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Tunneling recombination of trapped electrons and holes in KCl:AgCl and KCl:TlCl[†]

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It is well established that exposure of KCl:AgCl (or KCl:TlCl) crystals at 77 K to ionizing radiation results in the trapping of holes as Cl_2^-, V_K centers, and electrons as Ag^0 (Tl^0). These crystals emit luminescence at 77 K which persists for many hours after the irradiation. Evidence is presented that indicates that this afterglow results from electron-hole recombination between nearby metal-atom–Cl_2^- pairs, and that the recombination does not occur by a thermally activated process but by a tunneling process. The time dependence of the intensity of the afterglow is qualitatively understood on the basis of a simple model. When the Cl_2^- are preferentially oriented in the crystal it is observed that the afterglow is partially polarized with the electric vector of the dominant component parallel to the Cl_2^- molecular axis. If a crystal containing oriented Cl_2^- is warmed, the degree of polarization remains constant up to the temperature range where the Cl_2^- disorient at an appreciable rate; in the latter range the degree of polarization goes to zero and then reverses sign before finally going to zero again. This reversal of the polarization which occurs when the Cl_2^- change orientation is interpreted as indicating that the tunneling probability is anisotropic.

I. INTRODUCTION

During an investigation of the symmetry properties of the V_1 band, Lambe and West[1] investigated the phosphorescence emitted by a KCl:TlCl crystal which had been x rayed at 77 K. They found that excitation in the V_1-band region with polarized light produces a polarization in the afterglow and were able to conclude that this emission probably does not involve the V_1 center but does involve some center with ⟨110⟩ symmetry. Although their evidence was not conclusive, they suggested that the center involved might be the Cl_2^- molecule ion, V_K center, which had been recently discovered by Känzig.[2] Since this early work, considerable information has been obtained concerning the V_K center in KCl (hereafter called Cl_2^-),[3–5] Ag^0, and Ag^{++},[6] and Tl^0 and Tl^{++},[7–9] and their interactions.

A preliminary report on the reactions producing the afterglow and low-temperature glow peak in irradiated KCl:AgCl was presented some time ago.[10] Because of the considerable interest in trapped-exciton emission we have decided to publish a more detailed account of this different type of recombination luminescence, i.e., that involving the recombination of Cl_2^- and silver atoms and Cl_2^- and thallium atoms.

II. EXPERIMENTAL PROCEDURE

Similar to the procedures described in earlier papers,[6,7] single crystals of KCl containing about 0.02-mole % AgCl or about 0.01-mole % TlCl were irradiated at 77 K with 50-kV x rays, from a Machlett tube with a tungsten target, or ~1.2-MeV ^{60}Co γ rays from a 4000-Ci source. The intensity of the luminescence emitted from the crystals was measured by an EMI 9558QB photomultiplier tube in conjunction with a Keithley 417 pico-ammeter. Emission spectra were measured with a scanning monochromator described elsewhere.[11]

Whenever polarized light was involved in an experiment, i.e., analyzing the luminescence or producing and measuring the anisotropy of the Cl_2^- band, an Ahrens calcite prism having an acceptance angle of about 30° and a 1-in.^{2} aperture was used.

III. EXPERIMENTAL RESULTS

A. Afterglow decay

Crystals of KCl:AgCl and KCl:TlCl were x rayed at 77 K for 1–5 sec at 10–50 mA and the intensity of the afterglow was followed as a function of time after the end of the x irradiation. Short irradiations were used to minimize the decay of luminescence during the irradiation period. Thin crystals were used to minimize the nonuniformity of the concentration of centers through the crystal. The conditions of the experiment were such that the lowest irradiation dose gave an afterglow intensity which could be followed for 4 to 5 h.

Figure 1 shows a plot of the afterglow data using coordinates indicated by Eq. (8). The ordinate is proportional to the product $tI(t)$ and the abscissa is proportional to t. This data will be discussed further in Sec. IV B.

B. Polarization of luminescence

Single crystals (5×8×13 mm) of KCl : AgCl and KCl : TlCl were irradiated at 77 K by ~1.2-MeV ^{60}Co γ rays. The crystals were then warmed to 130 K and excited with either $[0\bar{1}1]$ or [001] polarized 365-nm light propagated in the $[\bar{1}00]$ direction; this light is absorbed by Cl_2^- and leads to its preferential orientation into either the [011] or the [110] and $[\bar{1}10]$ directions, respectively (see Fig. 2). It should be

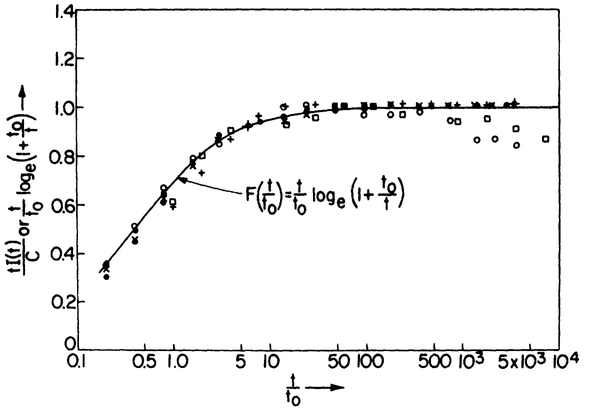

FIG. 1. Dependence of the intensity I (in arbitrary units) of the afterglow on the time t (in seconds) after the end of irradiation with x rays at 77 K. The solid curve shows the time dependence given by Eq. (8); the experimental data are normalized to fit Eq. (8) at $t/t_0 = 6$. The experimental points are (●), KCl : AgCl exposed to 50-kV, 50-mA x rays for 5 sec; (*x*), KCL : AgCl exposed to 50-kV, 10-mA x rays for 5 sec; (+), KCL : AgCl exposed to 50-kV, 50-mA x rays for 1 sec; (○), KCl : TlCl exposed to 50-kV, 50-mA x rays for 5 sec; (□), KCl : TlCl exposed to 50-kV, 50-mA x rays for 1 sec.

