Surface Studies of X-Ray Irradiated Potassium Chloride Crystals*†

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Multiple-beam interferometry has been used to investigate the surfaces of x-ray irradiated KCl crystals. Within the limits of the method there is no evidence for diffusion of vacancies or ions to or from the surface to account for the observed decrease in density. The change of density thus must be attributed to an internal mechanism, a possibility which finds tentative experimental support.

I. INTRODUCTION

It is known that the density of potassium chloride crystals decreases upon irradiation with x-rays,[1] and since there is no accompanying significant change in lattice parameter[2] one concludes that the lower density is associated with an increased concentration of vacancies. At saturation, the observed change of density and the number of vacancies calculated from it correlate reasonably with the number of F-centers formed during irradiation, as determined optically. In order to account for this excess of vacancies, Seitz[3] suggested that they diffuse into the interior of the crystal from the surface. In support of this hypothesis, Dienes[4] showed that the activation energy for diffusion of coupled pairs of positive and negative ion vacancies was 0.375 ev, which could account for sufficient diffusion at room temperature. Later, Seitz[5] pointed out that vacancies could be generated at dislocations, in which case the decrease in density as a result of x-ray irradiation could be an internal phenomenon and it would not be necessary for the vacancies to diffuse in from the surface. This mechanism was discussed in further detail by Markham,[6] while Dexter[7] has shown that one should also consider the formation of color centers from groups of associated vacancies.

The purpose of this investigation was to ascertain by an independent method whether there is any appreciable diffusion of vacancies into the crystal during irradiation or whether an internal mechanism is responsible for the decrease in density. That the latter is the more plausible mechanism finds support in the measurements made by Duerig and Markham[8] at temperatures of liquid helium. They obtained a high density of F-centers in spite of negligible diffusion expected at these temperatures. Of course, one might speculate that the diffusion coefficient increases during x-ray irradiation, but this hypothesis is contradicted by the results of measurements made by Mapother.[9]

The results of Estermann, Leivo, and Stern[1] showed that after an exposure to x-rays for $8\frac{1}{2}$ hours the density of a potassium chloride crystal decreased by $\Delta\rho=1.4\times10^{-4}$ g/cm^3. If the assumption is made that the change in density is completely due to diffusion of vacancies from the surface, then the surface of the crystal could conceivably rise. Depending upon geometry, this rise would be of the order

$$\Delta h=(\Delta\rho/\rho)h. \tag{1}$$

Inserting $\rho=1.987$ g/cm^3, $\Delta\rho$ as given above, and the thickness $h=0.025$ cm (the crystals in reference 1 were 0.05 cm thick, but were irradiated on both sides) one obtains $\Delta h=200$ A, which is well within the reported resolving power (25 A or less) of multiple-beam interferometry.

If the point of view that the surface of the crystal can rise uniformly as a whole is too simple, then it is necessary to consider growth on the surface in the vicinity of cleavage and slip lines or steps and surface cracks. This would lead to even greater changes of the surface configuration, since then the changes due to diffusion would be concentrated in smaller areas.

It appears thus that the multiple-beam interferometry can in principle determine whether or not the decrease in density is primarily due to diffusion of

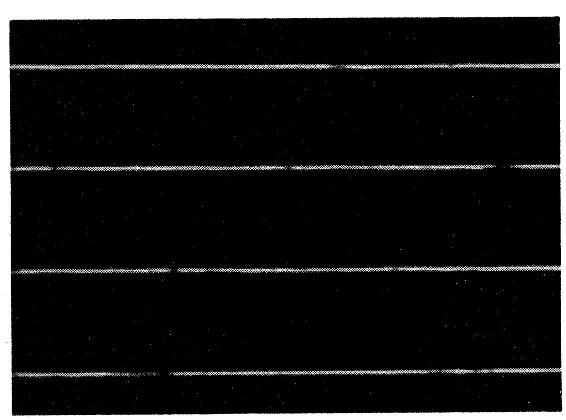

FIG. 1. An interferogram arising between two optical flats (100×).

