lationship with very little spread between them and, therefore, the total Cu concentration could be directly deduced from resistivity measurements. At Cu concentrations higher than 3×10^{15} cm^{-3}, the free hole concentration is lower than the Cu concentration, and corrections based on Fermi-Dirac statistics had to be made. This admittedly introduces a higher experimental error for higher Cu concentrations, but there is no better method to deduce acceptor concentration from electrical measurements in this case.

VIII. CONCLUSION

We have demonstrated that Cu has interstitial as well as substitutional properties in InSb. If the crystal is originally free from vacancies, the in-diffusion of vacancies from the surface is the rate-limiting factor ("dissociative diffusion"). Good agreement with meas-

urements of the self-diffusion is obtained from the dissociative process. If vacancies are already present in the bulk of the crystal, the reaction of interstitial Cu with vacancies (probably vacancy aggregates, e.g., divacancies) is the rate limiting factor. It is possible to free InSb crystals from vacancies inherited during growth by a low temperature heat treatment. The concept of fast diffusing divacancies has been introduced to explain the latter effect.

Low-Temperature Coloration in KCl and KBr near the Fundamental Edge

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Crystals of KCl and KBr have been cooled with liquid helium, x rayed, and investigated for coloration near their fundamental absorption edge. Three bands are seen in both materials with the largest band closest to the fundamental edge. In KBr the first band is broad and peaks at 2300 Å, the second is the α band at 2020 Å, and the third, called the γ band, is at 1895 Å. The areas of the three bands with respect to the F band are, respectively, 1:8:20. In KCl similar bands are found at 1940 Å, 1790 Å, and 1640 Å. The areas are, respectively, 1:6:16 as large as the F band. The α and γ bands are also found in KBr:H on bleaching in the U band, and the α and γ bands have similar bleaching rates on warming. It is concluded that the γ band arises when an exciton is created at a slightly larger distance from the negative-ion vacancy than is the case for the α band. It is proposed that the centers responsible for the first band, the α and γ bands, and the F and H bands all are formed from the creation of Frenkel defects but differ in the distance of separation of the interstitial and vacancy and in the resulting ability to trap electrons and holes. With this assumption the x-ray energy dissipated in producing a Frenkel defect is 240 eV for KBr and 450 eV for KCl using 50-kV x rays.

I. INTRODUCTION

TWO absorption bands near the fundamental absorption edge in alkali halides were first observed by Delbecq, Pringsheim, and Yuster[1] in KI. The longer wavelength band was called the α band and was associated with negative-ion vacancies; the shorter wavelength band was called the β band and was associated with F centers. It was proposed that the absorptions correspond to fundamental absorption transitions perturbed by the presence of the defects. Similar results have also been found for KBr, NaBr, NaF, NaCl, and KCl.[2-9]

Calculations have been made to test these proposed models of the α and β bands. In all cases, it has been assumed that the fundamental absorption band arises from the creation of excitons. The problem then is to calculate the properties of excitons perturbed by nearby negative-ion vacancies or F centers. Oscillator strengths for the transitions have been computed by Dexter[10] and by Fuchs.[11] The shift of the α and β bands from the first exciton band has been computed by Bassani and

[1] C. J. Delbecq, P. Pringsheim, and P. Yuster, J. Chem. Phys. 19, 574 (1951).

[2] C. J. Delbecq, P. Pringsheim, and P. Yuster, J. Chem. Phys. 20, 746 (1952).

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

[4] W. Martienssen and R. W. Pohl, Z. Physik 133, 153 (1952).

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[10] D. L. Dexter, Phys. Rev. 83, 1044 (1951).

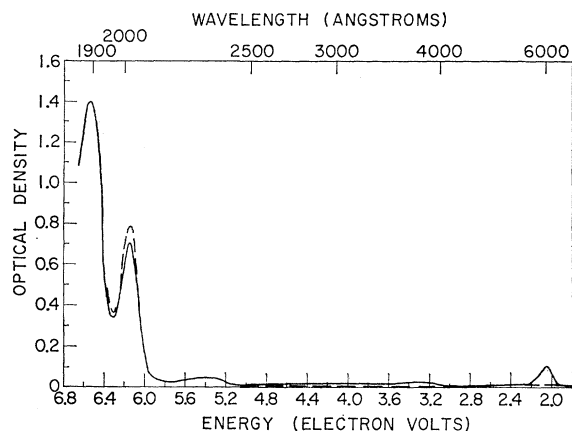[11] R. Fuchs, Phys. Rev. 111, 387 (1958).

FIG. 1. The solid curve is the absorption curve of KBr x rayed for 45 secs at liquid-helium temperature and measured at the same temperature. The absorption of the crystal before x raying has been subtracted so that the curves show induced bands. The dashed curve is the result of bleaching the F band (6000 Å) with light.