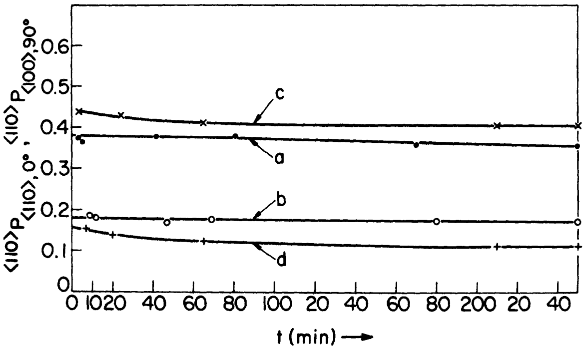

FIG. 3. Dependence, at 77 K, of the degree of polarization of the afterglow on t, the time after the Cl_2^- were oriented, for KCl : AgCl, (a) $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ and (b) $^{\langle 110\rangle}P_{\langle 100\rangle,90^\circ}$; KCl : TlCl, (c) $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ and (d) $^{\langle 110\rangle}P_{\langle 100\rangle,90^\circ}$.

pointed out that this excitation not only reorients the Cl_2^- but also releases trapped electrons from Tl^0 or Ag^0 to the conduction band causing a rapid decrease in concentration of Cl_2^- and metal atoms (these metal atom centers, M^0, have absorptions which overlap that of Cl_2^-); this effect is especially marked in the case of KCl: TlCl. The fact that a considerable loss of Cl_2^- and metal atoms occurs during light excitation is important for two reasons: (i) it limits, in a practical way, the degree to which the Cl_2^- can be preferentially oriented since the luminescence intensity also decreases rapidly and (ii) it accounts for the structure observed in the glow peak of the crystals treated in the above manner (see discussion of Fig. 4).

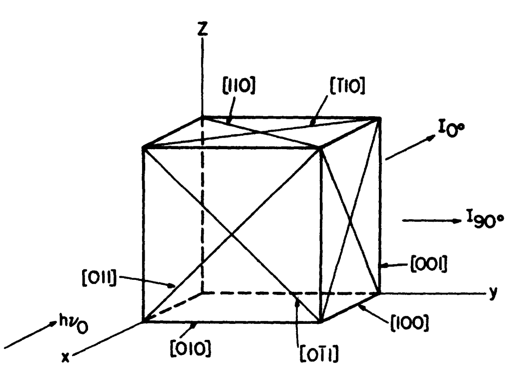

FIG. 2. Directions of propagation are shown of the (a) orienting light, $h\nu_0$, along [$\bar{1}$00], (b) afterglow luminenscence, I_{0°, along [$\bar{1}$00], and (c) afterglow luminescence, I_{90°, along [010]. The possible orientations of the Cl_2^- molecular axes are along the six ⟨110⟩ directions.

After excitation with [0$\bar{1}$1] light the intensity of the luminescence emerging from the rear of the crystal, I_{0°, (see Fig. 2) was resolved with an Ahrens prism into components having electric vector along [011], labeled $^{\langle 110\rangle}I_{\parallel,0^\circ}$, and along [0$\bar{1}$1], labeled $^{\langle 110\rangle}I_{\perp,0^\circ}$; thus the electric vector for $^{\langle 110\rangle}I_{\parallel,0^\circ}$ is parallel to the molecular axis of the preferentially oriented Cl_2^-. (The left superscript indicates the general direction of the electric vector of the exciting light used to produce polarization.) These two values are used to calculate the degree of polarization,

$$^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ} \equiv \frac{^{\langle 110\rangle}I_{\parallel,0^\circ} - {}^{\langle 110\rangle}I_{\perp,0^\circ}}{^{\langle 110\rangle}I_{\parallel,0^\circ} + {}^{\langle 110\rangle}I_{\perp,0^\circ}} .$$

The intensity of the luminescence emerging from the side of the crystal, I_{90°, is measured as components having electric vector along [001], labeled $^{\langle 110\rangle}I_{\parallel,90^\circ}$, and along [100], labeled $^{\langle 110\rangle}I_{\perp,90^\circ}$; these two values are used to calculate the degree of polarization, $^{\langle 110\rangle}P_{\langle 100\rangle,90^\circ}$.

After excitation with [001] polarized light, the intensities of the afterglow propagated along [$\bar{1}$00],

TABLE I. Initial values of $^{\langle 100\rangle}P_{\langle 100\rangle,0^\circ}$ for the afterglow obtained using orienting exposures at 365 nm similar to those used for the data of Fig. 3. The minimum values, during reversal, of $^{\langle 100\rangle}P_{\langle 100\rangle,0^\circ}$ were obtained about 2 h after the Cl_2^- has been oriented.

