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Tunneling-recombination luminescence between Ag^0 and Ag^{2+} in KCl:AgCl

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Appropriate treatment of a KCl:AgCl crystal results in the trapping of electrons as silver atoms, Ag^0, and positive holes as $AgCl_4{}^{2-}$, Ag^{2+}, centers. Optical excitation of Ag^0 in such a crystal at $T < 90$ K produces a luminescence which lasts for many hours after the excitation. Evidence is presented which indicates that this afterglow results from electron-hole tunneling recombination between nearby Ag^0 and Ag^{2+} pairs, similar to the Ag^0-$Cl_2{}^-$ tunneling-recombination studies we previously reported. We have shown that Ag^{2+} centers are involved in the emission process by preferentially orienting the anisotropic Ag^{2+} at 6 K by excitation with polarized light and observing that the afterglow is polarized. Upon warming to 50 K, where the preferentially oriented Ag^{2+} can change orientation, a strong reversal in the degree of polarization occurs which finally decays to zero. The characteristics of this luminescence can be understood if we assume: (i) a tunneling-recombination mechanism in which the orientation of the electric vector of the emitted radiation depends on the position of the Ag^0 relative to the Ag^{2+} and (ii) the tunneling is anisotropic and depends on the location of the Ag^0 relative to the anisotropic Ag^{2+}. The latter assumption is based on the tetragonal (d-like) symmetry of the Ag^{2+} complex. Good quantitative agreement between theory and experiment has been obtained on the decay kinetics, the degree of polarization, and the polarization reversal.

I. INTRODUCTION

After a crystal of KCl:AgCl has been exposed at 77 K to ionizing radiation, luminescence is observed from the unwarmed crystal, which decays with time but can be detected for many hours after the ionizing radiation source is removed. The intensity and rate of decay, which does not follow a single exponential, have been shown to be independent of temperature,[1] over the range 6–77 K. These facts show that the luminescence does not arise from a thermally activated process. It has been proposed[1] that this luminescence results from electron-hole tunneling recombination between nearby Ag^0 and $Cl_2{}^-$ separated by different distances; in this case the electrons produced by ionizing radiation are trapped by Ag^+ to form Ag^0 and the holes are self-trapped as $Cl_2{}^-$. When the $Cl_2{}^-$ are preferentially oriented by optical means, the tunneling recombination luminescence has a measurable polarization.[1]

Osminin[2] and Osminin and Zazubovich[3] have reported a long-lasting luminescence which they have attributed to a bound excited state of Ag^0 in KCl. This luminescence has some properties which are very similar to those of the Ag^0-$Cl_2{}^-$ tunneling recombination luminescence. In the following sections we shall show that the luminescence attributed to an excited state of Ag^0 is, in fact, another example of electron-hole tunneling recombination, but in this case the hole is trapped as Ag^{2+} and the electron as Ag^0.

II. EXPERIMENTAL PROCEDURE

Single crystals containing about 0.02 mol% AgCl, grown from the melt by the Kyropolous method, were exposed at 77 K to ~1.2-MeV ^{60}Co γ rays from a 6000-Ci source. The optical absorption spectra of the crystals were measured with a Cary 14 R specrophotometer. An afterglow was excited by using an EIMAC VIX-300 Xe arc lamp plus appropriate filters. The luminescence emitted from the crystals was detected by an EMI 9658 R photomultiplier tube; the signal from the photomultiplier tube was fed into a Keithley 417 picoammeter whose output was recorded on a strip chart. Emission spectra were measured with a scanning monochromator described elsewhere[4] using a grating blazed at 500 nm. An Ahrens calcite prism, with an acceptance angle of about 30° and 1-in.^{2} aperture, was used to analyze the luminescence or to produce and measure the anisotropy in the Ag^{2+} absorption bands.