Inchauspé[12] using the charge transfer model of the exciton. This work has been extended recently by Tsertsvadze[13] to transitions other than those considered by Bassani and Inchauspé. Fuchs[11] has also considered the symmetry properties connected with the creation of the perturbed exciton near an F center and has shown that the transition should split into six bands of which the two which are lowest in energy should appear on the long-wavelength side of the fundamental absorption band.

The perturbed exciton bands are normally studied at low temperatures where they are thermally stable and can be more easily separated from the fundamental absorption band. Coloration can be produced either by exposure to ionizing radiation at low temperatures or by additive coloration.[14] When ionizing radiation is used, the study of color center bands yields important information about the interaction of radiation with ionic solids. In alkali halides a good many facts about the effects of low-temperature irradiation are now clear. Optical[15,16] and spin resonance[17] studies have shown that, even in the perfect lattice, low-energy x rays produce interstitial halogen atoms (H centers) and leave halide ion vacancies which can trap electrons to form F centers. These F and H centers are normally separated by about ten lattice spacings or more since a closer spacing would be expected to produce effects

in the detailed spin resonance spectrum and such effects are not observed.[18] In the more efficient cases the formation of an F center requires an over-all average expenditure of 2000 eV from the x-ray beam.[16,19] Moreover, the efficiency of F-center production is dependent on the energy of the x rays.[19] In addition to the F and H bands, Rüchardt[5,6] observed that an α band was formed in KBr on irradiation at low temperatures and that it was several times as large as the F band. This effect has recently been studied further in mixed crystals of KBr-KCl.[20]

In the present work a large new ultraviolet absorption band has been found in KBr and KCl x rayed at low temperatures. It lies to the short-wavelength side of the α and β bands and will be called here the γ band. A variety of optical and thermal experiments have been performed which suggest that this new band may be associated with the creation of an exciton at positions only slightly removed from a negative-ion vacancy. The relative amounts of negative-ion vacancies and F centers and their thermal stabilities are interpreted in terms of the varying separation of radiation-induced interstitials and vacancies.

II. EXPERIMENTAL RESULTS

A. KBr

The experiments on pure KBr were done with thin cleaved plates of Harshaw crystals. They were mounted in a Dewar and cooled with liquid helium. The vacuum jacket of the Dewar had a rotatable bottom section with four ports. Two CaF_2 windows aligned with the sample, permitted measurement of its absorption spectrum. A 90° rotation of the Dewar jacket placed one of the other ports (containing a beryllium window) in front of the sample so that it could be x rayed. The x-ray source was a tungsten target tube in a constant-potential machine run at 50 kV, 20 mA unless otherwise stated. This provided an x-ray intensity of about 5×10^{19} eV/cm^2 h at the sample holder. The absorption spectra were measured with a Cary Model 14 Spectrophotometer. This instrument is a double monochro-

[12] F. Bassani and N. Inchauspé, Phys. Rev. **105**, 819 (1957).
[13] A. A. Tsertsvadze, Fiz. Tverd. Tela **3**, 336 (1961) [translation: Soviet Phys.—Solid State **3**, 24 (1961)].
[14] For a description of various techniques used in the coloration of alkali halides, see the article by J. H. Schulman and H. W. Etzel, in *Methods in Experimental Physics*, edited by K. Lark Horowitz and V. Johnson (Academic Press Inc., New York, 1959), Vol. VI, p. 324.
[15] W. D. Compton and C. C. Klick, Phys. Rev. **110**, 349 (1958).
[16] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).
[17] W. Känzig and T. O. Woodruff, J. Phys. Chem. Solids **9**, 70 (1959).

TABLE I. Energy of bands in eV.

	First exciton peak[a]	γ band[b]	β band	α band
NaCl	7.96	...	7.38[c]	7.16[c]
KCl	7.76	7.56	7.36[c]	6.95[c]
KBr	6.77	6.54	6.42[d]	6.10[d]
KI	5.80	...	5.48[e]	5.20[e]

a Reference 23.
b Present work.
c Reference 7.
d Reference 2.
e Reference 1.

[18] This argument was first proposed by W. Känzig.
[19] V. H. Ritz, International Symposium on Color Centers in Alkali Halides, 1962 (unpublished).
[20] H. Bauser and F. Lüty, Physica Status Solidi **1**, 608 (1961).

mator with a signal-to-scattered light ratio greater than 100 even at the end of its range in the ultraviolet. For the sample size used here, the instrument was operable to 186 mμ at which point the automatic slits were open to their maximum of 3 mm.

In Fig. 1 the solid curve shows the absorption spectrum of KBr x rayed at helium temperature for only 45 sec. A faint F band is seen at 6000 Å and a small H band at 3800 Å. In the ultraviolet there is a small broad band at 2300 Å, the α band at 2020 Å, and the new γ band at 1895 Å. The β band, at 1930 Å, does not appear in these curves because it is proportional to the F band which is small. In this curve, and all the others of this paper which involve x-ray induced coloration, the background absorption of the crystal before x raying has been subtracted so that the data represent the increase in absorption produced by the x-ray irradiation. In a typical case the background optical density rises to 0.6 at 1865 Å.

