PHYSICAL REVIEW VOLUME 137, NUMBER 3A 1 FEBRUARY 1965

# Recombination of Vacancies and Interstitials in KBr at Low Temperatures*

N. Itoh,† B. S. H. Royce, and R. Smoluchowski
*Solid State and Materials Program, Princeton University, Princeton, New Jersey*

(Received 9 June 1964; revised manuscript received 25 September 1964)

Measurements and a detailed analysis were made of the thermal annealing of the α band in KBr x rayed at temperatures below 20°K. Four distinct annealing stages at 11, 17, 19, and 21°K were resolved, the first three stages corresponding to first order reactions and the fourth stage to a second order reaction. The activation energies for the annealing stages were about 0.015, 0.03, 0.04, and 0.06 eV, respectively. The first three stages were interpreted as a correlated recombination of close pairs of bromide vacancies and interstitials, and the fourth stage as the recombination of more distant defect pairs through a free migration of an interstitialcy. The activation energy 0.06 eV is interpreted as the free migration energy of a bromide-ion interstitialcy. Interaction energies between a vacancy and an interstitial ion in several configurations were calculated and possible annealing sequences for the first three annealing stages are proposed. The observed low pre-exponential factor for the first stage is also discussed.

## I. INTRODUCTION

The formation of lattice defects in alkali halides by ionizing radiation has been discussed for several decades.[1] Among the several mechanisms proposed,[2–5] those which consider the formation of Frenkel pairs appear to be more probable, especially at low temperatures where the defect formation appears to be less structure sensitive[6] than at higher temperatures. Most of the lattice defects formed by ionizing radiation at low temperatures are expected to remain stable, the easiest to observe among them being the *F* and the much more numerous[7,8] α centers. It has been further established[9] that an *F* center and an *H* center constitute a neutral Frenkel pair. In contrast, the complementary center to an α center, which should be an interstitial halogen ion, is less understood, the very existence of alpha centers implying however that the displaced ion is not too far away since otherwise all isolated halogen vacancies would become *F* centers.[10,11]

It is known that α centers are also formed by the photolysis of *U* centers.[12] Studies of ultraviolet absorption, infrared absorption and ESR,[13,14] have established that there the complementary centers to the α centers are hydrogen interstitial ions. The two techniques of forming α centers, however, produce different effects on thermal resistivity[15]: a small increase in the low-temperature thermal resistivity in the uv-irradiated alkali halides containing *U* centers and a large increase in x-rayed alkali halides. Furthermore, in the latter case, the increase in thermal resistance anneals together with the α band. This fact suggests the existence of a complementary defect to α center with large lattice relaxation, most probably an interstitial halide ion.

The annealing of α centers and hydrogen interstitials has been studied by Fritz,[14] who observed several annealing stages between 100 and 200°K. The lower temperature annealing stages were attributed to the annihilation of close pairs, and the highest temperature annealing stage to that of distant pairs. In x-irradiated crystals, several stages have been observed[8,15] both in the annealing of α centers and annealing of thermal conductivity in the temperature range between 10 and 100°K, although no detailed analysis has been made. It is of great interest to establish which annealing stage actually corresponds to the migration of interstitials. A theoretical calculation[16] has shown that the activation energy for an intersititialcy mechanism for the migration of a negative ion is small and might correspond to the low-temperature annealing.

The purpose of this paper is to present the detailed analysis of the annealing experiments on α centers formed by x rays below 20°K. The results are interpreted to be an annihilation of both close and distant Frenkel pairs through an interstitialcy migration process. Possible configurations of Frenkel pairs are discussed.

## II. EXPERIMENTAL TECHNIQUES

The specimens used in the present work were cleaved from a single block of Harshaw KBr. They were

---

* Supported in part by U. S. Atomic Energy Commission and National Science Foundation contracts.

† On leave from Faculty of Engineering, Osaka University, Osaka, Japan.

[1] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962), Chap. 7.

[2] F. Seitz, Rev. Mod. Phys. **26**, 7 (1954).

