PHYSICAL REVIEW VOLUME 127, NUMBER 5 SEPTEMBER 1, 1962

Photochemical Behavior of Alkali Halide Crystals Containing OH^- and $SO_4^=$ Ions

P. W. M. JACOBS AND H. A. PAPAZIAN*
Department of Chemistry, Imperial College, London, England

(Received April 2, 1962)

The irradiation with uv light of KCl crystals containing K_2SO_4 produces three new absorption bands at 213, 236, and 258 mμ. Simultaneously, the absorption due to $SO_4^=$ ions in the infrared decreases. KCl crystals doped with KOH show on irradiation only the 236- and 213-mμ bands. A comparison of the absorbance at these wavelengths after irradiation with that due to the OH^- and $SO_4^=$ ions prior to irradiation leads to the conclusion that the 236-mμ band is due to absorption by an oxygen species while that at 213 mμ comes from the photolysis of OH^- ions which are present to some extent even in crystals which have not been doped with KOH. It is likely that the 213-mμ band is identical with the hydride band. KBr doped with K_2SO_4 shows broadly similar results.

I. INTRODUCTION

THE irradiation of alkali halides with x rays or ultraviolet light induces new absorption bands in both the visible and the ultraviolet regions of the spectrum, and this phenomenon has been intensively studied over a number of years. Recently, there has been renewed interest in the possible roles in photochemical processes of H^- ions[1] and OH^- ions[2–5] incorporated in alkali halide crystals. In this communication, we describe some optical measurements on potassium chloride crystals containing K_2SO_4 or KOH and on potassium bromide containing K_2SO_4, which we believe may assist in an assessment of the contributions from oxygen to the ultraviolet absorption spectra of irradiated alkali halides.

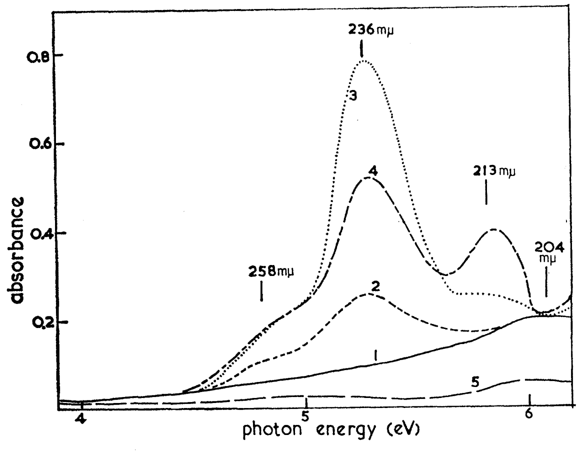

FIG. 1. The absorption spectrum of KCl:K_2SO_4 at 80°K. Curve 1: background prior to irradiation with uv light. Curve 2: after 10-min irradiation. Curve 3: after 30-min irradiation. Curve 4: after 105-min irradiation. Curve 5: KCl without added K_2SO_4, after irradiation for 1 h. Curves 1 to 4, crystal *A*, 1.1 mm in thickness. Curve 5, crystal *D*, 1.2 mm in thickness.

II. EXPERIMENTAL

A. KCl:K_2SO_4

Crystals of KCl containing 2×10^{-3} mole ratio of K_2SO_4 were grown by the Stockbarger method; they were beautifully transparent and cleaved readily. The charge, in a quartz container, was pretreated at temperatures up to 500°C with a mixture of purified hydrogen chloride and nitrogen to remove water. The quartz container was then evacuated and sealed off. In the resulting crystals there was some absorption due to OH^- as evidenced by a slight band near 204 mμ (see Fig. 1). In addition, there was a steady rise in the background absorption below 250 mμ. As this was not found in crystals which were not doped with K_2SO_4 but were otherwise similarly treated, it must be due to the presence of $SO_4^=$ ions in the crystal. Considerable absorption in the region of 8–10 μ (Fig. 2) was apparent in agreement with the recent results of Coker, Decius, and Scott[6] on the infrared absorption of the $SO_4^=$ ion in KCl.

