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Thermal Motion of Holes in Potassium Iodide*

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Previous studies of the anisotropic absorption of oriented V_K centers (self-trapped holes) in KI showed that thermal reorientation occurs by a jumping motion in which the V_K axis changes direction by 60° and is characterized by a thermal activation energy of 0.27 eV. An investigation of a possible motion along the V_K center's axis, which cannot be detected by anisotropic absorption methods, is reported here. The thermal activation energy for the long-range diffusion of V_K centers was measured in two ways: (a) by monitoring the isothermal decrease of the principal V_K absorption band, and (b) by monitoring the luminescence which is the result of diffusing V_K centers annihilating trapped electrons. The activation energy needed for diffusion was found to be the same, within experimental error, as that needed for reorientation. On this basis it is concluded that the dominant mode of motion for holes in the temperature range of these experiments is by a series of reorientation jumps.

INTRODUCTION

THE trapping of holes in otherwise perfect regions of a crystal at low temperatures has been observed in several alkali halides.[1,2] The model of the self-trapped hole (V_K center) has been well established as a (halogen)$_2^-$ molecule-ion (I_2^- in KI). In order to form stable self-trapped holes in a crystal, the crystal must contain an electron-trapping defect or impurity. Otherwise the dispossessed electrons will move freely in the lattice and annihilate the holes.[3] Exposing a properly doped crystal to ionizing radiation at low temperatures causes the formation of self-trapped holes and impurity-trapped electrons.

Since self-trapped holes in alkali halides exhibit prominent absorption bands, one can study the motion of holes in these materials by optical techniques. If a crystal containing V_K centers is maintained at a temperature where holes are being released from the self-trapped state and are capable of annihilating electron-excess centers, then one would observe a corresponding decrease in absorption in the V_K region of the optical absorption spectrum. One might also expect these annihilation events to result in excited centers at the sites where the annihilated electrons had been trapped (impurity or defect sites) and that the decay of the excitation might be radiative. If such is the case, then the luminescence from the crystal is directly proportional to the rate of annihilation. The 105°K thermoluminescent glow peak in irradiated KI(Tl) is an example of this process.[4,5] This luminescence has been attributed to the thermal release of self-trapped holes which subsequently annihilate electrons trapped at thallous ion (Tl^+) sites. The emission is characteristic of the Tl^+ impurity (peak wavelength of 425 mμ).

Owing to their axial symmetry and their property of selective absorption of polarized light, one can preferentially orient V_K centers among the six distinguishable $\langle 110 \rangle$ orientations. The loss of preferential orientation can be detected by optical absorption measurements with polarized light. If a V_K center takes one step to its nearest-neighbor position in the lattice of possible V_K-center sites (lattice made up of the midpoints between anion sites), then it has changed its orientation. Therefore, thermal-reorientation experiments allow one to detect hole motion over the smallest free path possible.

The thermal reorientation of V_K centers in KI has been measured in the temperature range from 76 to 88°K.[6] These experiments showed that, within our ability to discern experimentally, V_K centers always change their orientation by 60° and never by 90°. Figure 1 illustrates that in moving through the lattice a V_K center could reorient by either 60° or 90°. If the center should jump to one of its eight first-nearest-neighbor positions, then its orientation would change by 60°. If, on the other hand, the center should jump to one of its four second-nearest-neighbor positions, then its orientation would change by 90°. Therefore, the thermal-reorientation experiments indicate that V_K centers change their orientation by jumping to first-nearest-neighbor sites and that one of the two iodine constituents that made up the original V_K center is also a member of the new V_K center after reorientation. These experiments also give the value of the probability per unit time that a V_K center will reorient through 60° as a function of temperature, which is equivalent to the

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[1] T. G. Castner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957).

[2] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961).

[3] R. K. Ahrenkiel and F. C. Brown, Phys. Rev. **136**, A223 (1964.)

[4] H. N. Hersh, J. Chem. Phys. **31**, 909 (1959).

[5] R. B. Murray and F. J. Keller, Phys. Rev. **137**, A942 (1965).

[6] F. J. Keller and R. B. Murray, Phys. Rev. Letters **15**, 198 (1965).

jump frequency for a first nearest-neighbor jump Γ_1.

$$\Gamma_1 = 4.0\times10^{13}\exp(-0.273/kT)\ \mathrm{sec}^{-1}, \tag{1}$$

where k is Boltzmann's constant in eV per °K, and T is the temperature in °K. There are eight first-nearest-neighbor sites to a given site so that the probability per unit time that a V_K center will jump from a given site to one of its first-nearest-neighbor sites γ_1 is $\frac{1}{8}\Gamma_1$.

The thermal-reorientation experiments also give evidence supporting the model of the V_K center as being a self-trapped hole rather than an impurity-trapped hole. The thermal activation energy for reorientation was the same, within experimental error, in KI(Tl) as it was in KI(NO_3). It would seem reasonable to assume that a hole trapped at a cation impurity would have a substantially different thermal activation energy from a hole trapped at an anion impurity.

Thermal-reorientation experiments have one inherent weakness; that is, motion of a hole from a given site to a site having the same orientation cannot be detected using this technique. A jump from a given site to the closest site having the same orientation is a fourth-nearest-neighbor jump in the lattice of possible V_K-center sites. It might not be correct to argue that the potential barrier for a fourth-nearest-neighbor jump (jump distance = 5.0 Å) must be greater than that for a first-nearest-neighbor jump (jump distance = 2.5 Å) on the grounds of jumping distance alone. Also, the fact that the thermal-reorientation experiments showed that the potential barrier for a second-nearest-neighbor jump (jump distance = 3.5 Å) is greater than that for a first-nearest-neighbor jump is not sufficient proof to exclude motion along the V_K-center's axis. The purpose of the experiments described here was to determine whether or not this proposed motion along the V_K-center's axis is appreciable compared to the known first-nearest-neighbor jumping motion.