Because the γ band occurs near the end of the range of the spectrophotometer, special care was taken to insure that it was not an erroneous result arising from instrumental limitations. Samples were measured with differing amounts of γ band such that the transmission at the peak of the band varied from 1.4 to 10%. Stray light would be expected to be most important in the sample with the largest ultraviolet absorption since stray light, essentially unaffected by the crystal, becomes a proportionately larger part of the signal. Over this range of concentrations, however, the ratios of γ band to α band and F band remained constant. Also the peak position of the γ band did not vary. Finally, varying the sensitivity of the spectrophotometer, which changes the slit width of the instrument, produced only minor changes in the spectrum.

The energies for the α, β, and γ bands in various materials are given in Table I and the separation of these energies from the first exciton peak along with theoretical estimates of these values for the α and β bands are given in Table II. For KBr it is seen that the γ band is 0.23 eV from the exciton peak. The separation of the α and γ bands is 0.44 eV.

In the γ band, only the long-wavelength side can be measured with accuracy because of the increasing fundamental absorption band on the short-wavelength side. Assuming that the γ band is symmetrical about its peak, a width at half-maximum can be obtained and

FIG. 2. The change in height of the α and γ bands in KBr as a function of time after the end of the x-ray exposure. At 10 min the liquid gases were removed from the Dewar and the Dewar was allowed to warm up. The temperature is given on the right-hand scale.

its size compared with those of the F and α bands. If the width at half-maximum for the F, α, and γ bands are taken, respectively, as 0.14, 0.20, and 0.22 eV, then their relative areas are 1:8:20, respectively.

In Fig. 1, the dashed curve results when the sample is bleached with white light at liquid-helium temperature. Both the F and H bands disappear while the α band grows as expected since the removal of electrons from F centers increases the number of negative-ion vacancies. No change is indicated in the height of the γ band, but this may not be completely accurate since, under the conditions of high sensitivity and optical density, the instrumental noise might have obscured a small change.

It has previously been shown that a large fraction of the α band produced in KBr by x raying at low temperatures is bleached by warming to temperatures as low as 30°K.[5] Experiments were conducted here to determine whether or not the γ band showed similar behavior. A crystal was x rayed at liquid-helium temperature and the height of the α and γ bands were measured. Then the coolant liquids were removed from the Dewar and it was allowed to warm up. Temperature measurements were made with a copper-constantan thermocouple placed near the sample. The results are shown in Fig. 2 where the relative heights of the α and γ bands are plotted on the left-hand ordinate and the temperature is plotted on the right-hand ordinate. The abscissa is time measured from the end of the x-ray exposure. For 10 min after the end of the x-ray exposure no change is observed in the height of the α and γ bands. Then the coolant liquids are removed and the sample is remeasured. The changes occurring in all the curves during this operation are shown by dashed sections followed by the slow continuous variation as

TABLE II. Energy difference from first exciton peak in eV.

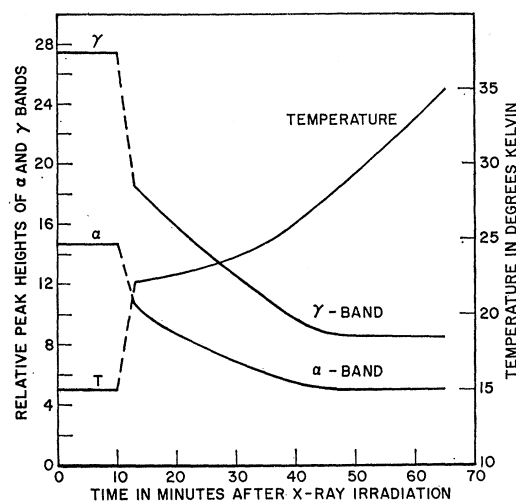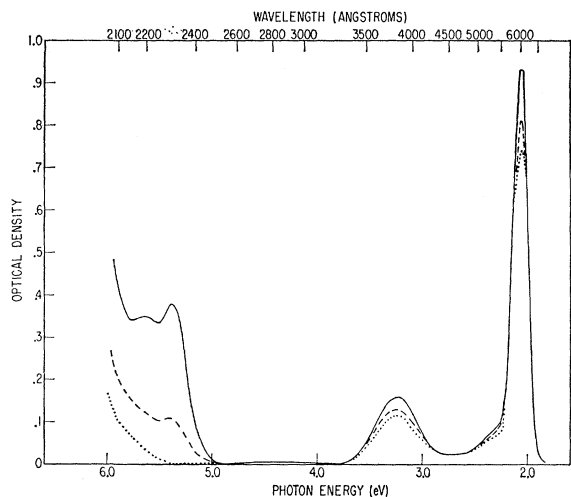|	γ band exp.	β band exp.	theoret.[a]	α band exp.	theoret.[a]	theoret.[b]
NaCl	...	0.58	0.19	0.80	0.50	0.33
KCl	0.20	0.40	0.28	0.81	0.53	0.41
KBr	0.23	0.35	0.29	0.67	0.49	0.38
KI	...	0.32	0.23	0.60	0.44	0.33

[a] Reference 12.
[b] Reference 13.

