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Characteristic Volume Expansion of Point Defects in KBr*

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The change in volume of crystals of KBr, x irradiated at low temperature, has been measured using a capacitive dilatometer. Simultaneous measurement of volume expansion and optical density permitted a determination of the relaxations around individual defect pairs. By assuming that the F-center Frenkel pair relaxation volume was constant between 78 and 5 K, and by using previously measured values for the α-center and F-center relaxations, the relaxations around the interstitial defect could be evaluated. It was found that at 78 K the F-center associated interstitial had a relaxation $(0.7\pm0.3)\frac{1}{2}a^3$. Over the temperature range 5–30 K, an apparent change in the relaxation due to the α-center Frenkel pair is observed. Optical bleaching of the F band between 5 and 20 K produced no change in the crystal volume. A possible reason for this is presented.

I. INTRODUCTION

It has been demonstrated by Peisl *et al.*[1] that x irradiation of KBr and other alkali halides at low temperature produces Fenkel defects in the negative-ion sublattice. Crowe *et al.*[2] have suggested that during room-temperature x irradiation of NaCl, Schottky defects are also generated, but this has not yet been substantiated by other workers. The introduction of Frenkel defects causes a crystal to undergo an increase in volume and to exhibit optical absorption bands which have been attributed to specific defect models.[3] Therefore, by measuring the optical absorption spectrum of an irradiated crystal, the number and type of Frenkel pairs generated by the irradiation may be obtained. By simultaneously measuring the change in volume of the same crystal, the volume change associated with an individual Frenkel pair can be determined.

Lüty *et al.*[4] have used a photoelastic technique to measure the volume expansion produced in crystals of KBr:KH by the introduction of Frenkel pairs of two kinds: those comprised of F centers and neutral hydrogen interstitials, and those consisting of α centers and negative hydrogen interstitials. Since the contribution to the volume expansion made by the hydrogen interstitials is believed to be small, an upper-limit estimate of the relaxations associated with the F center and the α center may be obtained. The use of these values in conjunction with measured relaxations for intrinsic Frenkel pairs in KBr enables one to estimate the relaxation associated with the interstitial halogen member of the pair. Ritz and Mascarenhas,[5] again using the photoelastic technique, have reported measurements on both pure KBr and mixed crystals of KBr:KCl. In pure KBr at 66 K they find that the volume expansion associated with the neutral bromine interstitial is essentially the same as that produced by a neutral hydrogen interstitial and that the interstitial accompanying the α center has a positive volume expansion associated with it.

This paper reports volume expansion measurements made on single crystals of KBr using a capacitive dilatometer. Data were obtained at 78 K and in the temperature range 5–30 K. Fixed temperatures between 5–30 K were chosen on the basis of the α-center annealing data of Itoh *et al.*,[6] and an apparent temperature dependence of the interstitial relaxation was observed. At 78 K, the interstitial center accompanying the F center was found to make a positive contribution to the volume expansion, in disagreement with the findings of Ritz and Mascarenhas. A similar positive expansion of an interstitial accompanying an F center at room temperature has been reported in pure KCl by Balzer *et al.*[7] These workers[8] also obtain a positive value for the relaxation around the H center in crystals of KBr irradiated at 6 K and annealed to 300 K.

II. EXPERIMENTAL TECHNIQUE

The x-ray-induced volume expansion of single crystals was obtained from a measure of the change in a linear dimension of the irradiated specimen at constant temperature. A capacitive dilatometer (Fig. 1) was developed that was small enough to fit into the nose section of a standard helium Dewar designed for optical absorption studies. The capacitive dilatometer has the advantage of working over a wide temperature range, being less subject to noise than an inductive dilatometer, and being a more direct method of volume expansion measurement than the photoelastic technique.

Single-crystal specimens of Harshaw KBr having a $2.5\times2.5\text{-cm}^2$ cross section and a thickness of 0.4 cm

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[1] H. Peisl, H. Splat, and W. Waidelich (unpublished).

[2] G. J. Crowe, W. Fuchs, and D. A. Weigand, Phys. Rev. Letters **16**, 1154 (1966).

[3] J. H. Shulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962).

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

[5] V. H. Ritz and S. Mascarenhas (unpublished).