	$^{\langle 100\rangle}P_{\langle 100\rangle,0^\circ}$ Initial values	Minimum values
KCl : AgCl	+0.248	−0.115
KCl : TlCl	+0.432	−0.061

$^{\langle 100\rangle}I_{\parallel,0^\circ}$ with electric vector parallel to [010] and $^{\langle 100\rangle}I_{\perp,0^\circ}$ with electric vector parallel to [001], were used to calculate $^{\langle 100\rangle}P_{\langle 100\rangle,0^\circ}$.

Figure 3 shows the degrees of polarization, $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ and $^{\langle 110\rangle}P_{\langle 100\rangle,90^\circ}$ for KCl:AgCl and KCl:TlCl at 77 K as a function of time after orienting Cl_2^-; both are positive and decrease somewhat with time for both crystals, the decrease being more pronounced for KCl:TlCl. The value of $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ is greater in the case of KCl:TlCl than in the case of KCl:AgCl; whereas the reverse is true for $^{\langle 110\rangle}P_{\langle 100\rangle,90^\circ}$.[12] Table I shows that the initial values of $^{\langle 100\rangle}P_{\langle 100\rangle,0^\circ}$ are also positive. The fact that $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$, $^{\langle 110\rangle}P_{\langle 100\rangle,90^\circ}$, and $^{\langle 100\rangle}P_{\langle 100\rangle,0^\circ}$ are all positive shows that the electric vector of the dominant component of the polarized emission is parallel to the Cl_2^- molecular axis. The maximum initial values of the polarization of the afterglow which have been obtained are $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ} = +0.40$ for KCl:AgCl and $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ} = +0.57$ for KCl:TlCl. These values can be obtained only with a very high degree of orientation of Cl_2^-.

The polarization of the luminescence was also followed as a function of temperature. Figure 4 shows data for a KCl:TlCl crystal which had been irradiated at 77 K with ^{60}Co γ rays for 15 min, excited at 130 K for 2 min with 365-nm $[0\bar{1}1]$-polarized light, and then cooled to 77 K. The luminescence intensities, $^{\langle 110\rangle}I_{\parallel,0^\circ}$ and $^{\langle 110\rangle}I_{\perp,0^\circ}$, and $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ are plotted as a function of crystal temperature as the crystal is warmed at a rate of about 1.5 K per minute. The degree of polarization stays nearly constant up to the temperature range in which Cl_2^- begins to disorient[4] at an appreciable rate; as the temperature increases above 150 K the polarization decreases rapidly to zero at 170 K (the low-temperature foot of the glow peak), becomes negative, goes rapidly through a minimum and then gradually increases, going finally to zero near the maximum in the glow peak. The structure in the glow peak results from the 365-nm excitation (see glow curve in Ref. 7); this excitation probably favors the formation of some other species of trapped Cl_2^- with a somewhat different thermal stability. A comparison of the emission spectra during this glow peak, of bleached and unbleached crystals, reveals no differences within experimental error. Figure 5 shows similar data for a KCl:AgCl crystal which had been irradiated with ^{60}Co γ rays for 20 min and then was excited at 130 K for 20 min with 365-nm $[0\bar{1}1]$-polarized light. The behavior of the degree of polarization upon warming is very similar to that of KCl:TlCl discussed above.

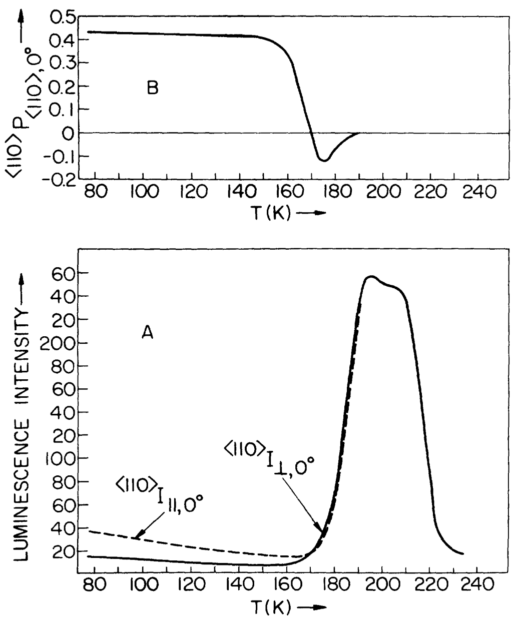

FIG. 4. (A) Plot of the intensities, $^{\langle 110\rangle}I_{\parallel,0^\circ}$ and $^{\langle 110\rangle}I_{\perp,0^\circ}$, as a function of temperature as the crystal is warmed. Before warming, the KCl : TlCl crystal containing Tl^0 and Cl_2^- centers had been excited at 130 K with $[0\bar{1}1]$-polarized 365-nm light. (B) Plot of $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ as a function of T.