FIG. 3. The solid curve is the absorption curve of KBr x rayed for 15 min at liquid-helium temperature. In addition to the F band at 6000 Å and the H band at 3800 Å, there appear to be two close bands at 2200 and 2300 Å. The α and γ bands are off scale. After warming the crystal to 30°K and cooling to liquid-helium temperature once more, the dotted curve is observed. An additional 2 min of x-ray exposure results in the dashed curve.

the Dewar gradually warmed. It seems clear that over this temperature range the α and γ bands have approximately the same thermal bleaching properties.

The behavior of the other color center bands on warming over the same range was studied. In order to bring these relatively weak bands up to an easily measured intensity, the x-ray exposure was extended to 15 min. Under these conditions the α and γ bands were too large to be measured. The results are given in Fig. 3. The solid curve shows the crystal after x raying at liquid-helium temperatures. In addition to the F and H bands, there seem to be two bands in the 230-mμ region. The sample was then warmed to 30°K and recooled to liquid-helium temperature. The remaining coloration is shown in the dotted curve. The bands near 230 mμ have bleached almost completely while the F and H bands have bleached by about 25%. The bleaching of these latter bands may be due either to the complete disappearance of the centers involving ionic displacement, or it may be due to the capture of electrons or holes involving only a redistribution of electronic charge. This latter process is predominant in optical bleaching of the F and H bands at low temperatures since it has been observed that the bleached centers are quickly reformed by short re-x-raying.[15] In this case an F center, for example, which has lost its electron through the action of bleaching light, quickly recaptures one of the many free electrons produced by the second x raying and reappears as an F center. A similar experiment was performed here by x raying the thermally bleached crystal again for only 2 min. The resulting coloration is shown in the dashed curve. Only a fraction of the bleached bands recover and it, therefore,

appears that all of these bands bleach by thermally induced motion of ions or atoms even at these low temperatures. A crystal of KBr was x rayed at low temperature, warmed to 77°K, and recooled. In this case also the α and γ bands were greatly reduced but they still maintained the same relative sizes.

The solid curve of Fig. 4 shows the coloration of KBr x rayed at 77°K for 20 min and then cooled to liquid-helium temperature for the measurement. The principal bands are the F band, the α band, and the β band at 1930 Å. The α band produced in this way is identical in peak position and half-width to that produced at liquid-helium temperature. Since a relatively large F band is present, a strong β band is also seen. A small shoulder appears on its short-wavelength side. After bleaching with white light the dashed curve is obtained. In order to see more clearly the effect of the optical bleach on the coloration, the difference between the two curves of Fig. 4 is plotted in Fig. 5. Points below the horizontal zero line indicate bleaching. It is apparent that the F band, the β band, and several small bands bleach while the α band and a band in the γ band region grow. In the α, β, and γ band region, the magnitude of the bands is distorted because of their strong overlap.

These results on pure KBr seem to indicate that the α and γ bands are strongly correlated. While the α band seems clearly to be due to a negative-ion vacancy, the defect responsible for the γ band is not yet clear. Two simple possibilities will be considered. One is that the γ band may arise from a negative-ion vacancy just as the α band does. Then, of course, the α and γ bands would always have the same relative size. The other possibility is that the γ band arises from interstitial halide ions. Studies of the F and H centers indicate that at low temperature x rays can produce interstitial-vacancy pairs. Since the interstitial and vacancy are
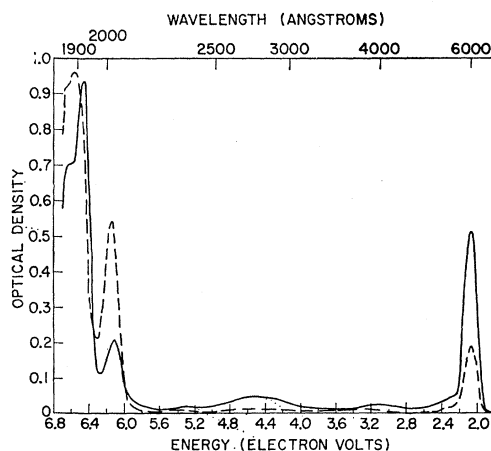

