Ionic Disorder in X-Irradiated KBr Crystals

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The production by x-rays of anion vacancies in KBr crystals was studied quantitatively in the liquid helium temperature range. The thermal stability of the vacancies was investigated in detail. A series of recombination steps was observed in the 10°K to 30°K region associated with activation energies of the order of 0.03 to 0.09 ev. A green luminescence was observed during the irradiation by x-rays and during the annealing of the crystals. This luminescence is attributed to electronic recombinations rather than to vacancy recombination. A semiquantitative electrostatic model is proposed to explain the very limited thermal stability of single vacancies. This analysis predicts remarkably high local concentrations of vacancies.

INTRODUCTION

POTASSIUM bromide crystals which have been x-irradiated at low temperatures show an absorption band at 2020 A, called the α band.[1] Its absorption constant is directly proportional to the number of single anion vacancies produced by the energetic radiation. In a previous investigation[2] the production and recombination rates of these centers were studied at temperatures above 20°K. The crystals exhibited drastic changes with temperature in the vicinity of 20°K, the lowest temperature achieved. For this reason the same problem has now been studied in the liquid helium temperature range.

EXPERIMENTAL

The KBr crystals were obtained from the Harshaw Chemical Company. Measurements were made on crystals as cleaved, as well as on samples well annealed after cleaving. In order to maintain the samples at helium temperatures, standard cryogenic technique was used. The metal cryostat allowed optical measurements and x-irradiation at sample temperatures down to 4.9°K without pumping on the helium. Higher temperatures were achieved by heating the crystal holder electrically. After evaporation of all the helium, the crystals warmed up from 4.9°K to 30°K in about 90 minutes. A resistance thermometer and a gold-cobalt *vs* copper thermocouple were used to measure the crystal temperature. The x-irradiation was carried out with a tungsten-anode x-ray tube at 70 kv and 10 ma. The distance from anode to crystal was 13 cm. A Nestor hydrogen lamp, a Bausch and Lomb quartz monochromator, and a RCA-S5 Phototube with quartz window were used for the optical measurements. A Keithley vacuum tube electrometer measured the photocurrent. The detector had a time constant of 20 seconds. Most of the annealing data were automatically recorded. A few measurements of the earlier investigation[2] were repeated in order to determine the absolute x-ray intensity values for the present work, since absolute values were determined in the earlier work.

RESULTS

In Fig. 1 the number of anion vacancies per electron volt of absorbed x-ray energy is plotted *versus* crystal temperature. We are dealing here with initial efficiencies; with continued irradiation the rate of vacancy production decreases steadily at all temperatures.[1] There is a very strong increase in production rate between 25°K and 10°K. Well-annealed and freshly cleaved crystals cooled down in a few minutes or in several hours showed no systematic differences in these efficiencies.

Much additional information was achieved by observing the x-irradiated crystals during a slow annealing procedure from 5°K to about 30°K. Here a superposition of two effects complicated the analysis. The complication arose because the phototube which was being used to measure the transmission change at 2020 A was exposed simultanously to a recombination luminescence. This luminescence had also appeared very strongly during the x-irradiation at any temperature below 30°K. Its spectrum was not observed explicitly, but from measurements with different filters the luminescent energy was located between 4000 and 6000 A with a maximum in the green and without any appreciable component in the ultraviolet. The sensitivity of the S5-photocathode was unfortunately still appreciable at wavelengths as long as 6000 A. Further-

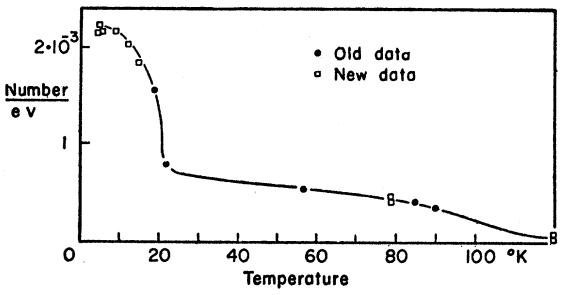

FIG. 1. α-center (anion vacancy) production efficiency *versus* crystal temperature during x-irradiation of KBr. The "old data" are from reference 2.

[1] Delbeq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951); W. Martienssen, Z. Physik **131**, 488 (1952).
[2] H. Rüchardt, Z. Physik **140**, 574 (1955).