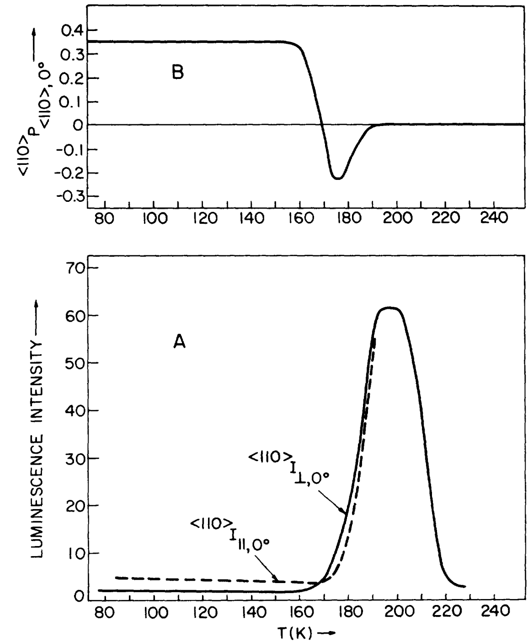

FIG. 5. (A) Plot of the intensities, $^{\langle 110\rangle}I_{\parallel,0^\circ}$ and $^{\langle 110\rangle}I_{\perp,0^\circ}$, as a function of temperature as the crystal is warmed. Before warming, the KCl : AgCl crystal containing Ag^0 and Cl_2^- centers had been excited at 130 K with $[0\bar{1}1]$- polarized 365-nm light. (B) Plot of $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ as a function of T.

Experiments similar to those described in the previous paragraph also show a reversal in sign

TABLE II. Dependence of the minimum value of P (during the reversal) on the length of time the Cl_2^- remain preferentially oriented.

${}^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ Initial values	Time Cl_2^- remained oriented (in min)	${}^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ Minimum values
	KCl : AgCl	
+0.377	10	−0.103
+0.375	37	−0.130
+0.375	350	−0.228
	KCl : TlCl	
+0.494	8	−0.056
+0.474	35	−0.099
+0.445	345	−0.138

of ${}^{\langle 110\rangle}P_{\langle 100\rangle,90^\circ}$ at about 170 K. In related experiments, warming of a crystal of KCl:AgCl or KCl:TlCl containing Cl_2^- which had been oriented by excitation with [001]-polarized 365-nm light also produces a reversal in the degree of polarization, ${}^{\langle 100\rangle}P_{\langle 100\rangle,0^\circ}$, near 170 K. Table I shows minimum values of ${}^{\langle 100\rangle}P_{\langle 100\rangle,0^\circ}$ obtained during the reversal.

Table II shows the dependence of the minimum value of ${}^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ (during the reversal of the polarization) on the time the Cl_2^- remain preferentially oriented. The strength of the reversal increases markedly with increasing time, at least during the first 6 h. A comparison of these data for KCl:AgCl and KCl:TlCl brings out the fact that the latter crystal, which shows a larger initial polarization, shows a much weaker reversal of the polarization.

Table III shows the relationship between the polarization of the afterglow and the anisotropy in the optical absorption at 360 nm for a KCl:AgCl crystal which had been irradiated at 77 K for 0.7 min with ^{60}Co γ rays. The purpose of the experiment was to investigate the relationship between the degree of orientation of Cl_2^- and the polarization of the afterglow. As the degree of preferential orientation of Cl_2^- increases (indicated by the increasing ratio of the optical densities taken with polarized light having electric vector in the [011] and [0$\bar{1}$1] orientations, respectively) the polarization of the afterglow increases, and as the Cl_2^- are disoriented by excitation in the 750-nm band[4] the polarization of the afterglow decreases. Qualitatively the connection is quite clear but we have not examined this

TABLE III. Relationship at 77 K between the degree of polarization of the afterglow and the optical absorption anisotropy (D is the optical density) at 360 nm in a KCl : AgCl crystal upon (A) orienting Cl_2^- at 130 K by excitation with ⟨110⟩ light in the 365-nm band and (B) disorienting Cl_2^- by excitation in the 750-nm band.

A

Excitation at 130 K with 365-nm [0$\bar{1}$1] light (in min)	$\frac{D_{[011]}}{D_{[0\bar{1}1]}}$ (at 360 nm)	${}^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$
$\frac{1}{2}$	1.54	+0.130
1.5	2.18	+0.222
2.5	2.65	+0.270
4.5	3.40	+0.329
7.5	3.64	+0.353

B

Excitation at 77 K with nonpolarized 750-nm light	$\frac{D_{[011]}}{D_{[0\bar{1}1]}}$ (at 360 nm)	${}^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$	Time after end of excitation (in min)
$\frac{1}{2}$	3.31	+0.275	2
		+0.306	6
1	2.87	+0.209	2
		+0.239	4
		+0.281	18
2	2.40	+0.052	2
		+0.107	4
		+0.206	21
5	1.63	−0.056	2
		0.000	6
		+0.078	33
17	1.04	−0.074	2
		−0.056	15
		−0.048	33

relationship quantitatively for the following reasons: (i) The M^0 bands overlap the Cl$_2^-$ 365-nm band making it difficult to estimate the Cl$_2^-$ contribution at a specific wavelength and therefore impossible to make an accurate determination of the degree of preferential orientation of the Cl$_2^-$; (ii) the reversal of the polarization of the luminescence upon disorientation (thermally or optically) of the Cl$_2^-$ adds another complication; and (iii) for a given degree of orientation of Cl$_2^-$ the degree of polarization is not time independent (Fig. 3).