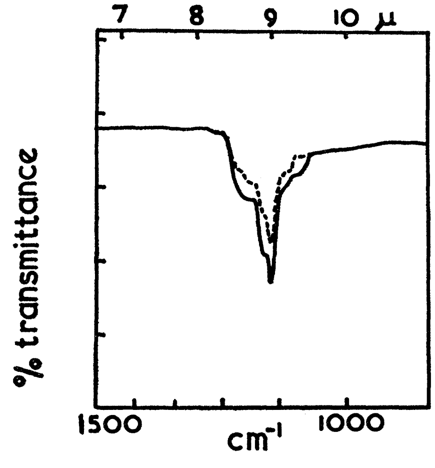

FIG. 2. The infrared spectrum of a KCl:K_2SO_4 crystal, measured at 80°K (full line). The dotted curve shows the spectrum after the crystal had been irradiated for 30 min with uv light. Crystal *C*, 3.7 mm in thickness.

---

* National Academy of Sciences—National Research Council Postdoctoral Fellow, on leave of absence from the Space Sciences Laboratory, General Dynamics Astronautics, San Diego, California.

[1] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **104**, 599 (1956).

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

[3] F. Kerkhoff, Z. Physik **158**, 595 (1960).

[4] J. Cape, Phys. Rev. **122**, 18 (1961).

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

[6] E. H. Coker, J. C. Decius, and A. B. Scott, J. Chem. Physics **35**, 745 (1961).

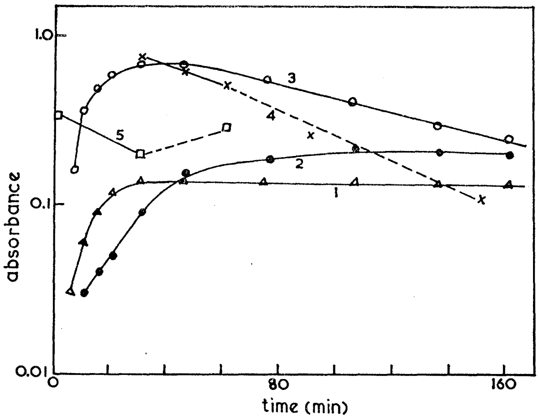

FIG. 3. Growth curves at 80°K for KCl:K_2SO_4 crystals. Broken lines show the changes in absorbance on standing in the dark at 80°K. Curve 1: 258-mμ band. Curve 2: 213-mμ band. Curve 3: 236-mμ band. Curves 1, 2, 3 all for crystal *A*. Curve 4: 236-mμ band, crystal *B*, 1.2 mm in thickness. Curve 5: infrared absorption, crystal *C*.

The intrinsic ionic conductance[7] was similar to that for pure crystals, indicating either that extra anion vacancies are not introduced by the $SO_4^=$ ions, or that they are so firmly bound in complexes that they do not contribute to the conductance even at 700°C. In the impurity-controlled region, the conductivity was smaller[7,8] than that of undoped crystals, indicating that the cation vacancy concentration had been reduced by the removal of M^{++} ions by the $SO_4^=$. Probably, the $SO_4^=$ ion occupies two nearest-neighbor anion vacancy sites. The clarity of the crystals indicates true solution rather than a precipitated sulphate phase.

On irradiation at liquid nitrogen temperature with ultraviolet light from an unfiltered low-pressure mercury source, the infrared absorption decreases (Fig. 2) and simultaneously, bands appear in the ultraviolet at 213, 236, about 258 mμ, and beyond the limit of the spectrophotometer (Fig. 1). There is no visible coloration.

