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# Optical Detection of Vacancies Created by High-Energy Radiation in Sodium Chloride

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The presence of vacancies created by high-energy radiation in sodium chloride single crystals has been detected by comparing the *F*-center coloration produced by ultraviolet light after irradiation and optical bleaching to that obtained before irradiation. The behavior of the *F*-center coloration as a function of time of irradiation under ultraviolet light after exposure of the crystals to high-energy radiation is different for synthetic and natural sodium chloride. This difference is attributed to the presence of hydroxyl ions in the synthetic crystals which are inadvertently introduced into the lattice during the growth of the crystals in air. The results obtained are the same whether 40-kvp x-rays, 2-Mev electrons, or $\mathrm{Co}^{60}$ $\gamma$ rays are used to create the *F* centers.

## INTRODUCTION

IN a previous publication[1] the creation of vacancies by x-rays was demonstrated in the following manner. The growth of the *F* band in a synthetic single crystal of NaCl was measured as a function of the time of exposure to ultraviolet light. Using this coloration as a reference, the crystal was then exposed to a flux of 40-kvp x-rays at 13 ma and the resulting coloration was bleached optically. The crystal was then re-irradiated with ultraviolet light and the resulting growth curve compared to that obtained before x-raying. The data obtained from this work indicated that (a) vacancies were created by the x-rays, (b) x-ray created vacancies were ultimately destroyed by ultraviolet light, and (c) the enhanced *F*-band absorption, observed in those crystals which were colored by ultraviolet light after being x-rayed and optically bleached, was not due to an increased ultraviolet absorption.

In the present work, the effects of other high-energy radiations, such as 2-Mev electrons and $\mathrm{Co}^{60}$ $\gamma$ rays, as well as x-rays, on several synthetic crystals as well as on a specimen of halite are reported. Recently the presence of the hydroxyl ion as an impurity in air-grown synthetic crystals has been established.[2,3] It is the presence of the hydroxyl ion in the synthetic crystals investigated that is responsible for the marked difference in the behavior of synthetic and natural crystals on the optical detection of radiation created vacancies.

## EXPERIMENTAL DETAILS

The single crystals produced in this laboratory were grown in air by the Kyropoulos technique using NaCl from which heavy metal ion impurities have been removed by a dithizone extraction process. Other synthetic single NaCl crystals were obtained from the Harshaw Chemical Company. The halite came from Baden, Germany.

All irradiations of these crystals were made at room temperature. A 2-Mev Van de Graaff generator operating at a beam current of 3 microamperes supplied the high-energy electrons. The x-rays of 40-kvp (beam current 13 ma) were obtained from a Machlett OEG-60 tube with a tungsten target. $\gamma$ rays of 1.1 and 1.3 Mev were provided by a $\mathrm{Co}^{60}$ source.

The ultraviolet light source was an Allen hydrogen-arc lamp with a lithium fluoride window. The *F* band created by high-energy irradiation was optically bleached using a glass-envelope 100-w tungsten lamp with a water filter. Optical absorption measurements were made with a Cary Model 14M spectrophotometer in the region from 1850 A through the visible, and with a Baird Associates vacuum monochromator below 1850 A.

## RESULTS

In Fig. 1 the curve labeled "pre-irradiation" is the growth curve for the *F* band created by ultraviolet light prior to exposure of the crystals to high-energy radiation. For simplicity only one curve is shown, although there is some slight variation in the pre-irradiation growth curves, depending upon the nature of the crystal. The NRL Lot C crystal colors about 30% more than the natural crystal, and the Harshaw crystals are intermediate. The initial ultraviolet exposure produces a negligible number of vacancies relative to the number to be created by the high-energy irradiation.

The effect produced by irradiating various crystals with 40-kvp x-rays at 13 ma for 15 minutes on each side[4] (about $4\times10^{20}$ ev/cm$^3$ absorbed in a crystal 0.009 in. thick), followed by optical bleaching of the x-ray created *F*-centers and subsequent exposure of the crystal to the same number of ultraviolet quanta as used prior to x-raying, is shown in Fig. 1. With irradiation of 2-Mev electrons or $\mathrm{Co}^{60}$ $\gamma$ rays the shape of the curves are the same for the same energy absorbed (about $4\times10^{20}$ ev/cm$^3$). The magnitude of the effect in any given crystal appears to depend upon the flux density

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

[2] J. Rolfe, Phys. Rev. Letters **1**, 56 (1958).

