

Photoelastic Measurements of the Volume Expansion by the $U \rightarrow F$ and $U \rightarrow \alpha$ Transformation in KBr

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Volume expansion by the introduction and transformation of point defects in alkali halide crystals was measured using the photoelastic technique. KBr crystals containing U centers were used as convenient model cases, which allow the transformation of U centers into F or α centers and hydride interstitials by uv or x irradiation. All products of these reactions can be quantitatively controlled in their formation and annealing behavior. Their concentrations can be monitored by optical absorption measurements, and their microscopic structure models are well known. Volume-expansion measurements with an improved automatic photoelastimeter were performed parallel to the formation and annealing processes, and could thus be correlated to specific center transformations. From the dilatation, which is found to be strictly proportional to the $U \rightarrow F$ transformation at room temperature, the volume expansion per F center can be determined. $U \rightarrow \alpha$ conversion by uv irradiation at low temperature produces volume expansion proportional to the α -center concentration. Thermal annealing of the α centers occurs in correlation with the annealing of the volume expansion. This allows the accurate determination of the volume change per vacancy H^- -interstitial pair. Using Eshelby's theory and previous data on the lattice parameter of KBr:KH crystals, values for the microscopic dilatations around F centers and α centers are obtained.

I. INTRODUCTION

A LARGE amount of experimental and theoretical effort has been made to determine dilatations caused by the introduction of point defects into alkali halide crystals. Different experimental techniques have been developed to a high degree of perfection and accuracy for these measurements. Relative changes of the macroscopic dimensions of the crystal,^{1,2} the crystal density,^{3,4} the lattice parameter,^{5,6} and the strain in the crystal⁷⁻⁹ (using photoelastic methods) have been detected with an accuracy of 10^{-5} to 10^{-6} . Nearly all investigations made so far were concerned with dilatation caused by high-energy radiation damage. In spite of a considerable amount of experimental and theoretical work the mechanism of high-energy radiation damage in alkali halides is not yet thoroughly understood. Moreover, in these processes always several types of defects are created, not all of them being accessible to optical control or known in their micro-

scopic structure. Thus, in most of the earlier work, correlations between observed macroscopical dilatations and microscopic size effects from specific point defects were either not possible or were achieved only under neglect of certain types of defects (like α centers at low temperatures and V -type centers at room temperature). Only very recently more sophisticated approaches were begun using a combination of different experimental techniques (like lattice parameter and density measurements) in order to achieve a more thorough interpretation of the measured dilatations.¹⁰⁻¹²

With the work reported here a series of experiments was started, aiming at the measurement of dilatation in point-defect systems which are more fully understood, controlled, and accessible to direct interpretation. Crystals containing U centers (substitutional H^- ions) appeared to be attractive in this respect, allowing two types of well-investigated center transformations:

(a) At room temperature, uv light and x irradiation produce a conversion of U centers into F centers and interstitial hydrogen molecules.

(b) At low temperatures, uv-light absorption produces from U centers complementary pairs of anion vacancies and interstitial hydrogen ions and, to a small degree, pairs of F centers and interstitial hydrogen atoms.

These processes have been extensively studied by

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optical,¹³⁻¹⁵ magnetic,¹⁶ and thermal-conductivity¹⁷ techniques. All point imperfections involved in these reactions have well-established microscopic models and can be controlled optically. Moreover, the above-mentioned reactions $U \rightarrow F$ and $U \rightarrow \alpha$ are cases of "low-energy radiation damage," which show remarkable similarities to the high-energy radiation effects in pure crystals.¹⁸ The two optical U -center conversions clearly show that (a) a *single* excitation process can produce extrinsic Frenkel pairs in the crystal down to lowest temperatures; (b) the probability of finding the electron trapped at either the vacancy or the interstitial follows the same general behavior as in high-energy radiation damage (preferentially empty vacancies and interstitial ions at low temperature, F centers and neutral interstitials at high temperature).

It has been suggested earlier¹⁸ that these conversions by single excitation may serve as model cases for the complicated high-energy radiation effects. This seems especially valid in view of recent speculations¹⁹ and rising evidence that single excitations may be the origin of intrinsic Frenkel pair production by high-energy radiation as well.