[3] J. H. O. Varley, Nature **174**, 886 (1954) and Phys. Chem. Solids **23**, 985 (1962).

[4] C. C. Klick, Phys. Rev. **120**, 760 (1960); see also Ref. 1.

[5] R. E. Howard, D. Vosko, and R. Smoluchowski, Phys. Rev. **122**, 178 (1962).

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

[7] F. Lüty, Z. Physik **145**, 249 (1956); see also C. C. Klick and D. A. Patterson, Phys. Rev. **130**, 2169 (1963).

[8] H. Rüchardt, Z. Physik **140**, 574 (1955); Phys. Rev. **103**, 873 (1956).

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

[10] F. Lüty, Zeit. Physik **153**, 247 (1958); *Halbleiterprobleme* (F. Vieweg and Son, Braunschweig, 1960), Vol. 6, p. 276.

[11] R. N. Euwema and R. Smoluchowski, Phys. Rev. **133**, A1724 (1964).

[12] W. Matienssen, Z. Physik **131**, 488 (1952).

[13] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **104**, 599 (1956); and C. J. Delbecq and P. H. Yuster, Phys. Rev. **104**, 605 (1956).

[14] B. Fritz, Phys. Chem. Solids **23**, 375 (1962).

[15] W. Gebhardt, Phys. Chem. Solids **23**, 1123 (1962).

[16] K. Tharmalingam, Phys. Chem. Solids **25**, 255 (1964).

mounted in a liquid-helium cryostat equipped with a pair of quartz windows and a pair of aluminum windows. The windows were rotatable so that the x-ray irradiation and optical absorption measurements were made from the same direction. The specimens were irradiated by 100-kV 10-mA x rays from a tungsten target constant potential tube having an inherent filtration of 3 mm of Al. An additional 1.5-mm KBr filter assured a fairly uniform coloration.

Optical measurements were made using a Cary 14R spectrophotometer. Typical alpha center concentrations were about $10^{17}$ cm$^{-3}$, assuming an oscillator strength[17] of 0.9 and a half-width of 0.2 eV. It should be noted that the spectrophotometer is a double-beam monochromator with a chopped light, and that the output signal is amplified by tuned ac amplifier; it is therefore insensitive to the steady thermoluminescent light emitted from the specimen during annealing experiments.

Temperature measurements were made using an Allen-Bradley carbon resistor calibrated at fixed temperatures and embedded in the copper block which surrounded the specimens. For the isothermal studies an electrical heater was used to maintain the copper block at higher temperatures than the liquid refrigerant contained in the Dewar. For the isochronal studies, the absorption coefficient at the alpha-band maximum was measured during warm up at about 0.6° K/min. As the change of the half-width of alpha band between 6 and 21°K is less than 3%, this technique for obtaining relative concentration changes is adequate.

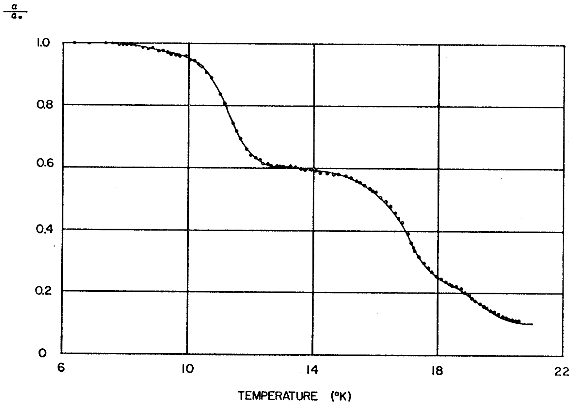


FIG. 1. Isochronal annealing curve of $\alpha$ centers in KBr x rayed at 6°K. The initial concentration of $\alpha$ centers was nearly $3.0\times10^{16}$ cm$^{-3}$.