[6] N. Itoh, B. S. H. Royce, and R. Smoluchowski, Phys. Rev. **137**, A1010 (1965).

[7] R. Balzer, H, Peisl, and W. Waidelich, in Proceedings of the Color Center Conference, Rome, 1968 (unpublished).

[8] H. Peisl (private communication).

were divided into three connected posts by string saw cuts. After polishing the top of the three posts to reduce surface irregularities to less than 4 μ from the mean surface, the top of the center post was coated with evaporated aluminum. This aluminum-coated face was used as the bottom plate of a parallel-plate capacitor. The outer posts were used to support the top plate of the capacitor, an 0.04-mm gap between this and the center post having been obtained by inserting 1-mm-diam Al rods into *V* grooves in the top electrode. Both the crystal and the electrode assembly were sprung against sapphire rods located in *V* grooves in the copper sample holder. A *V* groove and flat in the top electrode determined its position with respect to these sapphire rods. The top electrode was pushed against the crystal by a Teflon-insulated spring, which also served to hold the crystal in contact with the base plate of the copper sample holder. This semikinematic mounting produced a vacuum capacitor between the top electrode and the plated center post of the crystal that was stable against mechanical shocks and showed little drift with time. Typically, the drift corresponded to a length change of 2×10^{-8} cm in 12 h. Such a change in length would be produced by the introduction of about 10^{15} (*F* centers)/cm^3 into the crystal.

When assembled, the copper sample holder completely surrounded the sample except for two ports, which served as final collimators for the x rays and as windows for the optical absorption measurements. To maintain the continuity of the thermal shielding, these ports were covered with Corning No. 7940 fused-silica windows. Even after 100 h of x irradiation at various temperatures these windows were found to be uncolored. The alignment of the ports was such that the center post of the crystal could be irradiated from both sides over a predetermined length while the support posts were shielded from irradiation.

To exploit the inherent sensitivity of the dilatometer, it was necessary to obtain a temperature stability of about 1 mdeg during a capacitance measurement. Over the range 5–30 K, the temperature of the sample was measured and controlled by germanium resistance thermometers. A thermal resistance was incorporated between the dilatometer assembly and the cryogenic reservoir. The temperature of the sample was maintained at the desired value by a proportional controller that regulated the power supplied to a heater in the sample holder. Typical power dissipations were less than 100 mW. The capacitor assembly is shown in Fig. 1.

Throughout the volume expansion measurement, the Dewar containing the capacitance assembly was mounted in a Cary 14 MR spectrophotometer used to make the optical absorption measurements. The optical spectrum was recorded from 1700 to 190 nm after each measurement of the capacitance change. In order to measure accurately the absorption at 190 nm, the optics of the Cary were purged with dry nitrogen. Even with this purging, however, scattered light in the instrument prevented accurate measurements of optical densities greater than 1.5 below 195 nm, and greater than 2.5 below 210 nm. In some of the experiments, the α band at 200 nm grew beyond the range of the Cary, and measurements at 205 and 207 nm were extrapolated to obtain the peak height of the band. The optical density at these points was observed to be proportional to that at the band peak, and the proportionality constant was determined during each measurement.