FIG. 4. The solid curve shows the absorption of KBr x rayed for 20 min at 77°K and then cooled to liquid-helium temperature. The sample was bleached with white light from a tungsten lamp and the resulting absorption is shown in the dashed curve.

created simultaneously, and on diffusing together they disappear simultaneously, the number of interstitials could remain proportional to the number of vacancies. This would also have the γ band proportional to the α band. In order to decide between the interstitial and vacancy as the source of the band, further experiments were required. One possibility was to use additively colored crystals which contain few, if any, interstitials. Bleaching the F band with light at low temperatures would produce vacancies which could be seen as the α band and as the γ band if vacancies were its source. Attempts at performing this experiment were not successful because only a fraction of the F centers could be bleached and the remaining F centers gave rise to a strong β band which made accurate measurement in the γ-band region impossible. Attention was shifted to the use of potassium bromide with hydrogen addition, in which a different interstitial could be produced.

B. KBr:H

It has been shown by Thomas[21] and Martienssen[3] that when a crystal of KBr:H is irradiated with light in the 2280 Å hydride absorption band (U band) at low temperatures, a strong α band is produced and smaller amounts of F band and U'' band. A study of KCl:H by Delbecq, Smaller, and Yuster[22] shows a band similar to the U'' band. From paramagnetic resonance and optical investigations this band is identified with an interstitial hydride ion.

Experiments were performed in which the U band in KBr:H was bleached by the cadmium arc line at 2280 Å isolated by passage through a quartz monochromator. The solid curve of Fig. 6 shows the absorption of the KBr:H crystal at liquid-helium temperature.

Fig. 6. The solid curve shows the optical absorption of a crystal of KBr:H at liquid-helium temperature. The dashed curve shows the results of bleaching in the U band with a cadmium arc line at 2280 Å for 40 min.

After 40 min of bleaching with 2280 Å light the dashed curve results. The difference between the original curve and curves after bleaching for times varying between 10 and 40 min is plotted in Fig. 7. The small insert in this figure shows the growth of the F band. As bleaching continues it is seen that the main U band bleaches and that a variety of bands grow. As previously seen by Thomas, the α band grows. However, the apparent position of the band in Figs. 6 and 7 is displaced from 2020 to 1970 Å. This appears to be due to two effects. First, the U band is decreasing and, since it overlaps the α band, the long-wavelength side of the α band is depressed. Second, there appears to be a background absorption increasing to high energies which increases the high-energy side of the α band.[22a] The absorption in the region from 2400 to 3100 Å is the U'' band. The F band (plotted on an expanded scale in Fig. 7) is seen to grow slightly.

It appears from Figs. 6 and 7 that the γ band appears along with the α band as the principal products of the optical bleach. These results indicate strongly that the γ band, as well as the α band, arises from negative-ion vacancies. If the γ band were due to interstitials, then the interstitial Br⁻ ion and the interstitial H⁻ ion would have to produce the same absorption band. This seems unlikely because of the different ionic sizes and chemical properties of these two ions. In addition, there is the evidence mentioned previously that the interstitial H⁻ ion is thought to give rise to the U'' band on the long-wavelength side of the U band.

C. KCl

If the α and γ bands both arise from negative ion vacancies, there remain two attractive explanations
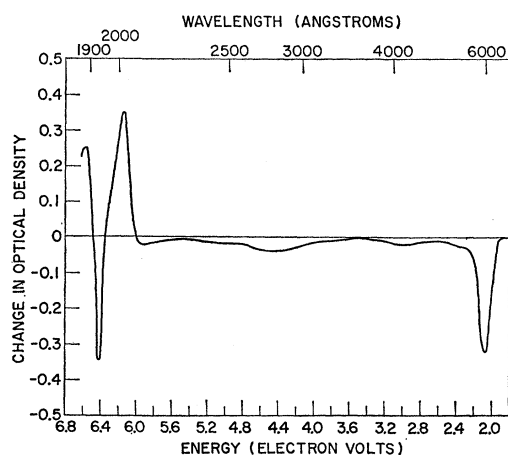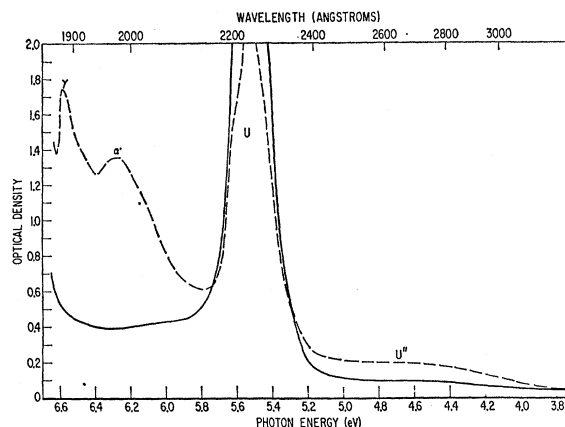
Fig. 5. The difference between the two curves of Fig. 4 is plotted to show the effect of optical bleaching. Portions of the curve below the zero line show bleaching, those above the line show enhancement of coloration.