## III. EXPERIMENTAL RESULTS

Figure 1 shows the results of a typical isochronal annealing of the alpha band formed by x rays at 6°K. The structure in the annealing curve is more clearly exhibited in Fig. 2 which is obtained from the curve in Fig. 1 by numerical differentiation with respect to temperature. Three distinct annealing stages at 11, 17, and 19°K are resolved. Detailed measurements around 20°K were made on more heavily colored specimens and also on specimens irradiated at 17°K. Figure 3 shows the results for these experiments; a fourth stage at 21°K is clearly resolved.

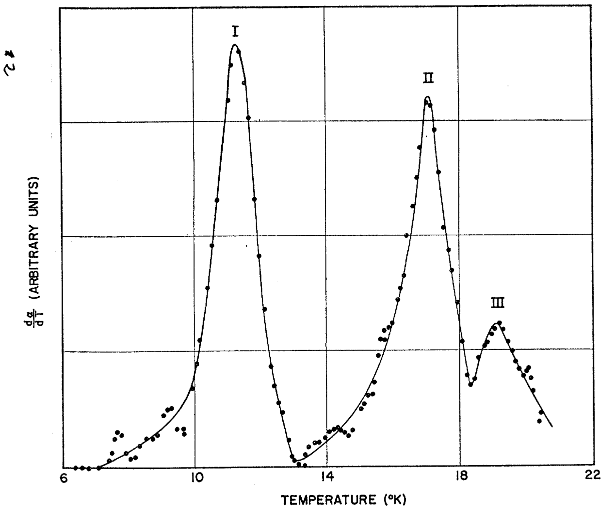


FIG. 2. Slope of the isochronal annealing curve shown in Fig. 1 obtained by numerical differentiation.

An analysis of the annealing curves was undertaken assuming a simple rate equation[18]

$$-dn/dt=n^xK\exp(-E/kT)\,, \qquad (1)$$

where $n$ is the concentration of alpha centers belonging

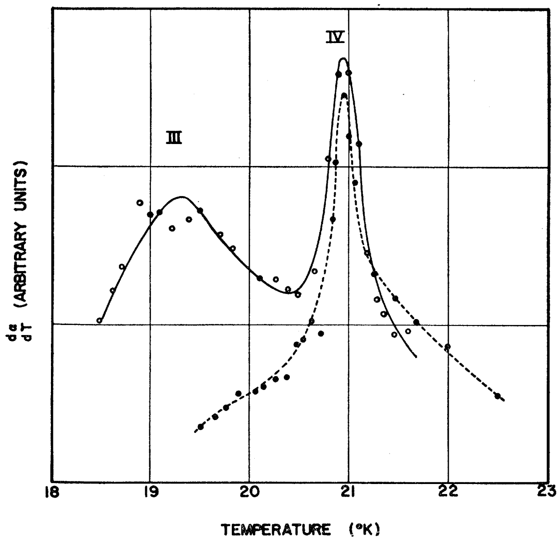
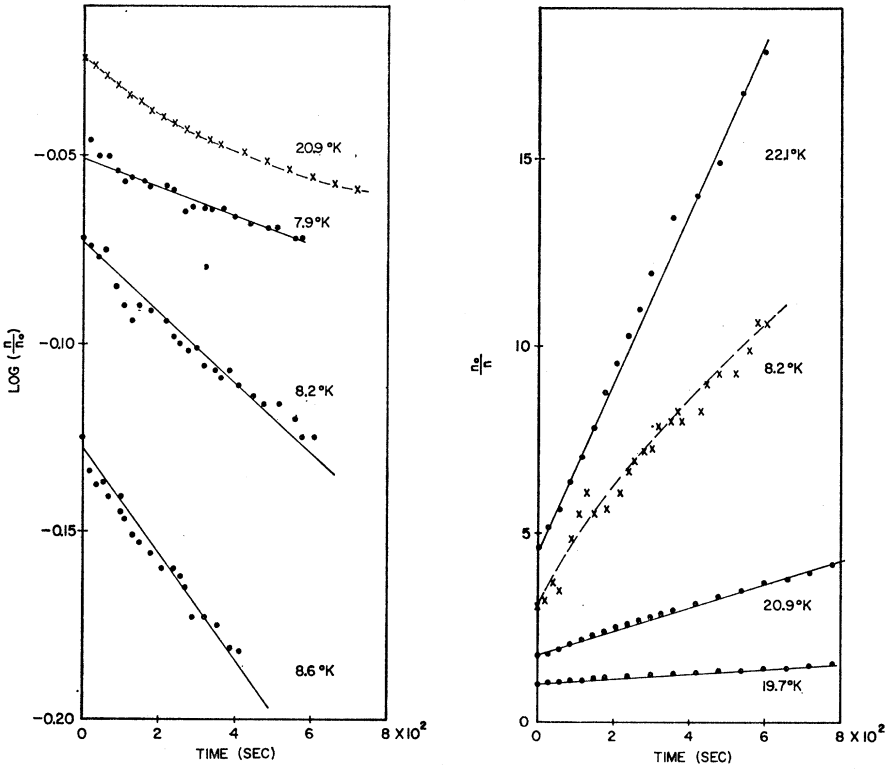