If the Cl$_2^-$ are oriented by excitation at 77 K instead of 130 K, upon warming the crystal the first reversal of the polarization is observed as usual and at about 190 K a second weak reversal occurs which persists to about 205 K. For example, for data comparable to that shown in Figs. 4 and 5 a typical maximum value of P during this second reversal is $+0.04$ for KCl : TlCl and $+0.01$ for KCl : AgCl. The process responsible for the very small second reversal is separate and distinct from the processes giving rise to the large initial polarization and the first reversal; this conclusion is substantiated by two experiments: (1) As shown in Figs. 4 and 5, excitation at 130 K produces no second reversal, and (2) if, after orientation of Cl$_2^-$ in KCl : AgCl at 77 K, the crystal is immediately warmed to 175 K (Cl$_2^-$ disorient and the first reversal is minimized) for a period of about 10 min, P goes from the initial large positive value to a negative value and finally becomes $+0.04$ after cooling to 77 K; at this point in the experiment, an investigation of the optical absorption spectrum revealed no detectable anisotropy. Upon warming the crystal, P remains almost constant at $+0.04$ until it goes to zero at about 205 K. From these two experiments we conclude that a very large fraction of the electrons and holes are trapped as normal M^0 and Cl$_2^-$ and that it is these species which are responsible for the polarization effects shown in Figs. 4 and 5; a small fraction of the holes are trapped, perhaps as Cl$_2^-$ in an "abnormal" configuration which produces the small component of polarization which persists to 205 K.

IV. DISCUSSION

A. Mechanism producing the afterglow and the first glow peak

It is well established that at 77 K after exposure to ionizing radiation, KCl : AgCl and KCl : TlCl crystals contain Ag^0 and Cl$_2^-$ and Tl^0 and Cl$_2^-$, respectively[6–8]; they also show an afterglow with peaks in the emission spectrum at 530 nm for KCl : AgCl and 410 nm for KCl : TlCl. Although the afterglow can be measured for as long as one or two days in fairly heavily irradiated crystals there is a decay of less than 10% in the concentrations of metal atoms and Cl$_2^-$ during this period. The fact that Cl$_2^-$ is involved in the luminescence process is shown by the dependence of the polarization of the afterglow on the degree of preferential orientation of Cl$_2^-$. It seems reasonable that the other partner in the luminescence process is the metal atom and that luminescence occurs upon recombination of the electron from the metal atom with Cl$_2^-$. We propose that a radiative tunneling recombination occurs between nearby neighbor (M^0-Cl$_2^-$) pairs. These pairs are defined as a metal atom and the Cl$_2^-$ closest to it. The time dependence of the afterglow intensity is not a simple exponential but can be decomposed into a series of exponentials; we have observed components in the decay with lifetimes of less than 10^{-4} sec and greater than 10^5 sec. We have ascertained that the decay rate and the intensity of the afterglow are not functions of temperature in the range 4–77 K; thus the luminescence does not result from a thermally activated process. All of the above described properties are consistent with the proposal that the luminescence results from a tunneling recombination of the electron of the metal atom (6p electron of Tl^0 and 5s electron of Ag^0) with the hole of a nearby Cl$_2^-$ and that the tunneling probability depends strongly on the separation of the pair. The very fast decay times observed are associated with (M^0-Cl$_2^-$) pairs having small separation while the long decay is due to pairs with greater separation. Such an array of (M^0-Cl$_2^-$) pairs which annihilate by a tunneling process might be expected to yield a temperature-independent decay composed of a large number of simple exponentials, in agreement with observation. Most of the (M^0-Cl$_2^-$) pairs formed by the irradiation have a sufficiently large separation so that they are not destroyed during the time scale of our measurements.

Figure 6 shows an energy-level scheme for the ground states of Ag^0, Tl^0, and Cl$_2^-$ in KCl. From previous work[7] it was determined that the ground state of Tl^0 lies about 1.0 eV below the conduction

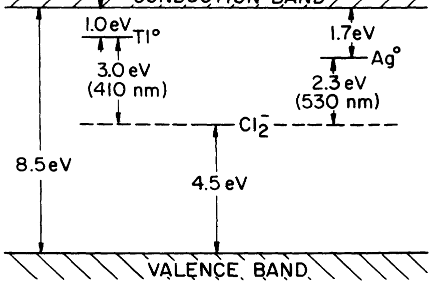

FIG. 6. An energy-level scheme for the ground states of Ag^0, Tl^0, and Cl$_2^-$ in KCl.