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† Part of a dissertation submitted by Walter J. Smith in partial fulfillment of the requirements for the degree of Doctor of Science in the Physics Department of the Carnegie Institute of Technology.
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[1] Estermann, Leivo, and Stern, Phys. Rev. 75, 627 (1949).
[2] C. R. Berry, Phys. Rev. 98, 934 (1955).
[3] F. Seitz, Revs. Modern Phys. 18, 384 (1946).
[4] G. J. Dienes, J. Chem. Phys. 16, 620 (1948).
[5] F. Seitz, Phys. Rev. 80, 239 (1950).
[6] J. J. Markham, Phys. Rev. 88, 500 (1952).
[7] D. L. Dexter, Phys. Rev. 93, 985 (1954).
[8] W. H. Duerig and J. J. Markham, Phys. Rev. 88, 1043 (1952).
[9] D. E. Mapother, Phys. Rev. 89, 1231 (1953).

vacancies into the crystal. If the change in density is due to an internal process which results in an over-all expansion or bending, then no surface changes should be observed.

The theoretical and experimental details of the technique of multiple-beam interferometry have been reported in detail.[10] The main advantage of the method over the two-beam technique is that the silvering of the reference flat and of the specimen leads to an extreme sharpening of the interference fringes. Stating the fringe width as a fraction of the distance between fringes, its dependence on reflection coefficient is as follows:

Reflection coefficient	Fringe width
0.04 (glass)	1/3
0.90	1/30
0.94	1/50

Under the best conditions it is possible to measure height changes with an accuracy of 3 A. However, the experimental requirements for the attainment of such precision are severe, and for present purposes the fringe width will be assumed to be one tenth of the distance between fringes. Furthermore, one can easily see a fringe shift one fifth of its width, which, upon using the mercury blue line of wavelength 4358 A, gives for the lower limit of resolution about 44 A. (Actually, the lower limit appears to be about one-half of this or less.) Thus, if in our experimental setup no change is observed, then it is possible to state that diffusion accounts for no more than 20% of the observed change in density, and an internal mechanism for change in density must be considered.

II. EXPERIMENTAL PROCEDURE

The KCl crystals used in this experiment were obtained from the Harshaw Chemical Company. The crystals were cleaved to suitable size and annealed in a stream of helium at 700°C for approximately 15 hours. The rate of heating was 5°C per minute and the rate of cooling was 3°C per minute. The crystals were cleaved again after annealing to obtain fresh surfaces.

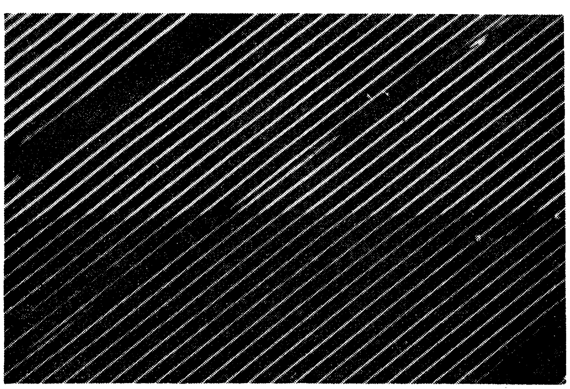


FIG. 2. An interferogram of an x-rayed crystal. The lower part of the crystal has been irradiated (50×).

In order to make any changes which may occur due to x-ray irradiation easily visible, the crystals were irradiated through a slit in a thick piece of brass, thus forming a colored strip between two uncolored regions in the same crystal. The crystal and the slit were mounted on a microscope slide, wrapped in cellophane or DuPont Mylar Polyester Film, and sealed with cellophane tape.

The cleaving and mounting of the crystals were done in air since a comparison with a series of trials in which the crystals were cleaved in an atmosphere of dry helium using a glove box and mounted in gas tight cells indicated that there was no observable difference in the two methods. However, it appeared necessary to seal the crystals in a dust-free atmosphere during irradiation because the ejection of photoelectrons causes the crystals to become charged and to attract dust.

