effects because intermediate coupling theory is not valid near $2E_G$ (the variational displacement g_K of the Kth oscillator diverges due to a vanishing energy denominator). However, it is highly plausible that the trends in photoemissive yield predicted by our theory would be unchanged by these effects.

The main feature of the calculated two-quantum rates is that their ratio with one-exciton absorption increases with valence shell polarizabilities; i.e., $f^{(2)}/f^{(1)}$ increases in the sequence KCl, KBr, KI. Turning to Metzger's data,[35] we see that these qualitative predictions are consistent with the trends observed. The dip near $2E_G$ becomes more prominent towards the iodides, for all alkalis, and is nearly indistinguishable in RbF and CsF, which solids are characterized by large gaps and weak electron-exciton coupling.

The two-exciton process in solid rare gases is also weak. These crystals have very small Bohr radii and small coupling constants due to their large energy gaps and small dielectric constants. On the other hand, semiconductors correspond to values of x much larger than unity in Fig. 1. Our theory might well predict $f^{(2)}/f^{(1)} \approx 1$ for some systems characterized by small energy gaps. However, as noted above, the Toyozawa model breaks down for these crystals because the oscillator strength for the (longitudinal) exciton field is spread over a wide energy range compared to E_G,[38] and so cannot properly be renormalized into a single exciton band below threshold. Moreover, the one-exciton line is often difficult to resolve in semiconductors, and the much broader two-exciton structure will likely elude identification.

ACKNOWLEDGMENTS

The author is grateful to Professor F. Brown, Professor Y. Toyozawa, Professor T. Sagawa, and Professor E. Hanamura for stimulating discussions on the subject of two-quantum excitations. We express special gratitude to Dr. C. Swenberg for helpful remarks and a careful reading of the manuscript.

---

[38] H. R. Phillipp and H. Fhrenreich, Phys. Rev. **129**, 1550 (1962).

PHYSICAL REVIEW VOLUME 177, NUMBER 3 15 JANUARY 1969

Vacancy Production and Volume Expansion in KBr and KBr-KCl Mixed Crystals*

VICTOR H. RITZ
U. S. Naval Research Laboratory, Washington, D. C.† *20390*

AND

S. MASCARENHAS
Escola de Engenharia, São Carlos, S. P., Brazil‡

(Received 5 June 1968)

The generation of Frenkel defects in KBr and KBr–KCl mixed crystals after x irradiation at 66°K has been investigated. The growth of the optical absorption bands induced by the defects was studied, and the volume expansion was measured with the photoelastic technique. The relative defect production rate at 66 and 87°K can be explained simply in terms of the thermal stability of the vacancy-interstitial pairs. The energy required to produce a Frenkel defect pair at 66°K does not depend upon the quality of the x rays used to irradiate the crystals. The variation in the α/F ratio indicates that recombination luminescence is not an important factor in determining this ratio at 66°K. The volume expansion associated with the F-center Frenkel pair in pure KBr agrees with the results due to Lüty *et al.* for KBr–KH, indicating that the interstitial Br^0 atom causes little expansion. No volume expansion could be attributed to the V_4 center; thus, it cannot be the exact antimorph of the F center, but must involve a localized hole as in Kanzig's V_F center or Itoh's model of the V_4 center. Analysis of the α-center expansion data yielded an expansion at 66°K caused by the interstitial bromine ions which was smaller than that produced at 5°K. The expansion caused by F-center Frenkel pairs was larger in KBr–KCl crystals than in pure KBr. This indicates that the F-center production process involves the displacement of Cl^- ions from their substitutional sites. The expansion induced by α-center Frenkel pairs in the mixed crystals was half that observed in KBr. Possible explanations for this anomalous result would appear to be aggregates of α centers which are not additive in their effect and overlap to change the bulk compressibility of the crystal in their vicinity, or a similar change produced by the vacancy-interstitial pairs.

I. INTRODUCTION

It is now well established that the coloration induced in alkali halide crystals exposed to ionizing radiation at low temperatures arises from the creation of Frenkel defects and self-trapped holes in the perfect lattice.[1–4] In this process halide ions are displaced from their

---

* Based on the Ph.D. thesis of V. H. Ritz, University of São Paulo, 1967 (unpublished).

† Supported by a Fulbright American Research Scholar Grant (1965–1966) and the Naval Research Laboratory Sabbatical Study Program (1966).

‡ Supported by the U. S. Office of Naval Research, National Research Council of Brazil, and FAPESP.

[1] J. M. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., London, 1962).

[2] W. Känzig and T. Woodruff, J. Phys. Chem. Solids **9**, 70 (1958).

[3] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

[4] M. N. Kabler, Phys. Rev. **136**, A1296 (1964).

normal lattice positions to produce Frenkel pairs consisting of vacancies and interstitials.[5] In pure KBr irradiated near liquid-helium temperature the majority of Frenkel pairs formed consist of α centers and interstitial Br^- ions[6,7]; lesser numbers of Frenkel pairs in the form of F centers and H centers are created. At higher temperatures, in the neighborhood of 65°K, F centers and interstitial bromine atoms dominate; smaller numbers of α centers and bromine ions of unknown configuration are formed. Lüty[8] found that the α-center production in this higher temperature region could be greatly enhanced if one doped KBr with KCl. The Frenkel pair in this case presumably consists of an α center and an isolated interstitial Cl^- ion. Lüty came to the conclusion that the Cl^- ion is displaced from its substitutional position by drawing an analogy between this system and the conversion processes in the KBr:KH system in which one produces Frenkel pairs consisting of α centers and interstitial hydrogen ions or F centers and interstitial hydrogen atoms. Thus one has available for study three systems in which one can produce Frenkel pairs either in the form of α centers and associated Br^-, Cl^-, or H^- interstitial ions, or in the form of F centers and the associated Br^0, Cl^0, or H^0 interstitial atoms.

The generation of these defects in a crystal causes a macroscopic volume expansion.[1] It is of interest to connect this macroscopic expansion with the details of the microscopic relaxation of the lattice around the individual defects. Measurements have been made on the KBr:KH system at low temperature by Lüty *et al.*[9] The volume expansion was measured by means of the photoelastic technique and a correlation with the local lattice relaxation around the F- and α-center Frenkel pairs was made by using Eshelby's theory in which the defects are treated as inclusions in a continuous elastic medium.[10] The object of the present investigation was to make similar measurements on the KBr and KBr–KCl systems in which the nature of the vacancies should be similar but in which the interstitial products could be quite different. In this way one might be able to determine the lattice relaxation around interstitial bromine and chlorine ions and atoms in a KBr lattice. An additional object of the experiment was to explore at higher temperatures some of the characteristics of the coloration process which had previously been investigated between 4 and 10°K in KBr.[11,12] In particular, the dependence of the vacancy production efficiency upon temperature, and x-ray "quality" and intensity was to be investigated.

II. EXPERIMENTAL TECHNIQUES

A. Samples

Pure KBr crystals were obtained from the Harshaw Chemical Company. Mixed crystals of KBr+5% KCl and KBr+10% KCl were very kindly supplied by the II Physikalisches Institut der Technischen Hochschule, Stuttgart, Germany. Samples were cleaved into plates 6×8×1 mm thick with a razor blade. By exercising reasonable care in the cleaving process, strain-free samples could be obtained which did not require the high-temperature annealing found necessary by some workers.[13,14] Two sets of matched crystals were used in the experiments; one for photoelastic measurements and one for optical absorption measurements.

The sample was mounted by placing it in an aluminum-foil box which was 8×10×1 mm thick. The box had a pair of 5-mm-diam holes in it to permit optical measurements. Dow-Corning vacuum grease was used to glue the crystal to one face of the box directly over one of the holes. This left a 1-mm border of aluminum foil around the edges of the crystal which absorbed the thermal stresses as the crystal and copper cold finger of the cryostat were cooled. The opposite side of the box, with its matching hole, was not glued to the crystal. The outer edges of this small box containing the crystal were then glued into a rectangular hole in the copper cold finger of the cryostat.

A brief search was made for the presence of impurities in the crystals by looking for impurity-induced optical absorption bands. The 215-nm absorption characteristic of OH^- was present in both the pure and mixed crystals and corresponded to OH^- concentrations of $\approx 10^{15}/cm^3$, $10.5\times10^{15}/cm^3$ and $1.5\times10^{15}/cm^3$ for Harshaw KBr, KBr+5% KCl and KBr+10% KCl, respectively.[15] An additional impurity was found in the KBr+5% KCl crystals. At 65°K the KBr+5% KCl crystals exhibited a strong absorption at about 200 nm. This anomalous absorption was attributed to an impurity-induced absorption band whose peak was in the 190–195-nm region, beyond the limit of the spectrophotometer. Iodine introduces an absorption band in this region[16] and quantitative analysis of the KBr+5% KCl crystals showed the presence of ≈2 ppm of this impurity. Sodium was also present in concentrations of ≈5 ppm; Ca, Sr, Mg, Pb, and Ag were present in concentrations of less than 1 ppm. One should note for later discussion that iodine was *not* present in the KBr+10% KCl crystals.

---

[5] For a summary of vacancy production mechanisms see V. H. Ritz, Phys. Rev. **133**, A1452 (1964); **142**, 505 (1966).

[6] C. C. Klick and D. A. Patterson, Phys. Rev. **130**, 2169 (1963).

[7] G. Kurz and W. Gebhardt, Phys. Status Solidi **7**, 351 (1964).

[8] H. Bauser and F. Lüty, Phys. Status Solidi **1**, 608 (1961).