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

[4] The fact that the same energy is absorbed in each of the various crystals is of primary importance. The resulting *F*-band coloration will vary from crystal to crystal and depends upon the hydroxyl ion concentration.[3]

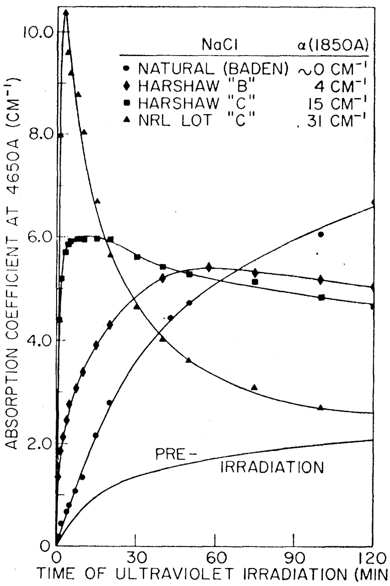

FIG. 1. Optical absorption measured at the peak of the *F* band in NaCl as a function of ultraviolet irradiation. All crystals have, prior to exposure to ultraviolet light, been irradiated for 15 minutes per side with 40-kvp x-rays and the resulting color optically bleached. The table in the upper right hand corner indicates the optical absorption at 1850 A prior to irradiation.

of the high-energy radiation. In comparing the effect of 2-Mev electrons and 40-kvp x-rays, where the flux density can be made equal, the same curves (magnitude and shape) are obtained within 30%. The flux density of the $\gamma$ rays, however, is 100 times lower than the previously mentioned radiations and the resulting coloration is about 3 times less.

The shape of the growth curve for the synthetic crystals is quite different from that of the natural crystal. The natural crystal growth curve produced by ultraviolet light, as shown in Fig. 1, has the same increasing monotonic growth after exposure to x-rays as before exposure to x-rays. The synthetic crystal growth curves all have a high rapid initial coloration after exposure to x-rays followed by a decrease in the *F*-center concentration as the ultraviolet irradiation continues. It is also of interest to note that in the synthetic crystal having the highest initial coloration (NRL Lot C) the final value of the *F*-center coloration approaches the "pre-irradiation" curve. The same effect occurs in all the synthetic crystals and is dependent on the hydroxyl ion concentration present in all the crystals measured. The hydroxyl ion concentration has been shown in NaCl to be related to an absorption band in the unirradiated crystal at 1850 A.[3] The amount of hydroxyl present is proportional to the 1850 A absorption band and the magnitude of this band for the crystals used is given in Fig. 1. This band was observed some years ago,[1] but its origin was unknown until recently. It was detected in a measurement designed to show that the increase in sensitivity of a crystal to ultraviolet radiation was not due to an increased absorption of ultraviolet quanta after the crystal had been x-rayed and optically bleached. This is illustrated in Fig. 2 where it can be seen that there is some increase in absorption in this short wavelength region. This is now known to be significant, contrary to the opinion stated in the earlier paper. The difference of the two curves indicates the presence of a band at 1920 A which is attributed to hydride ions (*U* centers). The source of the hydride ion is the hydroxyl ion. The initial enhanced ultraviolet created coloration in synthetic crystals which have been exposed to high-energy radiation is due then to the presence of *U* centers as a source of *F* centers.

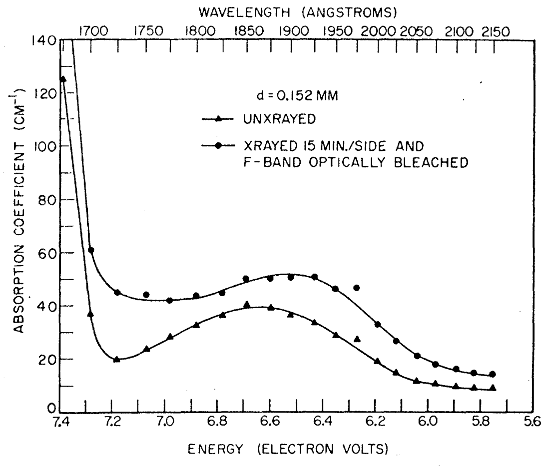

FIG. 2. Optical absorption spectra of synthetic NaCl showing the growth of the hydride band at 1920 A.