The methods used in detecting hole motion were to measure (a) the isothermal decrease of the V_K-absorption bands, and (b) the isothermal post-irradiation luminescence (afterglow). These measurements were made after warming the crystal rapidly to temperatures where V_K centers are known to have an appreciable diffusion coefficient from the reorientation studies. Processes (a) and (b) are assumed to be the result of diffusing V_K centers annihilating trapped electrons, as described above in the second paragraph. If the diffusion coefficient D is the result of random jumps to the eight first-nearest-neighbor sites and to the two fourth-nearest-neighbor sites along the V_K center's axis, then

$$D = \tfrac{2}{3}a^2(\gamma_1+\gamma_4). \tag{2}$$

γ_4 is the jump frequency to one of the two fourth-nearest-neighbor sites being considered (closest sites along the molecular axis), and a is one-half of the lattice constant, i.e., $a = 3.53$ Å. Equation (2) is the result of adding jump probabilities and has been derived elsewhere.[7] The reason γ_1 and γ_4 enter the equation with equal weights is the following: γ_1 represents jumps to one of a possible eight sites, whereas, γ_4 represents jumps to one of a possible two sites. However, the jump distance, which enters squared in the equation, is twice as far for a fourth-nearest-neighbor jump as for a first-nearest-neighbor jump. Therefore, the weights are the same. We find that

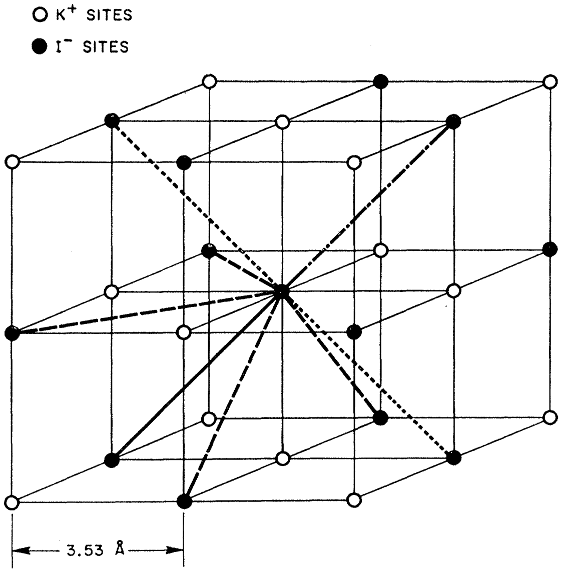

FIG. 1. Illustrating the orientations of neighboring V_K-center sites. V_K-center sites are represented here by lines between I^- sites. The reference V_K-center site is indicated by a heavy solid line. Its first-nearest neighbors (four of the eight are shown) are indicated by dashed lines and are oriented at an angle of 60° with respect to the reference site. Its second-nearest neighbors (two of the four are shown) are indicated by dotted lines and are oriented at an angle of 90° with respect to the reference site. The two closest sites along the axis of the reference site (the one shown is indicated by alternate dashes and dots) are fourth-nearest neighbors and have the same orientation as the reference site.

$$\gamma_1 = s_1 e^{-E_1/kT}, \tag{3}$$

and we assume that

$$\gamma_4 = s_4 e^{-E_4/kT}. \tag{4}$$

From the thermal-reorientation experiments

$$s_1 = 5\times10^{12}\ \mathrm{sec}^{-1}, \tag{5}$$

and

$$E_1 = 0.273\pm0.004\ \mathrm{eV}. \tag{6}$$

We also assume that s_1 and s_4 are not greatly different so that the activation energies alone determine whether the hole jumps to a first or to a fourth-nearest-neighbor site.

In measurements of (a) and (b) it is very difficult to determine the absolute magnitude of D accurately.

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[7] F. J. Keller, in Oak Ridge National Laboratory Report, ORNL-TM-1422 1966, p. 140 (unpublished).

This is because the product of D times several inaccurately known parameters is gotten from the experiments. Therefore, we wish to determine the temperature dependence of D in the experiments. In analyzing the data we ask whether or not D is of the form

$$D=D_0e^{-E_D/kT}. \tag{7}$$

There are three possibilities: (a) $E_1=E_4$ within experimental error; (b) $E_1>E_4$; and (c) $E_4>E_1$. Possibility (a) cannot be distinguished from (c) with these experiments if E_4 is sufficiently greater than E_1 so that $\gamma_1\gg\gamma_4$. However, (a) might be considered an unlikely coincidence. At any rate, the difference between (a) and (c) represents only a factor of 2 in the diffusion coefficient and we consider this to be relatively unimportant. Therefore, (a) shall be disregarded in future discussions. The important difference is between (b) and (c). In particular we wish to know if E_4 is significantly less than E_1. If this is the case, then a semilogarithmic plot of D versus $1/T$ will indicate two branches, one for E_1 and one for E_4. However, if $\gamma_1\gg\gamma_4$, then there will be only one branch which will be characteristic of E_1.

EXPERIMENTAL METHODS

The crystals used in these experiments were of two types which shall be referred to as KI(NO_3) and KI(Tl). The KI(NO_3) samples were cleaved from a boule purchased from Semi-Elements. A chemical analysis performed on this boule showed that it contained more NO_2^- ions than NO_3^-, and that the distribution of the impurities was inhomogeneous. The mole fraction of NO_2^- varied from 4×10^{-4} to 4×10^{-5}, and that of NO_3^- varied from 2×10^{-4} to 0, depending on the region of the boule from which the sample was cleaved. NO_2^- was also detected in absorption during each experiment and the size of the bands was about the same in all cases.[8] Presumably one or both of these impurities acted as the electron trap in the experiments, and evidently one or both also acted as a hole trap. The KI(Tl) samples were cleaved from a boule purchased from Harshaw. This boule contained $\sim10^{-3}$ mole fraction of thallium. The samples were always single crystals and were generally $1-2\times10\times10$ mm^3. The propagation direction of the ionizing radiation and measuring light was along the crystal's shortest dimension.

The samples were mounted in a variable-temperature stainless steel cryostat that has a rotatable base. The rotatable base allows alignment of a thin aluminum window for the passage of ionizing radiation and then quartz windows for optical studies while the sample is at low temperature. Liquid nitrogen was used as the cryogenic fluid. The sample could be maintained at a temperature close to that of the cryogenic fluid by allowing the fluid to pass through a tube that is in good thermal contact with the sample holder. The sample could be warmed rapidly by passing room-temperature gas through this tube. Constant temperatures above that of the cryogenic fluid were maintained by closing the tube and passing a current through an electrical heater.