[9] F. Lüty, S. Costa Ribeiro, S. Mascarenhas, and V. Sverzut, Phys. Rev. **168**, 1080 (1968).

[10] J. D. Eshelby, *Solid State Physics* (Academic Press Inc., New York, 1956), Vol. 3, p. 79; J. Appl. Phys. **25**, 255 (1954); **24**, 1249 (1953).

[11] V. H. Ritz, Phys. Rev. **133**, A1452 (1964).

[12] V. H. Ritz, Phys. Rev. **142**, 505 (1966).

[13] S. Mascarenhas, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **134**, A485 (1964).

[14] M. Merriam, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **125**, 52 (1962).

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

[16] C. J. Delbecq, J. E. Robinson, and P. H. Yuster, Phys. Rev. **93**, 262 (1954).

B. Cryostat and X-Irradiation Techniques

Low-temperature measurements were made with the cryostat used by Lüty *et al.*[9] The lower part of the cryostat had four windows which could be moved into different positions relative to the sample by rotation on a lubricated O ring. Two of the windows were made of 0.13-mm-thick aluminum to allow entry of the x rays. The other two windows were used for optical measurements. Quartz windows were used for optical absorption measurements; these windows were replaced with strain free Pyrex glass for photoelastic measurements.

The geometry for the photoelastic measurements was the same as that used by Wiegand and Smoluchowski.[17] The sample was in the form of a thin rectangular plate. One half of it was irradiated with x rays. The other half was protected by a tiny shield positioned directly in front of the sample. A mechanical linkage attached to the cryostat head moved this shield out of the light beam during subsequent measurements in a photoelastimeter. This permitted photoelastic measurements on both sides of the boundary between the irradiated and unirradiated halves of the crystal. Studies of the optical absorption bands induced by irradiation were made with the shield retracted from the beam for both x irradiations and spectrophotometer measurements. This arrangement provided a larger aperture for the spectrophotometer beam and, hence, improved the resolution near the limit of the spectrophotometer range in the ultraviolet.

X irradiations were made with a Philips tungsten-target beryllium-window x-ray tube energized by a Müller MG150 constant potential high-voltage generator. The x-ray tube (type FA 100/25) could be operated continuously at 100-kV and 20-mA emission current. The total filtration between the x-ray tube and irradiated crystals was increased by the addition of 5.7 mm of aluminum plus 0.87 mm of copper to ensure uniform colorations of the crystals. These particular thicknesses of aluminum and copper filters were chosen to be the same as those used by Hettinger and Starfelt[18] so that use could be made of their published x-ray emission spectra to calculate the distribution of absorbed x-ray energy in the samples. The calculated gradient of energy absorption in an 0.75-mm-thick KBr crystal was about 20% between the front and back faces. Measurements of the energy absorbed by the crystals (eV/cm^2) to determine the vacancy production efficiencies were made with the silver-activated glass block dosimeters described previously.[3,11,19] The response of the dosimeters to 100-kV heavily filtered x rays was obtained by an interpolation procedure which increased the absolute errors to about ±15% for this particular radiation quality.

C. Temperature Control

It was considered desirable to have as large an α-center-to-F-center ratio as possible in the measurements of the KBr–KCl mixed system. Unpublished data of Strähle[20] indicate that a maximum in this ratio occurs at about 20° below liquid-nitrogen temperature. By pumping on liquid nitrogen we were able to lower its temperature from 77.4°K to its triple point at 63.3°K and freeze it. Temperature measurements were made with a copper-constantan thermocouple whose thermoelectric power was measured at 77.4 and 63.3°K before its installation in the cryostat and found to be within 0.5°K of the nominal values listed in the *American Institute of Physics Handbook*.[21] The thermocouple junction was attached to the copper block rather than to the sample and it was assumed that the crystal was at the same temperature as the block.[12]

The method used to maintain the crystal at temperatures below 77°K depended upon a balance between the refrigeration provided by the pumping process and the heat influx inherent in the cryostat design. The nitrogen was pumped on for a few minutes to lower the temperature. When the pump was turned off, the temperature rose very slowly because of the natural heat leak of the cryostat. By cycling the vacuum pump we could maintain the temperature to ±1°K at any temperature between 66 and 77°K. This cycling process was done automatically by a relay in a Philips Model PR2216U/21 potentiometric recorder.

Samples were also held at temperatures between 77 and 150°K to study the annealing of the radiation-induced defects. For these experiments, the liquid nitrogen was poured out of the cryostat which was allowed to warm up under the influence of its natural heat leak. Small quantities of liquid nitrogen were then poured into the cryostat from a Dewar flask to make the temperature oscillate around a desired point. In addition, a fixed temperature point at 87°K was obtained by filling the cryostat with liquid argon.

The use of the photoelastic technique at low temperature requires that the crystal be cooled very slowly from room temperature to avoid thermal strains.[13] Mascarenhas[22] has described a slow cooling system in which pressurized gas forced liquid nitrogen into the cryostat a few drops at a time. We used a variation of this system in which a vacuum pump periodically sucked liquid nitrogen into the cryostat from a small storage Dewar. With this arrangement it was possible to cool the crystal smoothly at rates as low as 5°K/h. In practice, it was found, for the crystals and crystal mounting techniques used here, that much more rapid cooling rates ($\approx$40°K/h) could be employed without the introduction of excessive thermal strain.

---

[17] D. A. Wiegand and R. Smoluchowski, Phys. Rev. **116**, 1069 (1959).

[18] G. Hettinger and N. Starfelt, Acta Radiol. **50**, 381 (1958).

[19] V. H. Ritz and C. H. Cheek, Radiation Res. **25**, 537 (1965).

[20] U. Strähle, Diplom, Stuttgart, 1963 (unpublished).

[21] *American Institute of Physics Handbook*, edited by Dwight E. Gray (McGraw-Hill Book Co., New York, 1957).

[22] S. Mascarenhas, Rev. Sci. Instr. **34**, 1053 (1963).

D. Optical Absorption Measurements

Optical absorption measurements were made at low temperature by placing the cryostat in a Beckman Model DK2 automatic scanning spectrophotometer. Defect concentrations were derived from the measured optical densities by the use of Smakula's equation,[23] using appropriate constants. In this case of the F center in KBr at 65°K $n=1.55$,[24] $W_{1/2}=0.18$,[25] and $f=0.78$,[26] where $n=$ the refractive index at the absorption peak, $W_{1/2}=$ the half-width in eV, and $f=$ the oscillator strength. For the α center in KBr at 65°K $n=2.06$,[24] $W_{1/2}=0.254$, and $f=1.02$.[27] These constants may be used with negligible error for the KBr–KCl mixed crystals. The change in n because of peak shifts of the bands is extremely small for the addition of 10% KCl.[28,8,24] We found no systematic variation in measurements of $W_{1/2}$ of the bands in pure KBr and the mixed crystals, within, our experimental error, and used the average value obtained at 65°K. Similarly, values of the oscillator strength in KBr and KCl differ by less than 15%,[26,27] so the error involved in using an oscillator strength characteristic of KBr for the mixed KBr–KCl crystals is again, very small. Some experiments were done in which the crystals were warmed to 150°K. A correction of about 15% was applied for the variation of $W_{1/2}$ over this temperature range.[25]

In many cases the optical densities of the α and F bands exceeded the range of the spectrophotometer. A common technique used in such a situation is to make an extrapolation from the tail of the absorption band. This makes the important assumption that no smaller bands exist under the main band which grow at a different rate. Ritz[12] has shown that this is a valid technique for the α band at 5°K and studies of the α band in the present experiment indicated that this method could be used at 65°K. The same process was used for high F-band optical densities, following the example of Faraday and Compton.[29]

E. Photoelastic Measurements

Photoelastic measurements were made with the automatic photoelastimeter described by Costa Ribeiro.[30] Using this equipment it has been possible to detect volume changes in KBr of the order of one part in 10^7. It was desirable to be able to scan both sides of the boundary between the irradiated and unirradiated halves of the crystal. This meant that optical measurements had to be made on the heavily colored half of the sample. A relatively transparent spectral region of the crystal existed between 400 and 550 nm. Accordingly, 475-nm light was used in the experiments. Repeated scans of a sample in the photoelastimeter demonstrated that no optical conversion processes were induced by the measurements.

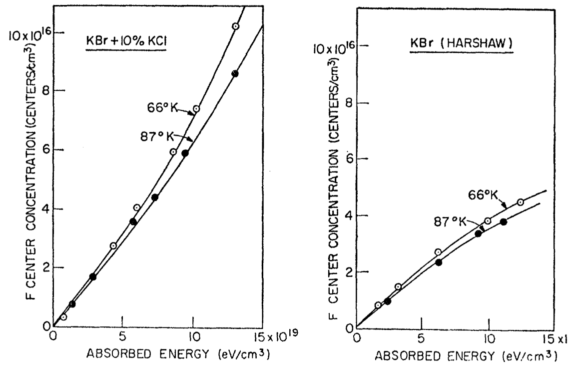

FIG. 1. F-center concentration versus absorbed energy as a function of irradiation temperature.

For the geometry used in the experiment,[17] the free fractional volume expansion can be written as the product of three terms:

$$\frac{\Delta V}{V}=\left[\frac{3(S_{11}+S_{12})}{C_\lambda}\right]\left[\frac{1}{1-2b/l}\right]\left(\frac{\Delta\theta}{t}\right). \qquad (1)$$

All of the temperature-dependent constants have been grouped in the first bracket which contains the elastic constants S_{11} and S_{12}, and the photoelastic constant C_λ. The second bracket contains a correction to the experimentally measured strain pattern which has been described in detail by Wiegand and Smoluchowski. The constants b and l are defined in Fig. 1 of their paper.[17] The last term in Eq. (1) contains the experimentally measured quantities $\Delta\theta$ and t which are the rotation of the plane of polarization of the light used to scan the boundary, and the crystal thickness, respectively.