band in KCl. We propose that the energy of the emitted radiation in the tunneling recombination luminescence is just the difference between the energies of the Tl^0 and Cl_2^- levels, namely, 410 nm or 3.0 eV. Since the band gap in KCl is 8.5 eV, this proposal requires that the ground state of Cl_2^- lies 4.5 eV above the valence band. Gilbert[13] has estimated that both the $^2\Sigma_g$ and $^2\Sigma_u$ levels of Cl_2^- lie in the band gap. Since the energy of the transition $^2\Sigma_u \rightarrow {}^2\Sigma_g$ is about 3.4 eV, his estimate places the ground state of Cl_2^-, $^2\Sigma_u$, a minimum of 3.4 eV above the valence band, which is not inconsistent with the above estimate using the luminescence energy. Once having located the position of the Cl_2^- level we can estimate the position of the ground state of Ag^0. Recombination luminescence in KCl : AgCl peaks at 530 nm or 2.3 eV, which places the ground state of Ag^0 1.7 eV below the conduction band. From earlier work[6] we believe that the Ag^0 lies less than 2.9 eV below the conduction band. The thermoluminescence peaks[6,7] caused by the instability of Ag^0 and Tl^0 are at about 350 and 300 K, respectively, which indicates that Ag^0 is more stable thermally than Tl^0 in KCl; these facts place the ground state of Ag^0 below Tl^0, which is consistent with the energy-level diagram. In this energy-level diagram we are concerned with the ground state of isolated M^0 and Cl_2^-; we assume that these ground states are inappreciably perturbed, at least for those (M^0-Cl_2^-) pairs which have lifetimes greater than 10 sec. We believe that this approximation is rather good since (a) the afterglow spectrum shows no detectable change over the time period we were able to measure it (10 sec to several hours),[14] and (b) an estimate we have made from the maximum number of centers which can be produced in a KCl : AgCl crystal suggests that the tunneling we observe occurs over distances of about two to six lattice constants.

Upon warming either a KCl : AgCl or KCl : TlCl crystal which had been irradiated at 77 K the afterglow emission shifts slightly and continuously to longer wavelength, there being no discontinuity upon coming into the glow peak at about 200 K. Cl_2^--molecule ions disorient with a half-life of somewhat less than 2 min at 170 K and begin to migrate through the lattice jump by jump, faster and faster as the temperature increases; they all disappear during the first glow peak. The Ag^0 and Tl^0 are thermally stable in this temperature range and so we conclude that the glow peak arises from mobile Cl_2^- wandering into the neighborhood of an Ag^0 or Tl^0 with resultant electron-hole recombination producing the luminescence. (A large fraction of the migrating Cl_2^- are also destroyed by combination with Ag^+ or Tl^+ to produce Ag^{++} or Tl^{++},[6,7] respectively, and do not yield any luminescence in the observed region of the spectrum.) Since the emission spectra of the afterglow and the glow peak are identical, within experimental error, we conclude that the same tunneling process is responsible for both.[15]

The low-temperature edge of the glow peak occurs at a temperature where Cl_2^- is becoming thermally unstable and is beginning to migrate or jump through the lattice; the lifetime of Cl_2^- in a particular position and orientation is long at this temperature and decreases as the temperature increases. This increase in the jumping rate of the Cl_2^- increases the concentration of Cl_2^- which are within tunneling distance of metal atoms and therefore increases the luminescence intensity without changing the emission spectrum and gives rise to the glow peak.

Experiments show that neither the intensity nor the decay rate of the afterglow change on cooling from 77 to 4.2 K; thus the efficiency of luminescence must be constant over the temperature range. On the other hand, the efficiency of luminescence in KCl : AgCl at 77 K is about 25 times larger than the average efficiency during the glow peak; we also find that the efficiency decreases with increasing temperature in the temperature range of the glow peak. The comparison of luminescence efficiences of the afterglow and the glow peak is meaningful since we believe the same tunneling process is responsible for the luminescence in both cases. Thus the efficiency appears to decrease rapidly in the temperature region where the Cl_2^- mobility increases rapidly; this decreasing efficiency may result from the decreasing lifetime (time between jumps) of Cl_2^-.

Kabler,[16-18] Murray and Keller,[19] and Pooley and Runciman[20] have studied a different kind of recombination luminescence involving the V_K centers. They observed that at a sufficiently low temperature the recombination of electrons from the conduction band with V_K centers results in the emission of trapped-exciton luminescence. This luminescence generally consists of two bands; the short wavelength band is σ polarized and the long wavelength band is π polarized. In KCl only the π polarized component of the exciton emission is observed, however, at temperatures above about 20 K it is strongly quenched. The spectrum of the exciton emission in KCl is close to that of the afterglow in KCl : AgCl (but much different from that of the afterglow in KCl : TlCl). In NaCl the exciton emission spectrum is measurably different from that of the afterglow of NaCl : AgCl.

Although the spectra of the exciton emission and the afterglow in KCl : AgCl are very similar, other evidence shows that these emissions do not result from transitions between the same two states. The exciton emission is π polarized while the afterglow is σ polarized and the exciton emission is quenched at temperatures above 20 K whereas the afterglow efficiency is essentially temperature independent between 4.2 and 77 K.

B. Qualitative analysis of the time dependence of the afterglow at 77 K

The probability per second, $p(R)$, of the radiative tunneling recombination of the electron at a neutral impurity atom (Ag^0 or Tl^0) and the positive hole at a Cl_2^- center, separated by distance R, is assumed to be a rapidly decreasing function of R, behaving like

$$p(R) = \frac{1}{\tau}\, e^{-2\alpha R}\,, \tag{1}$$

at least within a small range of ΔR ($\ll R$). It should be those pairs of centers with the smallest separation R which are responsible for the afterglow, in view of the fact that only a small fraction (less than 10%) of these centers are observed to decay. Let us start, for simplicity, from the initial condition (just after x-ray irradiation) that the neutral impurity atoms and Cl_2^- centers are distributed completely at random with concentration N_0. The concentration of nearest-neighbor pairs of these two kinds of centers, having a separation in the interval (R, $R+dR$) is then given by

$$n(R) = N_0^2\, 4\pi R^2 dR\,, \tag{2}$$

as long as $N_0 R^3 \ll 1$ (otherwise, one would have to consider the factor $[\exp(-4\pi N_0 R^3/3)]^2$ in order to exclude the possibility that the pair is not the nearest-neighbor one).