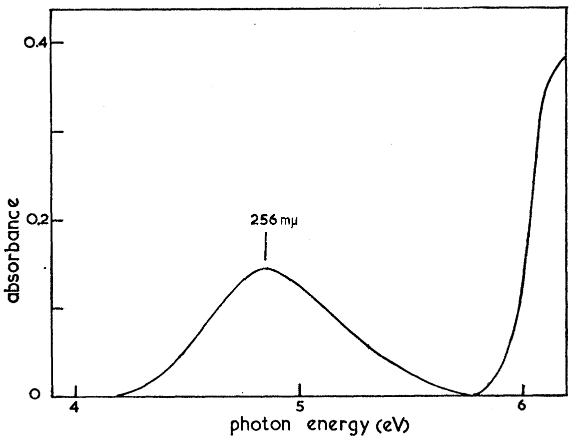

FIG. 4. The absorption bands produced by irradiation of a KCl:K_2SO_4 crystal at room temperature. Crystal *E*, 1.05 mm in thickness.

The wavelengths for the peak maxima were obtained by subtracting the background and carrying out a Gaussian analysis for the strongest band (i.e., 236 mμ). Subtraction of this curve yielded a band at 258 mμ and another at 213 mμ. The resulting full widths at half maximum absorption were 0.29, 0.41, and 0.36 eV for the 258-, 236-, and 213-mμ bands, respectively.

In Fig. 3 is shown the growth of these bands under ultraviolet illumination at liquid nitrogen temperature. The 258-mμ band saturates after 30 min, that at 213 mμ continues to grow up to 110 min, while the 236-mμ band grows for about 40 min and then begins to decrease. This phenomenon appears to be related directly to the thermal stability of the corresponding center at liquid nitrogen temperature. As shown in Fig. 3, on standing in the dark at 78°K, the 236-mμ band bleaches at a somewhat greater rate than when uv illumination is continued. The 258- and 213-mμ bands are stable at least up to room temperature and the band below 200 mμ grows during warmup. At no time, either during irradiation or during warming, is there any visible coloration.

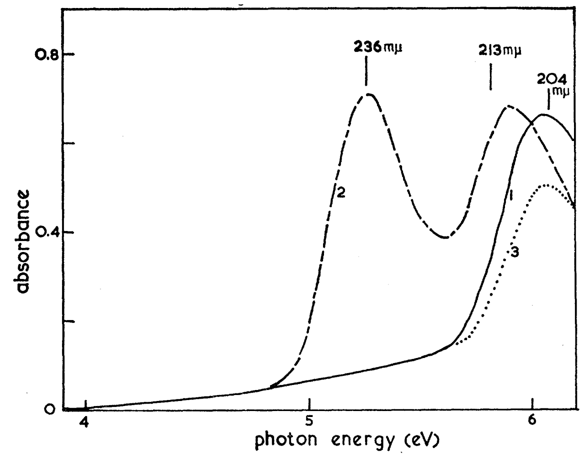

FIG. 5. The absorption spectrum of a KCl:KOH crystal at 80°K. Curve 1: spectrum before irradiation, showing the OH^- band. Curve 2: after irradiation at 80°K. Curve 3: estimated background after irradiation. Crystal *F*, 1.5 mm in thickness.

In Fig. 4 is shown the result of irradiating a crystal at room temperature. A band develops at about 256 mμ and another below 200 mμ. This latter band would appear to be the one which is also formed at liquid nitrogen temperature and which increases during warmup after a low-temperature irradiation. Again, there is no coloration.

Comparative experiments with "pure" KCl crystals grown by exactly the same technique from the same batch of A.R. salt, but without added sulphate, show only a trace of the 236-mμ band (about 5% of the absorption shown by the $SO_4^=$-doped crystal). On pro-

---

[7] P. W. M. Jacobs and J. N. Maycock (to be published).

[8] P. M. Gruzensky and A. B. Scott, J. Phys. Chem. Solids **21**, 128 (1961).

longed irradiation this weak band decreases in a manner similar to that formed in the doped crystals.

A crystal doped with $MgSO_4$ instead of K_2SO_4 showed neither the $SO_4^=$ infrared bands nor did it develop any bands upon irradiation with uv light. The crystal was highly polycrystalline and the $MgSO_4$ appeared to be substantially precipitated.

