurer,[11]

$$n=1.2\times10^{23}\exp(-2.02\text{ ev}/2kT)\text{ cm}^{-3}. \quad (2)$$

In the low temperature or structure-sensitive range below the knee of the conductivity curve the number of thermally generated vacancies becomes small, in accord with Eq. (2), and the vacancy content of the crystal is controlled by vacancies which are required to compensate for the charge of multivalent impurities (the so-called principle of charge compensation). It is expected, for example, that the introduction of positive divalent impurities results in the production of positive ion vacancies, and under conditions of thermodynamic equilibrium the number of negative ion vacancies is suppressed in accord with the mass action law. The difficulty in estimating negative ion vacancy concentrations in the structure-sensitive range rests with the fact that it is not clear if thermodynamic equilibrium exists in the crystal. Under nonequilibrium conditions, vacancies are "frozen" into the lattice and the mass action law is no longer applicable. Thus to apply Eq. (2) safely one should at least be at the temperature of the knee of the conductivity curve.

The knee of the conductivity curve for NaCl has been observed by Compton[22] to fall as low as 467°C. Assuming that all NaCl crystals are in thermodynamic equilibrium at this temperature (regardless of the fact that their conductivity knees might lie at higher temperatures), Eq. (2) yields a negative ion vacancy content of about $1\times10^{16}/\text{cm}^3$. This concentration agrees with the room temperature estimate of the Harshaw crystal of Table II and yet it corresponds to a temperature well above room temperature, and probably above the actual temperature of thermodynamic equilibrium. It is clear that the disagreement is larger for the other crystals of Table II which have negative ion vacancy concentrations in excess of the Harshaw crystal. The disagreement is particularly widened for the crystals with positive divalent addition. For example, in the case of the calcium doped crystal (assuming a calcium addition of 5×10^{-4} mole fraction in the crystal) the requirements of charge compensation imply a positive ion vacancy concentration of about $10^{19}/\text{cm}^3$. Invoking the mass action law at 467°C leads to a negative ion vacancy concentration of $(10^{16})^2/10^{19}$ cm^3 or $10^{13}/\text{cm}^3$. This is to be compared with the room temperature estimate for the calcium-doped crystal of $6\times10^{17}/\text{cm}^3$. It becomes apparent that the estimates of negative ion vacancy concentration based on the principle of charge compensation and the law of mass action are incompatible with the negative ion vacancy concentrations of Table II. To resolve this incompatibility a more complete understanding of the kinetics of the coloration process is no doubt needed.[23]

C. Calcium-Doped NaCl

Within the framework of the two-stage interpretation of the data of Fig. 7, the calcium-doped crystal was observed only during the first stage which is characterized by disagreement with the theoretical model. The second stage agreement with the theoretical model that was observed for other crystals would be expected to occur in calcium-doped NaCl at longer irradiations than those produced in this study. Thus the estimate of Table II put the lower bound on the initial negative ion vacancy content at about $6\times10^{17}/\text{cm}^3$, which was considerably larger than any of the other crystals investigated. In the light of this estimate the enhancement of the coloration of calcium-doped NaCl over undoped NaCl (Fig. 6) can be simply attributed to its larger initial negative ion vacancy content. The lightly doped cadmium crystal presumably did not show a similar coloration enhancement because its initial negative ion vacancy content was not increased above the undoped crystal. This explanation for the *F*-band sensitization of calcium-doped NaCl and lack of sensitization of cadmium-doped NaCl is considerably different than the two previous proposals put forth by Etzel[7] and Seitz.[15] Etzel's explanation depended on the degree of association of the positive ion vacancy and the positive divalent impurity which was in turn related to the hole trapping efficiency and the ultimate stability of the *F* center. Seitz's mechanism was based on the dispersal of negative ion vacancies created at dislocation jogs; this dispersal was promoted by the action of unassociated positive ion vacancies.

Unfortunately few experiments have been carried out which give information on the low-temperature concentration of negative ion vacancies in the alkali halides. Although conductivity measurements have amply reflected on the positive ion vacancy content in the low-temperature range, they have said virtually nothing with respect to the negative ion vacancy content owing to the negligible mobility of the negative ion. There are two experiments, however, which can be considered in regard to the negative ion vacancy content of calcium-doped alkali halides. First, there is the work performed by Pick and Weber[24] in which the density change in KCl was determined as a result of the introduction of the calcium ion. These investigators observed a density decrease in KCl doped with $CaCl_2$ that was approximately 25% short of the decrease expected from the charge compensation model in which each substitutional calcium ion produces a potassium ion vacancy. If, in addition, one requires the presence of simple negative ion vacancies according to the results of Table II, the discrepancy would be even greater than 25%. Perhaps the detailed manner in which negative ion vacancies occur in the lattice is such as to reconcile these inconsistencies. A second experiment, which is favorable to the initial presence of

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[22] W. D. Compton (unpublished).

[23] J. H. Schulman, J. Phys. Chem. **57**, 749 (1953).

[24] H. Pick and H. Weber, Z. Physik **128**, 409 (1950).

a large negative ion vancancy content as a result of calcium doping, was performed by Etzel.[25] Etzel observed that F-band sensitization that is produced in x-ray irradiated NaCl doped with calcium is also produced with ultraviolet radiation. Under the assumption that the ultraviolet is capable of creating only a small number of vacancies compared to the number created by the x-rays, Etzel concludes that excess negative ion vacancies are initially present in the calcium-doped crystal. Certainly additional experiments with respect to the low-temperature negative ion vacancy content of the alkali halides would be of interest.

As pointed out earlier a characteristic of the calcium-doped NaCl not observed for any other crystal investigated was the contraction of the crystal after the x-ray beam was turned off. It was interesting to see if this contraction was accompanied by a corresponding fading of the F band. It was found that the percent fading of the F band in the dark in the calcium-doped crystals was actually smaller than most of the other crystals in this study. If the great abundance of F centers are created from vacancies originally in the calcium crystal as proposed, it is not necessary that the disappearance of x-ray created vacancies be accompanied by a sizeable depletion of F centers.

D. Summary

The leading observations and conclusions of this investigation can be summarized as follows:

First, the presence of impurity atoms (calcium, cadmium, and potassium) does not sizeably alter the x-ray induced expansion of NaCl crystals; the only exception was a heavily doped cadmium crystal that was heated and quenched prior to irradiation to remove an initial turbidity.

Second, a highly strained natural NaCl crystal was observed to expand and color less under x-rays than any of the synthetic crystals. The presence of a large dislocation density in this crystal would tend to argue against the dislocation-jog mechanism for the creation of vacancies under x-ray irradiation.

Third, x-ray induced expansion occurs simultaneously with the commencement of irradiation and terminates simultaneously with the cessation of irradiation contrary to the observations of Lin.

Fourth, x-ray expansion and coloration are simply related to one another (one vacancy pair per F center) only after vacancies originally present in a crystal are transformed to F centers. This interpretation supports the two stage coloration mechanism of Gordon and Nowick and allows for an estimate of the initial negative ion vacancy concentration of a number of the crystals investigated. These concentrations are in excess of the concentrations expected from simple thermodynamics.

Fifth, the enchanced sensitivity of calcium-doped NaCl to the production of F centers under x-ray irradiation is attributed to a large initial concentration of negative ion vacancies of unknown origin.

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[25] H. W. Etzel (unpublished).