The photoelastic constant C_λ, which relates the rotation of the plane of polarization to stress, has been measured[31] at room temperature for KBr and found to be 0.80 deg-kg^{-1}-cm for 530-nm light. Using the data of Bangisir and Iyengar[32] this constant was corrected to a value of 0.86 for 475-nm light. In the case of the mixed crystals C_λ was calculated to be 0.85 and 0.84 for KBr+5% KCl and KBr+10% KCl, respectively. In view of the small differences between C_λ in the various crystals, one can assume an average $C_\lambda=0.85$ deg-kg^{-1}-cm. The values used for the elastic constants S_{11} and S_{12} were 4.0×10^{-6} kg^{-1}-cm^2 and -1.2×10^{-6} kg^{-1}-cm^2, respectively. The latter values are those which have been measured for KBr,[33] and it was assumed that they

---

[23] A. Smakula, Z. Physik **59**, 603 (1930).

[24] Z. Gyulai, Z. Physik **46**, 80 (1927).

[25] G. A. Russell and C. C. Klick, Phys. Rev. **101**, 372 (1956).

[26] W. T. Doyle, Phys. Rev. **111**, 1072 (1958).

[27] R. Onaka and J. Fujita, J. Quant. Spectry. Radiative Transfer **2**, 599 (1962).

[28] H. Ivey, Phys. Rev. **72**, 341 (1947).

[29] B. J. Faraday and W. D. Compton, Phys. Rev. **138**, A893 (1965).

[30] S. Costa Ribeiro, Rev. Sci. Instr. **38**, 705 (1967).

[31] C. Argüello and S. Mascarenhas (private communication).

[32] N. G. Bansigir and K. S. Iyengar, Proc. Phys. Soc. (London) **71**, 225 (1958).

[33] R. F. S. Hearmon, Rev. Mod. Phys. **18**, 409 (1946).

were the same for the mixed crystals. The temperature dependence of the first term on the right-hand side of Eq. (1) has been evaluated by Merriam[14] for NaCl at temperatures above room temperature. We used the same techniques to evaluate the temperature dependence for KBr at temperatures below room temperature. This involved a combination of low-temperature elastic constants taken from the literature[34] and a judicious extrapolation of the photoelastic data of Bhagavantam and Murty[35] to lower temperatures. The result indicates that the temperature-dependent term is about 10% larger at 65°K than it is at room temperature. This is consistent with measurements made by Costa Ribeiro[9] who found that a strain profile produced at room temperature varied by less than 15% when the crystal was cooled to 90°K. Putting these constants in the above equation one obtains finally

$$\frac{\Delta V}{V}=1.08\times10^{-5}\left[\frac{1}{1-2b/l}\right]\left(\frac{\Delta\theta}{t}\right), \tag{2}$$

where $\Delta\theta/t$ is given in degrees per cm of crystal thickness. The Wiegand-Smoluchowski correction factor in square brackets was 1.10 in our experiments. Typically, $\Delta\theta$ and t were about 2° and 0.1 cm, respectively.

III. RESULTS AND DISCUSSION

A. Optical Absorption Measurements

1. Growth and Annealing Studies

A measurement of the free volume expansion by the photoelastic technique combined with a knowledge of the molar concentrations of the defects will enable us to measure the lattice relaxation around the various point defects generated by x irradiation. Since there are several unknowns, one varies the relative concentrations of the defects to generate a system of simultaneous equations. This was done by making measurements after successive x irradiations, i.e., at different points along the "growth curve" and by measurements on x-rayed crystals as they were warmed to higher temperatures. In addition to being necessary for the solution of the volume expansion problem, a comparison of the rate of defect production as a function of irradiation temperature with the annealing of the defects as a crystal was warmed to higher temperatures yielded some information about the generation and subsequent stability of the defects.

Figures 1 and 2 show the results of successive x irradiations in which the crystals were x-rayed and measured at the same fixed temperature. The crystals were held at 66°K for one set of experiments; the other set of experiments was done with liquid argon in the cryostat; i.e., at 87°K. In Fig. 1, one sees that the F-center production rate is relatively insensitive to temperature. The addition of 10% KCl to KBr produces some enhancement of the F-center production rate which becomes more pronounced as the irradiation progresses. This is in contradiction to earlier work reported by Bauser[8] and Strähle[20] who found no enhancement in the F-center production. The possibility that the enhancement in our crystals might be due to different trace impurities should be considered. The only impurity found in large quantities was OH^- which was present in all three crystals. The OH^- concentration in the Harshaw and KBr+10% KCl crystals was about the same, while the concentration in the KBr+5% KCl crystals was seven times as great. Since the enhancement of F-center production in the KBr+5% KCl crystals was within 10% of that observed in the KBr+10% KCl crystals, it would appear that the enhancement was independent of OH^- concentration and more likely due to the addition of KCl. In Fig. 2, one sees that, in contrast to the F-center results, very large changes are produced in the α-center production rate by the addition of KCl to the KBr host lattice. Note that the vertical concentration scale for the KBr+10% KCl crystal is ten times larger than that of the Harshaw KBr shown on the right-hand side of Fig. 2. Thus the α-center production rate at 66°K in the doped crystal is almost 30 times that in pure KBr. This is shown more clearly in Fig. 3. One also notes from Fig. 2 that the α-center production rate is more sensitive to irradiation temperature than the F-center production rate and falls to about half of the 66°K rate at 87°K.

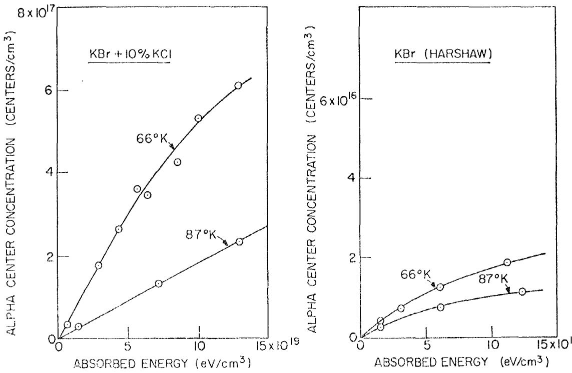

FIG. 2. α-center concentration versus absorbed energy as a function of irradiation temperature.

Isothermal annealing curves were obtained in which crystals x rayed at 66°K were warmed to higher temperatures in increments of 10–15°K. Optical absorption measurements indicated that the defects attained an equilibrium value after about 20 min at the higher temperature. As a precaution all samples were held at the higher temperature for 1 h before measurements were made. The results of these measurements are shown in Fig. 4. The concentrations have been nor-

---

[34] J. K. Galt, Phys. Rev. 73, 1460 (1948).

[35] S. Bhagavantam and Y. Krishna Murty, Proc. Indian Acad. Sci. A46, 399 (1957).

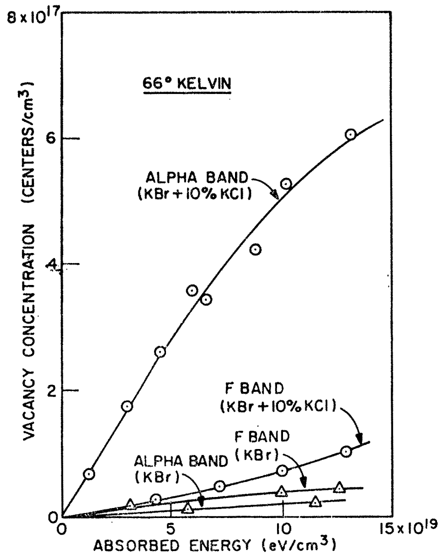

FIG. 3. Vacancy production in KBr and KBr+10% KCl x-rayed at 66°K.

malized to unity at 66°K. As one might suspect from the data of Figs. 1 and 2, the α band anneals out much more rapidly than the F band as the temperature is raised. The F band is much more stable in the 66–100°K range and is reduced to about half of its original value at 145°K, while the α band has dropped to a tenth of its original size in the same temperature interval.

It is of interest to see if the growth-curve data of Figs. 1 and 2 are consistent with the thermal annealing data of Fig. 4. This comparison is made in Table I in which the concentration of a particular center at 87°K has been divided by its concentration at 66°K. One sees that the ratios obtained by these two different methods are in good agreement. This implies very strongly that the relative vacancy production at a given temperature can be explained simply in terms of the thermal stability of the centers produced. Thus, the difference in production rates shown in Figs. 1 and 2 for x irradiations at temperatures of 66 and 87°K can be predicted from the thermal annealing data of Fig. 4. The difference is not due to a change in efficiency of the basic vacancy production mechanism, but rather, to differences in the thermal stability of the reaction products.

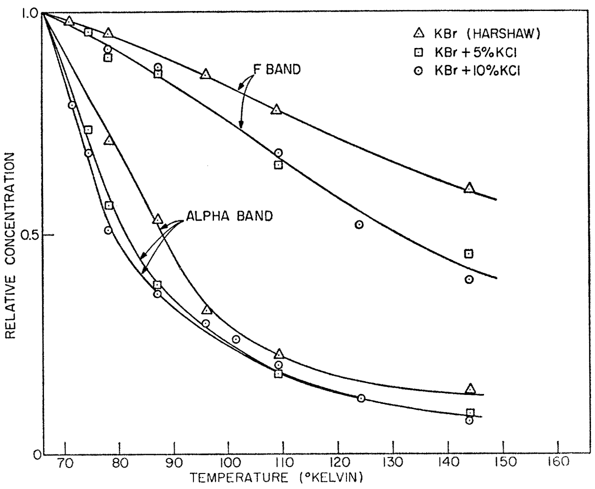

FIG. 4. Thermal annealing of defects produced at 66°K.