FIG. 3. Detailed annealing spectra of $\alpha$ centers around 20°K: *Solid line*, x rayed at 6°K (initial concentration about $1.0\times10^{17}$ cm$^{-3}$), *dotted line*, x rayed at 17°K (initial concentration about $1.2\times10^{17}$ cm$^{-3}$).

---

[17] R. Onaka and I. Fujita, J. Quant. Spectr. Radiative Transfer **2**, 599 (1962).

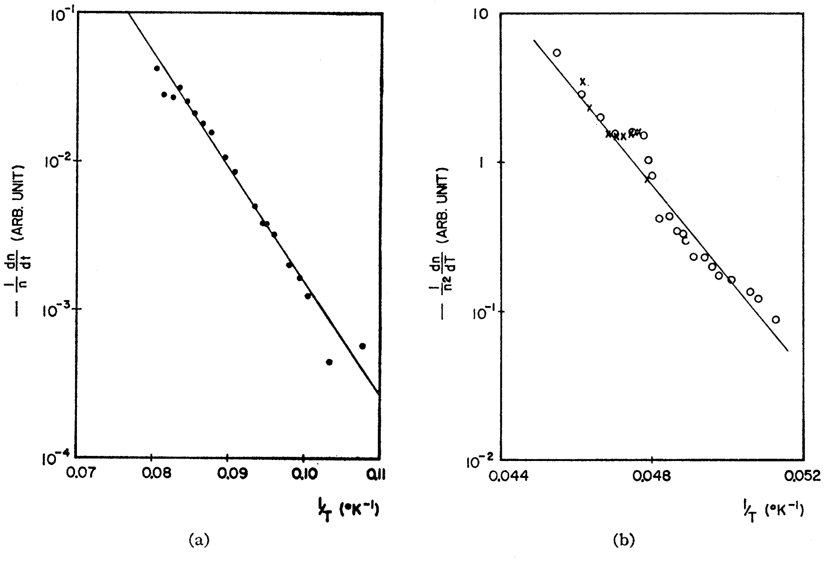
[18] A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach, New York, 1964), Chap. 2.



(a) (b)

FIG. 4. Isothermal annealing curves for stages I and IV. (a) Plot of $\log(n/n_0)$ versus $t$; (b) plot of $n_0/n$ versus $t$.

to each stage, $x$ the order of reaction, $E$ the activation energy, and $K$ the frequency factor. In order to determine $x$, isothermal annealing experiments were done for each annealing stage. Figure 4(a) shows plots of $\log(n/n_0)$ versus time while Fig. 4(b) shows plots of $n_0/n$ versus time, where $n$ and $n_0$ are concentrations of $\alpha$ centers for each annealing stage at a given time and at the beginning of annealing at each temperature. Straight lines correspond to stage I in Fig. 4(a) and to stage IV in Fig. 4(b), showing that the former is a first-order reaction and the latter a second-order reaction. The order of reaction was also determined using the results of isochronal annealing experiments, in which a plot of $(1/n^x)(dn/dt)$ versus $1/T$ should give a straight line if the value of $x$ is properly chosen. In Figs. 5(a) and 5(b), such plots for stages I and IV are shown. Similar