All the above considerations suggest that the controlled conversion from U centers into other fundamental defects are attractive and interesting for the study of volume changes and their interpretation by microscopic center dilatations.

II. EXPERIMENTAL TECHNIQUE

The photoelastic technique was first introduced by Primak *et al.*,²⁰ and later modified by Wiegand and Smoluchowski,⁷ Merriam *et al.*,⁸ and Mascarenhas *et al.*⁹ For the present work an automatic photoelastimeter was constructed.²¹ This allows one to record within a short time the full strain pattern of the crystal before and after irradiation [Figs. 1(a) and 1(b)], the difference between both directly yielding the defect induced strain profile (curve c in Fig. 1). While the instrumental accuracy is about $\Delta V/V \approx 5 \times 10^{-8}$, several factors such as background strain, temperature fluctuations, and uncertainties in the photoelastic constant limit the actual accuracy considerably. Typical errors for absolute measurements of $\nabla V/V$ are about $2-3 \times 10^{-6}$.

For the room-temperature (RT) measurements the crystals were fixed in aluminum holders, half shielded with a detachable iron piece. For the low temperature experiments the crystals were placed inside a liquid-

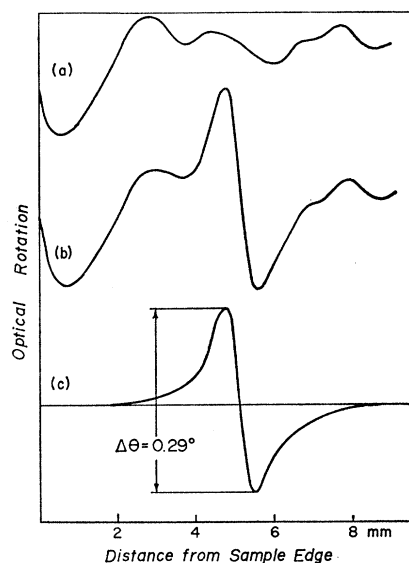


Fig. 1. Records of strain profile taken with the photoelastimeter scanning over a 10-mm-long crystal (a) before irradiation (background strain), (b) after x irradiation of half the crystal, (c) irradiation-induced strain (b minus a).

nitrogen-temperature (LNT) dewar. In the crystal holder of this dewar a special mechanical system allowed the shield to be moved on and off the non-irradiated half of the crystal, so that optical and photoelastic measurements could be made on both the irradiated and the nonirradiated part of the crystal. The design and building of these mechanical parts required great care because reproducibility of the shield position at low temperatures is very important for the method as applied. Thermocouples were fixed in the crystal holder, but could not be placed directly in the sample because of background strain problems. Blank runs were made, however, with the thermocouple directly in the sample and temperature differences of the readings were unimportant for the present experiments. The dewar was provided with a rotating external neck with two pairs of windows: one for x irradiation purposes, the other for optical and photoelastic measurements, which require special nonstrained windows. Irradiation of the crystals was performed either with uv (LNT measurements) from a low-pressure mercury lamp or with 50-kV, 30-mA x rays from a Mo tube, with the crystal positioned 2 cm from the target (RT measurements).

The KCl and KBr crystals used contained circa 10^{18} (U centers)/cc and were grown in Stuttgart by the Kyroupos technique, additively colored, and subsequently doped with hydrogen by heating them in a high-pressure hydrogen chamber. Crystals for the optical-density measurements were cleaved to about 0.1–0.2 mm thickness, the other dimensions being circa 0.5 and 1 cm. For the photoelastic measurements the samples were cleaved to 0.3 to 0.8 mm in thickness.

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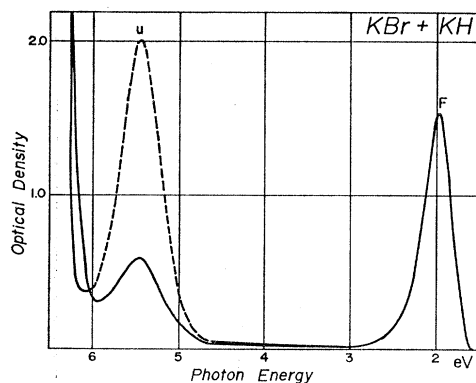


FIG. 2. Spectrum of the $U \rightarrow F$ conversion. Dashed curve: KBr:KH crystal before irradiation. Full curve: Crystal after x irradiation at RT.