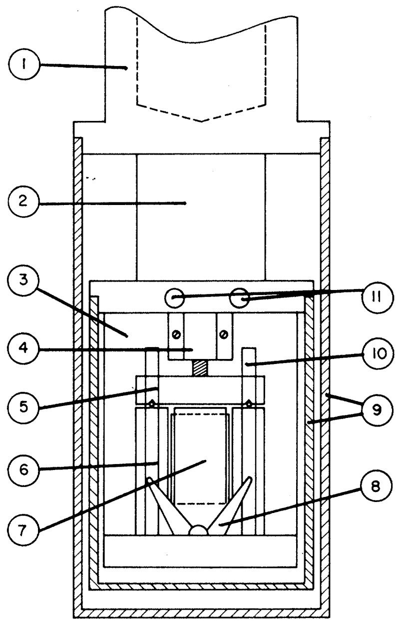
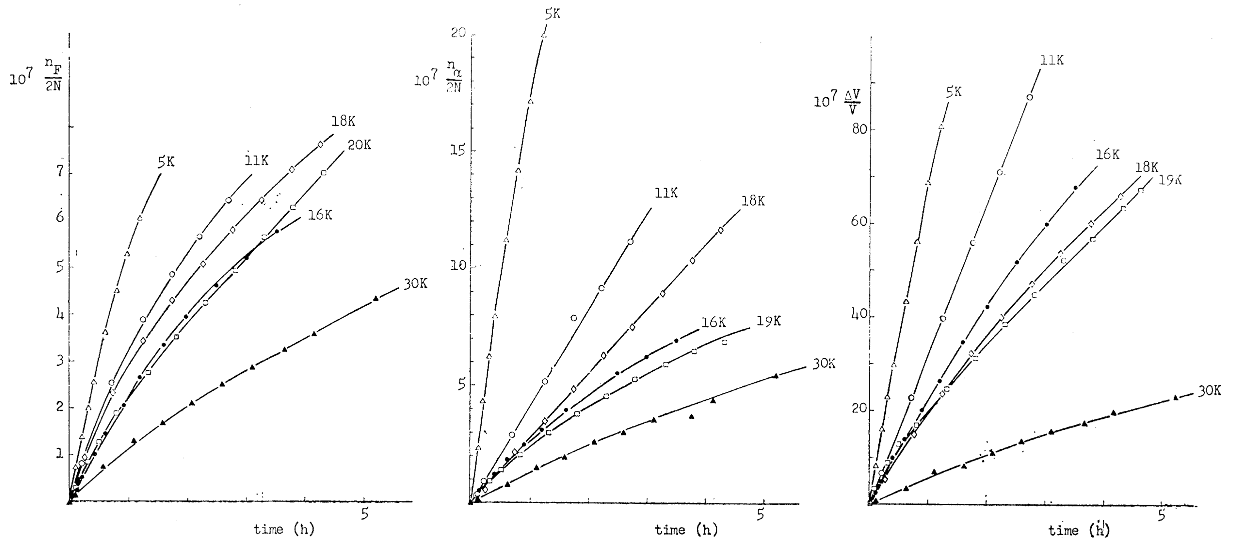


FIG. 1. Diagram of capacitive dilatometer: 1, copper tail section of helium Dewar; 2, stainless-steel thermal resistance; 3, copper sample holder; 4, insulated spring; 5, top plate of dilatometer; 6, support post of crystal specimen; 7, irradiated center post; 8, retaining spring; 9, thermal radiation shields; 10, sapphire rods; 11, germanium resistance thermomenters.

An x-ray tube that was mounted in the cell compartment of the spectrophotometer produced an x-ray beam perpendicular to the light beam of the Cary. In this way it was only necessary to rotate the Dewar in order to change from an x irradiation to an optical absorption measurement. The crystal was held at about 8 cm from the tungsten-tube target and was irradiated with 100-keV x rays at 15 mA filtered by 1.6 mm of Cu, 3.6 mm of Al, and 0.75 mm of fused silica. With this filtration, it was estimated that x irradiation from both sides produced a gradient of less than 5% in the amount of ionization per unit volume.

The capacitance was measured with a General Radio 1615A capacitance bridge. The bridge was driven at 10 kHz with 30-V rms across the capacitor plates. The out of balance signal from the null detector was used to monitor the capacitance throughout the run. Actual capacitance values, obtained at null, were recorded after each x-irradiation period. To convert the measured values of capacitance into relative length changes of the



F Center Growth

α Center Growth

Volume Expansion

FIG. 2. Growth curves for F and α centers and $\Delta V/V$.

irradiated column of the crystal, it was necessary to know the dimensions of this part of the sample. These dimensions were measured at room temperature using a Vickers metallographic microscope, and were corrected for the thermal expansion of KBr between room temperature and the temperature of the experiment.

III. EXPERIMENTAL RESULTS

The macroscopic relative volume expansion $\Delta V/V$ produced in a crystal by the introduction of n_i point defects of type i per unit volume may be written

$$\Delta V/V=\sum_i K_i(n_i/2N)\,, \tag{1}$$

where N is the number of ion pairs per unit volume and K_i is a relaxation constant for the ith type of point defect. Since the type of Frenkel pair that is most prominently produced by x irradiation is a function of the irradiation temperature, experiments made in different temperature ranges permit comparisons between the various pair contributions to the volume expansion.