(a) (b)

FIG. 5. Isochronal annealing curves for stages I and IV: (a) plot of $(1/n)(dn/dT)$ versus $1/T$; (b) plot of $(1/n^2)(dn/dT)$ versus $1/T$.

analyses were also made for stages II and III leading to the conclusion that stages I, II, and III correspond to first-order reactions and stage IV to a second-order reaction.

The activation energies were obtained from the isochronal annealing experiments by two methods: firstly, from the slope of the straight line drawn to fit the plots of $\log(-n^{-x}dn/dt)$ versus $1/T$ as shown in Figs. 5(a) and 5(b), and secondly from the least square fit of the isochronal annealing curves to the integrated form of Eq. (1). The least-squares fit was obtained with respect to the two variables $K$ and $E$, using Gauss's method. An example of such a fitting for stage I is shown in Fig. 6. There is some ambiguity in this method when there is a large overlap of annealing stages because it is necessary to assume an appropriate value for $n_0$. The results of these studies are shown in Table I, the agreement between the values obtained by the two methods being very good for stages I and II.

## IV. DISCUSSION

The order of the reaction kinetics of each stage indicates that it is reasonable to assume that stages I, II, and III correspond to correlated annihilations of close pairs, and that stage IV corresponds to non-correlated, i.e., random-walk annihilation of more distant pairs. The activation energy 0.06 eV for stage IV is so low that it excludes the motion of negative ion vacancies.[19] The activation energy for motion of an interstitial halogen ion has been theoretically estimated by Tharmalingam[16] as 2.21 and 1.89 eV for a normal interstitial motion of a negative ion, and as 0.19 and 0.44 eV for the motion of a negative ion interstitialcy in KBr and KCl, respectively. Schatterly and Compton[20] suggested on the basis of their experiments the value 0.07 eV for the interstitial motion in KCl without specifying, however, the mechanism.

It thus seems reasonable, in view of the theoretical uncertainties, to identify the stage IV with the random motion of an interstitial ion by an interstitialcy mechanism. The frequency factor for this stage given in Table I is the value of $(Kn_0)$, where $n_0$ is the initial concentration of interstitials. As this value is approximately equal to the frequency factor for jumping divided by the number of jumps for annihilation, the result is not unreasonable.

It is of interest to note that the band at 230 mμ observed by Markham *et al.*[21] and Klick *et al.*[7] bleaches in the same manner as these four annealing stages of the α band. No 230-mμ band was produced by irradiation at higher temperatures than 21°K. The ratio of the height of the 230-mμ band to that of the α band is approximately maintained during irradiation below 17°K. In view of the results of the annealing experiments, the interpretation that the 230-mμ band is related to interstitial bromine ions appears to be probable.

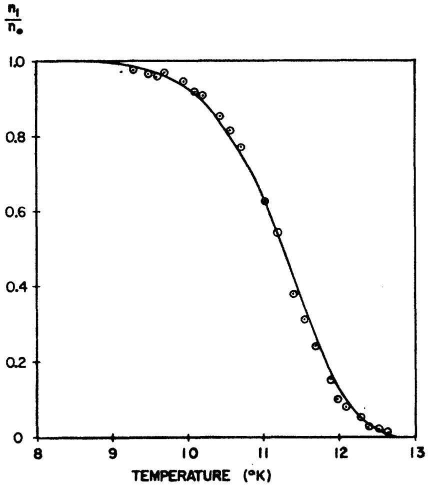


FIG. 6. Least-square fit of a first-order reaction equation to stage I isochronal annealing curve.