In some of the thinner samples, points could be taken simultaneously for the optical and photoelastic measurements. The samples had to be chosen so as to present a reasonable background strain pattern. High-temperature annealing of U -center-containing crystals to remove strains can evaporate U centers from the surface, and thus cannot be used. The photoelastic constants of the samples used were measured directly in our laboratory,²² and they compared well with the pure-crystal values, even for the highly doped samples. The optical-absorption measurements were made with a DK-2 Beckman spectrophotometer.

The crystal was bombarded with x rays or uv, and optical absorption measurements were taken, after which the sample was transferred to the photoelastimeter to take the strain profile. In the case of growth curves this procedure was repeated several times. For thermal annealings the temperature of the dewar was allowed to vary slowly, optical density and photoelastic measurements being taken successively. In some cases iso-

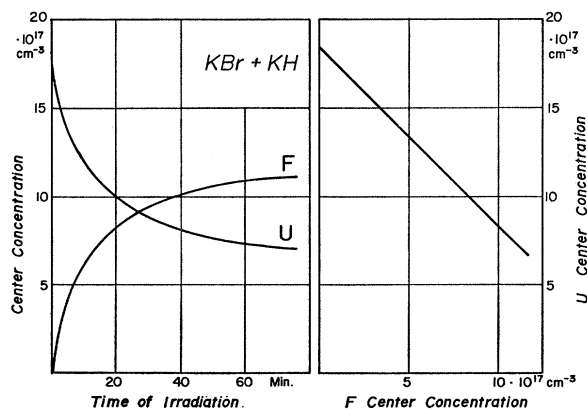


FIG. 3. F -growth curve and U -decay curve for KBr:KH under x irradiation at RT. Plot of U versus F -center concentration (right side) confirms a 1:1 conversion between U and F centers.

²² C. Arguello and S. Mascarenhas, U. S. Office of Naval Research Technical Report No. 3534, 1963 (unpublished).

thermal annealings were also performed. In all cases temperature changes were made so as not to introduce thermal strains in the sample. The measuring light for the photoelastimeter was chosen so that one could measure both the irradiated and nonirradiated halves of the crystal, a special electronic system compensating for differences in optical density along the sample.

III. EXPERIMENTAL RESULTS

A. $U \rightarrow F$ Conversion at Room Temperature

Figure 2 shows a typical absorption spectrum for a KBr:KH crystal before and after x irradiation at RT. The initial pure U -center system is converted into F centers without any trace of F -aggregate or V centers. X irradiation was continued up to the saturation of the $U \rightarrow F$ transformation. As can be seen in Fig. 3, saturation is obtained after about one hour of bombardment when about 60% of the original U centers are converted to F centers. In the same figure the U -center concentration has been plotted against the F -center concentra-

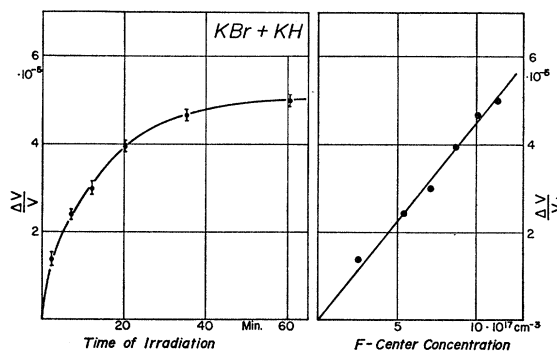


FIG. 4. Volume expansion in dependence of x irradiation time for KBr:KH crystal at RT. A plot of the measured $\Delta V/V$ against F -center concentration (right side) yields a linear dependence.

tion. The plot is linear, as expected if no other side reactions are present.