A. 78 K Measurements

At 78 K, the F-center Frenkel pair is predominant. The F-center vacancy is accompanied by a neutral interstitial and this is normally stabilized in the lattice by forming a molecule of the Br_2^- type with one atom on a lattice site. The F' and α bands are also present in the optical absorption spectrum of the irradiated crystal. Both of these bands were saturated after approximately 2 h of x irradiation and, since the intrinsic α-center Frenkel pair is not stable above 25 K, they are probably both formed from bleached F centers and accompanied by the same type of interstitial as the F center.

In this temperature range, therefore,

$$\Delta V/V=(K_F+K_V)(n_F/2N)+(K_{F'}+K_\alpha+2K_V)(n_\alpha/2N)\,. \tag{2}$$

Since $n_\alpha/n_F\simeq 0.1$ at this temperature, $\Delta V/V$ is almost entirely due to the creation of the F-center (with V-center interstitial) Frenkel pair. $\Delta V/V$ was found to be a monotonically increasing function of time with a negative second derivative. It was linearly dependent upon n_F and, from the slope of these plots, a mean value[9]

$$K_F+K_V=1.5\pm0.1$$

was determined. Lüty *et al.*[4] obtained a value for $K_F=0.8\pm0.2$ from $U\rightarrow F$ conversion studies at room temperature, while Ritz[5] has found that K_F is temperature-independent between 300 and 66 K. Therefore, the above data can be compared, with the result that $K_V=0.7\pm0.3$.

B. Measurements between 5 and 30 K

In this temperature region the α-center Frenkel pairs play an important role in the volume expansion process. Between 5 and 20 K the intrinsic α-center Frenkel pair is formed, but above this temperature the interstitial must be stabilized, presumably by being trapped at impurities or other lattice defects. Over the complete temperature range, the F center is accompanied by an H-center interstitial. Therefore, the fractional volume expansion in this region can be written

$$\Delta V/V=(K_F+K_H)(n_F/2N)+(K_\alpha+K_I)(n_\alpha/2N)\,. \tag{3}$$

Figure 2 shows the dependence of the growth of α and F

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

centers upon the irradiation temperature together with the measured volume expansion at each of these temperatures.

In order to obtain a value for $K_\alpha + K_I$ from these measurements, it is necessary to know the value of $K_F + K_H$. Since an independent measurement of this parameter was not possible, it was assumed to be temperature-independent between 5 and 30 K and to have the same value as $K_F + K_V$ measured at 78 K. The value of $K_\alpha + K_I$ was then determined as a function of temperature. It was assumed that the relaxation associated with the α center was also independent of temperature in the 5–30-K range, and that the value $K_\alpha = 1.1 \pm 0.1$ obtained by Lüty *et al.*[4] from $U \rightarrow \alpha$ conversion was applicable. The values of K_I obtained in this way are summarized in Table I and are seen to be dependent upon the temperature of irradiation.

C. Optical Bleaching

Crystals irradiated at 5, 11, and 19 K were optically bleached for periods up to 1 h after the cessation of irradiation. At 5 K, 1 h of bleaching with 600-nm light from a Bausch and Lomb grating monochromator reduced the F, K, and H bands by $(57 \pm 2)\%$, while the α and I bands remained constant to within 1%. During this bleach, $\Delta V/V$ decreased by only 0.8%. Similar effects were observed at 11 K, the F, "H," and K bands decreasing by 44%, while the α and I bands remained constant and $\Delta V/V$ decreased by 1%. A crystal irradiated at 19 K was bleached for 5 min with white light from a fluorescent lamp, resulting in a decrease of 85% in the F and H band, as well as in the K band. At this temperature, no change in $\Delta V/V$ or in the concentration of the α and I centers could be detected. Because of the high optical densities obtained at the end of these runs, the peak of the α band was not accessible to the Cary spectrophotometer, and the optical density change was estimated from measurements on the side of the band at 205 and 207 nm and from the I bands. Any change in the number of α centers represented by a change in asymmetry of the band (such as an increase in the high-energy side of the band) would not be measured during the bleaching. Since a change in $\Delta V/V$ of about 10^{-8} could be detected, any change in $\Delta V/V$ induced by the bleaching of more than 0.05% could be measured accurately. Table II summarizes this data.

