Electrical Conductivity of X-Irradiated KCl†

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The conductivity of Harshaw KCl crystals has been measured isothermally as a function of time in the temperature range 150–200°C, after exposing the crystals at room temperature to x-ray doses sufficient to produce about $10^{16}F$ centers/cm^3. Besides the F band, a V band at about 5.75 ev is produced. If the F band is eliminated by optical bleaching before the measurement but the V band remains, the conductivity increases monotonically to an asymptotic value, which is equal to the conductivity of the unirradiated crystal for virgin samples but is lower for samples which have been annealed in air at 260°C beforehand. If both the F band and the V band are present, the conductivity increases more rapidly at first, and then decreases to an asymptotic value. The behavior is qualitatively similar to that previously observed in NaCl, though there are significant differences in the optical absorption spectrum and temperature dependence of the conductivity changes.

I. INTRODUCTION

IT is well established that the imperfection responsible for the F-band absorption in the alkali halides is an electron trapped at an anion vacancy. Seitz proposed[1] that the V bands in the ultraviolet were due to holes trapped at cation vacancies or vacancy aggregates. If this is so, the electrical conductivity of crystals containing V centers should be affected, since charge in the alkali halides is normally transported by the cation vacancy. Although Seitz's models of the V centers may now be considered doubtful, because of more recent studies,[2,3] nevertheless, large changes in conductivity are actually observed in colored crystals.[4] A correct model of the absorption centers should account also for their effect on the electrical conductivity.

Because the absorption bands produced by irradiation depend strongly on the conditions of the irradiation and the previous and subsequent treatment of the crystals, it is important to seek correlations between simultaneous optical and electrical measurements. Also the production and destruction of the color centers differs in detail considerably among the various alkali halides. We have repeated the previous measurements on KCl in order to compare its behavior with NaCl. We have also measured the optical absorption after various stages of the conductivity changes. For these measurements, KCl has the advantage that the V bands within the range of our spectrophotometer are more clean-cut.

II. EXPERIMENTAL DETAILS

The experimental procedure used in the present investigation was generally similar to that previously reported.[4] The samples used were cleaved from potassium chloride single crystals obtained from the Harshaw Chemical Company. The sample size was 1.0×1.0×0.2 cm. Electrodes were painted on the two large faces, using Dupont No. 5584 silver paint. Some samples were irradiated as received from Harshaw without further heat treatment, and others were annealed in air before the irradiation and measurement.

The x-rays with which the crystals were irradiated were obtained from a Norelco FA-60 tungsten target x-ray tube, operated at 40 ma and 50 kvp. The large faces of the specimen were perpendicular to the x-ray beam, about 3 cm from the tube window. A 1-mm thick KCl filter was placed in front of the sample in order to cut out the softest x-ray component, and the samples appeared uniformly colored.

The electrical resistance of the crystals was measured within one-half to one hour after the irradiation, using a General Radio Company electrometer-amplifier Type 1230-A. The sample was put into a preheated furnace and was at temperature after 3 minutes in the furnace. Earlier readings were corrected using the temperature dependence of the unirradiated sample. The warmup corresponds to an effective starting time about 1 minute later than the actual time of insertion into the furnace.

Optical absorption of the samples was measured with a Unicam SP 500 spectrophotometer. The optical path was through the thin edge of the specimen (perpendicular to the direction of the x-ray beam), since the electrodes were not removed.

III. RESULTS

1. Electrical Conductivity

The effect of x-ray irradiation on the conductivity of KCl is qualitatively similar to that previously observed in NaCl. In Fig. 1 the behavior of virgin KCl and NaCl crystals which have been exposed to identical 20-minute x-ray irradiations at room temperature is shown as a function of time at 173°C. The ordinate is the ratio of the conductivity σ of the colored crystal to the "normal" conductivity σ_0 of the same crystal measured before the irradiation. Although the x-ray dose

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[1] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).
[2] T. G. Castner, W. Känzig, and T. O. Woodruff, Suppl. Nuovo cimento **7**, 612 (1958).
[3] H. N. Hersh, Phys. Rev. **105**, 1410 (1957).
[4] R. W. Christy and W. E. Harte, Phys. Rev. **109**, 710 (1958). References to other work are given here.

was the same for the two crystals, the optical absorption, in particular the relative height of F- and V-type bands, was quite different. The optical absorption will be discussed in detail in the next section. The rapid rise of the conductivity from a low value, followed by a slower decrease to less than the normal conductivity, was characteristic of the colored crystals.