These close-by pairs are expected to decay with the rate $p(R)$ without being much influenced by the existence of other centers situated more distant, in view of the R dependence of $p(R)$ mentioned above. The concentration of the pairs surviving at time t is then given by

$$n(R, t) = N_0^2\, e^{-p(R)t}\, 4\pi R^2\, dR\,. \tag{3}$$

For large t ($\gg \tau$), Eq. (3) has a fairly sharp step at $R = R_c(t)$ defined by

$$p(R_c)t = 1\,. \tag{4}$$

The width of the step, which is of the order of α^{-1}, is much smaller than

$$R_c(t) \sim (2\alpha)^{-1} \ln(t/\tau)\,, \tag{5}$$

since τ is assumed to be of the order of 10^{-9} sec while t, the time of measurement, is larger than the order of a second. This means that sweeping of pairs proceeds with a well-defined frontier $R_c(t)$ as time goes on, if the ensemble of pairs is considered as a function of R. It should be noted that the frontier proceeds very rapidly in the initial stage but more and more slowly as time goes on. For instance, from $t = 3$ min to $t = 300$ min, the increase in R_c is only 17% as large as the increase between $t \sim 0$ and $t = 3$ min.

The intensity of the afterglow per unit volume, $I(t)$, is proportional to

$$\int \left(-\frac{dn(R, t)}{dt}\right) = \int N_0^2 p(R)\, e^{-p(R)t}\, 4\pi R^2\, dR\,. \tag{6}$$

Noting that the main contribution comes from a narrow region around the maximum point of $p(R)e^{-p(R)t}$, namely, $R = R_c(t)$, given by Eq. (4), we can extract the slowly varying factors outside the integral, to get

$$\begin{aligned} I(t) &= -t^{-1} A \left[4\pi R^2 N_0^2 \left(\frac{d}{dR} \ln p(R)\right)^{-1}\right]_{R=R_c(t)} \\ &= t^{-1} A \left[8\pi R^2 N_0^2 \alpha\right]_{R=R_c(t)}\,. \end{aligned} \tag{7}$$

In this way, $tI(t)$ is given as a function of the frontier radius $R_c(t)$, where A is a proportionality constant. One can expect that $tI(t)$, and perhaps also the degree of polarization, will remain constant for a fairly wide time interval during which $R_c(t)$ changes by a small fraction, as mentioned above.

We now discuss the fact that the experimental values of $tI(t)$ are not constant during the initial stage ($t < 1$ min) of the afterglow. In the above argument, it was assumed that all the pairs were created at the same instant $t_0 = 0$. Actually, however, the x-ray irradiation was continued for a finite duration t_0 (1 or 5 sec), while t was measured from the end of this irradiation. We can use Eq. (7), $I(t) \sim C/t$, only if $t \gg t_0$. Since the pairs are created with a constant rate during the time interval $-t_0 < t < 0$, we must integrate (average) over the compiled initial conditions in order to obtain the exact afterglow curve:

$$I(t) = \frac{C}{t_0} \int_{-t_0}^{0} \frac{dt'}{t - t'}\,,$$

therefore,

$$tI(t) = C\,\frac{t}{t_0} \ln\left(1 + \frac{t_0}{t}\right) \equiv CF\left(\frac{t}{t_0}\right)\,. \tag{8}$$

The quantity $tI(t)$ tends to C for $t \gg t_0$ (this situation corresponds to the one already discussed) but it deviates from a constant value when $t \lesssim t_0$. A plot to t/t_0 versus the properly normalized experimental values of $tI(t)$ is expected to fit the theoretical $F(t/t_0)$ curve. The comparison is made in Fig. 1, where the full line is the theoretical curve. The fitting of the ordinate was made at $t/t_0 = 6$. The agreement is satisfactory, at least qualitatively.

In this way, we can conclude that the shapes of the afterglow curves as well as the approximate constancy of the degree of the polarization are quite consistent with the radiative tunneling process. One must assume the pre-exponential time constant τ to be of the order of 10^{-8} sec or smaller, in order to assure the constancy of $tI(t)$. In order to explain the polarization reversal phenomena, it would be necessary to take into account the angular dependence (see Sec. IV C) of the recombination probability p, but this will not change the essential points of the above argument.