TABLE I. Concentrations of centers at 87°K divided by the concentrations at 66°K.

	KBr		KBr+10% KCl	
	F centers	α centers	F centers	α centers
Growth[a]	0.92	0.61	0.84	0.35
Anneal[b]	0.90	0.53	0.86	0.37

[a] From the growth curves of Figs. 1 and 2.
[b] From the annealing curves of Fig. 4.

2. *Efficiencies for Vacancy Production*

The efficiency for the production of a particular lattice defect may be defined as the total energy (eV) absorbed by the crystal divided by the number of those particular defects which are produced by the irradiation. The results, taken at the points in Figs. 1 and 2 where 10^{20} eV/cm³ have been absorbed, are 5800 eV/α center and 2500 eV/F center for KBr irradiated at 66°K. The efficiencies for KBr+10% KCl measured under the same conditions are 190 eV/α center and 1400 eV/F center. Thus 6000 eV absorbed in pure KBr produces one α center and two F centers. The same energy absorbed by a KBr+10% KCl crystal produces about 30 α centers and four F centers.

A more interesting comparison involves the total vacancy production efficiency, i.e., the total absorbed energy divided by the total number of vacancies (F centers+α centers) produced. This comparison is made in Table II. We see that the addition of 10% KCl to a KBr host crystal increases the vacancy production efficiency by a factor of 10 at 66°K. It is interesting to consider what fraction of the ionizations produced by x irradiation are involved in the creation of defects. About 20 eV, i.e., twice the band gap, is required to produce one ionization. In the case of the KBr+10% KCl mixed crystal at 66°K one sees that one in eight ionizations is involved in the vacancy production process if it proceeds by a single ionization mechanism. On the other hand, if a mechanism of the Klick-Williams type which requires the ionization of two adjacent

TABLE II. Vacancy production efficiencies in KBr and KBr–KCl mixed crystals at various temperatures.

	eV/vacancy		
	5°K	66°K	87°K
KBr	190[a]	1750	410
KBr+10% KCl	360[b]	170	2150

[a] From V. Ritz, Phys. Rev. 142, 505 (1966).
[b] U. Strahle, Diplom, Stuttgart, 1963 (unpublished).

halide ions is operative, than one in four ionizations is involved in the vacancy production process.

The efficiency for vacancy production in the KBr-KCl mixed system at 66°K is about the same as in pure KBr at 5°K. A theoretical calculation of the vacancy production efficiency in KBr by means of a Klick-Williams mechanism has been made by Ritz.[11] The most optimistic calculation yielded values of 270-580 eV/vacancy. These values are, as Crawford[36] has pointed out, "inconveniently large." However, in view of the strong variation of vacancy production efficiency with radiation quality,[37] it was possible to conclude that mechanisms of the Klick-Williams type dominated the coloration process at 5°K (Refs. 11, 12) since none of the other proposed mechanisms would seem to depend upon the spatial distribution of ionizations along the electron tracks. In view of the ease of vacancy production in the KBr-KCl mixed system, it was considered of interest to measure the effect of different x-ray qualities on the coloration process. Accordingly, the following experiment was performed: Crystals were x-rayed at 66°K with very heavily filtered (5.7-mm Al+0.87-mm Cu) 100-kV x rays and with lightly filtered (beryllium window of x-ray tube +0.13-mm Al) 50-kV x rays. In the case of the 100-kV x irradiations the crystals were uniformly colored and the concentration of centers per cm^3 could be calculated quite simply from Smakula's equation and the crystal thickness. However, the 50-kV x irradiations colored the crystals very nonuniformly, so a meaningful concentration per cm^3 could not be calculated simply from the geometrical crystal thickness. Accordingly, Smakula's equation was rearranged so that the concentration in units of centers per cm^2 could be evaluated. The results of these measurements are given in Figs. 5 and 6.

One sees that both the α- and the F-center production rates are depressed for the 50-kV irradiations in both KBr and KBr+KCl crystals. This is exactly ***opposite*** to the effect observed in pure KBr at 5°K where an ***increase*** in the vacancy production rate occurs as the x-ray photon energy is lowered in this kilovoltage range.[11,12] However, the vacancy production rate at 5°K depends upon the gross intensity of the radiation field (more accurately, on the rate of energy absorption in the crystal, eV/cm^3 sec) as well as upon the radiation quality.[12] One measures this effect by varying the emission current of an x-ray tube or a Van de Graaff accelerator. An increase in intensity causes a decrease in the vacancy production rate. Since the rate of energy absorption in the crystal for the 50-kV x irradiations was several orders of magnitude greater than that for the 100-kV irradiations, an analysis of this effect may explain the data of Figs. 5 and 6.

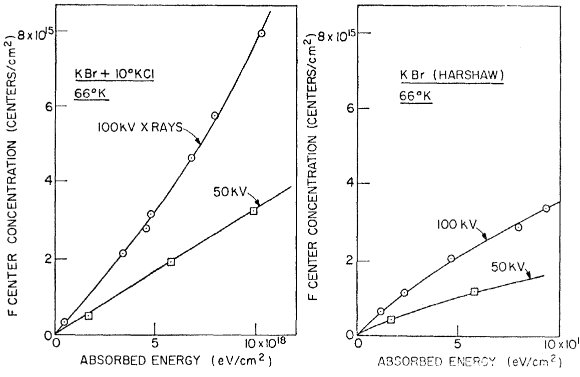

FIG. 5. F-center concentration versus absorbed energy as a function of x-ray energy.

An increase of the x-ray emission current by a factor of 3 was found to cause a 5% decrease in the rate of α-center production in the KBr+10% KCl system at 66°K. This effect was not measurable for the F band because of the small optical densities involved. Thus it would appear that the intensity dependence measured previously at 5°K in pure KBr is also operative in the doped crystals at 66°K. In Fig. 7, we plot data from previous work[12] and the present experiment to show the relative vacancy production as a function of the rate of energy absorption (eV/cm^3 sec). One sees that a smooth curve is obtained for the data and that the KBr+10% KCl points fall on a straight line extending the KBr, 5°K, data to lower intensities. All of these measurements were made with crystals which were uniformly irradiated, so the rate of energy absorption was calculated quite simply from the thickness of the crystal and the results of the glass block dosimeter measurements. In the case of the 50-kV x irradiations, in which the crystals were irradiated nonuniformly, we can only estimate an approximate average. This was done by using the 50-kV x-ray spectrum measured by Ehrlich[38] and various data obtained in a study of the α-center-to-F-center ratio at 5°K.[39] The horizontal error

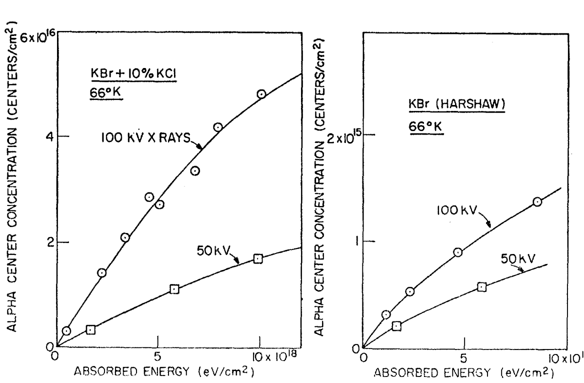

FIG. 6. α-center concentration versus absorbed energy as a function of x-ray energy.

---

[36] J. H. Crawford, International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, 1965 (unpublished).

[37] By a change in radiation quality, we mean a change in the average kinetic energy of the electron flux generated in the sample by irradiation.

[38] M. Ehrlich, J. Res. Natl. Bur. Std. (U. S.) 54, 107 (1955).

[39] V. H. Ritz and M. N. Kabler, Phys. Letters 19, 259 (1965).

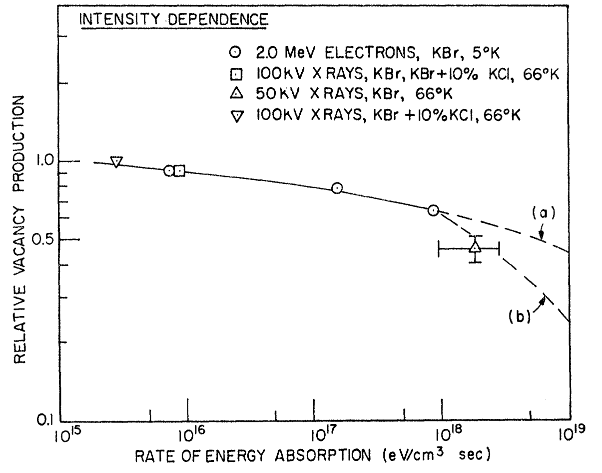

FIG. 7. Relative vacancy production versus rate of energy absorption.

bars on the 50-kV x-ray point in Fig. 7 represent what are thought to be reasonable limits for this estimate. At 5°K it was found that both the α- and F-center production rates varied in the same way with intensity.[12] The data of Figs. 5 and 6 indicate that the behavior of the F and α bands may be slightly different. For simplicity, we averaged them. The vertical error bars then show the uncertainty involved in this approximation.