III. EXPERIMENTAL RESULTS

A. Afterglow decay

Crystals of KCl:AgCl were exposed to γ rays at 77 K for 0.5–2 min, warmed to 250 K in the dark for about 2 min, and then cooled to 77 K. After this treatment the crystal contains Ag^0 and Ag^{2+} (see Sec. IV of Ref. 5). Excitation of the crystal at 77 or 6 K with light absorbed by the Ag^0 band, which peaks at 425 nm, redistributes trapped electrons among the silver impurities in the crystal and produces an afterglow. Figure 1(a) shows a plot of the logarithm of the intensity I of the afterglow at 6 K as a function of the logarithm of the time after the end of a 30-sec exposure at 6 K to 490-nm light. The data can be approximately fitted to a straight line but show undulations about the straight line which are both marked and reproducible. It is obvious from Fig. 1(a) that the afterglow does not follow a simple exponential decay, but much more closely an $I \propto t^{-0.9}$ law.

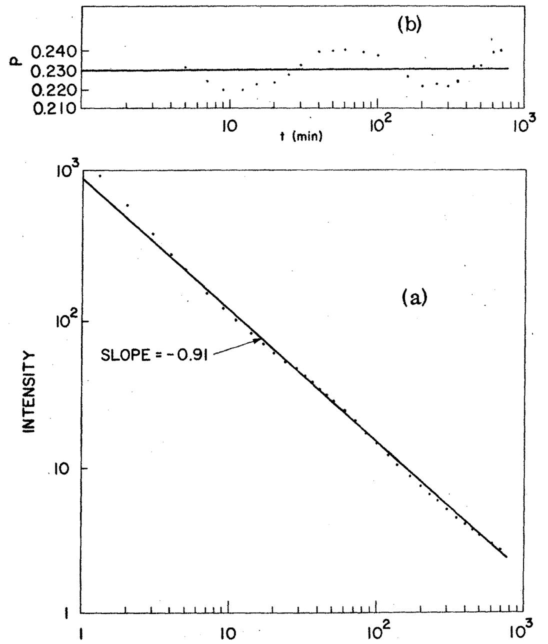

FIG. 1. (a) Intensity of the afterglow, in arbitrary units, is plotted as a function of time at 6 K for a KCl:AgCl crystal which had been exposed to 0.8 min γ rays at 77 K, then warmed to 250 K for 2 min, and finally excited for 30 sec at 6 K with 490-nm light. (b) This crystal was then excited at 6 K for 3 min with [001] polarized 641-nm light followed by 1.5 min with [001] polarized 490-nm light. The degree of polarization P of the afterglow at 6 K is plotted as a function of time on the same scale.

B. Polarization of luminescence and anisotropic tunneling

When a crystal at 6 K containing Ag^0 and Ag^{2+} is excited with [001] polarized light propagated along [010] and absorbed by the 630- or 460-nm band (both are π transitions[5]) of Ag^{2+}, the Ag^{2+} complexes can be oriented[5] such that almost all of them have the fourfold symmetry axis along the [001] direction (see Fig. 2); subsequent excitation of Ag^0 results in an afterglow which is polarized. Figure 1(b) shows data for such a crystal in which the Ag^{2+} were preferentially oriented by exciting with 641-nm [001] polarized light and then Ag^0 was excited with 490-nm [001] light (which also improved slightly the preferential orientation of Ag^{2+}). The degree of polarization of the luminescence,

$$P \equiv \frac{I_{[100]} - I_{[001]}}{I_{[100]} + I_{[001]}} = \frac{I_x - I_z}{I_x + I_z},$$

where the subscripts indicate the orientation of the electric vector of the light detected, is plotted as a function of time after the end of the second excitation. P is observed to be nearly constant at about 0.23 but goes through maxima at times which correspond to an undulation above the straight line in Fig. 1(a), and through minima at times which correspond to an undulation below that straight line.

The degree of polarization of the afterglow was

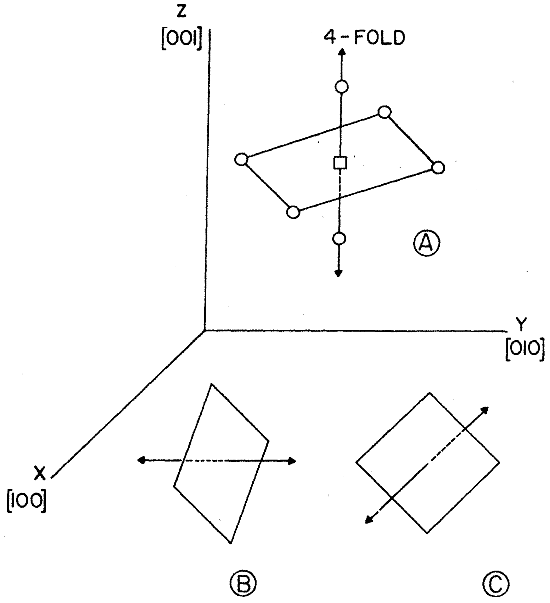

FIG. 2. The x, y, z coordinates, the ⟨100⟩ directions of the crystal, and the model of the Ag^{2+} center and its three possible orientations. The square indicates the silver and the circles the nearest-neighbor chlorines in the KCl lattice.