After mounting, the crystals were placed as close as possible to one of the beryllium windows of a *CA*-6 crystal analysis tube in a General Electric *XRD*-1 x-ray unit. The tube had a molybdenum target and the exposure in the dark varied from 8 to 60 hours at 45 kvp and 15 ma. After exposure to x-rays, the crystals were removed from the microscope slide, and placed along with an optical flat in a vacuum evaporation system. There they both received a film of silver suitable for multiple-beam interferometry. (The technique of vacuum deposition has been treated in detail in the literature.[10–12])

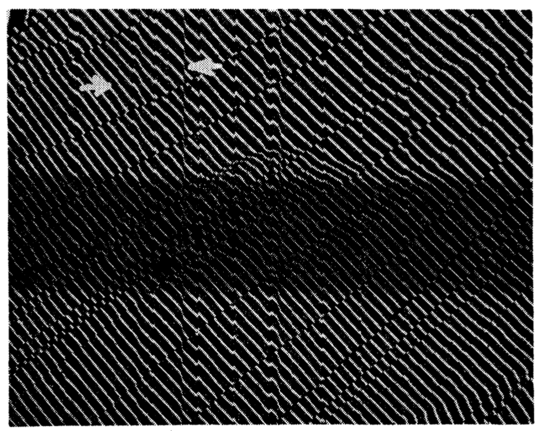


FIG. 3. Slip lines on an irradiated crystal. The small vertical slip line (left arrow) corresponds to a step of approximately 175 A and the larger one (right arrow) to a step of 1350 A.

For the production of the multiple beam photographs, a Vickers Projection Microscope was used. This apparatus is especially suited for this purpose, the only modification necessary being the addition of a diaphragm at the image of the mercury arc produced by the

[10] S. Tolansky, *Multiple Beam Interferometry of Surface and Films* (Oxford University Press, Oxford, 1948). For a review of the effectiveness of the method, see S. Tolansky, J. Sci. Instr. **22**, 161 (1945).

[11] S. Tolansky, Vacuum **1**, 75 (1951).

[12] L. Holland, Vacuum **1**, 23 (1951). This article has an excellent bibliography.

lamp condenser. On account of the very low transmission of the silver films resulting in only feeble illumination reaching the photographic plate, it was necessary to use Super Ortho Press Plates developed in *SD* 19*a*.[13] This combination had an effective speed of *ASA* 1000 and the exposures required were of the order of minutes, instead of hours as would have been necessary with the materials and solutions usually used.

III. RESULTS

An idea of the accuracy of multiple-beam interferometry as used in the present work can be obtained from Fig. 1 which is an interferogram (100×) which arose between the two optical flats used. The fringes are parallel within the accuracy of measurement and any error due to the flats themselves was estimated to be less than 10 A.

Figure 2 is an example of an interferogram (100×) of a crystal which received a strong x-ray irradiation, in this case 44½ hours. The density of color centers in this crystal was so high that, even though this interferogram was made using the 4358 mercury line, the colored region is plainly visible in the lower half of the print. There is no evidence for any changes in the crystal surface due to irradiation. If there had been any diffusion of ions to the surface, and the resulting height change were uniform, one would expect discontinuities or bends in the fringes to occur near the dividing line between the colored and uncolored regions.

In crystals which were weakly colored, the boundary of the colored region was not discernible on the interferograms made with the 4358 A line. In such cases, another interferogram was made using the green mercury line 5461 A. This wavelength falls in the *F*-band absorption region of KCl and produces a sharp outline of the x-ray irradiated portion of the crystal. A comparison of the two interferograms permits then an unambiguous analysis. An example of such a pair is Fig. 5 which will be discussed later. In not one case out of the many crystals thus investigated was there found any evidence of surface irregularities which could be associated with diffusion of vacancies during x-ray irradiation.

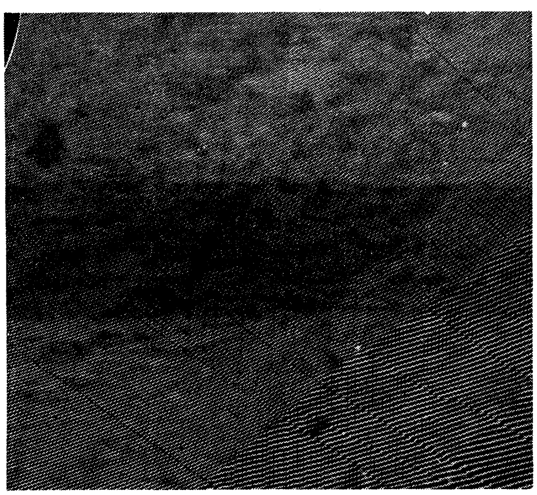


FIG. 4. Clustering of slip lines about the colored region (25×).