The 50-kV point is seen in Fig. 7 to lie beyond the limits of the data taken at 5°K, so we must extrapolate the intensity data to higher intensities. A close inspection of the curve shows that it has a decided curvature at higher intensities. The dashed curve (a) represents an extrapolation on the assumption that the rate of change between 10^{18} eV/cm^3 sec and 10^{19} is the same as between 10^{17} and 10^{18}. The dashed curve (b) assumes that the rate of change doubles in the 10^{18}–10^{19} range. In this way, we obtain a correction for the intensity dependence which we will apply to the data of Figs. 5 and 6. This is done in Table III for pure KBr at 66°K. We see that intensity-dependence corrections bring the 100- and 50-kV data into approximate agreement. Since the absolute accuracy of the efficiency measurements is about 15%, we can say that the vacancy production rate is either unaffected by the x-ray quality at 66°K or is weakly dependent upon it in a direction opposite to that observed at 5°K. In this respect we might mention the experiments of Sharma and Smoluchowski[40] in which the x-ray photon energy was varied around 13.5 keV in 78°K irradiations of KBr. They detected a small photon energy dependence of about 10% in this region. They were, however, working with x rays of much lower energy so their results are not directly comparable to the ones reported here. The general indication is, however, that the rather striking quality dependence measured at 5°K in pure KBr is either not observed at 66°K or is much smaller. The dependence of the vacancy production rate upon the rate of energy absorption in the KBr+10% KCl mixed system has not been measured over the wide range shown for KBr in Fig. 7. However, it would appear from the discussion that there is little difference between the KBr and KBr–KCl systems in their response to x rays of different qualities.

TABLE III. Vacancy production efficiencies for x rays of different energies.

	eV/vacancy			
	66°K	66°K[a]	66°K[b]	5°K[c]
100-kV x rays	1750	1750	1750	270
50-kV x rays	3500	2250	1950	190

[a] Corrected by extrapolation (a) of Fig. 7.
[b] Corrected by extrapolation (b) of Fig. 7.
[c] From V. Ritz, Phys. Rev. **142**, 505 (1966).

In view of these results, one might well ask if mechanisms of the Klick-Williams type are operative in the alkali halides at 66°K. Aesthetically, one would prefer to have Frenkel defects produced by the same basic mechanism at all temperatures. One can assume that the defect production yield is independent of temperature and that the increased energy required to produce the defects at higher temperatures is a reflection of the thermal stability of the defects. Support for this viewpoint for pure KBr can be derived from the annealing curves of Strähle[20] and Itoh *et al.*[41] Using this data one can derive an efficiency of 2100 eV/vacancy at 66°K from the 5° data. This result may be compared with the value of 1750 eV/vacancy which was measured directly from the growth curves at 66°K. It is seen that good agreement is obtained for pure KBr. A similar analysis for the KBr–KCl mixed system is not possible at low temperature since the addition of KCl to KBr at 5°K apparently depresses the vacancy production rate.[20] It is interesting to note the the efficiency in the mixed crystal at 66°K is about the same as in pure KBr at 5°K; this suggests that this may be the maximum yield of vacancies obtainable. While the above discussion can account for the gross changes in relative vacancy production in pure KBr as a function of temperature, one is left with the problem of the disappearance of the quality dependence at some temperature below 66°K.

Another viewpoint would be to assume that, in addition to the Klick-Williams mechanisms, another mechanism is operative at 5°K which is independent of radiation quality. This sort of possibility has been considered earlier[11] in connection with the role played by low-energy Auger electrons in the coloration process, and cannot be excluded. The excitonic mechanisms

---

[40] J. Sharma and R. Smoluchowski, Phys. Rev. **137**, A259 (1965).

[41] N. Itoh, B. S. H. Royce, and R. Smoluchowski, Phys. Rev. **138**, A1766 (1965).

proposed recently by Pooley[42] and Hersh[43] would fit into this class of mechanisms. One might suppose that, for some reason, the Klick-Williams mechanisms become inoperative at some temperature between 5 and 66°K, leaving the quality-independent mechanism. According to Pooley, the yield of the excitonic mechanism would be expected to increase rapidly near 100°K, and this could account for the observed coloration rates at higher temperatures. In KBr, where one could use a mixture of a very efficient Klick-Williams mechanism together with an inefficient mechanism of the second type, a good fit could probably be obtained in the 5–66°K range. In the KBr–KCl mixed system one has a problem in mixing two mechanisms so as to produce the same approximate efficiency at 5 and 66°K. One would have to postulate that the yield of the second energy-independent mechanism was greater at 66 than at 5°K. The data necessary for a quantitative evaluation of this possibility is, however, not available at present.

An interesting possibility arises in connection with the Klick-Williams mechanisms in a mixed KBr–KCl crystal. In particular, the Williams mechanism derives momentum for the displacement of the ions to interstitial positions from the interaction of the halogen molecule ions with the asymmetric crystalline field.[44] This asymmetry would be larger if one of the participating ions or neighboring ions was a Cl^- ion instead of a Br^- ion. One might conjecture that the increased yield of vacancies in the mixed crystal was due to this effect, rather than to the differences in thermal stability of the reaction products. However, this possibility would seem to be obviated by the fact that the presence of KCl in a KBr crystal does not increase the yield at temperatures below 20°K.[20]

Although the problem of vacancy production mechanisms between 5 and 100°K obviously needs further study, one can account for the general features of the temperature dependence of vacancy production by using a temperature-independent production mechanism of high yield combined with different thermal stabilities at irradiation temperatures above 5°K. An explanation for the disappearance of the radiation quality-dependence characteristic of the Klick-Williams mechanism would seem to be rather obscure at present and further experiments will be required to resolve this problem.

3. *Recombination Luminescence*

Two effects seem to be operative at 5°K which can explain the large ratio of α centers to F centers formed after irradiation. The first, proposed by Lüty,[45] involves the electric field of the interstitial ion which prevents the vacancy from trapping an electron to become a F center. The second, suggested by Kabler,[4] involves the strong luminescence produced in alkali halides under x irradiation at low temperatures which is due to the recombination of electrons and holes at V_K centers. Kabler has shown that this luminescence spectrum overlaps the F-center absorption band and may bleach some of the F centers, leaving α centers. Evidence supporting this latter proposal at low temperature has been reported by Ritz and Kabler.[39] The variation of the α-to-F ratio in KBr is shown by the solid curve in Fig. 8. The initial sharp rise in the α/F ratio is thought to be due to the bleaching effect of the recombination luminescence. The final decline after the bleaching saturates reflects the trapping of electrons by the α centers.

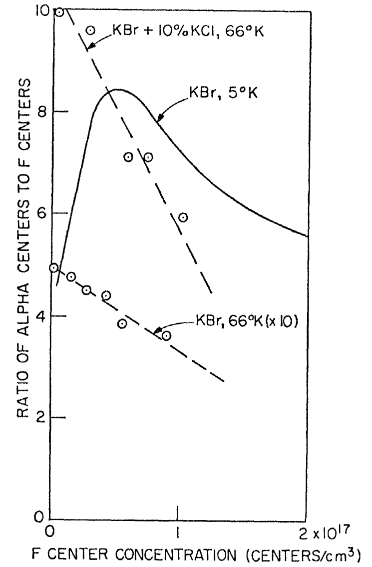

FIG. 8. Ratio of α centers to F centers versus F-center concentration.

The data plotted in Fig. 8 for pure KBr irradiated at 66°K indicates that the recombination luminescence plays no role in determining the α/F ratio at that temperature. No initial rise characteristic of the recombination luminescence is observed, just a gradual decrease in the ratio due to electron trapping by α centers. This result is consistent with the work of Kabler[46] in which the intensity of the recombination luminescence in KBr was observed directly with a photomultiplier and observed to fall to between 5 and 10% of its 5°K value at 55°K. The same behavior of the α/F ratio is observed in both the pure and the mixed crystal systems at 66°K. This implies that the large α/F ratio observed in the KBr+10% KCl crystals is not due to a recombination luminescence, but rather to the thermal stability of the Cl^- ions in a KBr lattice which enables them to prevent electron trapping

---

[42] D. Pooley, Proc. Phys. Soc. (London) **87**, 245 (1966); Solid State Commun. **3**, 241 (1965).

[43] H. N. Hersh, Phys. Rev. **148**, 928 (1966).

[44] F. E. Williams, Phys. Rev. **126**, 70 (1962).

[45] F. Lüty, *Halbleiter Probleme* (Vieweg und Sohns, Braunschweig, 1961), Vol. VI, p. 238.

[46] M. N. Kabler (private communication).

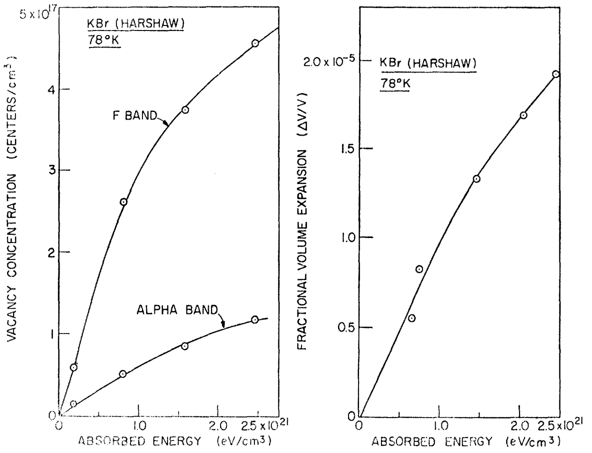

FIG. 9. Vacancy concentration and fractional volume expansion ($\Delta V/V$) versus absorbed energy in KBr.

through the influence of their electric field on the vacancy.