B. KCl:KOH

These crystals were grown by the Stockbarger method but were not pretreated with HCl. Doping with 2×10^{-3} mole ratio KOH resulted in a polycrystalline sample. A good crystal was obtained, however, when 0.4×10^{-3} mole ratio KOH was used. In Fig. 5 are shown the bands which develop after irradiation with the low-pressure Hg lamp. The hydroxyl band clearly decreases after the irradiation. The broken line in Fig. 5 is a reasonable estimate of the OH^- absorption after irradiation. On subtraction of this background, two bands are obtained with peak maxima at 236 mμ and 213 mμ. Assuming symmetrical band shapes, the corresponding full widths at half maximum absorption are 0.40 eV and 0.38 eV, respectively. In Fig. 6 are shown the growth curves for these two bands under uv illumination at liquid nitrogen temperature.

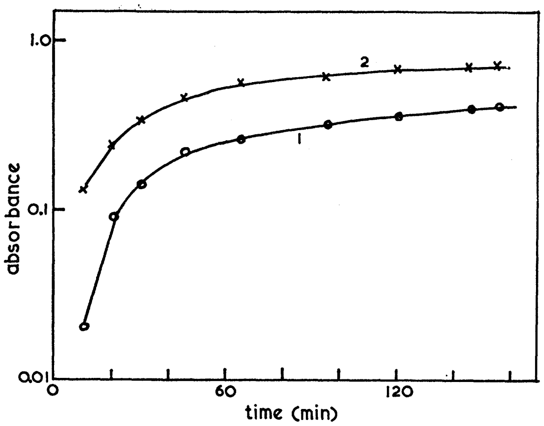

FIG. 6. Growth curves at 80°K for a KCl:KOH crystal. Curve 1: 213-mμ band. Curve 2: 236-mμ band. Crystal *F*.

On warming, the 236-mμ band decreased and it had disappeared by approximately 130°K. The 213-mμ band persists to room temperature. There is no regeneration of the 204-mμ band. After standing overnight, there is some reduction in the 213-mμ band and some regeneration of the 204-mμ band. After two days at room temperature, the 213 mμ has disappeared with complete regeneration of the hydroxyl band at 204 mμ. Similar results were obtained with a Harshaw crystal containing OH^-.

Upon irradiation at room temperature, the band at 213 mμ develops but not the band at 236 mμ. The crystal also develops visible coloration. Upon warming a crystal which has been irradiated at liquid nitrogen temperature, to approximately 130°K, visible coloration appears. Figure 7 shows the corresponding absorption bands in the visible region of the spectrum. The appearance of these bands on warming to 130°K is in agreement with the results of Kerkhoff.[3] Both bands could be bleached at liquid nitrogen temperature by radiation from an unfiltered tungsten lamp and again regenerated by warming to 130°K (Fig. 7).

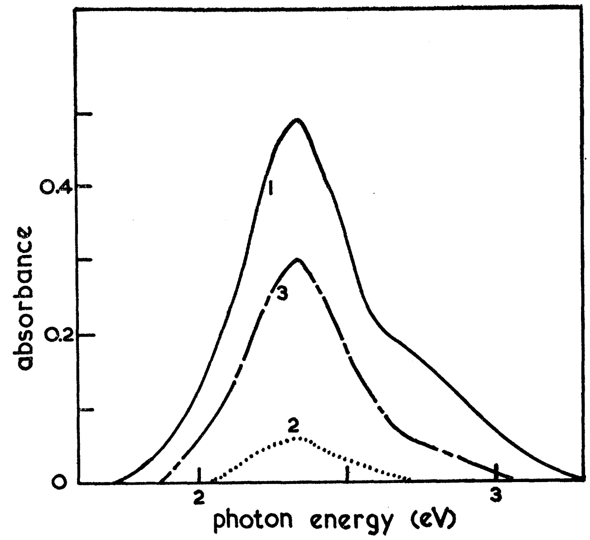

FIG. 7. Absorption spectrum, in the visible region, of a KCl:KOH crystal. Curve 1: after irradiation for 1 h at 80°K and warming to 130°K. Curve 2: after bleaching at 80°K with an unfiltered tungsten lamp. Curve 3: after warming again to 130°K. Crystal *G*, 1.2 mm in thickness.