Parallel to the optical measurements, the corresponding growth curve for the volume expansion $\nabla V/V$ was measured. By comparison with the optical data (Fig. 4) it can be inferred that the volume expansion increases proportionately to the extent of the $U \rightarrow F$ transformation. For comparison and a check of the method, measurements of the same type were done with a KCl:KH crystal, yielding very similar results to those with KBr:KH. Experimental errors for the KCl:KH crystal were larger, because of a lower value of the photoelastic constant and smaller U -center concentration. Again a linear dependence between volume expansion and $U \rightarrow F$ transformation was found.

The $U \rightarrow F$ photochemical transformation is reversible in the sense that illumination with F light bleaches the F band, restoring the original U band, with negligible M -band formation. This process could

not be followed in quantitative detail along with the $(\Delta V/V)$ process, because, owing to the high absorption of the samples, the bleached region "creeps" into the crystal. This effect eliminates the possibility of correct interpretation of the birefringence pattern, which is realized only for uniformly damaged samples. However, the final pattern of the completely bleached crystal could be measured, and it was found that indeed the strain profile had been reduced practically to the initial background profile. This is further proof that all of the measured volume expansion was due to the $U \rightarrow F$ transformation.

The proportionality of volume expansion and $U \rightarrow F$ transformation brings out the experimental fact that always—even in the saturation region—the volume relaxation due to a $U \rightarrow F$ transformation is additive. The slope of the straight line in Fig. 4 gives directly the quantity $(\delta V/V)$ per unit $U \rightarrow F$ transformation. We can write

$$\delta V/V = K_{u \rightarrow F} (n_F/2N), \quad (1)$$

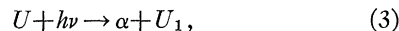
where n_F is the number of F centers, and N the number of ion pairs per unit volume. If r_0 is the interionic distance, and $2Nr_0^3$ the unit volume, K has the direct meaning of a volume change per dilation center measured in units of r_0^3 .

$$K_{u \rightarrow F} = (\Delta V/r_0^3)n_F. \quad (2)$$

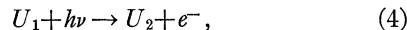
Our data from Figs. 3 and 4 yield a value $K_{u \rightarrow F} = 1.26$ for KBr:KH (A similar value $K_{u \rightarrow F} = 1.2$, though with larger error, was obtained for the comparison measurement in KCl:KH.)

B. $U \rightarrow \alpha$ Conversion at Low Temperatures

At low temperatures (e.g., LNT), optical irradiation into the U band converts the U centers according to the following primary reaction:



i.e., an anion vacancy (α) and an interstitial hydrogen ion (U_1) are formed.¹⁴⁻¹⁶ Unavoidable excitation by the uv light in the U_1 absorption (which overlaps the U band) leads to the secondary reaction.



i.e., the ionization of the interstitial hydrogen ion (U_1) forming an interstitial H atom (U_2 center); the electron becomes captured at the anion vacancy, forming an F center:



Thus, depending on the amount of secondary light absorption in the primary reaction product U_1 , pairs of U_2 and F centers are formed. Figure 5 shows an example of this conversion measured at a highly doped thin sample. The initial spectrum (containing only the U band) is transformed by the uv irradiation into the α , U_1 , U_2 , and F bands.

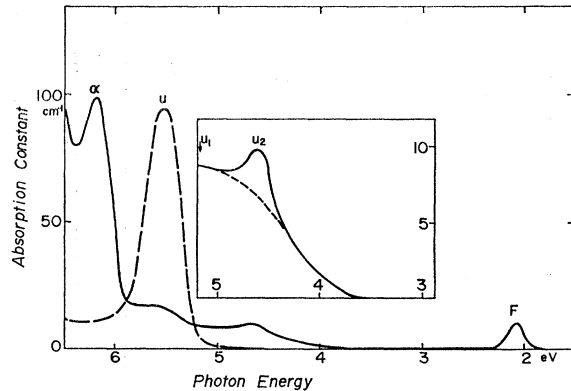


FIG. 5. Spectral transformations of KBr:KH crystal under uv irradiation at LNT. Dashed curve: Crystal before irradiation. Full curve: Crystal after almost complete bleaching of the U band. (The inset shows details of the U_1 and U_2 band in expanded scale.)