C. Polarization of the afterglow and its reversal

The results of the polarization experiments which have been described make it clear that the polarization of the afterglow is made observable by the preferential orientation of Cl_2^-; increasing the degree of orientation of Cl_2^- increases P, and either thermal or optical disorientation causes a decrease in P. It is concluded that the polarization of the emission resulting from the decay of a given $(M^0\text{-}Cl_2^-)$ pair is at least primarily determined by the orientation of the Cl_2^- molecular axis; the slight decrease of P with time at 77K, (Fig. 3) suggests that P also may depend somewhat on the distance separating the $(M^0\text{-}Cl_2^-)$ pairs which are being annihilated. The higher values of $^{\langle 110\rangle}P_{\langle 110\rangle,0^\circ}$ and $^{\langle 100\rangle}P_{\langle 100\rangle,0^\circ}$ (Fig. 3 and Table I) which are consistently observed for KCl : TlCl crystals are not to be attributed to the higher degree of orientation of Cl_2^- in this crystal, but are to be attributed to the fact that the polarization of the $(Tl^0\text{-}Cl_2^-)$ emission is inherently higher. (We believe that the degree of orientation of Cl_2^- is appreciably higher in the KCl : AgCl crystals because of the longer allowable excitation time with the orienting light.) If we assume that the emission consists of three components σ (along $\langle 110\rangle$ and parallel to the Cl_2^- molecular axis), π_1 (along $\langle 110\rangle$ and perpendicular to the molecular axis), and π_2 (along $\langle 100\rangle$ and perpendicular to the molecular axis), we can conclude from the data in Fig. 3 and Table I that the σ component predominates for both $(Tl^0\text{-}Cl_2^-)$ and $(Ag^0\text{-}Cl_2^-)$ recombination and that the ratio of the transition strengths σ/π_1 is greater for $(Tl^0\text{-}Cl_2^-)$ recombination. We have been unable to determine accurately the population distribution of the preferentially oriented Cl_2^- among the six $\langle 110\rangle$ directions in these crystals; however, a rough analysis of our results indicates that for

$$(Tl^0\text{-}Cl_2^-)\text{ emission: } \sigma \approx 10\,\pi_1, \quad \pi_1 \approx \pi_2,$$

and for

$$(Ag^0\text{-}Cl_2^-)\text{ emission: } \sigma \approx 3\,\pi_1, \quad \pi_1 \approx \pi_2.$$

We suggest that the reversal of the luminescence polarization near 170 K results from anisotropic tunneling between $(M^0\text{-}Cl_2^-)$ pairs after the Cl_2^- have been oriented; the tunneling probability per unit time is assumed to depend on the angle θ between the Cl_2^- molecular axis and the $(M^0\text{-}Cl_2^-)$ line of centers. For example, considering a given pair separation, if it is arbitrarily assumed that the tunneling probability is high when θ is small [Fig. 7(A)] and is low when θ is near 90° [Fig. 7(B)], then some time after the preferential orientation of the Cl_2^-, configuration B will predominate among the close pairs. Upon warming to a temperature where Cl_2^- can disorient, the Cl_2^- in configuration B can, through a succession of 60° jumps, rotate 90° in the plane of the paper to produce configuration A. In this configuration the tunneling probability is much increased and the luminescence intensity increases but now the dominant σ component, which is determined by the orientation of the molecular axis, is rotated by 90° and this emission would contribute to a reversal of P. This model can be used to understand the change in afterglow polarization whenever the Cl_2^- are disoriented, whether the disorientation results from thermal processes or from optical excitation (see Table III, Part B).

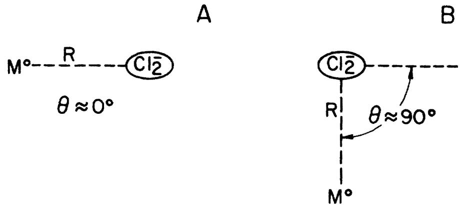

FIG. 7. Examples of $(M^0\text{-}Cl_2^-)$ pair configurations which are proposed to have different probabilities for tunneling recombination.

The data in Tables I and III show that the reversal of the polarization, upon disorientation of Cl_2^-, is stronger in the case of KCl : AgCl than in the case of KCl : TlCl, and this is in spite of the fact that the initial degree of polarization and the intrinsic σ character are greater in the latter case. This observation indicates a more anisotropic tunneling probability in the case of $(Ag^0\text{-}Cl_2^-)$ recombination.

Preferential orientation of Cl_2^- in NaCl : AgCl and Br_2^- in KBr : AgBr also has been found to yield a partially polarized afterglow with the electric vector of the dominant component parallel to the molecular axis of the oriented halogen-molecule ion; upon warming these crystals, a reversal in the polarization at the low-temperature foot of the glow peak has also been observed. This general behavior probably also occurs in other alkali halides where the Ag^+ and Tl^+ ions are good electron traps.

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[14] A combination of rapid decay, low intensity, and broad emission bands, especially in the case of KCl : AgCl, makes it difficult to estimate the peaks of these bands to better than 0.2 eV.

[15] The case of (Tl^0-Cl_2^-) tunneling recombination is a bit more complicated in that two emission bands occur in the glow peak (Ref. 8). On the low-temperature side of the glow peak only the 410-nm band occurs but as the temperature is raised, a second band at 298 nm appears and grows relative to the 410 band. Excited Tl^+ ions in the ${}^3P_1$ state are known to emit at 298 nm. We believe that the 298-nm emission during the first glow also arises from tunneling between a Tl^0 and a nearby Cl_2^-, but in this case a $6s$ electron of Tl^0 recombines with the Cl_2^- (this process involves a thermally activated step) and results in a Tl^+ in an excited state, $6s6p\,{}^3P_1$, from which 298-nm emission occurs (Ref. 8).

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