As far as the earlier stages are concerned, it should be borne in mind that certain close vacancy-interstitial pairs may be inherently unstable during irradiation and will not be observable. On the other hand, the sharp and well resolved peaks in the annealing spectrum, Figs. 2 and 3, indicate that the corresponding defects are distinct close pairs; otherwise the peaks would be broad or merge into a wide band. On this basis, a simple model in which specific lattice sites are considered can be proposed and the corresponding activation energies estimated (see Appendix): Let $E_i$ be the total attraction between the vacancy and the interstitial ion in its initial unrelaxed state, $E_s$ the total attraction between the vacancy and the interstitialcy pair-configuration in the unrelaxed saddle point, $E_{di}$ the correction to the above interaction due to relaxation of ions surrounding an interstitial ion, $E_{ds}$ a similar correction for the saddle configuration, and finally, $E_{ri}$ and $E_{rs}$ the repulsive interactions between the two point defects

TABLE I. Results of analysis of isochronal annealing experiments.

| Stages | $x$ | Method | $K$ (sec$^{-1}$) | $E$ (eV) |
|---|---|---|---|---|
| I | 1 | a | $5\times10^4$ | 0.015 |
| | | b | $1\times10^4$ | 0.014 |
| II | 1 | a | $3\times10^7$ | 0.032 |
| | | a | $3\times10^6$ | 0.029 |
| | | b | $1\times10^6$ | 0.027 |
| III | 1 | a | $2\times10^{11}$ | 0.053 |
| | | a | $6\times10^{11}$ | 0.054 |
| | | b | $2\times10^8$ | 0.040 |
| IV | 2 | a | $2\times10^{13}$ | 0.070 |
| | | b | $1\times10^{10}$ | 0.061 |

[a] Least-square fit to the integrated form of Eq. (1).
[b] Slope of $(1/n^x)(dn/dt)$ versus $(1/T)$.

---

[19] See, for example, G. Chiarotti, in *Radiation Damage in Solids*, edited by D. S. Billington (Academic Press Inc., New York, 1962), p. 398.

[20] S. Schnatterly and W. D. Compton, Phys. Rev. **135**, A227 (1964).

[21] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

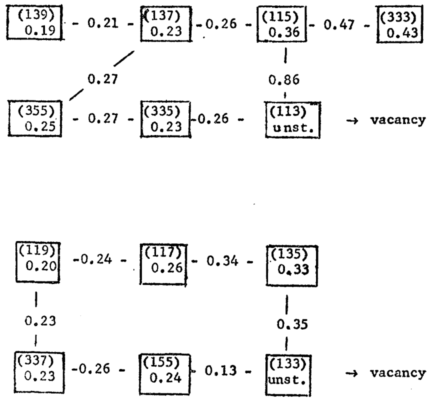


FIG. 7. Typical sequences of commutable interstitial positions (*pqr*) around a vacancy located at (000). Coordinates *pqr* are expressed in units of half the interionic distance in a perfect lattice. Numbers below each (*pqr*) are the energies in eV of interaction between an ion at (*pqr*) and the vacancy. The other numbers correspond to the interaction energies of an interstitialcy at the saddle point between the two particular cube center interstitial sites.