[21] H. Thomas, Ann. Physik **38**, 601 (1940).
[22] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **104**, 599 (1956).

[22a] *Note added in proof.* T. Timusk and W. Martienssen have kindly shown us a manuscript in which they find a similar shift of the α band. They interpret this as arising from the influence of the nearby interstitial hydride ion.
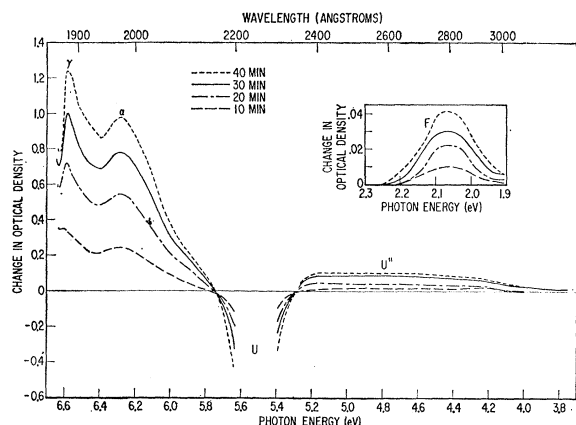
FIG. 7. The difference between the absorption of the KBr:H crystal of Fig. 6 and its absorption after different times of bleaching with 2280 Å light is plotted. Portions of the curves above the zero line show enhanced coloration. The enclosed box shows the growth of the F band plotted to an expanded scale.

about their origin. One is that the α band arises from an exciton created near a vacancy while the γ band corresponds to an exciton created at a greater distance from the vacancy and thus is less perturbed. The other explanation is that the difference between these bands is due to the splitting of the ground-state levels of Br^0 which amounts to 0.46 eV and which appears in the splitting of excitons for pure KBr and other bromides.[23,24] This effect also is the basis for the splitting of the β band calculated by Fuchs[11] but which has not yet been observed. Both the simple theory[25] of this effect and the observations on excitons in the pure bromide[23] indicate that the longer wavelength band of the two should be larger. However, just the reverse condition is found in the case of the α and γ bands of KBr.

Experiments were performed on KCl to attempt to decide between these possible explanations. In atomic chlorine the ground-state splitting is only 0.11 eV. If the α and γ bands are due to this effect they should strongly overlap or merge into a single band in KCl. On the other hand if the γ band arises from excitons formed at a larger distance from the negative-ion vacancy, the α and γ bands in KCl might be expected to resemble those in KBr since the lattice constants and polarizabilities of the two materials are not widely different.

The KCl measurements were made using a vacuum ultraviolet monochromator to which the Dewar was fitted. The samples were measured, x rayed, and remeasured all at liquid-helium temperature. In obtaining the final curves, ratios are taken between runs

taken a half hour or more apart. Variations in the lamp output or detector sensitivity or changes in sensitivity resulting from the removal and replacement of the Dewar appear in the data as changes in the baseline of the absorption curves.

At low temperatures most commercial crystals of KCl have a strong absorption band at 1660 Å first seen by Kobayashi and Tomiki[26] at slightly longer wavelengths in room temperature measurements. They have traced this band to small amounts of Br impurities. By using crystals prepared in our own laboratory in which this band was substantially reduced, observation of the x-ray induced bands could be made without serious interference.

The absorption spectrum induced in KCl at liquid-helium temperatures by 2 minutes of x raying is shown in the solid curve of Fig. 8. The F band is shown in the insert. In addition to the F band there is a broad weak band at 1920 Å, the α band at 1780 Å, and a new band at 1640 Å. Because of the general similarity of this spectrum to that observed in KBr, the 1640 Å band will also be called the γ band. The areas under the α and γ bands are, respectively, 6 and 16 times that of the F band. Bleaching with white light produces the dashed curve. The F band bleaches and there is a general rise in the region of the α band; there may also be a small change in the height of the γ band.

The difference in energy between the α (6.96 eV) and γ (7.56 eV) bands is seen to be 0.60 eV for KCl. This separation is even larger than was found for KBr and it argues strongly for the first explanation mentioned above: that the γ band is an exciton less strongly perturbed by the vacancy. From Table II it is seen that the γ bands in both KBr and KCl are shifted about 0.2 eV from the first exciton peak. It is possible, of course, that the halogen doublet splitting makes
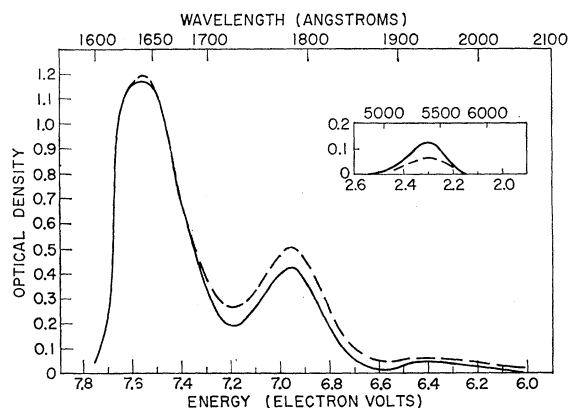

FIG. 8. The solid curve shows the absorption curve of KCl x rayed for 2 min at liquid-helium temperature. The insert shows the F band. Bleaching the crystal with white light results in the dashed curve.