When the visible bands are bleached at low temperatures, the band at 236 mμ in the ultraviolet is partially regenerated.

C. KBr:K_2SO_4

This crystal was also grown by the Stockbarger method in a quartz container but the charge was not pretreated with HCl. Doping with a 2×10^{-3} mole ratio of K_2SO_4 resulted in a polycrystalline sample; however, some clear portions were obtained and these did show the $SO_4^=$ infrared vibration as found in KCl. From the infrared band we may estimate that the clear portions of the KBr crystal contained about 0.25 as much $SO_4^=$ as did the KCl crystals used.

Figure 8 shows the bands obtained after irradiation with the low-pressure Hg lamp. After subtraction of the background, four bands were identified with peaks at 303, 273, 226, and 205 mμ. Full bandwidths at half maximum absorption were 0.38, 0.24, and 0.20 eV for the 273-, 226-, and the 205-mμ bands, respectively. (The low intensity of the 303-mμ band made it impractical to estimate its half-width.) There was no visible coloration. After warming to approximately room temperature, there are bands at 303, 226, and 214 mμ while a new band develops beyond the range of the spectrophotome-

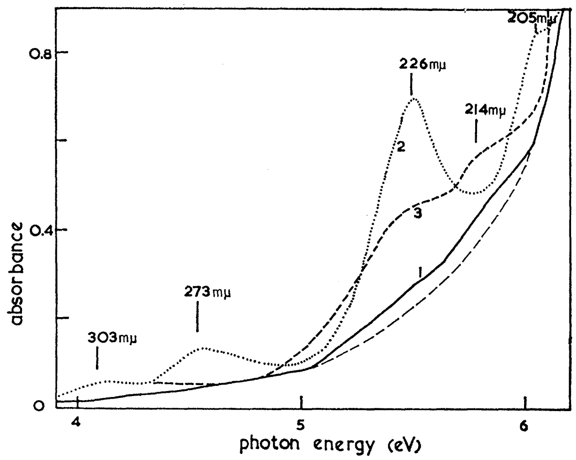

FIG. 8. Absorption spectrum of a KBr:K_2SO_4 crystal. Curve 1: background prior to irradiation. Curve 2: after irradiation for 1 h with uv light at 80°K. Curve 3: after warming to room temperature (measured at room temperature). Crystal H, 1.0 mm in thickness.

ter. There is no visible coloration. Except for the 205-mμ band these results are analogous to the KCl:K_2SO_4 crystal. From the background spectra before irradiation, it can be seen that both the KCl:K_2SO_4 and the KBr:K_2SO_4 contained OH^- as an "impurity." The 213-mμ band in KCl and the 226-mμ band in KBr are usually ascribed to the presence of H^- ions.[9] From their thermal behavior, it seems that the 303-mμ band in the bromide, and the 258-mμ band in the chloride, are associated with the same center. A similar identification may be made for the 273- and the 236-mμ bands. Both bromide and chloride show regeneration of the hydroxyl band (204 mμ in KCl and 214 mμ in KBr). The α band found at 205 mμ in KBr would be beyond the limit of the spectrophotometer in KCl.

The spectrophotometer used in all the work described was a Perkin-Elmer "Spectracord" 4000.