Also shown in Fig. 1 is the relative conductivity of a colored crystal which had a 3-hour anneal in air at 260°C before the irradiation. After annealing at this temperature the normal conductivity between 150° and 200°C is about half that of the virgin crystal, and the conductivity of the colored crystal is decreased even more. After the first anneal at 260°, however, the behavior is fairly reproducible. If the crystal is subsequently irradiated, annealing at 260° restores the resistance to approximately its value before the irradiation, and the relative conductivity curves are similar after succeeding irradiations. An anneal at 600°C in-

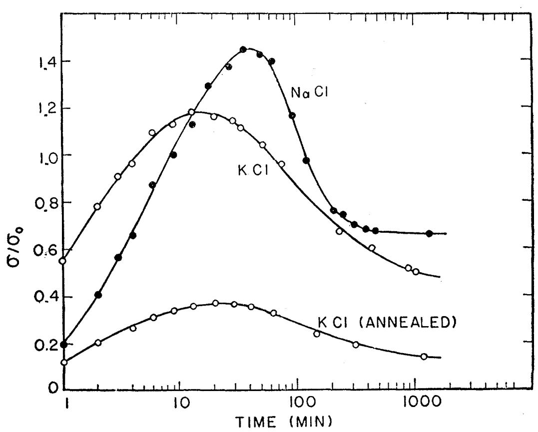

Fig. 1. Relative conductivity at 173°C of NaCl and KCl irradiated 20 min as received, and of KCl annealed at 260° before the irradiation.

creased the resistance of the unirradiated crystal to the extent that the behavior could not be investigated.

The temperature dependence of the conductivity changes is shown by Fig. 2, for an annealed KCl crystal. These data were all taken on the same crystal, which received a 3-hour anneal at 260° between successive irradiations. The dependence on temperature in the range 150 to 200°C is similar to that for NaCl, but three differences should be noted. First, the initial rate of increase of conductivity, relative to the normal conductivity, is approximately independent of temperature in KCl, but in NaCl it increased with temperature with an activation energy of about 17 kcal/mole. Secondly, the temperature dependence of the slow conductivity decrease is much stronger than in NaCl; in KCl an activation energy of 48±8 kcal/mole can be estimated, compared with about 26 kcal/mole for NaCl. The duration of the conductivity decrease appears to be insensitive to thermal history and to the amount of irradiation.

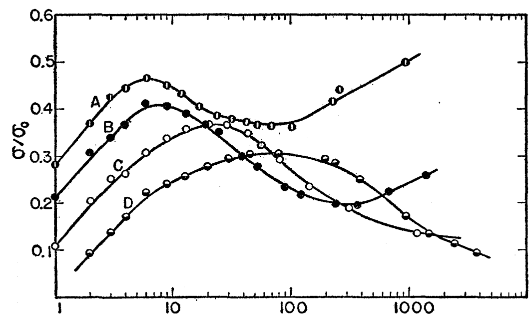

Fig. 2. Effect of temperature on relative conductivity of KCl annealed in air, irradiated 20 min (A) 203°C, (B) 187°C, (C) 173°C, (D) 159°C.

Thirdly, the conductivity ultimately returns toward the normal value even at temperatures in the range 150–200°C, whereas this tendency was not seen in NaCl.

The effect of optically bleaching the crystal before the conductivity measurement is shown in Fig. 3. After the irradiation the samples were bleached with white light from a tungsten lamp until they were colorless. The most striking effect of bleaching the F band is that the conductivity peak is absent. The simplest behavior was that of the bleached virgin crystal (curve B), which returned monotonically to its normal conductivity.

2. Optical Absorption

Optical absorption measurements were made on the conductivity samples (removed from the furnace) before, during, and after the conductivity measurements. The general results are illustrated by Fig. 4.