[23] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. 116, 1099 (1959).
[24] R. S. Knox and N. Inchauspé, Phys. Rev. 116, 1093 (1959).
[25] N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals (Oxford University Press, Oxford, 1948), 2nd ed., pp. 95–100.
[26] K. Kobayashi and T. Tomiki, J. Phys. Soc. Japan 15, 1982 (1960).

some contribution to the spectra seen for both KCl and KBr. In KBr the higher level of the α band would lie under the γ band; in KCl both components would appear in the α band. The principal cause of the γ band, however, does not appear to be the halogen doublet.

In Fig. 9 the solid curve plots the results obtained with KCl on x raying at liquid nitrogen temperature for 20 min and measuring the absorption at liquid-helium temperature. In addition to a small α band at 1780 Å there is a β band at 1680 Å and a sharp band at 1620 Å which is only 0.07 eV from the first exciton peak. This band is probably somewhat distorted because of its overlap into the fundamental absorption, but it clearly is not the γ band. Perhaps it is due to an exciton formed near an F center but less strongly perturbed than the β-band exciton. No serious attempt has been made here to examine this possibility. The curve with long dashes in Fig. 9 shows the absorption curve after bleaching with white light at liquid-helium temperature and the curve with short dashes plots the differences between the curves. It is seen that the optical bleach gives rise to an increase in both the α- and γ-band regions as was also the case for KBr.

III. DISCUSSION

One conclusion that has been drawn from these measurements is that the γ band arises from an exciton formed near a negative-ion vacancy but not so close as is the case for the α band. Bassani and Inchauspé[12] and Tsertsvadze[13] have computed the energy to be expected for an exciton using the electron-transfer model. This assumes that an electron is transferred from a halide ion to an alkali ion which is one of the nearest neighbors to a negative-ion vacancy. An obvious choice for the γ band is to consider a similar model in which the electron is transferred from a more distant halide ion to the second nearest neighbor positive ion. This calculation is not yet complete,[27] but the qualitative results are clear. In the calculations an important effect is the Coulomb energy gained by the electron transferring from a negative ion to a positive ion closer to the vacancy which has an effective positive charge. If a more remote positive ion is used, the energy gained will be less and the exciton energy will be more nearly that of the pure lattice.

One of the most striking things about the low-temperature α and γ bands is their large size in comparison with the F band. It would be expected that the negative-ion vacancy with its effective positive charge would have a large cross section for capture of an electron and would appear as an F center rather than an α center. In addition, Compton and Klick[15] have shown that if the F center is bleached by light at low temperatures the negative-ion vacancies which are formed are easily able to trap electrons to re-form F
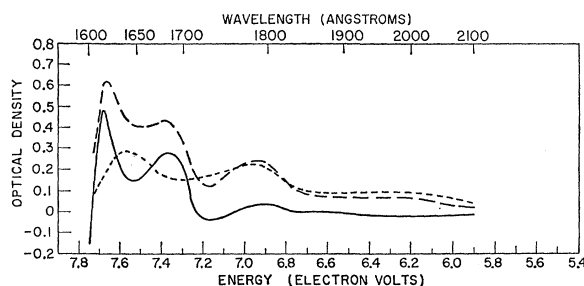
[27] H. B. Rosenstock (unpublished).

FIG. 9. The solid curve shows the absorption curve of KCl x rayed at liquid-nitrogen temperature for 20 min and then cooled to liquid-helium temperature. The curve with long dashes was measured after bleaching with white light. The difference between the curves is given by the curve with short dashes.

centers. It appears that there are two different kinds of α centers, one of which may capture electrons and one of which may not.

A suggestion has been made by Fedders and Lüty[28] that the electric field of a nearby interstitial negative ion prevents the negative-ion vacancy from trapping an electron. This suggestion is made especially plausible because of the probability that when the electron is trapped it first goes into a high lying state corresponding to the excited state of the F center. It is known that the lifetime here is several microseconds[29] which may allow field ionization of this relatively shallow trap. As a result the vacancies which are close to interstitial negative ions may remain unpopulated.