III. DISCUSSION

The photolysis of OH^- ions in a KCl crystal would be expected to produce all or some of the species: H^-, O, O^-, H. Some of these would presumably have to be located in interstitial positions. The situation is evidently more complicated[4] at 15°K, where both H and F centers are found. The growth curves (Fig. 6) for the 236- and 213-mμ bands in irradiated KCl:KOH are closely parallel, indicating that they both arise from the decomposition of OH^- ions. There is no doubt that the OH^- ions do undergo photolysis, since a decrease in absorption at 204 mμ on irradiation has been observed by Rolfe,[2] Cape,[4] and Kerkhoff,[3] as well as by ourselves. The possibility that the new bands arise from the decomposition of some other center is discounted because of the behavior under irradiation of a KCl crystal prepared by the same method from the same batch of salt, but without added KOH. Such a crystal showed only very faint evidence of absorption due to OH^- ions and correspondingly very slight absorption at 236 mμ (the larger of the two bands) after two hours irradiation at 80°K. Furthermore, the same two bands are produced in the same proportion on irradiation of an untreated Harshaw crystal (Table I). The thicknesses of the two crystals corresponding to the last two lines in the table were chosen so as to make the original OH^- absorption at 204 mμ comparable. The difficulty in computing the increase in absorption at 213 mμ, because of the simultaneous decrease in the 204-mμ absorption, has already been stressed. Because of this, there is an uncertainty in the values for the ratio r_1 given in the second last column of about ±10%.

A 212-mμ[10] absorption band in KCl is generally attributed to the H^- ion substituting for Cl^- on a normal lattice site.[1,5,9] Martienssen's value for the full width of the band at half the maximum absorption is $H = 0.31$ eV at 90°K. Our value, which must be subject to some uncertainties because of (a) the much smaller absorption which results from irradiating KCl:KOH crystals, compared with that in hydrided crystals and (b) the overlapping of the 236-mμ band, is ~0.36 eV at 80°K. Thus, on the basis of the values of $\lambda_{\max}$ and of the half-width, we identify the absorption band at 213 mμ in irradiated OH^--doped KCl crystals with that generally considered to be due to H^- ions on lattice sites.

Both Rolfe[2] and Kerkhoff[3] have observed an absorption band at 236 mμ in uv-irradiated KCl:KOH and, following Delbecq, Smaller, and Yuster,[1] attributed this to the presence of interstitial H atoms. The presence of interstitial H atoms in the latter's experiments was established unequivocally from the electron spin resonance (ESR) measurements, but we believe that the 236-mμ band observed by Rolfe, Kerkhoff, Cape,[4] and ourselves arises from an oxygen fragment produced by the photolysis of OH^- ions. The principal evidence that this 236-mμ band is due to oxygen and not hydrogen comes from a comparison of the value of the absorbance

TABLE I. Values of the absorbance at 204, 213, and 236 mμ in various KCl crystals. The first two KOH crystals were grown from a melt containing 4×10^{-4} mole ratio KOH:KCl. In the second last column are given values of the ratio r_1 of the absorbance at 236 mμ to that at 213 mμ, measured after 30 min. r_2 is the ratio of the absorbance at 236 mμ after 30 min to the original absorbance at 204 mμ.

Crystal	204 mμ	213 mμ	236 mμ	r_1	r_2
KCl:KOH	0.50	0.13	0.34	2.6	0.68
KCl:KOH	0.68	0.17	0.48	2.8	0.71
Harshaw	0.60	0.13	0.41	3.1	0.68
Mean				2.8±0.3	0.69

---

[9] W. Martienssen, Z. Physik **131**, 488 (1952).

[10] Owing to the difficulties of resolution, the discrepancy between this value and that of 213 mμ found in this work, is not regarded as significant. A similar remark applies to the 226-mμ band found in KBr.

ratio r_2 in the $SO_4^{=}$- and OH^--doped crystals. This ratio, which is that of the absorbance at 236 mμ to that at 204 mμ, has the value 13.6 in a $KCl:K_2SO_4$ crystal. Comparison of this value with those for the ratio r_2 given in Table I shows that the absorption at 236 mμ is some 20 times more intense in the $SO_4^{=}$-doped crystals than in OH^--doped crystals. Since both bands possess the same half-width (0.4 eV) and show their maximum absorption at the same wavelength (236 mμ), the possibility that one is due to oxygen and the other to hydrogen can be discounted. Moreover, the $SO_4^{=}$-doped crystal could not have contained some unsuspected hydrogen source (e.g., HCl, from the pretreatment), since crystals grown from the same KCl batch with the same pretreatment but without added K_2SO_4 showed on uv irradiation only a barely perceptible absorption at 236 mμ. Further confirmation that the 236 mμ comes from photolysis of $SO_4^{=}$ ions lies in the decrease in the infrared absorption which accompanies the development of the uv band and in the fact that no such band develops when the $SO_4^{=}$ ions are precipitated with Mg^{++}.