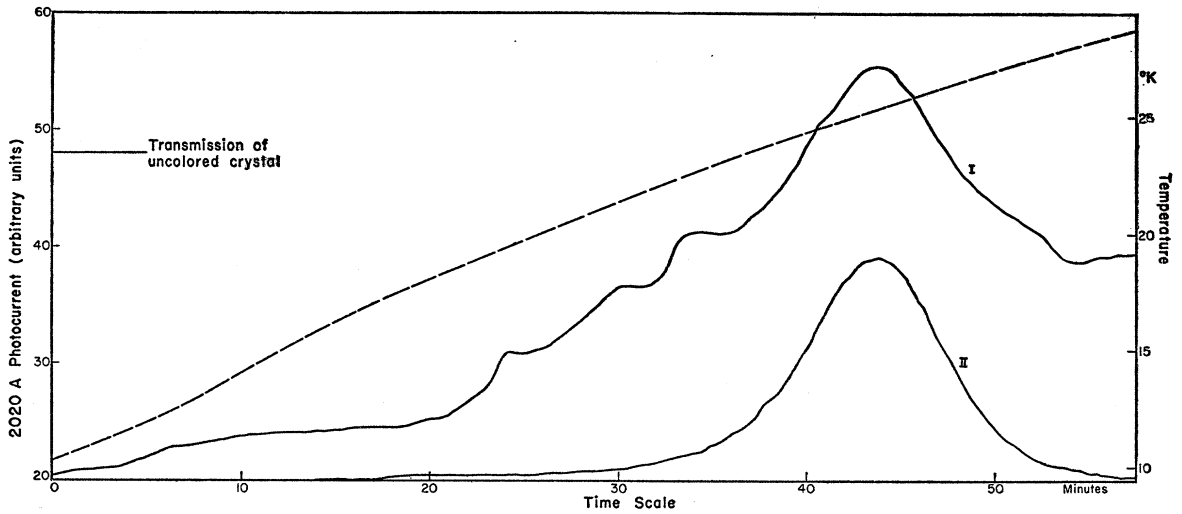

FIG. 2. Recorder trace of photocurrent in RCA–S5 phototube during annealing of a KBr-crystal x-irradiated at 5°K. Curve I (ordinate shifted) shows the transmission at 2020 A and a superimposed luminescence. Curve II shows the luminescence contribution alone. Here the ordinate should start at zero. The dotted curve gives the temperature-time relation. The data between 5°K and 10°K are not shown here.

more the ultraviolet light for the transmission measurement could not be made sufficiently intense to make this disturbance negligible.

In order to correct for luminescence, the whole coloring and annealing procedure had to be exactly repeated with an identical crystal, which was adjacent to the originial slab before the samples were cleaved. This time only the luminescence was measured. A separate check was made to establish the fact that irradiation by the measuring ultraviolet light during the annealing did not affect the luminescence behavior at all. Therefore the luminescence contribution could be subtracted very accurately, particularly since the main transmission change and the luminescence peak are shifted by several °K relative to each other.

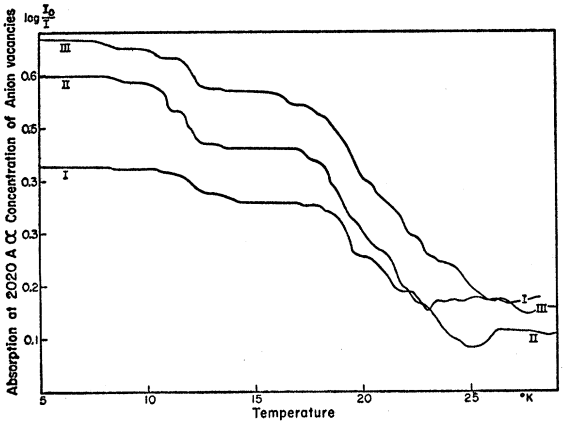

FIG. 3. Anion vacancy concentration *versus* temperature for three different annealing runs. The plotted range was covered within 80 to 90 minutes. The data above 23°K are less reliable because of the large luminescence correction. Here we could expect a new α-center production by dissociation of F-centers.

Figure 2 gives in curve I the direct recording of both effects. Curve II shows the luminescence peak, measured separately. The temperature-time relation is represented by the dotted curve. In the range of strong luminescence above 23°K the transmission values, obtained by subtraction, are not reliable.

Figure 3 presents the absorption (proportional to the vacancy concentration) *versus* temperature, derived from the data of Fig. 2. A quite extensive structure is apparent and shows the complexity of the recombination processes. The three curves, resulting from different runs, show quite a similar pattern and most of the steps can be found in all of them. The remaining variations below 23°K were probably not caused by lack of accuracy in measurement but are probably attributable to individual differences in the samples and to possible different treatments. Above 23°K the disagreement may be caused also by measuring errors.

The result of Duerig and Markham[3] for F-center production was confirmed by our measurements; production by x-rays is as efficient at 5°K as at 80°K. This seems to be in contradiction to results from Göttingen[4] obtained at 20°K.