Temperatures below 100°K were measured with a germanium resistance thermometer calibrated with an accuracy of ±0.1°K traceable to the National Bureau of Standards. Temperatures above 100°K were measured with a copper-constantan thermocouple. The thermocouple was calibrated using fixed points at 100°K (using the germanium resistance thermometer as standard) and at 273°K by the "difference curve" method.[9] The thermometers were mounted in the copper sample holder. A supplementary experiment with the thermocouple mounted in a drill hole in the sample (the thermocouple was shaded from room temperature radiation) showed that the sample was 0.04±0.02°K warmer than the sample holder at 78°K. This difference was considered to be negligible compared to other uncertainties. During the rapid heating from 78°K to the control temperature, the temperature increased at about 10°K per minute. Control temperatures were maintained within ±0.05°K.

The crystals were irradiated with 1.7-MeV electrons from a Van de Graaff accelerator at a current density of the order of 10^{-2} μA/cm^2 in the experiments concerned with optical absorption. In the afterglow experiments the crystals were x irradiated. The x-ray tube has a molybdenum target and was operated at 40 kV and 15 mA. The x rays were unfiltered in that they passed through only the mica-beryllium window of the tube and the 0.008-in. aluminum window of the cryostat.

The absorption spectra were measured with a Cary model-14 recording spectrophotometer. The emission spectra were measured with a Bausch and Lomb grating monochromator in conjunction with a photomultiplier tube. The monochromator's dispersion is 3.3 mμ/mm, and it has a 500-mm focal length. An RCA 6903 photomultiplier tube was used which is sensitive in the range from 200 to 600 mμ. The spectral response of the monochromator-detector system was measured with a National Bureau of Standards calibrated lamp and all the emission spectra reported here have been corrected.

THEORY

The data from these experiments were consistent with the theory advanced by Waite.[10] For the random-walk diffusion-limited reaction $A+B\rightarrow AB$, Waite gives

$$\frac{dC_A}{dt}=\frac{dC_B}{dt}=-4\pi r_0D\left[1+\frac{r_0}{(\pi Dt)^{1/2}}\right]C_AC_B. \tag{8}$$

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[8] T. Timusk and W. Staude, Phys. Rev. Letters **13**, 373 (1964).

[9] W. F. Roeser and A. T. Louberger, Natl. Bur. Std. (U. S.), Circ. No. 590 (1958).

[10] T. R. Waite, Phys. Rev. **107**, 463 (1957).

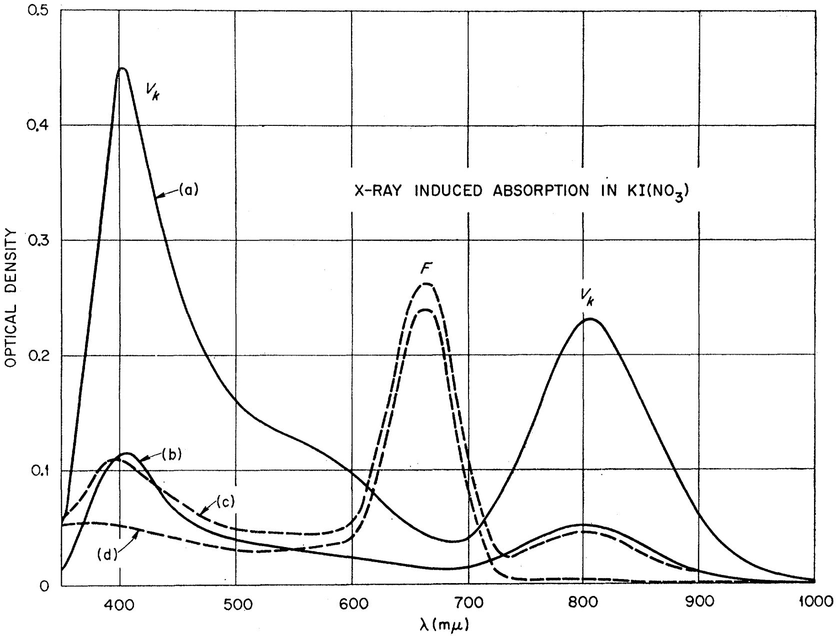

FIG. 2. X-ray-induced absorption in KI(NO$_3$). All measurements were made at 78°K: (a) After the crystal was x rayed at 78°K. (b) After the crystal was warmed to 122°K for one hour. The crystal was then heated to room temperature and exposed to room light, which reduced the radiation-induced absorption to zero. (c) After the crystal was x rayed at 125°K. (d) After the crystal was heated to 150°K.

C_A and C_B are the concentrations of A's and B's, respectively, D is the diffusion coefficient, and r_0 is the separation at which the two particles combine (capture radius). If A's and B's are both diffusing, then $D=D_A+D_B$. Since we are concerned with only one species diffusing, we set $D_B=0$. Equation (8) is valid for particles that combine because of the influence of short-range forces only and have a random initial distribution. If the particles are attracted by long-range Coulomb forces (as in our case), Waite suggests that this equation may be used as a first approximation by substituting a temperature-dependent capture radius.[11] The capture radius given by Waite for this case is

$$r_0=e^2/\epsilon kT, \tag{9}$$

where e is the electronic charge and ϵ is the dielectric constant.

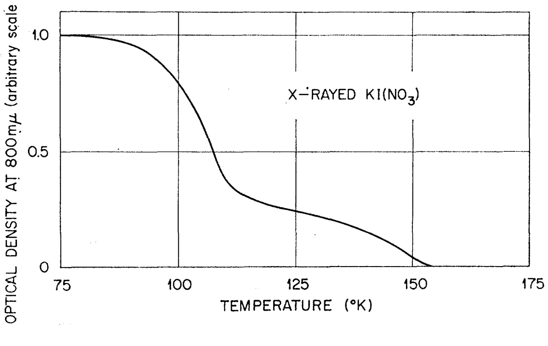

FIG. 3. Decrease of the 800-mμ V_K absorption band upon warming in KI(NO$_3$).