The correlation of the 236-mμ band in KCl and the 273-mμ band in KBr with the initial $SO_4^{=}$-ion absorption in the ir, and of the 213-mμ band in KCl and 226-mμ band in KBr with the initial OH^--ion absorption is shown in Table II. The KBr crystal showed twice the absorbance of the KCl crystal in the OH^- band but about one-fourth the absorbance due to $SO_4^{=}$.

The band formed at 226 mμ, the position of the hydride band in KBr,[9] is rather more than twice as intense as the H^- band in the KCl crystal showing its connection with the original OH^--ion absorption. In contrast, the bands at 273 mμ and 303 mμ are much less intense in the KBr than in the KCl crystal, verifying their connection with the original $SO_4^{=}$-ion absorption.

The band at 236 mμ in KCl has already been ascribed to oxygen. The one at 258 mμ appears in the same spectral region as that in which a crystal grown in oxygen[11] absorbs. It has been shown by Känzig and Cohen[12] from ESR measurements that the entity responsible is the O_2^- ion occupying a halide-ion lattice site. Our band is much narrower than that shown by Rolfe,[11] but there is some indication from the shape of his curve, that two or more unresolved bands may be present.

Table II. Values of the absorbance at various wavelengths in $KCl:K_2SO_4$ and $KBr:K_2SO_4$ crystals.

Absorbing species	$KCl:K_2SO_4$ λ	Absorbance	$KBr:K_2SO_4$ λ	Absorbance
$SO_4^{=}$	9 μ	0.33	9 μ	0.08
OH^-	204 mμ	0.05	214 mμ	0.10
H^-	213 mμ	0.17	226 mμ	0.42
Oxygen	236 mμ	0.61	273 mμ	0.08
Oxygen	258 mμ	0.09	303 mμ	0.02

The correlation is less good for KBr since the crystal grown in oxygen does not show extensive absorption at 303 mμ. This is, however, a weak band in irradiated KBr. On leaving a $KCl:K_2SO_4$ crystal which had been irradiated for 30 min, in the dark at 80°K, the 236-mμ band decreases and the ir absorption simultaneously recovers (Fig. 3). This indicates a recombination reaction between the two fragments produced by the photolysis of the $SO_4^{=}$ ions. If this were the only reaction, however, the concentration of the species responsible for the 236-mμ band would reach a steady-state value, whereas under continued irradiation the intensity of the absorption at 236 mμ decreases (Fig. 3). No new bands form in the spectral region scanned (200–370 mμ) and nor does any color develop. The oxygen species responsible for this band must, therefore, be transformed to a state which does not show an absorption band within our range. This state could well be responsible for the absorption band, the tail of which can just be seen in Fig. 1, for this band appears to develop more strongly as the temperature is raised. It may be identical with the band at 185 mμ found by Kerkhoff[3] and by Cape[4] in irradiated KCl:KOH crystals. This band was ascribed by them to the O^- ion, but it could equally well be due to interstitial oxygen atoms.

ACKNOWLEDGMENTS

We should like to thank J. N. Maycock for growing the crystals used in the work described in this paper.

One of us (H. A. P.) acknowledges gratefully support from the U. S. Air Force Air Research and Development Command and the National Academy of Sciences in the form of a postdoctoral fellowship.

---

[11] J. Rolfe, F. R. Lipsett, and W. J. King, Phys. Rev. **123**, 447 (1961).

[12] W. Känzig and M. H. Cohen, Phys. Rev. Letters **3**, 509 (1959).