The change of the F-center as well as the H-center concentration was also checked during some of the annealing runs. Figure 4 shows that appreciable numbers of these centers do not disappear until the luminescence appears strongly. There seems to be a much more direct correlation between color center removal and luminescence than with vacancy recombination and luminescence. Figure 5 shows the absorption in the H-band at 5°K and after warming to 30°K. In addition to the H-band a relatively strong band can

[3] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).
[4] For example, F. Lüty, Z. Physik **145**, 249 (1956).

be seen at the wavelength where Dorendorf[5] found the V_7 band. This band is reduced in the same manner as the H-band as the temperature rises. At the same time a V_1 absorption appears, superimposed to the remaining H-band.

Another observation concerning the F'-centers should be mentioned: A KBr crystal, intensively irradiated with x-rays at liquid helium or hydrogen temperature and afterward exposed to light between 0.8 and 1.3 μ, also shows green luminescence. The luminescence disappears completely after a short while and seems to be caused by recombination of F'-centers with V-centers.

DISCUSSION

Vacancies

Our results for the production by x-rays of vacancies in KBr are in full agreement with the mechanism proposed by Seitz[6] and by Dexter,[7] as was shown explicitly in the earlier paper.[2] The theory of Seitz and Dexter is briefly the following: Any real crystal contains dislocations and vacancy clusters as intrinsic disorder. The x-irradiation produces photoelectrons, holes and excitons in the crystal. These excitations cause charge anomalies by changing the charge of lattice elements and thermal spikes from recombination and decay processes. These processes happen preferentially at disordered lattice points, particularily dislocations. There they cause spontaneous disorder changes, moving the dislocation and ejecting single ion vacancies into the surrounding lattice.

We attempted to extend this model in order to understand the temperature dependence of the production rate and of the recombination processes. The data of the pertinent measurements (Figs. 1 and 3; see also reference 2) show quite evidently that the dependence of the vacancy production rate on temperature can be traced to the more or less complete spontaneous recombination of vacancies at different temperatures, as observed in the annealing experiments. Therefore only the temperature dependence of recombination requires an explanation.

The basic proposal for the recombination processes is the hypothesis that there is a minimum distance bebetween opposite charged vacancies if they are to be stable. The magnitude of the distance must increase with temperature.

The new, much more detailed low-temperature data give quite valuable additional information. It is now apparent that the recombination occurs in a number of single steps. This fact was observed only indirectly in the previous work, but now the better resolution of the processes permits at least a rough estimate of the activation energies involved. By measuring the change of slope with temperature within single steps one evaluates

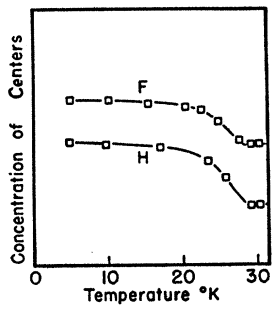

FIG. 4. Decrease of F-center and H-center concentrations during the annealing of a crystal, previously x-irradiated at 5°K.

numbers between 0.025 and 0.09 ev. The values increase with temperature and exhibit a gap between 0.04 and 0.07 ev. The accuracy of these numbers is poor since the separation of the individual processes is still not great.

Mott and Littleton[8] calculated the activation energies for the migration of cation and anion vacancies in NaCl as 0.51 and 0.56 ev; respectively and Dienes[9] calculated the similar energy for vacancy pairs to be 0.375 ev. In KBr we have to expect very similar values. All these numbers are much too high in order to explain our processes directly. But the attractive potential of oppositely charged centers provides a means of reducing these energies to smaller effective values. This has been shown explicitly by Reitz and Gammel.[10] They found absolute instability for oppositely charged vacancies in the second nearest neighbor position, but a barrier reduction of only 20% for twice this distance. In order to explain our effective values the barrier potential (about 0.5 ev) must almost equal the Coulomb potential effect, leaving only about 10% of the initial value. Since we observe a series of steps with activation energies close to each other, there must exist a number of possible positions with almost the same distance between the vacancies. A distance of at least 3 to 4 lattice constants is required. The pronounced structure in the recombination (particularily the gap around 15°K) show that the distances are not much larger. If they were, a practically continuous series of possible distances would exist. How can it be understood to have

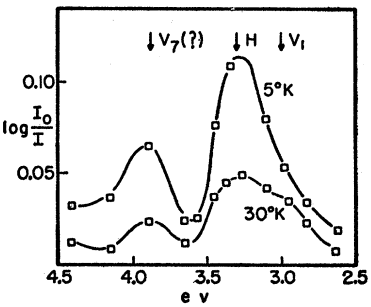

FIG. 5. V-center absorption in KBr, x-irradiated at 5°K. The lower curve shows the remaining absorption after annealing to 30°K.