Equation (9) gives an absolute value of r_0 that is evidently too large. In a typical experiment, assuming an oscillator strength of one-half for the 404-mμ V_K-absorption band, a crystal contains $\sim 2\times10^{17}$ V_K centers per cm^3 and an approximately equal number of trapped electrons. If these centers are spatially distributed so that they are a maximum distance apart, then a V_K center's first-nearest-neighbor trapped electron is 140 Å away. If the centers have a random spatial distribution, then the average distance from a V_K center to the nearest trapped electron is 75 Å. According to the above equation, r_0 is 400 Å at 85°K and 7000 Å at liquid-helium temperature, so that it would be impossible to form stable V_K centers with a concentration of the order of 10^{17}. Therefore, for reasonable assumptions about the oscillator strengths of the V_K absorption bands this equation gives an absolute value of r_0 that is too large. However, we retain the temperature dependence of r_0 predicted by this equation because it is a result of taking into account the Coulomb attraction of the centers.

ISOTHERMAL DECREASE OF THE 404-mμ V_K ABSORPTION BAND

Curve (a) of Fig. 2 shows the two prominent V_K bands (404 and 800 mμ) in x-rayed KI(NO$_3$) at 78°K. Figure 3 shows the behavior of the 800-mμ band upon warming. The 404-mμ band behaves in a similar fashion. We attribute the first annealing stage at about 100°K to the annihilation of self-trapped holes by their diffusion to trapped electron sites. We assume that the second annealing stage at about 150°K is due to the annihilation of holes trapped at impurity sites. A similar process occurs in KI(Tl), according to Hersh.[4]

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[11] T. R. Waite, J. Chem. Phys. 28, 103 (1958).

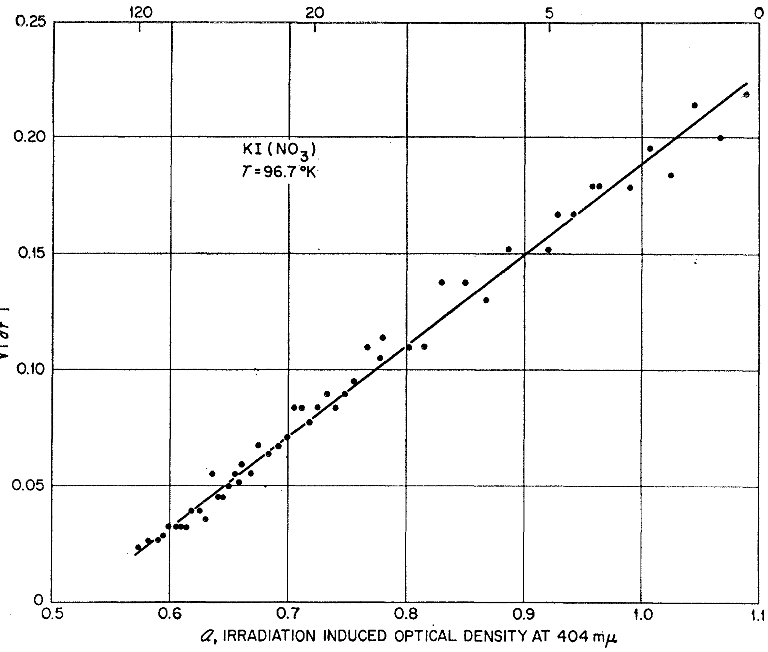

FIG. 4. Isothermal decrease of the 404-mμ V_K absorption band at 96.7°K.

Figure 2 shows that the absorption we attribute to impurity-trapped holes is quite similar to that of self-trapped holes. This figure also shows that impurity-trapped holes can be created either by irradiating at 78°K and warming to ~125°K, or by irradiating at ~125°K. This leaves open the question as to whether the impurity-trapped holes are present to an appreciable extent in a sample after irradiation at 78°K, or whether they are created by the diffusion of the V_K centers upon warming past ~100°K.

The best evidence we have that the absorption shown as curve (b) in Fig. 2 is due to impurity-trapped holes is the fact that optical bleaching at 78°K causes the re-creation of self-trapped holes. The details of this evidence are given in Ref. 7. Impurity-trapped holes have been discovered and studied in many systems other than KI(Tl) and KI(NO$_3$). Examples are NaF(Li), NaCl(Li), KCl(Li), and KCl(Na).[12,13]

There are two possibilities for the predominant mode of creation for the impurity-trapped holes: (a) by the diffusion of V_K centers upon warming past ~100°K, and (b) by the irradiation at 78°K. Let n = number of V_K centers per unit volume; n_e = number of trapped electrons per unit volume; n_a = number of impurity-trapped holes per unit volume; N_i = number of hole-trapping impurities per unit volume; r_0 = trapped-electron capture radius for V_K centers; and r_a = hole trapping impurity-capture radius for V_K centers. Conservation of charge gives

$$n_e = n + n_a. \tag{10}$$

For case (a)

$$\frac{dn}{dt} = -4\pi r_0 D\left(1+\frac{r_0}{(\pi Dt)^{1/2}}\right)nn_e - 4\pi r_a D\left(1+\frac{r_a}{(\pi Dt)^{1/2}}\right)nN_i, \tag{11}$$

$$\frac{dn_e}{dt} = -4\pi r_0 D\left(1+\frac{r_0}{(\pi Dt)^{1/2}}\right)nn_e, \tag{12}$$

and

$$\frac{dn_a}{dt} = 4\pi r_a D\left(1+\frac{r_a}{(\pi Dt)^{1/2}}\right)nN_i. \tag{13}$$

By using data at long times so that the transitory term involving $(t)^{-1/2}$ can be neglected, one can solve for n as

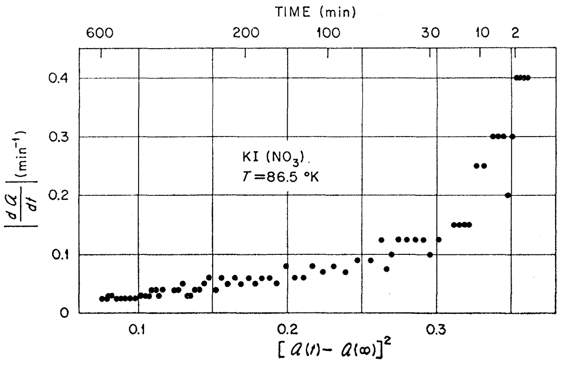

FIG. 5. Isothermal decrease of the 404-mμ V_K absorption band at 86.5°K.