The thermal annealing of this system of defects is summarized in Fig. 6. Two processes take place:

(1) The interstitial hydrogen ion (U_1) when becoming thermally unstable recombines with the vacancy, the α band decreases under corresponding increase of the U -band. This thermal annealing occurs in characteristic stages¹⁵ which correspond to different stabilities, which in turn are attributable to different configurations of the interstitial-vacancy pairs.

(2) The interstitial hydrogen atoms (U_2 centers) become thermally unstable at about 100°K. As seen in Fig. 6, they do not recombine with their "antcenters", as the F band remains constant up to room temperature. Thus one has to conclude that the interstitial hydrogen atoms, when they become mobile, form molecular hydrogen, which is not detectable optically or magnetically.

This group of defects, which has well-established microscopic models and is optically controllable in its formation and annealing behavior, constitute the system for our dilatation experiments. Basically, two different experimental procedures were applied.

In the first method thick crystals were irradiated with uv light at LNT to a state of saturation of the

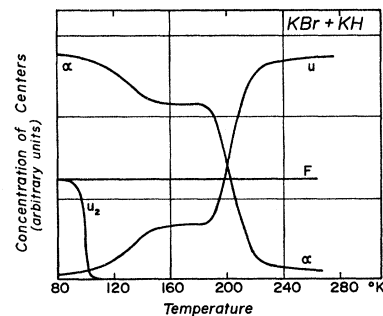


FIG. 6. Thermal annealing behavior of α , U_1 , U_2 , and F centers which were created by uv irradiation at LNT in KBr:KH.

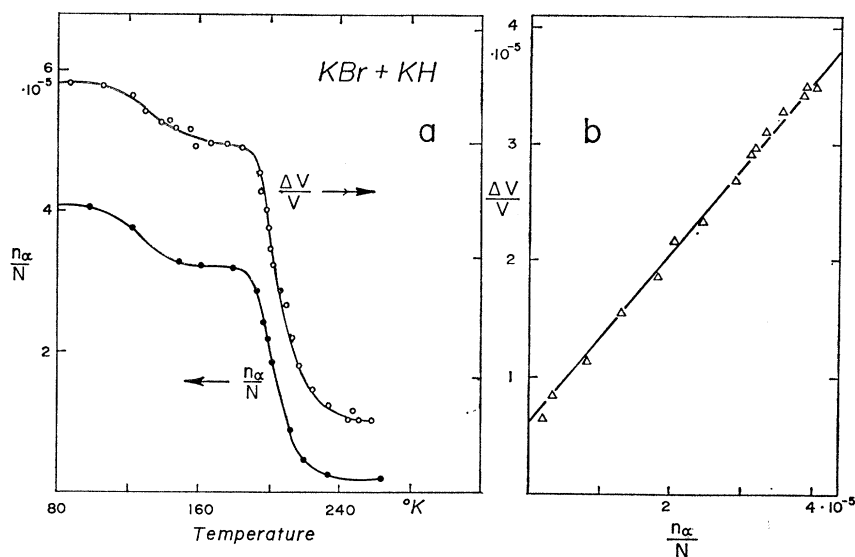


FIG. 7. (a) Thermal annealing of the α centers and volume expansion which were created by uv irradiation at LNT. (b) Plot of $\Delta V/V$ versus α -center concentration showing an accurate linear dependence. (Remaining $\Delta V/V$ for completely annealed α centers is contribution from F centers.)

U -center conversion. The irradiation-induced $\nabla V/V$ profile and its thermal annealing over temperature were measured; an example is given in Fig. 7(a). Because of the high optical densities involved, no detailed optical control of the formation and annealing behavior in the U - and α -band region was possible. Therefore, this control was performed in a parallel experiment with a thin sample of the same crystal, yielding the annealing behavior of the α band shown in Fig. 7(a). As can be seen the measured $\alpha \rightarrow U$ reaction is completely parallel to the $\Delta V/V$ annealing, yielding a straight line when the two quantities are plotted against each other [Fig. 7(b)]. The following conclusions follow directly from the results of Figs. 6 and 7: (i) No volume changes are connected with the annealing of the U_2 band, when the interstitial hydrogen atoms become mobile and form molecules. This was most clearly verified by observing the strain profile while holding the crystal near 100°K when only this annealing reaction occurs readily. From this we conclude that neither the interstitial hydrogen atom nor the molecule contributes appreciably to any $\Delta V/V$ effect. (ii) During annealing the F -center concentration remains constant (Fig. 6) and thus cannot contribute to changes in $\nabla V/V$. After complete α annealing the remaining strain profile (Fig. 7) should be attributed to these F centers. The volume expansion per F center $K_{u \rightarrow F}$ determined under this assumption from the remaining strain profile is in good agreement