produced by the overlap of the strain fields. In order to estimate the activation energy for the motion of an interstitialcy, the difference between the energies $(E_i+E_{di}+E_{ri})$ and $(E_s+E_{ds}+E_{rs})$ has to be subtracted from the observed 0.06 eV activation energy which is assumed to characterize the free motion of an ion by an interstitialcy mechanism. It is clear that as long as the interstitialcy moves towards the vacancy $E_i<E_s$. The calculation shows, however, that the quantities $E_{di}$ and $E_{ds}$ can be large and that they either increase the attraction $E_s-E_i$ between the defects or they lead to a net repulsion. The energies $E_{ri}$ and $E_{rs}$ turn out to be negligible. Furthermore, a simple topological consideration indicates that only ions occupying certain special positions can fill a particular vacancy by a pure interstitialcy mechanism. Other interstitials cannot do so except if in a saddle point-configuration, the pair of moving ions reorients itself from one cube diagonal direction to another. Examples of the "permitted" sites are the interstitial positions which are nearest to the vacancy and the third nearest. The second nearest and the fourth nearest are of the "forbidden" kind. Figure 7 shows some of the sequences of commutable interstitial positions which are identified by their cubic coordinates expressed in terms of half of the nearest distance between positive and negative ions in a normal lattice. The corresponding energies $(E_i+E_{di})$ and $(E_s+E_{ds})$ are also shown. The interesting conclusion of these calculations is the fact that the effect of the vacancy on the migration energy of the interstitial is not a monotonic function of the distance between them but depends on the direction of the motion and on the direction of the line joining the interstitial and the vacancy. It turns out that in some cases interstitials have a preferred direction of motion away from the vacancy rather than towards it. For example, from position (137), the migration energy towards (115) is 0.03 eV, while the migration energy toward (355) is 0.02 eV. Thus, until the temperature is high enough for the interstitial to overcome the higher energy barrier for the motion towards the vacancy, it will stay within the positions (137), (355), and (335). Similarly, an ion at (115) cannot move into (133). It is clear that the numerical values of $E_s$, $E_{di}$, etc., depend rather critically on the calculated displacement of nearest neighbors, on the distance between negative ions in the saddle point position, etc. It turns out, however, that they do not affect the sequences of interstitial sites nor the general conclusions discussed below. In particular they do not alter the possible Frenkel pairs which can be assigned to each annealing stage.

Taking all these considerations into account, one arrives at the following tentative model in which the vacancy is located at (000): Stage I can be ascribed to the annealing of interstitials which are initially in site (113) or those which reach this site immediately from their unstable locations at (115) or (333); similarly, stage II is due to interstitials at sites (137) and (335) and those which reach them earlier from such sites as (139) or (355); and finally stage III corresponds to the annealing of interstitials from sites (135) and those which reach it earlier from more distant sites. Interstitials in sites (111), (133), etc., are inherently unstable and cannot show up in the annealing spectrum. Among the nearest 376 interstitial sites located in the fourteen shells surrounding the vacancy, 32 are inherently unstable, 72 are repulsive, 56 anneal directly in stage I, 120 in stage II and 96 in stage III. A quantitative comparison of the last three values with the relative size of the peaks in Fig. 2, however, requires taking into account the initial probability of occupation of the various sites: The displacement mechanisms based on diffusion (Klick,[4] Varley[3] etc.) would lead to a roughly spherical very compact distribution; the mechanism based on crowdion motion[5] would lead to a broad distribution peaked in the 12 equivalent [110] directions. The calculated activation energies for stages II and III corresponding to the rate-controlling sites (137) and (135) are 0.03 and 0.04 eV, respectively. The activation energy for stage I corresponds presumably to the energy necessary to rotate an ion pair at the saddle position as discussed above. This energy is difficult to estimate but the experimental value 0.015 eV is probably right for this step. The low pre-exponential factor is accounted for by the low probability of this rotation, although again no quantitative estimates have been made.

Two aspects of this model should be emphasized: First, that many interstitials cannot return to the initial vacancy because of the repulsive interaction, and they are "frozen-in" until the fourth "random-walk" stage sets in. Secondly, the various annealing stages do not correspond to quasispherical volumes or shells of interstitial sites around the vacancy but rather to specific sequences of mutually connected sites each with a specific activation energy at the final step. In this respect there seems to be a profound difference between the vacancy-interstitial recombination in metals[18] and in ionic crystals. In the alkali halides there is no evidence of a correlated annealing peak having an activation energy of the "random walk" which is well identifiable in metals.

## APPENDIX

The interaction energy between a vacancy and an interstitial was calculated following the well known Mott and Littleton's approximation[22] as used by Reitz and Gammel,[23] Tosi and Fumi,[24] and other authors.[25,26] A further approximation was used in the present calculation since it concerns the interaction between more distant defects than those treated by previous authors.