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[12] I. L. Bass and R. Micher, Phys. Rev. Letters 15, 25 (1965).

[13] D. Schoemaker, in Proceedings of the International Symposium on Color Centers in Alkali Halides, Urbana, 1965 (unpublished).

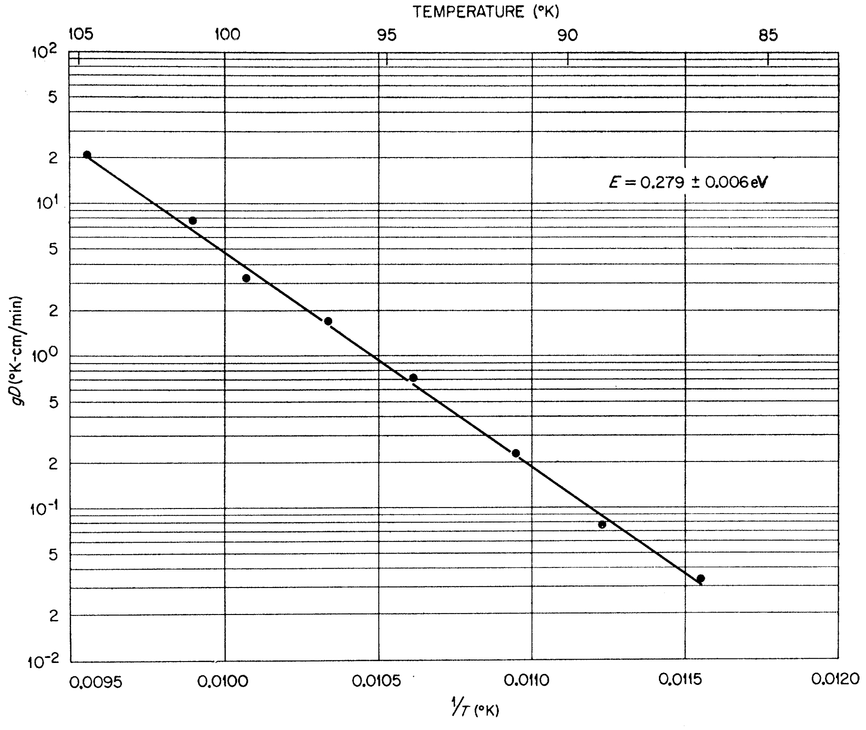

FIG. 6. Temperature dependence of the diffusion coefficient obtained from the isothermal loss of the 404-mμ V_K absorption band in KI(NO$_3$).

a function of n_e by using Eqs. (11) and (12) to obtain

$$n(t)=n_e(t)-n_e(\infty)+[r_aN_i/r_0]\ln[n_e(t)/n_e(\infty)]. \quad (14)$$

One can then eliminate n in Eq. (12) to obtain an equation in terms of n_e and t only. Assuming that the oscillator strengths for the 404-mμ band are the same for both self-trapped and impurity-trapped holes, we can let

$$n_e(t)\propto \mathcal{A}(t), \quad (15)$$

where $\mathcal{A}$ refers to the radiation-induced optical density at 404 mμ. Using Eqs. (12), (14), and (15) permits analysis of the measured quantities $\mathcal{A}$, $d\mathcal{A}/dt$, and t to get the diffusion coefficient D. For case (b)

$$\frac{dn}{dt}=-4\pi r_0 D\left(1+\frac{r_0}{(\pi Dt)^{1/2}}\right)nn_e, \quad (16)$$

$$dn_e/dt=dn/dt, \quad (17)$$

$$dn_a/dt=0. \quad (18)$$

Assuming $n\approx n_e$, we can let

$$n(t)\propto[\mathcal{A}(t)-\mathcal{A}(\infty)]. \quad (19)$$

In spite of the fact that there is strong evidence which indicates that case (a) is operative in KI(Tl),[4,14] our data for KI(NO$_3$) were accurately described by case (b) and were inconsistent with case (a). The reason our data do not support case (a) could be due to the assumption about the oscillator strengths rather than the fact that case (a) is the incorrect mode.

Experiments similar to those described in this section have been performed on KCl(Pb) by Neubert and Reffner.[15] These investigators also found that their data were satisfactorily described by case (b). However, they did not report any observations about the transitory term involving $(t)^{-1/2}$. They derived an activation energy of 0.53 eV from their data which they interpreted as that needed for the diffusion of V_K centers in KCl(Pb).

The procedure followed in these experiments was: (1) electron irradiate a crystal of KI(NO$_3$) at 78°K, (2) warm the sample rapidly to the control temperature, and (3) measure the optical density at 404 mμ as a function of time. Eight such experiments were performed. Uncertainty in determining the time $t=0$ made it advisable to use the differential form of the kinetic equations in analyzing the data. The time $t=0$ refers to the time when the centers are in a random spatial distribution. If this state of affairs exists at all, then it is immediately after the irradiation is stopped and before diffusion is allowed to begin.[10] Because of experimental difficulties, the sample was maintained at 78°K for 30 to 60 min between the time the irradiation ended and the time the crystal was rapidly heated to the control temperature. Since V_K centers diffuse, albeit quite slowly, at these temperatures the spatial distribu-

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[14] W. B. Hadley, S. Polick, R. G. Kaufman, and H. N. Hersh (unpublished).

[15] T. F. Neubert and J. A. Reffner, J. Chem. Phys. 36, 2780 (1962).