with the value obtained in the room-temperature $U \rightarrow F$ conversion experiments. (iii) With the conclusions (i) and (ii) it is evident that only the $\alpha \rightarrow U$ conversion should cause volume changes during annealing. The measured proportionality between $\Delta V/V$ and n_α/N (Fig. 7) confirms this and allows the determination of the volume change per $\alpha \rightarrow U$ conversion.

The above procedure can be criticized because the changing temperature may affect physical parameters important for the strain measurements and because optical and dilatation experiments were not performed on the same sample. A different method was applied, therefore, as a check. Crystals of medium thickness (0.3 mm) were subjected to uv irradiation of different duration at LNT and their $\nabla V/V$ profiles as well as their α and F bands were measured. It follows from the above conclusions that the volume expansion is due to the $U \rightarrow F$ and $U \rightarrow \alpha$ conversion only:

$$\Delta V/V = K_{u \rightarrow F}(n_F/2N) + K_{u \rightarrow \alpha}(n_\alpha/2N). \quad (6)$$

Because of reabsorption of the uv light in U_1 , the α -to- F ratio varies strongly with irradiation time; several values of $\Delta V/V$ for various α/F ratios can be obtained, and thus $K_{u \rightarrow F}$ and $K_{u \rightarrow \alpha}$ can be determined from Eq. 6. This method, using constant temperature and simultaneous dilatations and optical measurements, eliminates the uncertainties of the thermal annealing method. As summarized in Table I, the results for

TABLE I. Summary of $K_{U \rightarrow F}$ and $K_{U \rightarrow \alpha}$ values together with methods and center transformations from which they were obtained. $\langle \rangle$ denotes interstitial.

Method	Temperature	Center transformation	$K_{U \rightarrow F}$	$K_{U \rightarrow \alpha}$
X-ray growth curve	RT	$U \rightarrow F + \langle H_2 \rangle$	1.26	
Thermal annealing	LNT \rightarrow RT	$\alpha + F + \langle H^- \rangle + \langle H^0 \rangle \rightarrow U + F + \langle H_2 \rangle$	1.10	1.44
Variable α/F ratio	LNT	$U \rightarrow \alpha + F + \langle H^- \rangle + \langle H^0 \rangle$	1.14	-1.50
			$\bar{K} = 1.17$	$\bar{K} = 1.47$

$K_{u \rightarrow F}$ and $K_{u \rightarrow \alpha}$ obtained from the different methods are in good agreement, showing a very satisfactory coherence in the experiments.

IV. DISCUSSION

The data obtained for the constant K listed in Table I constitute macroscopical phenomenological quantities characterizing volume changes for specific center transformations. Besides the main centers involved (U, α, F), interstitial hydrogen is formed, transformed, or destroyed in all reactions described. What is the contribution of this interstitial hydrogen to the volume changes as measured by K ?

The answer to this question seems to be rather certain for the case of the interstitial hydrogen molecule or atom. The radius of the cavity centered at a $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ interstitial site in the KBr lattice is about 1 Å (using the ionic radii of Tosi and Fumi).²³ This should be ample space for the small hydrogen atom (radius 0.78 Å) or hydrogen molecule. The absence of any measurable volume change during the combination of the interstitial hydrogen atoms (U_2 centers) into hydrogen molecules (Figs. 6 and 7) is a direct confirmation for this assumption. Thus our $K_{u \rightarrow F}$ value should directly be interpreted as the volume difference between a U center and an F center.