It seems possible to understand the low-temperature coloration with the aid of this concept. There are three classes of Frenkel defects to consider. First is that in which the interstitial negative ion and the negative-ion vacancy are separated by a large distance of the order of ten interatomic spacings or more. In this case the interstitial ion can transfer an electron to the vacancy and F and H centers are formed. The large separation reduces the electric field interaction between the vacancy and ion so that an electron may be trapped to form an F center. That the F and H centers are widely separated is apparent from details of the low-temperature spin resonance spectrum.[18] It might be expected that only a relatively few Frenkel pairs are able to separate by such large distances and that this accounts for the relatively small F bands.

The second class of Frenkel defects are those in which the vacancy-interstitial separation is only a few lattice spacings—more than 2 but less than 10, for instance. In this case the electric field of the interstitial ion is large enough to prevent the vacancy from capturing an electron, and in a similar way the electric field of the vacancy may prevent the interstitial ion from capturing a hole. It is presumed that the separation of the Frenkel pair is such that the α-band

[28] H. Fedders and F. Lüty (to be published).
[29] R. K. Swank and F. C. Brown, Phys. Rev. Letters 8, 10 (1962).

transition is not appreciably distorted by the presence of the interstitial ion nearby. It is likely that the majority of Frenkel pairs fall into this category and give rise to the large observed α and γ bands.

The last class of Frenkel defects are those which are so close that the excitons formed in their vicinity are appreciably distorted compared to those of more isolated vacancies. These cases might be expected to be thermally unstable, to give rise to displaced absorption bands, and to be relatively few in number because of the high recombination probability of the closely spaced vacancy and interstitial ion. It is proposed that the weak ultraviolet absorption bands at 2300 Å in KBr and 1940 Å in KCl are of this type. As seen in the data of Fig. 3 this absorption may consist of more than one band and it bleaches completely on warming to 30°K. These are certainly the least stable thermally of any of the low-temperature bands.

This discussion views the creation of F and H centers, α centers, and closely spaced Frenkel defects as all arising from the same act of creation of Frenkel pairs in the pure lattice with different distances of separation between the interstitial ion and the vacancy. A different view of the creation of the α center has been proposed by Bauser and Lüty.[20] They add KCl to KBr and find that the efficiency of α center formation at 90°K increases up to a solid solution of 10% KCl in KBr. The maximum increase is about a factor of 5. At higher KCl concentrations the α-center efficiency again decreases. The F-center production decreases by about 40% as the proportion of KCl increases to 10% and remains essentially constant as the concentration increases to 25%. These authors ascribe the α band increase to the ejection of impurity ions (in this case Cl⁻) into interstitial positions. However, extension of this explanation to the α band production in pure KBr would require that some impurity, if it has the same coloration efficiency as does KCl, be present in concentrations of 1 to 2%. This is two orders of magnitude larger than has been found for carefully prepared alkali halides in many investigations. Recent measurements of Bauser, Lüty, and Strähle[30] have extended the temperature range down to that of liquid helium. Here the effect is just the reverse: The addition of 10% of Cl to KBr removes all the α band. It appears that the effects in mixed crystals are quite complex. One effect of incorporating a small ion such as Cl into a bromide lattice is to cause a loosening of the lattice which may favor both diffusion apart of Frenkel defects on creation and their subsequent recombination and annealing. Also the probability of "focusing collisions"

may be altered in mixed crystals and these collisions may be an important mechanism for the separation of the Frenkel interstitial and vacancy.

It is for these reasons that it is assumed here that both the F-center and α-center production occur in the pure lattice and are not dependent in an important way on the chemical impurities or dislocation densities found in normal crystals. This assumption has been confirmed for F-center production.[16] Measurements of the efficiency of production of the α band at liquid-helium temperatures and in the low-impurity concentration range would be most valuable in determining its validity in the α-center case.

Assuming that at low temperatures both the α center and F center have a common origin in Frenkel defect production, it is possible to estimate the efficiency of this process. Onaka and Fujita[31] have obtained the oscillator strength of the α band relative to that of the F band by bleaching experiments. The ratio of the oscillator strength of the α band to that of the F band is 1.39 in KCl and 1.31 in KBr. For KCl the size of the α band is 6 times that of the F band which, using the oscillator strengths above, indicates there are 4.3 times as many α centers as F centers. For KBr the corresponding ratio is 6.1. Ritz[19] has recently measured the F center production efficiency for the kind of x rays used here. The numbers are obtained by dividing the total energy absorbed from the x-ray beam by the total number of F centers formed. Ritz has found values of 2400 eV/F center for KCl and 1700 eV/F center for KBr. On the assumptions above, the energy dissipated by the x-ray beam in forming a Frenkel pair is 450 eV for KCl and 240 eV for KBr.

A number of models have been proposed to explain the production of interstitials in alkali halides by low-energy x rays.[32-35] The data above do not alone decide between these models but emphasize that the process is one of exceptionally high efficiency rather than a rare event.

ACKNOWLEDGMENTS

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