IV. DISCUSSION

At 78 K the present data, along with the data of Lüty *et al.*, indicate that the volume expansion associated with the F-center Frenkel pair is divided approximately equally between the constituents of the pair. This result is in direct contrast to that of Ritz and Mascarenhas,[5] who find that no measurable volume expansion can be attributed to the neutral bromine interstitial. At the present time there are the only two measurements that have been made on KBr in this temperature region. However, recent measurements by Balzer *et al.*[7] on samples irradiated at 6 K and annealed to 300 K give a volume relaxation for the H center in agreement with the present data. Farnum and Royce[9] have also made measurements on KCl at 78 K, and find a relaxation for the F-center Frenkel pair which agrees with that for KBr within experimental error. Room-temperature measurements of Balzer *et al.*[7] on additively colored KCl and KBr have shown that the F-center relaxations are the same in these two materials at room temperature with $K_F \simeq 0.6$. In x-irradiated KCl these workers[10] find that the room-temperature expansion associated with the Frenkel pair is twice as large as the F-center expansion, indicating that, at this temperature, interstitials have a positive, rather than zero, volume expansion associated with them. Similar results have been obtained by Bleckman and Thommen.[11]

TABLE I. Volume expansion data.[a]

Temp. (K)	$(\Delta V/V)/(n_F/2N)$	n_α/n_F	K_F+K_H	$K_\alpha+K_I$	K_I	Final n_F (cm^{-3})
5	12.1 ± 0.8	3.2 ± 0.05	1.5	3.3 ± 0.3 (0.3)	2.2	5×10^{16}
11–20	9.4 ± 1.0	1.2 ± 0.1	1.5	6.6 ± 1.0 (7.2)	5.5 (6.1)	$2 + 10^{16}$
30	5.1 ± 0.8	1.2 ± 0.05	1.5	3.0 ± 0.5 (3.0)	1.9 (1.9)	1.4×10^{16}

[a] Numbers in parentheses are calculated assuming a distribution of defects that is temperature-dependent. Those without parentheses are calculated directly from the experimental data.

Although the detailed form of the interstitial accompanying the F center is likely to change between room temperature and 78 K, it is highly probable that the neutral interstitial in KCl forms part of a Cl_2^- complex at both of these temperatures. If this is so, and if a positive volume expansion is associated with the interstitial at room temperature, it would be expected that a similar positive expansion should occur at 78 K, as the present KCl measurements show. Since at 78 K, KBr shows a volume expansion per F-center Frenkel pair very similar to that of KCl, and since the relaxations associated with the F center at room temperature in those two materials are the same within experimental error, these data strongly suggest that the Br_2^- inter-

TABLE II. Optical bleaching results.

Quantity	5 K	11 K	19 K
dF	−55%	−42%	−84%
d"H"	−58%	−46%	−85%
dI	0	+2%	0
$d\alpha$	0	0	0
$d(\Delta V/V)$	−0.8%	−1.0%	0
n_F (cm^{-3})	3.5×10^{16}	3.52×10^{16}	2×10^{16}
$\Delta V/V$	2.74×10^{-5}	1.89×10^{-5}	0.516×10^{-5}

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

[11] A. Bleckman and K. Thommen, Z. Physik **191**, 160 (1966).

stitial at liquid-nitrogen temperatures induces a positive volume expansion.

In order to compare the macroscopic experimental parameters K_i with theoretical calculations of the relaxation around specific point-defect configurations, it is necessary to find a formal connection between them. This type of problem has been treated by Eshelby,[12] who uses a continuum model. In this model the point defect is introduced into an elastic sphere of radius R and of the same elastic constant as the matrix. In an isotropic medium, a statistically uniform distribution of such defects will give rise to an isotropic macroscopically observable volume change of the specimen. Eshelby defines a "defect strength" C in terms of the radius of the sphere R, its relaxed strain ϵ, and Poisson's ratio σ for the material, such that $C=\epsilon\frac{1}{3}R^3(1+\sigma)/(1-\sigma)$. If the radius of this sphere is assumed to be equal to the distance from the substitutional defect to the nearest-neighbor ions, then both C and $\Delta V/V_0$ may be related to K_i as follows:

$$C=(V_0^3/12\pi)(1+\sigma)/(1-\sigma)\simeq 1.58K_i$$

and

$$\epsilon_d=\Delta V/V_0=K_i/8\pi\simeq 0.04K_i \text{ for KBr.}$$

No calculations have yet been performed on ionic relaxations around a Br_2^--type defect in KBr. However, Dienes *et al.*[13] have made such calculations for the $\langle 110\rangle$- and $\langle 111\rangle$-oriented Cl_2^- molecule in KCl. If the average ionic displacements in the nearest-neighbor shell, as computed by these authors, are used to determine $\Delta V/V_0$ in the above expression, the relaxations $K_{(110)}\simeq 1.1$ and $K_{(111)}=0.7$ are obtained for these two orientations of the Cl_2^- interstitial complex. The values for both orientations indicate a volume expansion from this type of molecular defect of the same order as that associated with an F-center vacancy, in agreement with the present experiment.

A. 5–30 K

The data presented above indicate that between 5–30 K the volume expansion per Frenkel pair is temperature-dependent. Since the irradiation temperatures were chosen to correspond to the high-temperature limits of the annealing stages of α-center Frenkel pairs, as reported by Itoh *et al.*,[6] the various growth temperatures should have produced pairs having different vacancy interstitial separations. For a 6 K irradiation temperature, the annealing data indicate that 40–50% of the α centers form close pairs that anneal by 13 K, that an additional 40% of the pairs anneal by 22 K, and that the final 10% are stable until above 80 K. For a crystal irradiated at 16 K, however, approximately 85% of the α centers anneal in an initial stage that is complete by 22 K, with the remaining 15% of the centers being stable to temperatures greater than 80 K. In interpreting the volume expansion data made in this temperature range, it is necessary to consider this changing spectrum of pair separations. If the temperature range is divided into three regions T_1 (6–12 K), T_2 (12–20 K), and T_3 (20–30 K), the values K_1, K_2, and K_3 of the α center Frenkel pairs in these three temperature regions can be determined from the ratios of the three pairs generated and the relaxations measured in each of the three temperature ranges. For crystals irradiated at 30 K, only centers of type K_3 will be formed and the measured relaxation per α-center Frenkel pair will determine K_3. The result is $K_3=3.0\pm 0.5$. Between 12 and 20 K, both K_2- and K_3-type pairs are present and, from the annealing data, approximately 85% of these are of the K_2 type. From the measured volume relaxation and this distribution of pair types, it may be determined that $K_2=7.2\pm 1.0$. For an irradiation at 6 K, all three types of pairs are present, with approximately 50% of K_1, 40% of K_2, and 10% of K_3. Using this distribution, the value of K_1 can be determined as 0.3 ± 0.5. The above data are summarized in Table I (numbers in parentheses).

In principle, it is possible to separate the volume expansion contributions due to the vacancy and the interstitial by assuming that the value of $K_\alpha=1.1$ obtained by Lüty *et al.*[4] applies over the complete temperature range. With this assumption, the interstitial formed between 6 and 12 K would have a negative volume expansion. This is unreasonable and suggests that because of the proximity of the two components of the pair their individual elastic and polarization contributions to the volume expansion are not simply additive, but partly cancel each other. Between 13 and 20 K the interstitial has a relaxation $K_I=6.1\pm 1.0$ (for $K_\alpha=1.1$), and at 30 K, $K_I=1.9\pm 0.5$. By 30 K, however, the interstitial ion is trapped by some other lattice defect, which could reduce the total contribution to the volume expansion in a way similar to the effect of the α center on the interstitial at 6 K. It would seem, therefore, that the intermediate temperature value for K_I ($K_I=6.1$) gives the best estimate of the relaxation due to a free negative-ion interstitial. It is important to note that while the value of K_3 is determined directly, the value of K_2 depends on K_3 and the relative number of 3-type centers. At 16 K this number is only 15%, and the effect of these centers on K_2 is small. However, at 6 K, the number of K_2-type centers is a large fraction of the total centers produced, and because K_2 is large, the value of K_1 obtained will be strongly influenced by the relative number of K_2-type defects. Since the numbers used for the relative defect concentrations at 6 K in this calculation are only approximate values, the value of K_1 cannot be considered a very accurate description of the relaxation around an α-interstitial pair at this temperature. It does,

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[12] J. D. Eshelby, in *Solid State Physics*, edited by F. Seitz and and D. Turnbull (Academic Press Inc., New York, 1956), 3rd ed., p. 79.