B. Volume Expansion Measurements

1. *Results*

The results of optical absorption and volume expansion measurements on KBr irradiated at 78°K are shown in Fig. 9. Irradiations were made at liquid-nitrogen temperature instead of 66°K because the low vacancy production rate in pure KBr necessitated irradiations of 90-h duration to produce a useable volume expansion. The growth of the optical absorption bands and the volume expansion parallel each other. One would expect that the volume expansion would follow the growth of the F band most closely since more F centers are formed than α centers. This expected correlation is not immediately evident from the growth curves of Fig. 9 because of the similarity in the shape of the F and α growth curves. However, the thermal annealing data of Fig. 10 show that the annealing behavior of the volume expansion is dominated by the F-center annealing characteristics as one might expect. This annealing curve was made after the crystal had been x irradiated to the last point of the growth curve shown in Fig. 9.

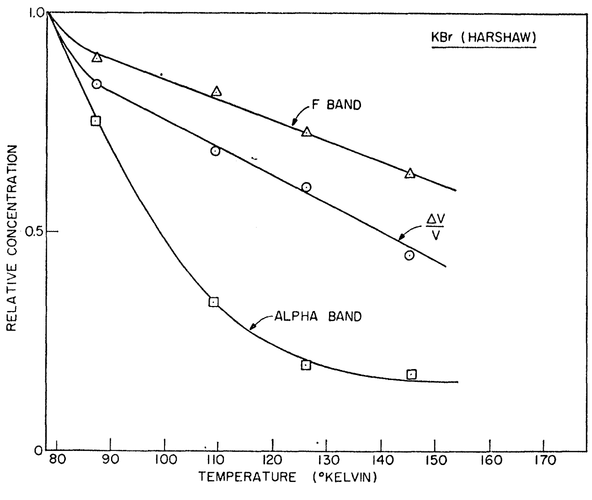

FIG. 10. Vacancy concentration and $\Delta V/V$ versus annealing temperature in KBr.

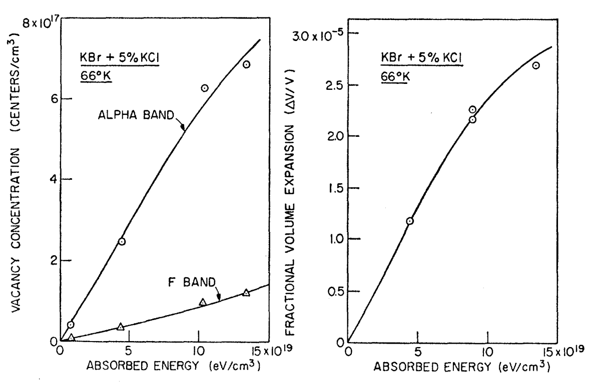

FIG. 11. Vacancy concentration and $\Delta V/V$ versus absorbed energy in KBr+5% KCl.

In Fig. 11, we have plotted similar data for the growth of the optical absorption bands and the volume expansion for KBr+5% KCl x irradiated at 66°K. In this system one expects the α-center growth to dominate. This is seen to be the case since both the α-band growth and volume expansion begin to saturate at about 15×10^{19} eV/cm^3 while the F band continues to grow at an increased rate at that point. The annealing curves of Fig. 12 show the dominant role played by the α center more clearly. Similar results were obtained for KBr+10% KCl and are shown in Figs. 13 and 14.

The V_4 center has been characterized by Kingsley[47] as the most important hole center formed near 80°K.

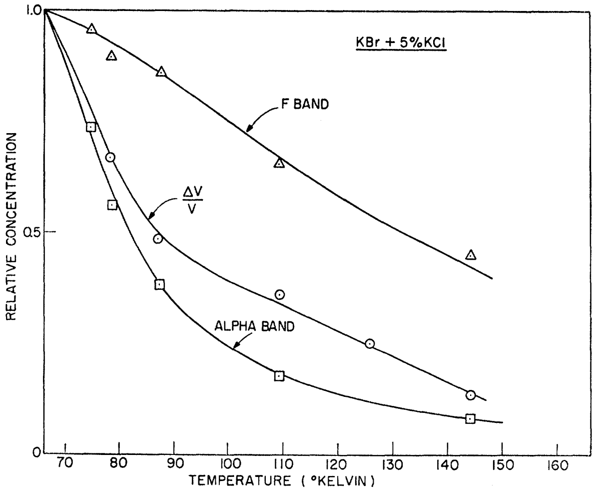

FIG. 12. Vacancy concentration and $\Delta V/V$ versus annealing temperature in KBr+5% KCl.

---

[47] J. D. Kingsley, J. Phys. Chem. Solids **23**, 949 (1962).

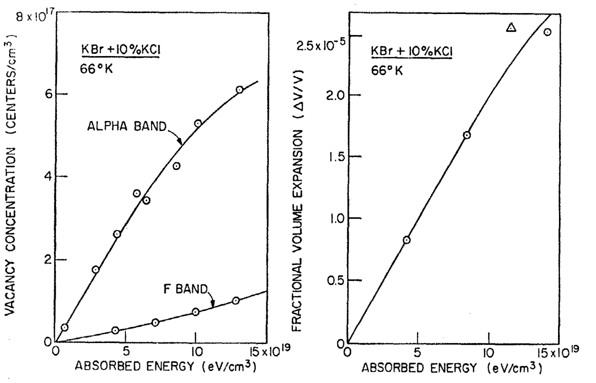

FIG. 13. Vacancy concentration and $\Delta V/V$ versus absorbed energy in KBr+10% KCl.

This viewpoint is supported by the work of Faraday and Compton[29] who found a linear relation between the absorption constants of the V_4 band at 274 nm and the F band. This suggests that the V_4 and F centers are formed in equal quantities. Attempts to follow the growth of the V_4 band at the beginning of the growth curves of Figs. 9, 11, and 13 were complicated by the small optical absorptions and large half-widths involved. It was observed however, that the band did grow linearly with the F band during the late stages of irradiation. We will assume, then, on the basis of this data and the results of Faraday and Compton, that the V_4 concentration is the same as the F concentration at all stages of the growth curves. We will also assume that the V_4 band anneals in the same way as the F band as the temperature is raised. This was observed to be the case for the first stages of the annealing curves where the optical densities were high and the bands were easily resolved. No differences in the V_4-band production rate or thermal annealing characteristics were observed between the KBr and KBr–KCl systems.

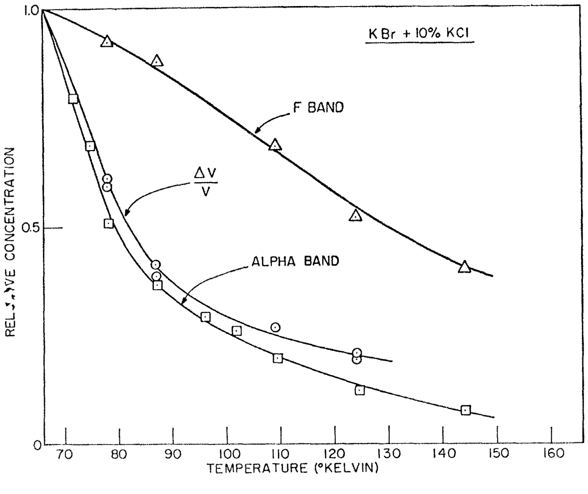

FIG. 14. Vacancy concentration and $\Delta V/V$ versus annealing temperature in KBr+10% KCl.

TABLE IV. Values of K_F and K_α for KBr and KBr–KCl mixed crystals. The upper number in each case was derived from the annealing data; the lower one from the growth curves.

	K_F		K_α	
KBr	0.78±0.06 0.60±0.02	0.70±0.10	1.86±0.16 2.14±0.22	2.00±0.12
KBr+5% KCl	1.06±0.26 1.36±0.42	1.22±0.22	1.16±0.24 0.96±0.06	1.08±0.08
KBr+10% KCl	1.26±0.14 1.26±0.18	1.26±0.10	0.88±0.16 0.86±0.02	0.88±0.06

Assuming that the volume expansions caused by the different defects are strictly additive, one can write[9]

$$\frac{\Delta V}{V}=K_\alpha\left(\frac{n_\alpha}{2N}\right)+K_F\left(\frac{n_F}{2N}\right), \tag{3}$$

where $\Delta V/V=$ the fractional volume expansion measured by the photoelastic technique, $K_\alpha=$ a constant which is a measure of the lattice relaxation around a Frenkel pair consisting of an α center and interstitial ion, $K_F=$ a constant which is a measure of the lattice relaxation around a Frenkel pair consisting of an F center and interstitial atom, n_α, $n_F=$ the concentrations of the various Frenkel pairs as determined by the optical absorption measurements, $N=$ the number of ion pairs per unit volume.

Since we can only measure the concentration of the α centers and F centers by optical absorption techniques, we will assume that the concentrations of the interstitial ions and atoms are the same, respectively, as the concentrations of the α centers and F centers. This is equivalent to saying that the defects are generated as Frenkel pairs.

One can use the above equation, together with the data of Figs. 9–14, to generate a system of simultaneous equations which may be solved for K_α and K_F. The data for the growth curves showed no systematic variation in the K's as the x irradiations progressed. Similarly, no systematic variation was observed in the annealing data as the temperature was raised. The results of these calculations are presented in Table IV. The growth and annealing results are listed separately, together with the probable errors of the mean value in each case. All of the results for these two types of measurements are in agreement within the given errors, except for the values of K_F for pure KBr which indicate the presence of some inconsistency between the growth and annealing results. Since we have no reason to favor either technique, we have treated them with equal weight and averaged them. The other averages in Table IV have been obtained by assuming that each of the experimental points on the growth and annealing curves was of equal weight and combining all of them to obtain the mean values. The number of annealing and growth points was not necessarily the same.