The situation is more uncertain for the $U \rightarrow \alpha$ conversion, where one H^- interstitial ion is formed together with each vacancy. Values for ionic radii of substitutional H^- vary considerably—between 1.0 and 2.0 Å—when determined from different substances and when different definitions of ionic radii are used. (For the substitutional H^- in KBr one obtains $r_{H^-} = 1.5$ Å using the ionic radii from Ref. 23) Size considerations about the H^- ion thus appear very unreliable, but they suggest some volume expansion from the H^- interstitial. As there is no way to separate from our measurements the contributions from the vacancy and the interstitial H^- ion, we must take the $K_{u \rightarrow \alpha}$ value as characteristic for the volume expansion of the whole Frenkel pair. The parallel variation of $\Delta V/V$ and the thermal annealing decay of the Frenkel pairs through all three annealing stages (Fig. 7) shows that the volume change for a closely associated and a disassociated Frenkel pair is apparently the same. More insight can be expected by a variation in the anticenter of the vacancy: Volume expansion experiments with x-ray induced α -center production in KBr:KCl²⁴ and pure KBr,²⁵ as well as optical $F \rightarrow F'$ conversion experiments, will be highly important to separate the volume expansion contributions from the vacancy and the interstitial. So far (with the assumption of a negligible H^- contribution) our $K_{u \rightarrow \alpha}$ value can only be regarded as

an upper limit for the volume difference between a U center and an anion vacancy.

We can connect our K values obtained from U -center reactions to values related to the pure KBr matrix, because the volume difference between the U center and the Br^- in KBr is known from lattice-parameter measurements²⁶:

$$3(\Delta a/a) = \Delta V/V = K_{Br^- \rightarrow u}(n/2N). \quad (7)$$

From the measurements of $\Delta a/a$ one obtains a value of $K_{Br^- \rightarrow u} = -0.36$. Thus our measured volume changes as related to a pure KBr matrix would be

$$K_{Br^- \rightarrow F} = K_{Br^- \rightarrow u} + K_{u \rightarrow F} = -0.36 + 1.17 = +0.8,$$

$$K_{Br^- \rightarrow \alpha} = K_{Br^- \rightarrow u} + K_{u \rightarrow \alpha} = -0.36 + 1.47 = +1.1.$$

A basic step now is the connection between the macroscopic quantities K and microscopic parameters, like the lattice relaxation around the defect. This connection can be achieved only with rather crude assumptions and simplifications. Following Merriam *et al.*,⁸ we apply Eshelby's continuum model²⁷ to the problem, assuming the validity of linear elasticity even in the badly strained regions around the dilatation center. The defect is visualized as a sphere of misfitting size (but unchanged elastic constant) substituted for the corresponding sphere of the perfect lattice. A statistically uniform distribution of n^* dilatation centers per unit volume in a crystal will give rise to an average strain $\bar{\epsilon}$ of the form

$$\bar{\epsilon} = 4\pi n^* C \frac{1-\sigma}{1+\sigma} \quad (\sigma = \text{Poisson's ratio}). \quad (8)$$

In this expression C is the strength of the dilatation center, which for a sphere of radius R and a relaxed misfit strain $\epsilon_d(\text{rel.})$ has the form

$$C = \epsilon_d(\text{rel.}) \frac{1+\sigma}{1-\sigma} R^3. \quad (9)$$

By forcing the misfitting sphere into the crystal matrix, an actual strain ϵ_d will result, which (for $\epsilon_d \ll 1$) should be one-half of the relaxed misfit strain $\epsilon_d(\text{rel.})$ due to the elastic constraint of the crystal. We chose the defect sphere to be formed by the octahedron of nearest-neighbor ions surrounding the substitutional defect, i.e., we take $R = r_0$ (r_0 = interionic distance). With n -dilatation defects in a crystal of N -ion pairs per unit volume, we thus obtain

$$3\bar{\epsilon} = \Delta V/V = 4\pi \epsilon_d(n/N), \quad (10)$$

where $\epsilon_d = \Delta r/r_0$ is now the fractional nearest-neighbor displacement at the defect in the crystal.

²³ F. Fumi and M. Tosi, J. Phys. Chem. Solids **25**, 31 (1964).
²⁴ V. Ritz and S. Mascarenhas, Bull. Am. Phys. Soc. **12**, 350 (1967).