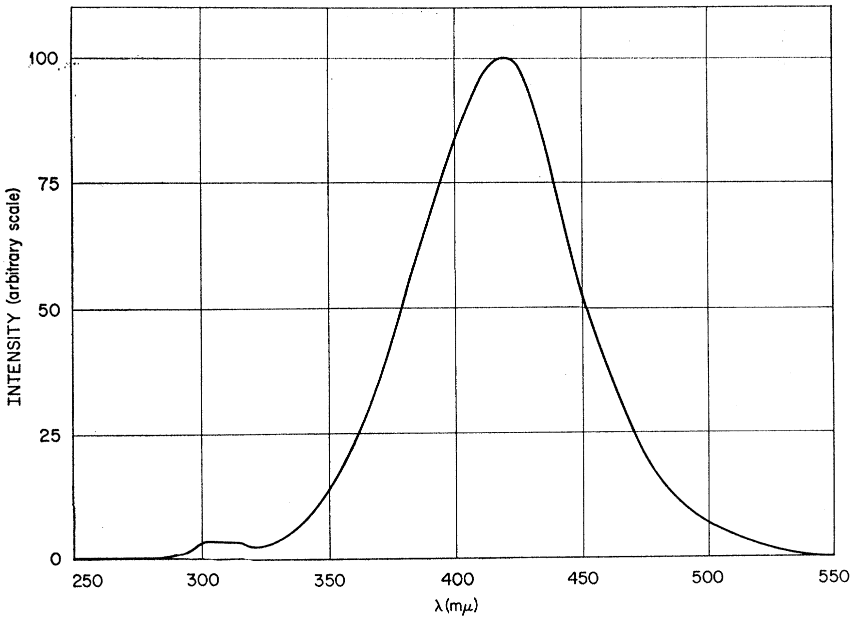

FIG. 7. Afterglow spectrum from KI(Tl) at 78°K.

tion at the time the control temperature was reached was surely not random. Therefore, the time $t=0$ was difficult to ascertain.

According to the kinetic equations for case (b), the optical density and the time are related by

$$|d\mathcal{A}/dt| = (C_1+C_2/\sqrt{t})[\mathcal{A}(t)-\mathcal{A}(\infty)]^2. \quad (20)$$

C_1 and C_2 are constants with respect to $\mathcal{A}$ and t. Since $C_2/C_1=r_0/(\pi D)^{1/2}$ the transitory term involving $t^{-1/2}$ is expected to be significant for long times only at low temperatures where D is small. At high temperatures the transitory term becomes negligible at early times and the simpler equation

$$\left|\frac{d\mathcal{A}}{dt}\right|^{1/2} = (C_1)^{1/2}\mathcal{A}(t)-(C_1)^{1/2}\mathcal{A}(\infty) \quad (21)$$

is followed. Figure 4 shows a plot of our data for a high-temperature run in which Eq. (21) was valid.

Figure 5 shows a plot of the data from our lowest-temperature experiment. The data points in this figure qualitatively support the transitory term involving $t^{-1/2}$, but are not accurate enough for a rigorous test of the theory.

Least squares fits of the data from each of the experiments gave the temperature dependence of C_1. The factor $h_a(T)TxC_1$ is proportional to the diffusion coefficient:

$$h_a(T)TxC_1=gD, \quad (22)$$

where g is a constant that has the same value for each experiment. $h_a(T)$ (called the "height" of the absorption band) is a correction factor that takes account of the thermal broadening of the absorption band since the width of the band was not measured during the runs. $h_a(T)$ varies only slightly with the temperature in the temperature range of these experiments so that this represents a small but systematic correction. T corrects for the temperature dependence of r_0, and x is the thickness of the crystal. A semilogarithmic plot of gD versus $1/T$ is shown in Fig. 6. The uncertainty in the activation energy quoted in the figure is derived from the least-squares analysis and pertains to random errors only. Systematic errors may result from systematic errors in the experimental measurements (e.g., $\mathcal{A}$ or T), incorrect analysis in determining C_1 [e.g., if case (b) is incorrect], or fitting D to the wrong function (e.g., if D is characterized by more than one activation energy, or if some process other than V_K-center diffusion is causing the decrease of the band). In view of these possibilities, a more realistic value for the activation energy E_a (the a stands for absorption) derived from the absorption measurements is

$$E_a=0.28\pm0.02 \text{ eV}. \quad (23)$$

ISOTHERMAL DECREASE OF AFTERGLOW

Previous investigations have shown that the luminescence in the 105°K glow peak in KI(Tl) is the result of diffusing V_K centers being annihilated by trapped electrons at impurity sites. We have performed isothermal measurements of this luminescence (afterglow) in order to determine the activation energy for the diffusion of V_K centers by another independent method. The afterglow spectrum shown in Fig. 7 indicates that the emission is characteristic of the thallous-ion impurity (peak wavelength ~425 mμ).

The luminescence intensity L is proportional to the

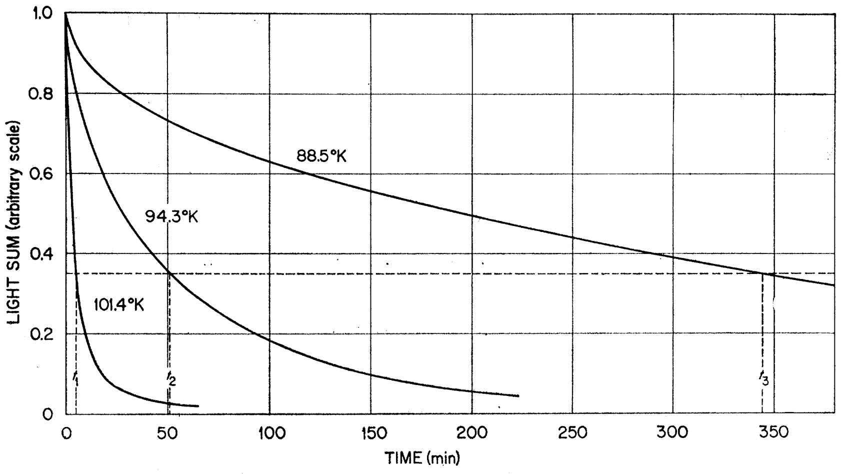

FIG. 8. Light sum versus time at various temperatures for the 420-mμ afterglow in KI(Tl).

rate of annihilation of trapped electrons.

$$L(t) \propto |dn_e/dt|. \tag{24}$$

We define

$$S(t)=\int_t^\infty L(t')dt'. \tag{25}$$

$S(t)$ is called the "light sum." Therefore,

$$S(t) \propto [n_e(t)-n_e(\infty)]. \tag{26}$$

$S(t)$ is to include luminescence due to the diffusion of V_K centers only so that it should result from an integration of all the luminescence in the 105°K glow peak and no more. $n_e(\infty)>0$ in (26) because some of the holes are trapped at impurities which leaves an equal number of stable electron-excess centers. The glow peaks at higher temperatures result from the annihilation of these charges.