2. Discussion of Pure KBr Results

We will now compare these results with those obtained by Lüty *et al.*[9] In their work they used transformations of U centers to α centers and F centers, so that the volume changes observed were due to the displacement of H^- ions from their normal lattice positions, rather than Br^- ions. To correct their results to those which would be obtained for the perfect lattice they used the following relation:

$$K_{U\to\alpha}=K_{U\to\mathrm{Br}^-}+K_{\mathrm{Br}^-\to\alpha}, \tag{4}$$

where $K_{U\to\alpha}$= the constant they measured experimentally, $K_{U\to\mathrm{Br}^-}$= a constant which can be derived from the lattice parameter measurements of Hilsch and Pohl,[48] $K_{\mathrm{Br}^-\to\alpha}$= the desired constant characteristic of the perfect lattice. From Hilsch and Pohl's data on mixed KBr–KH crystals they found $K_{U\to\mathrm{Br}^-}=0.36$ and were able to evaluate $K_{\mathrm{Br}^-\to\alpha}$. The same treatment was applied to their F-center results, so that their final values were characteristic of the pure KBr lattice. The validity of this type of correction down to the microscopic scale has been verified by Paus and Lüty for the KCl:KOH system.[49] It is important to note that this correction reflects only the difference in size of the Br^- and H^- ions in a substitutional position in the undamaged lattice and does *not* correct for the distortion produced by these ions when they go to an interstitial position. These results are listed in Table V.

Considering first the data for the F-center Frenkel pair we see that the value 0.70 obtained from the average of the growth and annealing curves is in good agreement with the value 0.87 measured by Lüty *et al.*[50] Since the Frenkel pair measured by Lüty *et al.* consisted of an F center and an interstitial hydrogen atom, their K_F was used to determine the relaxation around the F center by assuming that the distortion caused by the interstitial hydrogen atom was zero. In our case the Frenkel pair consists of an F center and bromine atom in an interstitial position. Since there is no reason to suppose that the F centers are different in these two systems, the agreement between the two K_F constants shows that the difference between the distortion caused by hydrogen atoms and by bromine atoms is small when they are in interstitial positions. This implies that the distortion caused by either atom alone is also small. Thus it would seem that the assumptions made concerning the hydrogen atom in the KBr–KH system were well justified. Farnum *et al.*[51] have measured the irradiation-induced volume expansion of KCl and KBr at low temperatures using a capacitive dilatometer. They derived an upper limit for the expansion caused by the neutral interstitial accompanying the F center at 80°K which was about 40% of that measured for the F center alone. This small expansion was obtained by comparison with the KBr:KH results of Lüty *et al.* who made photoelastic measurements and may reflect some systematic errors in the different methods of measuring the volume expansion. On the other hand, the F-center results of Peisl *et al.*,[52] obtained in pure KCl by the hydrostatic flotation technique, agree with those of Lüty *et al.* within experimental error and yield no expansion attributable to the interstitial Cl^0 atom.

Table V. Comparison of the KBr and KBr:KH systems.

	K_F	K_α
KBr	0.70±0.10	2.00±0.12
KBr:KH	0.87±0.12	1.26±0.22

This agreement between the KBr and KBr:KH systems brings up an interesting point in connection with the model of the V_4 center. Kingsley[47] proposed that the V_4 center in KBr was the antimorph of the F center and was similar to Känzig's V_F center in LiF.[53] Recently, Itoh[54] has proposed that the V_4 band corresponds to a center associated with an interstitial halogen atom. Since the V_4 center is present in the same concentration as the F center in KBr which has been x irradiated, but is not found in KBr:KH crystals in which $U\to F$ transformation has taken place, one may conclude from the agreement between the present experiment and the KBr:KH work that the V_4 center produces no volume expansion. This result is consistent with both of these models neither of which would be expected to produce a large volume expansion. It is interesting to note that an exact antimorph of the F center, in which the hole was shared equally by the ions surrounding the alkali ion vacancy instead of being localized as in the above two models, would have been expected to produce a volume expansion comparable to that of the F center.

Turning now to the results for the α-center Frenkel pair we see that the value 2.00 which was obtained for K_α in the present system is larger than that for the KBr:KH system which yielded 1.26.[50] According to Royce, the interstitials involved in the x-rayed KBr system are groups of bromine ions. The H^- ion is the product in the KBr–KH system. The above difference indicates that the distortion produced by the interstitial Br^- ions in larger than that produced by the H^- ion. Estimates of the size of the H^- ion radius vary from 0.7 to 2.08 Å and, for lack of adequate data, Lüty *et al.*[9] assumed that the volume expansion produced by the interstitial H^- ion was zero. If we make the same assumption, then we can attribute all of the difference in

---

[48] R. Hilsch and R. W. Pohl, Trans. Faraday Soc. **34**, 883 (1938).

[49] H. Paus and F. Lüty, Phys. Status Solidi **12**, 341 (1965).

[50] We have increased their reported value by 10% to include the temperature dependence of the elastic and photoelastic constants discussed earlier in the present paper.

[51] E. H. Farnum and B. S. H. Royce, Phys. Letters **26A**, 164 (1968).

[52] H. Peisl, R. Balzer, and W. Weidelich, Phys. Rev. Letters **17**, 1129 (1966).

[53] W. Känzig, Phys. Rev. Letters **4**, 117 (1960).

[54] N. Itoh, J. Phys. Chem. Solids **27**, 197 (1966).

K_α to the Br^- ions. We then obtain a difference in K_α due to Br^- ions of 0.75±0.25 in the 65–150°K range by the photoelastic technique. This may be compared to Farnum's value of 1.4±0.4 for KBr at 6°K. If we correct the results of Lüty *et al.* to be consistent with the photoelastic constants used in the present experiment, Farnum's value should be reduced to 1.35±0.4. This is just within the quoted uncertainties. However, if one believes that the results do indicate a real difference between the expansion due to isolated Br^- ions at 6°K and groups of Br^- ions at higher temperatures, then a reasonable explanation would be the "overlap" of Br^- ions at the higher temperatures where they do not exist as isolated single ions. We might also note here that the relaxations around the F or α centers alone which have been reported and discussed by Lüty *et al.*[9] are in good agreement with the theoretical calculations of the expected relaxations.

In the case of the F-center Frenkel pair we have found, then, that none of the expansion is attributable to the interstitial Br^0 atom. The α-center Frenkel pair yielded a large expansion associated with the α center and a smaller expansion due to the interstitial Br^- ions. In both cases we have obtained these results by comparing our measurements with those made by Lüty *et al.* on the KBr:KH system using the assumption that the volume expansion caused by interstitial H^0 atoms and H^- ions was very small.

3. *Discussion of KBr-KCl Mixed Crystal Results*

In the present experiment, it is of interest to adjust the pure KBr results to be characteristic of the expulsion of a Cl^- ion from its normal lattice position. This is done in the same way as was discussed in the preceding section:

$$K_{Cl^-\to\alpha}=K_{Cl^-\to Br^-}+K_{Br^-\to\alpha}, \qquad (5)$$

where $K_{Cl^-\to\alpha}$ = the desired constant characteristic of the expulsion of a Cl^- ion, $K_{Cl^-\to Br^-}$ = a constant we can evaluate from lattice parameter data,[55,56] $K_{Br^-\to\alpha}$ = the constant obtained from the pure KBr results. Using the lattice parameter data of Miessner and Pick[56] we find that $K_{Cl^-\to Br^-}=0.29$. The results obtained for the α and F centers in this way are listed in Table VI along the values for KBr and KBr-KCl crystals which were listed in Tables IV and V.

The data of Figs. 1–3 show that the F-center production is enhanced in KBr-KCl mixed crystals as well as the α-center production. One would suspect, then, that a large proportion of the F centers was generated by a process in which Cl^- ions were eventually displaced from their normal lattice sites. If this were the case, K_F for the mixed crystals should be slightly larger, by ≈0.29, than in the pure system, if one assumes that the interstitial atoms produce no additional volume expansion. Table VI shows that this is indeed the case.

TABLE VI. Comparison of the KBr-KCl mixed crystal results with those of KBr.

	K_F	K_α
KBr	0.79±0.10[a]	2.00±0.12
KBr+5% KCl KBr+10% KCl	1.24±0.16	0.98±0.10
KBr-KCl system Cl expulsion	1.08±0.10[b]	2.29±0.12[b]

[a] Average of the KBr and KBr:KH results in Table V.

[b] Obtained by taking the KBr results and adjusting them with lattice parameter data for the KBr-KCl system as described in the text.

The average value of K_F, 1.24, in the mixed crystals is larger than the value 0.79 characteristic of the pure KBr system. It is interesting to calculate the relative proportion of F centers produced by these two processes. The optical data of Figs. 1–3 can be used to calculate an average K_F, assuming that all of the enhancement of the F growth in the mixed crystals is due to the Cl^- ion expulsion. Using the average values in Table VI we obtain K_F equal to 0.96. This is only slightly different from the value characteristic of Cl^- ion expulsion and cannot be resolved in our data. Thus we can conclude that the majority of F centers which are formed involve eventual Cl^- ion expulsion, but cannot determine the smaller fraction due to Br^- ion expulsion. It seems reasonable, however, that the relative proportions are those which can be derived from the optical data.

Lüty[8] has suggested that the Cl^- ions in KBr:KCl mixed crystals are expelled directly. On the other hand, Itoh, Royce, and Smoluchowski[41] have suggested that the Br^- ions are displaced and then replaced by the more stable Cl^- ions during a second step in the vacancy creation process. It is impossible to differentiate between these two processes with the volume-expansion technique, since the expansion is only an indication of the difference between the initial and final states of the crystal.