A 20-min irradiation of a virgin crystal (curve A) produced the F band and a V-type band. The V_2 and V_3 bands were not resolved. The M and R bands were not observed except after longer irradiations. The height of the F band was 1.6 cm^{-1}, corresponding by Smakula's formula to $8\times10^{15}F$ centers/cm^3, and the height of the V band was 1.0 cm^{-1}. These values were reproducible to within about 10% in different samples

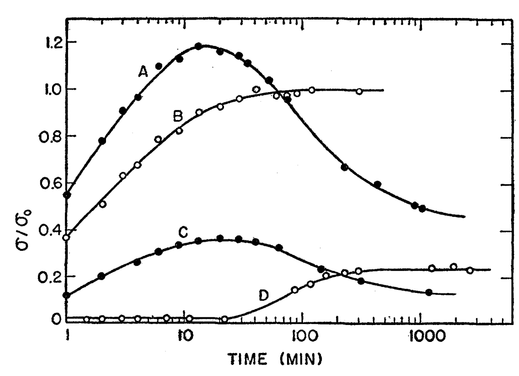

Fig. 3. Effect of optical bleaching on relative conductivity at 173° of KCl x-irradiated 20 min. (A) As received, colored. (B) As received, bleached with white light. (C) Annealed in air, colored. (D) Annealed, bleached.

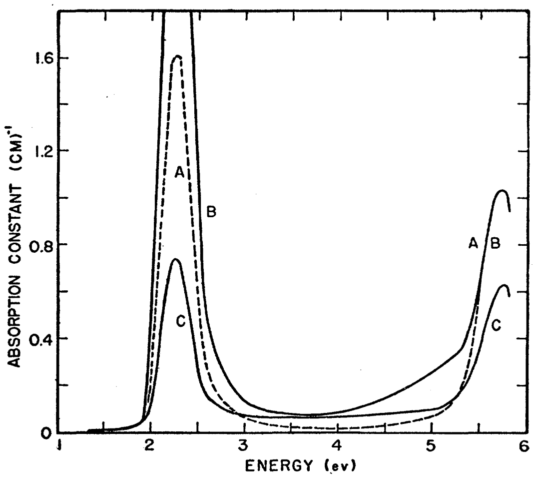

FIG. 4. Optical absorption of KCl x-irradiated 20 min. (A) As received. (B) Annealed in air at 260° before irradiation. (C) Same as B, after 30-min thermal bleaching at 173°C.

cleaved from the same crystal. By contrast, the same irradiation produced in NaCl an F-band height of 13.0 cm^{-1}, corresponding to 9×10^{16} F centers/cm^3, but a V band only about 15% higher than the V band in KCl.

After annealing in air at 260°, the height of the F band produced by a 20-min irradiation was greater, 3.0 cm^{-1}, but the height of the V band was about the same, 0.9 cm^{-1} (curve B). These values were reproducible to within 10% after repeated anneals and irradiations.

Therefore, the three conductivity curves of Fig. 1 correspond to crystals whose V bands were all approximately the same height immediately after irradiation. The annealed KCl contained roughly twice the F-center concentration of the virgin KCl, however, and the virgin NaCl contained eleven times the F-center concentration of the virgin KCl.

During thermal bleaching, the F band decayed very rapidly at first and the V band decayed more slowly. After the F band decreased to the height of the V band, the two bands decayed more or less together. In Fig. 4, curve B for an annealed KCl crystal decreased to curve C after 30 min at 173°C. Curve C was measured at the peak of the conductivity curve in Fig. 1. In general, the two bands were roughly the same height at the peaks of the conductivity curves. At the end of the conductivity measurement, when the conductivity curve had levelled off, both bands were essentially down to the background.

Optical bleaching with white light from a tungsten lamp eliminated the F band altogether, but left the V-band height virtually unaltered in both the virgin and the annealed KCl crystals. The V band was more stable against subsequent thermal bleaching, however, when the F band had been removed by optical bleaching.

IV. DISCUSSION

The relation between the electrical and optical properties of x-rayed crystals is apparently complex. Correspondances between the conductivity curves and the heights of the F and V bands can be sought on the basis of comparisons between KCl and NaCl, between virgin and annealed crystals, and between colored and optically bleached crystals.

Qualitatively, the peak in the conductivity curve seems to be associated with the presence of the F band. This peak is absent in both virgin and annealed KCl and NaCl in which the F band has been eliminated by optical bleaching, but is present in the other cases. In addition, the peak seems to be somewhat more pronounced in virgin NaCl than in KCl and the F band is much higher in NaCl.