The afterglow measurements were made with the cryostat in place in front of the x-ray machine. The rapid heating to the control temperature and the luminescence measurements were begun immediately after the irradiation was stopped. Therefore, these experiments were not hampered by the uncertainty in determining the time $t=0$, as was the case in the absorption experiments. This allowed us to use the powerful "cross-cut" method in analyzing the data.[16]

The following is a brief exposition of the cross-cut method. Suppose the rate of decrease of a certain defect is described by

$$d\nu/dt=-K_0e^{-E/kT}P(\nu). \tag{27}$$

ν is the fractional concentration of the defect; $P(\nu)$ is any continuous function of ν; and K_0 is a constant. Equation (27) is formally integrable to give

$$-\int_{\nu(0)}^{\nu(t)} \frac{d\nu}{P(\nu)}=K_0te^{-E/kT}. \tag{28}$$

Now suppose two isothermal experiments are performed at two different control temperatures T_1 and T_2. During each experiment ν is measured as a function of t. Comparing the times t_1 and t_2 when the concentrations are the same [i.e., when $\nu(t_1;T_1)=\nu(t_2;T_2)$], we can set

$$-\int_{\nu(0)}^{\nu(t_1;T_1)} \frac{d\nu}{P(\nu)}=-\int_{\nu(0)}^{\nu(t_2;T_2)} \frac{d\nu}{P(\nu)}. \tag{29}$$

Therefore,

$$t_1e^{-E/kT_1}=t_2e^{-E/kT_2} \tag{30}$$

or

$$\ln(t_1/t_2)=(E/k)(1/T_1-1/T_2). \tag{31}$$

If more than two experiments are performed, then for a given $\nu(t_i;T_i)$ the times and temperatures are related by

$$\ln(t_i)=(E/k)(1/T_i)+\text{constant}. \tag{32}$$

The subscript i stands for the ith experiment.

Figure 8 illustrates the method. This figure is a plot of $S(t)/S(0)$ versus time for three typical experiments. The horizontal dashed line indicates a typical cross cut. This method is useful in the present work because it does not require specification as to whether case (a) or case (b) discussed in the previous section is correct. By the same token it gives no information about which is the correct mode.

Before applying the cross-cut method to our data, we must take account of a process that has heretofore not been discussed. During the course of these experiments we observed an approximately temperature-independent afterglow. The following description of an experiment indicates some of the properties of this afterglow. This experiment was performed at temperatures lower than that needed for the thermal release of an appreciable number of V_K centers so that the contribution to the afterglow from diffusion can be neglected. A crystal of KI(Tl) was x rayed at ~20°K for 15 min, introducing V_K centers and trapped electrons. The afterglow at 420 mμ was monitored while the temperature of the crystal

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[16] A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach, Science Publishers, New York, 1963).

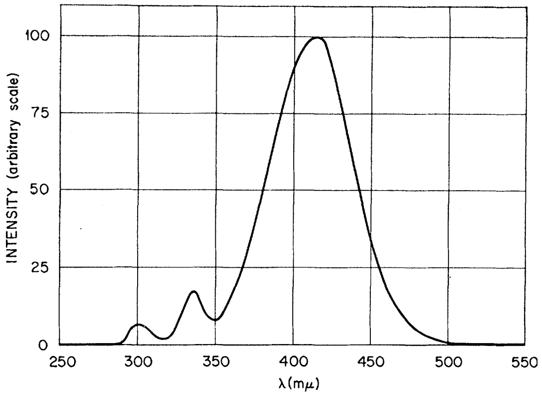

FIG. 9. Afterglow spectrum from KI(Tl) at 7°K.

was varied from 5° to 78°, and then back to 5°K. The afterglow intensity was found to decrease monotonically with time but was almost independent of temperature in this range. The spectrum of the afterglow at 7°K is shown in Fig. 9. This figure shows that the principal emission band peaks at practically the same wavelength as that of the afterglow at 78°K.

Delbecq, Ghosh, and Yuster[17,18] found that KCl(Ag) crystals that contained V_K centers and trapped electron centers (Ag°) exhibited a long and persistent afterglow that was almost independent of temperature in the range 5 to 140°K. V_K centers are thermally stable against diffusion in KCl to ~160°K.[15] Delbecq *et al.* attributed this afterglow to the recombination of nearby pairs of V_K centers and trapped electrons through an anisotropic tunneling process. We will refer to the temperature-independent phase of the afterglow in KI(Tl) as being due to a tunneling process by analogy with the work of these investigators.

We assume that the rate at which electrons are annihilated by the tunneling process is proportional to nn_e. Therefore,

$$dn_e/dt = -\{4\pi r_0 D(1+r_0/(\pi Dt)^{1/2})+\Lambda\}nn_e\,, \quad (33)$$

where Λnn_e is the rate of annihilation due to tunneling. Λ has the same dimensions as a second-order rate constant (volume per unit time). We made the cross cuts at long times ($t\gg 4r_0^2/\pi D$) so that the transitory term involving $t^{-1/2}$ could be neglected. After neglecting the transitory term and applying the cross-cut method to Eq. (33), we have

$$S_i(0)t_i/h_e(T_i)T_i = \text{constant}/(e^{-E/kT_i}+\Omega)\,. \quad (34)$$

$\Omega = \Lambda/4\pi r_0 D_0$ and is assumed to be independent of temperature, i.e., we are neglecting any possible temperature dependence in Ω compared to that in the exponential. The proportionality constant depends on photomultiplier efficiency, arrangement of the apparatus, etc. The factor $1/T_i$ on the left-hand side of the equation corrects for the temperature dependence of r_0. The factor $S_i(0)/h_e(T_i)$ normalizes the data of each experiment since we need to deal with fractional concentrations. This factor varied by only 3% among the experiments in a nonsystematic fashion owing to inadvertant variations in arrangement of the apparatus and irradiation dose. $h_e(T_i)$ (called the "height" of the emission band) corrects for the variation of the intensity at 420 mμ with temperature for a constant rate of excitation.