[13] G. J. Dienes, R. D. Hatcher, R. Smoluchowski, and W. D. Wilson (unpublished).

nevertheless, indicate a suppression of the full relaxation attributable to the free interstitial. Recent data obtained by Balzer *et al.*[7] on the volume expansion of KBr irradiated at 6 K are in agreement with the 6 K results above.

B. Optical Bleaching

When crystals colored by x irradiation at temperatures between 5 and 20 K were optically bleached, no change in the crystal volume accompanied the observed decrease in the number of F-center Frenkel pairs. The spectrophotometric measurements showed that the F-band absorption could be reduced 40–80%, with a corresponding decrease in the optical absorption in the H-band region of the spectrum. During the bleach, no change in the region associated with the negative-ion interstitial (I band) was observed, and this would seem to rule out a simple charge transfer process between the F and the H centers in which α centers and negative-ion interstitials were produced. This conclusion is in agreement with the previous observations of Itoh and Royce,[14] who as a result of thermal and optical bleaching experiments, suggested, that free negative-ion interstitials could not be created by F-light bleaching at low temperatures. In the present experiments the specimen thicknesses were such that direct measurements of the α-band absorption were not possible. Measurements in the long-wavelength wing of the band indicated that the changes in this region were less than 2% of the prebleaching value; however, from the magnitude of the F-center bleach it would be expected that the α band should increase by ~15%. As has been shown by Srinivasan and Compton,[15] the H- and V_K-center absorption bands have considerable overlap in KBr at 7 K, with the V_K center having the lower oscillator strength. The relative concentration of V_K to H centers was found to decrease with increasing irradiation time. Thus in the present experiments, where the F-center densities are low, V_K centers are expected to be relatively more important than H centers. During bleaching with F light, Srinivasan and Compton found that, in pure crystals, more V_K centers were bleached than were H centers. The absence of photoconductivity indicated that a tunneling process was taking place, and the results of subsequent x irradiation and bleaching experiments indicated that similar close pairs of F and V_K or H centers were formed upon re-x-irradiation. For low-temperature x irradiations, therefore, three groups of complementary centers are expected[14] to be present: $(\alpha+I)$, $(F+H)$, and $(F+V_K+I')$, where I' is used to indicate an interstitial negative ion trapped by some lattice defect, as is the interstitial accompanying the high-temperature α center. On the basis of this picture, the effect of the optical bleaching was to convert F centers into α centers, and to annihilate V_K centers through electron-hole recombination. If is is assumed that no other change in the point defects takes place, this model indicates that a volume expansion is to be associated with the V_K center that just compensates for the difference between the volume expansion of an α center and F center. Thus $K_{V_K}\simeq 0.4$. This is approximately half the value of the relaxation attributed to H centers.

If the above interpretation of the bleaching data is correct, then a similar assignment of complementary centers must be used to explain the volume expansion produced by the x irradiation. It is necessary to know the fraction of F centers accompanied by V_K centers at each of the growth temperatures, and to know the relaxation associated with the trapped negative-ion interstitial. It will be assumed, as a first approximation, that the number of F centers having V_K centers and trapped interstitials as their complementary centers is given by the number that were bleached at any given temperature. The volume expansion of the trapped interstitial will be taken to be the same as that of the interstitial accompany the α center at 30 K. Using these assumptions, the interstitial negative ion has an uncorrected K value of 1.2±0.5 at 30 K, 5.0±1 between 11 and 20 K, and 2.2±0.5 at 5 K. These values are within the estimated errors for the values given in Table I. This model is obviously an oversimplification of the physical situation, but the present data do not provide for a more detailed analysis.

It is of interest to note that Martel[16] has studied the effects of optical bleaching on the x-ray-induced volume expansion of KCl at 22 K. In these measurements also, no volume change was detected when the samples were bleached.

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[14] N. Itoh and B. S. H. Royce, J. Phys. Chem. Solids **27**, 1366 (1966).

[15] T. M. Srinivasan and W. D. Compton, Phys. Rev. **137**, A268 (1965).

[16] C. P. Martel, Ph.D. thesis, University of Toronto, 1965 (unpublished).