Turning now to the results of measurements of K_α, we have seen in Table IV that the KBr+5% KCl and KBr+10% KCl values agree fairly well with each other and an average value of 0.98±0.10 is obtained. However, as we can see in Table VI, this value is only half of that obtained for K_α in the pure KBr system and is comparable to that obtained for the F center. This result is quite unexpected and indicates that some factor in the KBr-KCl system causes the expansion around an α-center Frenkel pair to be much less than in the pure crystal. The optical absorption data did not indicate that there are any major differences in vacancy production in the two systems other than the enhanced vacancy production rate. The thermal annealing characteristics of both systems are not radically different as one warms from 66°K to higher temperatures, no differences in their response to the radiation quality or intensity of x radiation is observed, and recombination luminescence plays no major role in determining the α/F ratio in either system at these

---

[55] L. Vegard, Z. Physik **5**, 17 (1921).

[56] G. Miessner and H. Pick, Z. Physik **134**, 576 (1953).

temperatures. Moreover, the results for the F center in the mixed crystal systems seem fairly reasonable. In the following paragraphs we will discuss some possible explanations for this discrepancy in the α-center results.

First we will consider some possible sources of error in the experimental procedure itself. One might suspect that the distribution of KCl in the KBr–KCl mixed crystals was not uniform at concentrations of 5–10%, and that this produced nonuniform strains in the crystal which could introduce error in the photoelastic measurements. However, one sees that the K_α values are in good agreement for both 5% and 10% KCl concentrations. This close agreement would not be expected if there was appreciable nonuniformity of KCl distribution in the crystals. In addition, these crystals had a very uniform background strain profile and thus gave no evidence of areas of unusual strain. One might also wonder if appreciable plastic deformation was occurring in the mixed crystals which was absent from the pure KBr crystals or vice versa. However, the total volume expansion was about the same in all the experiments and the K_α value in the mixed crystals, as we have pointed out, was independent of KCl concentration. In addition, we did obtain values of K_F which were slightly larger in the KBr–KCl system. This would not be the case if appreciable plastic deformation had occurred.

Another source of error in the KBr–KCl system would be the ejection of impurities to interstitial positions instead of the Cl^- ions. In the case of OH^- the concentrations were $\approx 10.5\times10^{15}$ and $1.5\times10^{15}/\text{cm}^3$ in the KBr+5% KCl and KBr+10% KCl crystals, respectively. This is much smaller than the α-center concentrations used in the experiments and cannot account for the smaller K_α values which were the same in both mixed crystals in spite of quite different OH^- concentrations. In addition, the expulsion of OH^- instead of Cl^- or Br^-, would act in a direction so as to increase the measured K_α since the addition of OH^- contracts the lattice.[49] There was a large absorption band present in the KBr+5% KCl crystals which was attributed to iodine in a concentration of ≈ 2 ppm. Again this is much smaller than the total α-center concentrations which were used. More conclusive, perhaps, is the fact that the band attributed to iodine was *not* observed in the KBr+10% KCl crystal which yielded the same K_α value. Thus we can conclude that this impurity cannot account for the small K_α values.

One might look instead into the nature of the defects themselves for an explanation of the small K_α values. A possible reason for this effect could be a contraction of the lattice around the interstitial Cl^- ions. This would seem unlikely, however, in view of the fact that we found an expansion of the lattice in the pure KBr system which we attributed to interstitial Br^- ions. Since the Cl^- ion is only slightly smaller than the Br^- ion one would expect an expansion instead of a contraction of the order of $K\approx 1.0$ for the contribution of the interstitial ions to the total Frenkel-pair expansion.

A convenient assumption usually made in the continuous elastic theory is that the elastic constants of the continuum and the inclusion are the same. There is some evidence from the effect of pressure on the hyperfine structure of F centers in LiF that the compressibility near an F center may differ from the compressibility of the rest of the crystal.[57] Indeed, the methods of continuum elasticity themselves have been attacked recently by Hardy and Bullough.[58] However, we have found that the application of the continuum theory yields reasonable results for the α center and F center in pure KBr and for the F center in mixed KBr–KCl crystals. It would seem unlikely that the continuum theory would suddenly fail for randomly distributed α centers in the mixed crystals. A more likely possibility would be that the α centers are in a region of close aggregation so that appreciable "overlap" occurs and the expansions due to the individual centers are no longer additive.[14] This would certainly reduce the observed values of K_α. Thus one might attribute the small α-center-induced volume expansion in the mixed crystal to an aggregation of α centers which "overlap" to change the bulk compressibility in their vicinity. A similar effect could also be caused by aggregations of Cl^- ions.

Another possibility concerns the influence of the interstitial ion on the α center. Since the ion is known to be fairly close to the vacancy and has a strong electric field which prevents electron trapping by the vacancy,[45] one might inquire as to whether this field can contract the vacancy. In the case of KBr at 65°K, the interstitials are groups of bromine ions in an unknown configuration; for the KBr–KCl system, the interstitials are probably isolated Cl^- ions. The fact that the α-center size measured in the pure KBr lattice is larger than the F center size by a factor of 2 indicates that the groups of interstitial Br^- ions do not produce a contraction of the vacancy. In addition, Farnum[51] has seen no evidence of a contraction of the vacancy due to the isolated Br^- ion at 6°K. To account for the small K_α measured in the KBr–KCl system we would have to assume that the Cl^- ion is radically different in its effect on the vacancy, and is able to reduce the vacancy to the size of a F center. This would appear unlikely if the Br^- and Cl^- ions are both the same distance from the vacancy, but could occur if the interstitial Cl^- ion were much closer to the vacancy at 66°K than the interstitial Br^- ion. It is also possible that aggregates of the Cl^- ion vacancy pairs could act in a way to produce a smaller expansion. This argument assumes hat the spatial distribution of the interstitial Cl^- ions in KBr–KCl mixed crystals differs from that of the Br^- ions in pure KBr. This seems plausible in view of the

---

[57] H. Blum, Phys. Rev. **140**, A1998 (1965).

[58] J. R. Hardy and R. Bullough, Phil. Mag. **15**, 237 (1967).

difference in thermal stability of the two systems, but direct evidence of such a difference is lacking.

The exact configuration of the interstitial ions and atoms formed by irradiations above 20°K is not known. There is ample evidence that interstitials exist at these temperatures,[59,60] but they do not exist as the isolated products which produce optical absorptions correlated to each specific defect. From the above discussion it would appear that possible explanations for the small expansion produced by the α-center Frenkel pair in the KBr–KCl crystals are either aggregates of α centers which are not additive in their effect and overlap to change the bulk compressibility of the crystal in their vicinity, or similar changes produced by the vacancy-interstitial pairs.

IV. SUMMARY

(A) The optical absorption measurements have shown the following: (1) The relative vacancy production rates at 66 and 87°K can be explained simply in terms of the thermal stability of the vacancy-interstitial Frenkel pairs in both the pure and mixed crystal systems. (2) The energy required to produce a Frenkel defect pair in pure KBr at 66°K does not depend upon the radiation quality of the x rays used to irradiate the crystal. This is quite different from previous observations at 5°K where the strong dependence of coloration rate upon radiation quality was cited as support for the Klick-Williams mechanisms. Similar results were obtained for the KBr–KCl system. (3) The variation in the α-to-F-center ratio in either KBr or KBr–KCl crystals at 66°K is consistent with the absence of recombination luminescence, and hence an absence of F-center bleaching at this temperature.

(B) The volume-expansion measurements on the pure KBr system at 66°K showed that: (1) The volume expansion caused by an F-center Frenkel pair is in agreement with that measured by Lüty *et al.* in the KBr–KH system. The volume expansion caused by an interstitial Br^0 atom is comparable to that of an interstitial hydrogen atom and is probably quite small. The fact that no volume expansion could be attributed to the V_4 center indicates that either of the models of this center which have been proposed by Kingsley and by Itoh could be correct. (2) The volume expansion caused by an α-center Frenkel pair is larger than that measured by Lüty *et al.*[9] This may be attributed to the expansion caused by groups of Br^- ions in interstitial positions.

(C) The volume-expansion measurements on the KBr–KCl mixed crystal system at 66°K showed that: (1) The volume expansion caused by the production of F-center Frenkel pairs was larger in the mixed crystals than in pure KBr. This indicates that the F centers are formed by a process in which Cl^- ions are removed from their substitutional lattice sites. (2) The volume expansion caused by the production of α-center Frenkel pairs in the mixed crystals was half of that observed in pure KBr, and comparable to that produced by the F-center Frenkel pairs. Possible explanations for this anomalous result would appear to be aggregates of α centers which are not additive in their effect and overlap to change the bulk compressibility of the crystal in their vicinity or a similar change produced by the vacancy-interstitial pairs.

ACKNOWLEDGMENTS

The authors would like to acknowledge assistance in the laboratory from C. Trombélla, C. Biscegli, and S. Sanches. We would also like to thank F. Lüty and B. S. H. Royce for valuable discussions, and C. T. Butler and J. Allard for analysis of the crystals used in the experiments. The comments of B. S. H. Royce, M. N. Kabler, and C. C. Klick on the manuscript were quite helpful.

---

[59] W. A. Sibley and E. Sonder, J. Appl. Phys. **34**, 2366 (1963).

[60] J. S. Nadeau, J. Appl. Phys. **34**, 2248 (1963); **35**, 1248 (1964); **33**, 3480 (1962).