Six afterglow experiments were performed. The procedure for the experiments was: (1) x ray a KI(Tl) crystal at 78°K for 5 min, (2) raise the temperature rapidly to the control temperature, and (3) measure the luminescence intensity at 420 mμ as a function of time at constant temperature. Since the time measurement was critical, the increase in temperature from 78°K to the control temperature had to be as rapidly as possible. After the isothermal measurement was complete, the crystal was heated so that all the luminescence of the 105°K glow peak was taken into account (i.e., all the self-trapped holes were thermally destroyed).

Five cross cuts in the range $S(t)/S(0)=0.45$ to $S(t)/S(0)=0.25$ were made. The activation energies derived from each of the cross cuts varied by less than 1%, indicating that the requirement that cross cuts be made at long times is satisfied. Figure 10 shows a semilogarithmic plot of $S_i(0)t_i/h_e(T_i)T_i$ versus $1/T_i$. The data points of this figure are a result of a superposition of the five cross cuts normalized to the same scale by using different values for the proportionality constant in Eq. (34). The solid curve is a Newton's-method fit of Eq. (34) to the data. The fit indicated an uncertainty of ±0.003 eV in the activation energy due to random errors. Taking into account possible systematic errors, we give $E_e = 0.275 \pm 0.010$ eV for the activation energy obtained from these experiments (the subscript "e" stands

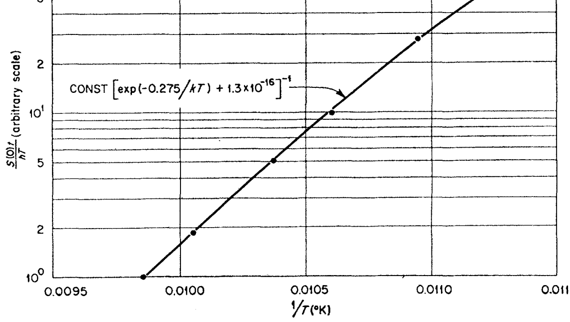

FIG. 10. Temperature dependence of the diffusion coefficient plus a temperature-independent tunneling term obtained from the 420-mμ afterglow in KI(Tl).

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[17] C. J. Delbecq, A. K. Ghosh, and P. H. Yuster, Bull. Am. Phys. Soc. 9, 629 (1964).

[18] C. J. Delbecq, A. K. Ghosh, and P. H. Yuster, in Proceedings of the International Symposium on Color Centers in Alkali Halides, Urbana, 1965 (unpublished).

for emission). Note that $\exp(-E_e/kT)=\Omega$ at 86°K. This indicates that the rate of annihilation due to "tunneling" is equal to that due to diffusion at 86°K (neglecting the transitory diffusion term involving $t^{-1/2}$). If $T<86$°K, then the "tunneling" term dominates the annihilation process according to these data.

A "tunneling" process in $KI(NO_3)$ similar to that found in KI(Tl) was not observed. However, we made no concentrated effort to search for such an effect. If such an effect does exist in $KI(NO_3)$, then we probably would not have observed it.

CONCLUSIONS

The two measured activation energies $E_a(0.28\pm0.02$ eV) and $E_e(0.275\pm0.010$ eV) were measurements of E_D. E_e is considered to be the more accurate of the two because it was derived from the cross-cut method of analysis. Both numbers are significantly less reliable than $E_1(0.273\pm0.004$ eV). E_1 was accurately determined because it was derived from the analysis of a first-order process.

A comparison of the activation energies indicates which of the three possibilities discussed in the introduction is probably correct. Since E_a and E_e are the same as E_1 within experimental error, it appears that $\gamma_1 \gg \gamma_4$ so that the data are describable in terms of possibility (c) rather than (b). To the extent that possibility (a) is an unlikely coincidence, the diffusion coefficient for holes in KI is

$$D=4.15\times10^{-3}\exp(-0.273/kT)\ \mathrm{cm}^2\,\mathrm{sec}^{-1}, \qquad (35)$$

where kT is expressed in units of electron volts. The experiments described here and the reorientation experiments taken together have shown that, aside from the tunneling effect, the motion of holes in KI is diffusive in character analogous to that of interstitials or vacancies, and that a hopping motion along the axes of the V_K centers is probably negligible compared to first-nearest-neighbor jumps.

The electron-hole annihilation at lower temperatures that we have attributed to the "tunneling" of charges may be an interesting problem for further research. Delbecq, Ghosh, and Yuster have shown that this is an anisotropic effect so that it may be due to a "tunneling" of charges along the V_K centers' axes. The theoretical treatment of the motion of polarons by Holstein[19] might be applicable to this problem. According to this investigator his model predicts a diffusive motion characterized by an activation energy at high temperatures and a band-type motion at low temperatures. He gives the transition temperature between the dominance of one mode over the other as approximately one-half the Debye $\Theta(\frac{1}{2}\Theta\sim80$°K in KI).

We have recently extended these studies to the system KCl(Pb). We have observed the preferential thermal reorientation of V_K centers in this crystal which indicates that reorientation occurs by virtue of a first nearest-neighbor jump and that $\gamma_1 \gg \gamma_2$. We have found that $\gamma_1=5\times10^{12}\exp(-0.54/kT)\ \mathrm{sec}^{-1}$, where again kT is expressed in electron volts. This activation energy is surely the same within experimental error as that given by Neubert and Reffner for the diffusion of V_K centers (0.53 eV). Therefore, it appears that in all likelihood $\gamma_1 \gg \gamma_4$ in KCl as well as KI, and that in the temperature range of these studies holes move predominantly by a diffusive hopping motion to first-nearest-neighbor sites.

ACKNOWLEDGMENTS

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[19] T. Holstein, Ann. Phys. (N. Y.) 8, 325, 343 (1959).