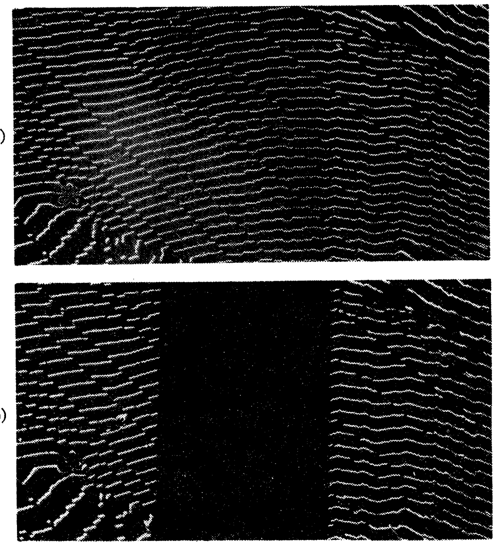
(a)
(b)


FIG. 5. Interferograms made with the (a) blue and (b) green lines of mercury respectively. Slip lines.

While no evidence was found for any striking phenomena near the boundary of the irradiated regions, there were many discontinuities in the interference lines observed elsewhere. These fall into two categories: cleavage lines, which have not specified crystallographic direction, are often curved, and radiate from the original point of initial cleavage, and slip lines, which are straight and oriented along the intersections of the possible active slip systems of the type (110) [011] with the surface of the crystal. A tentative observation was made that certain of the slip lines may be a direct effect of the x-ray irradiation. An initial indication in this direction was the ease with which the irradiated crystals could be slipped upon improper cleaving or handling. Of great help here was the fact that the presence or absence of slip lines on the surface of a crystal before irradiation could be easily checked by examination under glancing illumination.

A series of experiments was performed in an attempt to determine the origin of the slip lines. The results are plausible though not conclusive: Figure 3 is an interferogram of a crystal irradiated for 51½ hours which had not slipped prior to the exposure to x-rays as determined by the aforementioned examination. The change in height at the small slip line is 175 A and that at the large one is 1350 A subject to an error of 10%. (The slip lines are seen most easily by viewing the photograph at a glancing angle.)

The crystal of Fig. 4 (36×) was irradiated for 52 hours. This photograph shows clustering of the slip lines

[13] *Kodak Professional Handbook* (Eastman Kodak Company, Rochester, 1952).

FIG. 6. Microphotograph of growth on a KCl crystal surface due to annealing (280×).

about the irradiated region. In the authors' opinion, this is the most convincing evidence that the slip is connected with x-ray irradiation, and is accompanying the change in density. Further, since slipping or plastic flow may be initiated in the interior of crystals, the observation of slip lines indicates that there is an internal process occurring in the crystal during irradiation.

A further experiment to check the origin of the slip lines was as follows: A crystal was cleaved into two identical sections and the slit through which the x-rays passed was positioned on one face of the cut at right angles to what it was on the other face of the cut. Both crystals were then irradiated for $45\frac{1}{2}$ hours and Fig. 5 shows the results for one of the faces. As mentioned above, in order to locate properly the boundaries of the colored region, Fig. 5(a) was taken with mercury green line while Fig. 5(b) was taken with mercury blue line. On Fig. 5(a), besides a number of slanted cleavage lines, there are several slip lines discernible which are parallel to the length of the colored region. On the other face of the cut the situation was analogous; i.e., the slip lines were parallel to the length of the colored region. Since the two colored regions were perpendicular to each other, this means that the slip lines in the two sections of the crystal were perpendicular to each other. If the slip lines were due to plastic deformation produced during cleaving, the resulting slip lines would have been parallel on both faces rather than perpendicular as is observed. This result can be interpreted as another confirmation of the suggestion that the slip lines appeared as a result of x-ray irradiation.