²⁵ B. Royce, Bull. Am. Phys. Soc. **12**, 1062 (1967).

²⁶ R. Hilsch and R. W. Pohl, Trans. Faraday. Soc. **34**, 883 (1938).

²⁷ J. Eshelby, in *Solid State Physics*, edited by F. Seitz and S. Turnbull (Academic Press Inc., New York, 1956), Vol. 3.

TABLE II. Defect strength C and nearest-neighbor displacement $\Delta r/r_0$ for U , F , and α centers as obtained from experimental K values.

Defect	$K_{\text{Br}^- \rightarrow \text{Defect}}$	$C(\text{\AA}^3)$	$\Delta r/r_0$
U	-0.36	-0.57	-0.014
F	+0.8	+1.27	+0.032
α (upper limit)	+1.1	+1.74	+0.04

With this model we can express our experimental K values either as

(i) the defect strength

$$C = \frac{1}{12\pi} \frac{1+\sigma}{1-\sigma} r_0^3 K = 1.58K \text{ \AA}^3$$

or

(ii) the fractional nearest-neighbor displacement

$$\epsilon_d = \frac{\Delta r}{r_0} = \frac{1}{8\pi} K = 0.04K.$$

The values for C and ϵ_d obtained from the K values (related to the pure KBr matrix) are summarized in Table II.

In many theoretical treatments of the F center, attempts have been made to calculate the nearest-neighbor displacements at the defect. Among these calculations disagreement exists even about the sign of this displacement. Kojima,²⁸ Gourary and Adrian,²⁹ and Wood and Joy³⁰ predict inward displacements of the F -center neighbors for most alkali halides. Thommen³¹ in a recent calculation obtains for the F center in KBr a volume increase of $+0.35r_0^3$ which agrees in sign, and reasonably well in magnitude, with our experimental value of $0.8r_0^3$. Recent experiments by Balzer, Peisl, and Waidele¹² on additively colored KCl crystals determine a volume expansion of $+0.6r_0^3$ per F center, which is very close to our KBr value.

²⁸ T. Kojima, J. Phys. Soc. Japan **12**, 918 (1957).

²⁹ B. Gourary and F. Adrian, Phys. Rev. **105**, 1180 (1957).

³⁰ R. Wood and H. Joy, Phys. Rev. **136**, A451 (1964).

³¹ K. Thommen, Z. Physik **186**, 347 (1965).

Thus at least for the crystals KBr and KCl it is experimentally well established that F centers cause a net volume *increase* of about $(0.6-0.8)r_0^3$ per defect. This, under application of Eshelby's model, corresponds to an outward displacement of the nearest neighbors by 2-3%. These experimental values can now be used to test the validity of theoretical treatments of the F center in the future.

A microscopic interpretation is much more uncertain for the empty anion vacancy, where our value of $+1.1r_0^3$ constitutes only an upper limit for the volume expansion per anion vacancy. Even if the interstitial hydrogen ion would cause only negligible dilatation, the validity of Eshelby's model (which should be applicable only to mere elastic defects) is questionable for the anion vacancy. Electrostatic interaction between the charged vacancy and the surrounding ions should cause ionic polarization which has a different sign for the surrounding cations and anions. Thus the defect is not only surrounded by an elastic displacement field but also by a field of ionic-displacement dipoles, both together producing the observed net macroscopic volume increases of $1.1 r_0^3$ per vacancy. A thorough theoretical treatment of both elastic and electric effect would be needed to interpret this macroscopic value in terms of microscopic dilatations at the vacancy. Neglecting these complications, a simple application of Eshelby's model to our experimental K_α value would predict an outward displacement of the nearest neighbors of the vacancy by 4%. Tosi and Fumi³² calculate this value for NaCl as +1%, whereas Ferreira,³³ using the same calculation method, obtains +6% for KBr. The close agreement in sign and magnitude with the value obtained from our K_α with Eshelby's model has to be regarded as partly coincidental in view of the many simplifying assumptions made.

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³² M. Tosi and F. Fumi, Nuovo Cimento **7**, 95 (1958).

³³ G. Ferreira (unpublished).