The interaction energy $E$ can be considered to be the difference in the energy to form a vacancy in the presence of a nearby interstitial ion and in a perfect lattice. Following Mott-Littleton this is equal to

$$E=\tfrac{1}{2}(V_{v,i}+V_i)-\tfrac{1}{2}(V_v+V_0)\,, \qquad \text{(A1)}$$

where $V_{v,i}$ is the potential energy at the position of the vacancy in the presence of both an interstitial and the vacancy, $V_i$ the same energy in the presence of an interstitial only, $V_v$ and $V_0$ the corresponding potential energies in the absence of the interstitial. Equation (A1) can be rewritten

$$E=\tfrac{1}{2}(V_{v,i}-V_v)+\tfrac{1}{2}(V_i-V_0) \qquad \text{(A2)}$$

and the two terms assumed equal because the interstitial and the vacancy are not close neighbors and the distortion of the lattice around a vacancy is small compared to that around an interstitial. The energy $E$ can be evaluated for an interstitial in a cube center and for a saddle-point configuration of an interstitialcy.

The quantity $(V_i-V_0)$ was estimated by calculating the Coulomb term $(E_c)$, the polarization term $(E_p)$, the correction term $(E_d)$ due to the displacement of the nearest neighbors of interstitials, and finally the repulsive term $(E_r)$. The energies $E_{\mathrm{i}}$ and $E_{\mathrm{s}}$ referred to in the text are equal to $(E_c-E_p)$ for the two cases. This was done for various configurations of interstitial and vacancy pairs. In the polarization term, the electronic polarizations of all ions and the polarizations caused by displacements of all ions except the nearest neighbors were considered. For the displacement of the nearest-neighboring ions, the results of a calculation by Tharmalingam[16] were used, and the differences in the Coulomb potential before and after displacement were calculated. As long as the vacancy-interstitial distance is not very small an estimate of $E_{\mathrm{r}}$ can be made using Brauer's continuum model,[27] which assumed that the displacement decreases inversely as the square of the distance. It appears that $E_{\mathrm{r}}$ is small even for the interstitial position at (135) where one obtains 0.003 eV for the saddle-point position and a much smaller value for the cube-center position. $\Delta E$, the difference between the total interaction energy for each Frenkel pair in a cube center and in a saddle-point position, has to be subtracted from 0.06 eV which is the migration energy of an interstitialcy. Some results of these calculations are shown in Table II, where the coordinates of the ion are expressed in units of half an interionic distance with the vacancy taken to be at the origin. It is clear that the term $E_d$ makes a rather big contribution, so that the migration energy in some cases is increased above its value for a random diffusion.

TABLE II. Interaction energy $E$ (in eV) between a vacancy and an interstitial ion in a cube center or in a saddle point pair-state position. $E_c$, $E_p$, and $E_d$ correspond to the Coulombic, polarization, and correction terms.

| Position<br>Cube center | Pair state | $E_c$ | $E_p$ | $E_d$ | $E$ | $\Delta E$ |
|---|---|---|---|---|---|---|
| 335 | | 1.33 | −1.06 | −0.04 | 0.23 | 0.03 |
| | 224 | 1.92 | −1.51 | −0.15 | 0.26 | |
| 155 | | 1.22 | −0.97 | −0.01 | 0.24 | −0.11 |
| | 044 | 1.60 | −1.27 | −0.20 | 0.13 | |
| 117 | | 1.22 | −0.97 | 0.01 | 0.26 | 0.07 |
| | 026 | 1.36 | −1.08 | 0.05 | 0.33 | |

---

[22] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

[23] J. R. Reitz and J. L. Gammel, J. Chem. Phys. **19**, 894 (1951).

[24] F. Bassani and F. G. Fumi, Nuovo Cimento **11**, 274 (1954).

[25] M. P. Tosi and F. G. Fumi, Nuovo Cimento **7**, 95 (1958).

[26] M. P. Tosi and G. Airoldi, Nuovo Cimento **8**, 584 (1958).

[27] P. Brauer, Z. Naturforsch. **7a**, 372 (1952).