The above experiments do not imply necessarily that the slip is actually generated by x-rays. More likely, a Frank-Read source which happens to be inactive is activated by a local increase in the concentration of vacancies. One can easily propose models of obstacles which would hamper the function of a Frank-Read source and which disappear or become less effective as a result of the formation of vacancies. The orientation of the slip lines is presumably determined by the strain pattern produced by the gradient of density (gradient of expansion) within the crystal. Depending upon the dimensions of the crystal and of the colored band, the slip can occur either parallel or perpendicular to it.

An investigation was also made of the surfaces of annealed crystals. While there was no evidence of diffusion to or from the surface in the irradiated crystals, an examination of an annealed surface which was not exposed to x-rays showed what could be expected if diffusion did occur during x-raying and if the diffusion ions accumulated at cleavage steps. Figure 6 is a micrograph (280×) of growth features attributable to annealing on the surface of a KCl crystal. The diagonal line is a step due to cleaving before annealing. It is seen that there is considerable growth along the step. Figure 7 is an interferogram of another annealed surface. The fringes exhibit a definite curvature as they approach a cleavage line. This is the effect that presumably would be observed if diffusion occurred during x-raying and resulted in growth at discontinuities on the surface of the crystal.

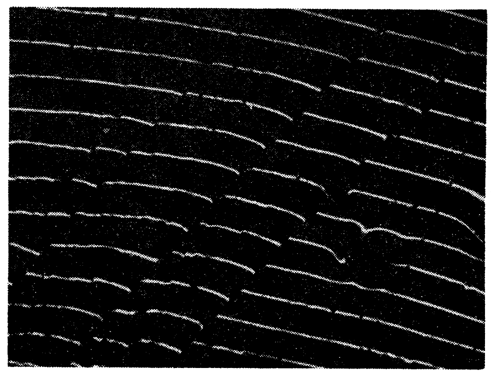


FIG. 7. Interferogram of an annealed surface (25×).

IV. CONCLUSION

As a result of these investigations, the conclusion can be made that the diffusion of vacancies from the surface of the crystal plays a very minor role, if any, in the decrease of density of KCl crystals upon x-ray irradiation. Further, an internal mechanism, possibly one involving dislocations, in the interior of subgrains or at their boundaries seems to find support.

Since the completion of this work Varley[14] has proposed a new mechanism for the production of vacancies, according to which the high-energy photons ionize the negative ions in the lattice, stripping them of maybe several electrons. The negative ions thus become positively charged and find themselves in a high-energy configuration because of the Coulomb repulsion of the positive nearest neighbors. Such halogen ions are then easily displaced into neutral interstitial positions and negative ion vacancies are formed. This mechanism, if otherwise verified, is not in disagreement with the results of our experiments.

VI. ACKNOWLEDGMENTS

The authors would like to express their appreciation to Elizabeth H. Smith for help with processing the photographs and typing the manuscript.

[14] J. H. O. Varley, Nature **174**, 886 (1954).

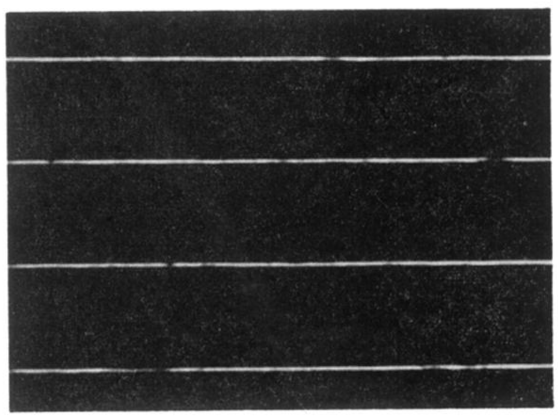


FIG. 1. An interferogram arising between two optical flats (100×).