[5] H. Dorendorf, Z. Physik **129**, 317 (1951).
[6] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).
[7] D. L. Dexter, Phys. Rev. **93**, 985 (1954).
[8] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).
[9] G. J. Dienes, J. Chem. Phys. **16**, 620 (1949).
[10] J. R. Reitz and J. L. Gammel, J. Chem. Phys. **19**, 894 (1951).

a strong enough effect of the Coulomb attraction over this distance?

Since we have presumably very high local concentrations of vacancies, the cumulative effects of many vacancies can increase the local potential reductions. The fact that at 30°K most of the vacancies have already recombined shows that the distance, which vacancies can be ejected out from their sources, must be limited very sharply. The thermal spike which produces the vacancy does not extend further. These high-concentration areas contain a large number of vacancy pairs and aggregates, produced by spontaneous recombination during the x-irradiation and in the lower temperature part of the annealing run. These empty spaces also can reduce the barriers. No data have been obtained for the fraction of vacancies which recombine spontanously during x-irradiation but our highest efficiency for production of stable α centers was one vacancy only per 400 ev (Fig. 1). Therefore abundant energy is still available.

One might expect observably different band shapes for anion vacancies in regions of so strong and varying disorder. The half-width of the α band is in fact quite large and is at least 0.2 ev at 5°K. Exact values have not been obtained since the absorption peak is not well isolated. This number is of interest in order to compare with the half-width of the first peak of the fundamental absorption, as measured by Martienssen[11] for KI. His measurements give a width at 20°K of 0.053 ev compared with 0.078 ev at 90°K and 0.174 ev at room temperature. Our measurements on the α band show a half-width reduction of only 10% between 78°K and 5°K.

No recombination was observed in the first few degrees of the warmup (the first 10 minutes of the run). The crystal temperature was not measurably influenced by the x-irradiation or by the ultraviolet light and the behavior is as yet unexplained.

Electronic Effects

After x-irradiation at 5°K, about 20% of the anion vacancies are filled with electrons, creating F-centers. This value depends, however, on the irradiation time, since saturation effects affect the vacancy and the F-center buildup to different extents.[2]

The observed luminescence during x-irradiation and during the vacancy recombination can be understood as a recombination of electrons from F- and F'-centers with holes from H-centers and eventually from other V-centers. This is proved by the analogous reduction of the F- and H-center concentration (Figs. 4 and 5) and by the observation of luminescence during optical bleaching of F'. The pronounced glow peak at 25.7°K, a temperature where most of the vacancies have recombined, demands an independent reason for electronic recombination at this temperature. The nature of this process has not yet been determined. The energy released during the production of vacancy pairs and the influence of vacancies passing by will lead to some recombination at lower crystal temperature. This can explain the long tail of the luminescence peak (Fig. 2) at lower temperatures. Additional experiments are necessary in order to understand these processes in detail.

The disagreement concerning F-center production efficiency in KBr between Duerig and Markham on one side and the Göttingen school on the other has already been mentioned. This disagreement could be attributed simply to this recombination process at 25.7°K, since only the American data were taken at liquid helium temperatures.

Other Alkali Halides

The preceding discussion concerning vacancy stabilization can also be applied to KI, NaBr, and NaI. In these crystals at sufficiently low temperatures, no stable single anion vacancies, nor any other coloration, can be produced by x-irradiation. In these crystals the barrier energy for cation vacancy migration is presumably smaller than in KBr. If this is true, all the distances which can be reached by single vacancies during their production by a thermal spike could be within the range, that leads to spontaneous recombination by Coulomb attraction.

An experiment on NaBr[12] of a quite different kind proves that changes in the ionic disorder also appear by irradiation in this material: One-half of a crystal was covered with a lead screen and then the crystal was x-irradiated for 12 hours at 78°K. No change in optical absorption was observed. The crystal was than warmed slowly. At about 0°C, moist air was induced in the cryostat at a pressure of 5 mm of Hg. The unirradiated half of the crystal was immediately contaminated on its surfaces, showing a large number of tiny circular holes of about 0.001 in diameter. On the other hand it took several minutes until the x-irradiated half showed the first spots, even at the face opposite to the x-ray tube. Obviously the number of contamination nuclei, presumably dislocations, is reduced by the irradiation.

ACKNOWLEDGMENTS

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[11] W. Martienssen, Nachr. Wiss. Göttingen Acad., 262 (1955).

[12] Supplied by Dr. K. Korth, Kiel Düvelsbeker Weg, Germany.