On the other hand, there is evidently no simple one-one correspondance between the conductivity and optical absorption. There are cases in which the optical absorption spectrum is the same but the conductivity is different. For example, after optical bleaching the F band is absent and the V band is approximately the same initially in both virgin and annealed crystals, but the conductivity is quite different in the two cases (curves B and D in Fig. 3). Also, at the end of the conductivity measurement the absorption is essentially zero, as in the normal crystal, but the conductivity differs in all cases.

It is perhaps surprising that something like the inverse of the last situation also appears to occur. Ingham[5] has concluded that immediately after the crystals are colored by irradiating at room temperature, the conductivity is essentially normal. He made measurements similar to ours at lower temperatures, in the range 65 to 135°C, and observed that initially conductivity decreased with time. His conclusion is based on an extrapolation to zero time.

Ingham's measurements are consistent with ours, since at higher temperatures the initial decrease was more rapid, and, by extrapolation, would be over in less than a minute at temperatures above 150°C. But his result means that our conductivity curves cannot be extrapolated to zero time.

It was previously suggested[4] that the decrease in conductivity observed after long times in the colored specimens might be consistent with a mechanism involving annihilation of excess positive ion vacancies produced by the irradiation. A similar conclusion is more directly suggested by a comparison of the present results with the experiment of Ewles and Jain,[6] in which they have observed the rate of relaxation of the enhanced conductivity produced by quenching KCl. They conclude, from the temperature and time dependence of the relaxation, together with the theory of Jain's,

[5] H. S. Ingham, Jr., Ph.D. thesis, Carnegie Institute of Technology, 1958 (unpublished).

[6] J. Ewles and S. C. Jain, Proc. Roy. Soc. (London) **A243**, 353 (1957).

that the relaxation is limited by migration of negative ion vacancies to sub-boundaries in the form of cubes of the order of 10^{-5} cm, with an activation energy of 43 kcal/mole. Our activation energy is consistent with this value, although the distance the excess vacancies diffuse before they are annihilated would have to be much smaller in our case.

The possibility cannot be excluded, however, that the peak in the conductivity curves is related instead to electrons released from the F centers during thermal bleaching. The observation of the peak only in samples containing the F band lends strength to this interpretation.

Crystals annealed in air are more easily colored than those as received from Harshaw, and the electrical behavior is markedly different. A possible explanation is that OH^- centers, which enhance colorability,[7,8] are formed during the anneal. The absorption curves of Fig. 4 are referred to an uncolored crystal, so that the OH^- absorption has been subtracted from them. Some of the uncolored virgin Harshaw KCl crystals had a peak absorption, relative to air, of the order of 1 cm^{-1} at 204 mμ. Consequently, the number of OH^- centers may have been comparable with the number of F centers produced by the irradiation. On the other hand, the uv absorption of the uncolored crystals was not strongly increased after an anneal in air at 260°C. Divalent cation impurities also increase the colorability,[9] and precipitated impurities may be expected to go into solution during annealing. This effect should give an increased conductivity of the annealed crystals, however, and the reverse was observed. Neutron activation analysis[10] of Harshaw KCl indicates that not more than 0.1 ppm of the relevant impurities are present. Also, in the case of NaCl it was not possible to return the crystal to its virgin state even by very slow cooling. Therefore, it seems more probable that hydrolysis products or oxygen are the impurities involved.

Whatever the cause of the differences between virgin and annealed crystals, the electrical and optical effects may be directly correlated. If a virgin crystal is irradiated longer than an annealed one, so that the two have roughly the same F-band absorption, the electrical behavior was found to be more nearly the same.

The relations between conductivity and absorption may be understandable after two fundamental problems have received completely satisfactory explanations. The identification of the V bands with trapped holes requires an understanding of the following questions. First, the F-band area can be greater than the V-band area (as, for example, in the annealed KCl). What is the source of the F-center electrons which are not created leaving holes? Secondly, the V band can be present without the F band (as in KCl bleached with white light). Where are the electrons which have left the F centers but have not annihilated the holes?

ACKNOWLEDGMENT

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[8] J. Rolfe, Phys. Rev. Letters **1**, 56 (1958).
[9] H. W. Etzel, Phys. Rev. **87**, 906 (1952).
[10] S. Anderson, Corvallis Color Center Symposium, 1959 (unpublished).