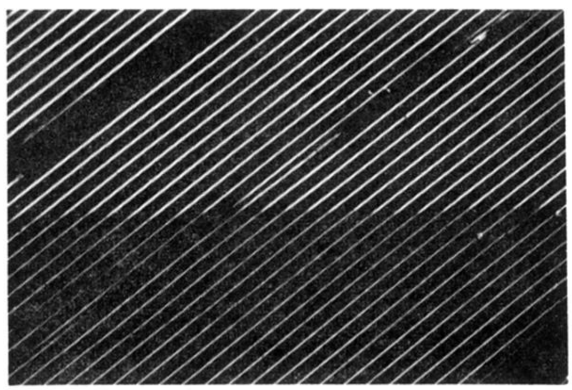
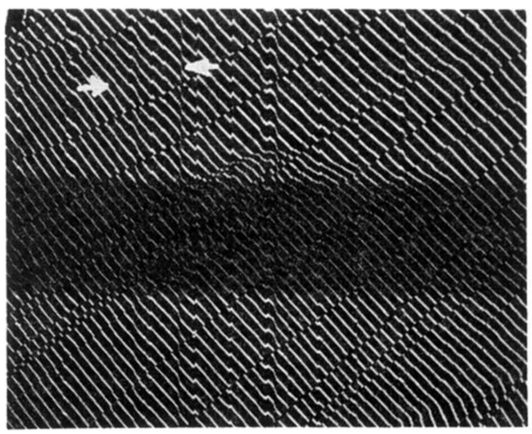


FIG. 2. An interferogram of an x-rayed crystal. The lower part of the crystal has been irradiated (50×).



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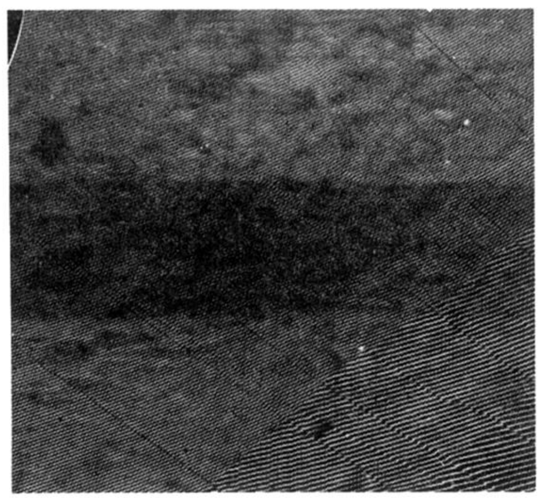

FIG. 4. Clustering of slip lines about the colored region (25×).

(a)

(b)

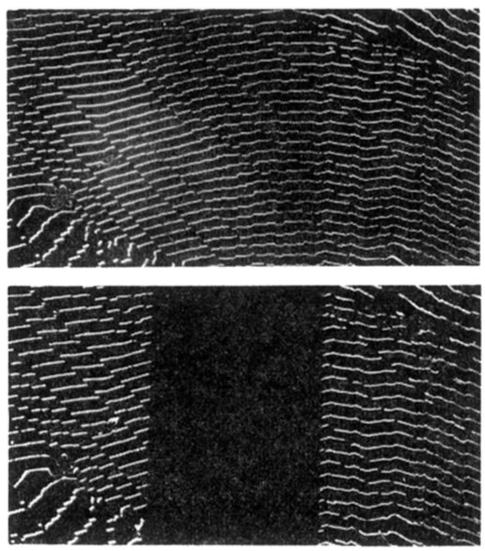

FIG. 5. Interferograms made with the (a) blue and (b) green lines of mercury respectively. Slip lines.

FIG. 6. Microphotograph of growth on a KCl crystal surface due to annealing (280×).

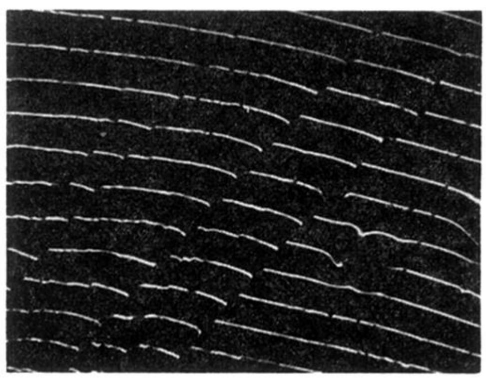

FIG. 7. Interferogram of an annealed surface (25×).