The loss of *F* centers under prolonged ultraviolet irradiation was originally attributed to "the destruction of the excess vacancies introduced by x-raying." Present re-cycling experiments indicate that these vacancies are still in the crystal but are agglomerated in such a way that they no longer can trap electrons to become color centers. This is demonstrated in the following way. If after x-raying, optically bleaching, and irradiating with ultraviolet light to the point where almost all the excess centers are removed, the crystal is then recycled, it is found that (a) the x-ray created *F* band is higher in the second cycle than in the first and (b) the peak of the ultraviolet created *F* band is higher in the second cycle than in the first. From this data it is concluded that the loss of *F* centers under prolonged ultraviolet irradiation does not represent a loss in the number of x-ray created vacancies but only a loss in isolated vacancies which are required for the production of *F* centers. No other absorption bands arise in the visible region of the spectrum during this loss of the *F* centers in the synthetic crystals.

From Fig. 1 it is seen that after about 80 minutes of ultraviolet irradiation the *F*-band coloration produced by the radiation in the synthetic crystals falls below that of the natural crystal. If only the excess vacancies created by the high-energy radiation were made unavailable for $F$-center formation by the prolonged ultraviolet irradiation, the coloration curves for the synthetic crystals should approach the coloration curve for the natural crystal. This assumes that the growth curve for the natural crystal is typical of a crystal containing vacancies created by high-energy radiation from a source not requiring the presence of hydroxyl ions. If this is so, then the agglomeration of vacancies under prolonged ultraviolet irradiation in the synthetic crystals includes those which would have arisen even in the absence of hydroxyl ions. There is then an entity which is introduced by the presence of hydroxyl ions or their dissociation and under the influence of sufficient ultraviolet radiation, that removes isolated negative ion vacancies from the crystal. Compton[5] has shown that massive doses of high-energy radiation produce a colloid band in synthetic crystals which is associated with the presence of hydroxyl ions in the crystals before irradiation. Under similar radiation doses a colloid band does not arise in natural sodium chloride because these crystals contain no hydroxyl ions. It is reasonable to assume that at much lower doses than those used by Compton some small number of colloids form in synthetic crystals. It is also possible that the loss of $F$ centers (electrons and isolated negative ion vacancies) under prolonged ultraviolet irradiation of high-energy irradiated crystals results in the formation of colloids. The electrons so released may contribute to the formation of sodium atoms from sodium ions and the vacancies may form a condensed cloud about the colloidal aggregate. If a hitherto unirradiated synthetic crystal which has been given sufficient high-energy radiation to provide a detectable colloid band in addition to the $F$ and $M$ bands, is completely optically bleached and then exposed to ultraviolet light, the colloid band grows instead of the $F$ band. This indicates that, at least under these conditions, the colloid can be made to grow under ultraviolet radiation. When natural crystals, which have been heated in moist air at a few hundred degrees below their melting point, are exposed to high-energy radiation, optically bleached, and then subjected to ultraviolet light their $F$-band growth curves have the same shape as those of the synthetic crystals.

Other properties appear to be affected by the presence of hydroxyl ions in the crystal lattice. The bleaching of the high-energy created $F$ centers is rapid and complete in those crystals containing the higher hydroxyl concentrations. In the halite from Baden, Germany, the $F$ centers in the crystal cannot be completely optically bleached. The absorption spectra show poorly defined bands at about 3900 A, 4700 A, and still others between 5500 and 8000 A. The 3900 A band may be the $K$ band, and the 4700 A band may be a perturbed $F$ band. The longer wavelength bands, of which there are 2 or 3, vary in wavelength from sample to sample. It was also noticed that the $N$ bands were absent in the high-energy irradiated crystals containing the higher hydroxyl ion concentrations whereas they were most prominent in the halite.

## SUMMARY

The effect of various high-energy radiations on the production of vacancies in single crystals has been studied. For a given crystal the shape of the growth curves were the same whether x-rays, $\gamma$ rays, or high-energy electrons were used, but striking dissimilarities were observed in comparing the results obtained on synthetic and natural crystals. It is clear that the presence of hydroxyl ions in the synthetic crystals provides a source of vacancies not present in the natural crystals.

## ACKNOWLEDGMENTS

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[5] W. Dale Compton, Phys. Rev. **107**, 1271 (1957).