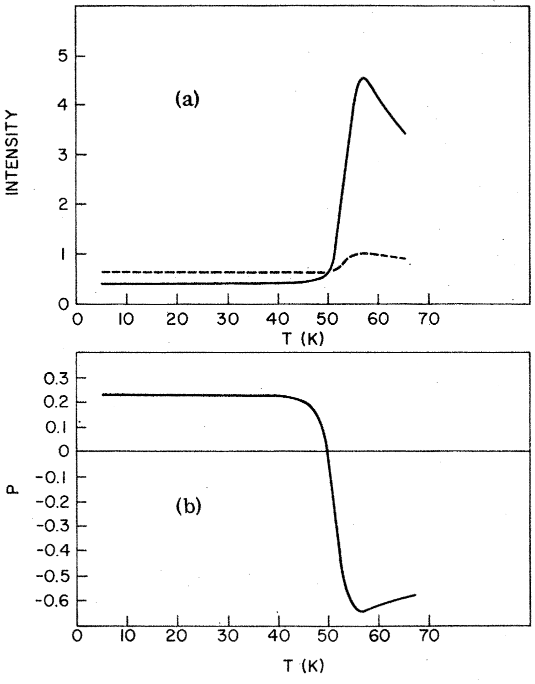

FIG. 3. KCl : AgCl crystal containing Ag^0 and preferentially oriented Ag^{2+} centers was excited for 2.5 min with [001] polarized 490-nm light at 6 K and then allowed to stand in the dark at 6 K for 3 h. After this "aging time" the crystal was warmed at a rate of 6 K per min and I_x and I_z were measured. (a) shows a plot of I_x (dashed line) and I_z (solid line), in arbitrary units, and (b) shows the degree of polarization as a function of T.

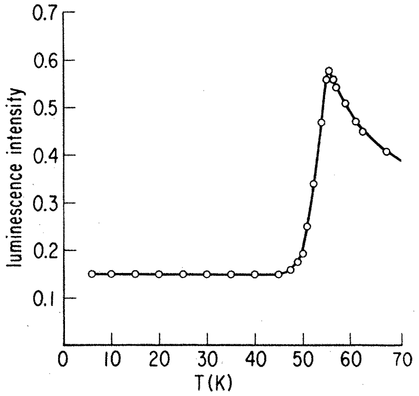

FIG. 4. Results for a crystal treated similarly to that of Fig. 3 *except* that the Ag^{2+} had not been preferentially oriented and the excitation was with unpolarized light. The intensity of the afterglow, in arbitrary units, is plotted vs T.

also followed as a function of temperature. Figure 3 shows data for a crystal containing Ag^0 and preferentially oriented Ag^{2+}; before warming, this crystal was allowed to stand at 5 K in the dark for an "aging time" of 3 h after Ag^0 excitation took place. The term "aging time" is defined as the time between initiation of the afterglow by Ag^0 excitation, during which time the crystal is in the dark at a fixed temperature, and some subsequent treatment. Figure 3(a) shows a plot of I_x and I_z versus temperature. As the crystal is warmed at a rate of about 6 K/min, as shown in Fig. 3(b), P stays constant at 0.23 until, at about 45 K, it begins to drop sharply. Above 45 K the Ag^{2+} reorients[5] at a rate which increases very rapidly with T; as the concentrations of Ag^{2+} in the three orientations approach equality, the degree of polarization goes to zero, reverses sign, and finally passes through a minimum of -0.63 at about 57 K. Above about 60 K the reorientation rate is sufficiently rapid that the course of the polarization does not depend on further warming, but it depends on time; P approaches zero as time increases. The strength of the reversal in P increases directly with the degree of initial orientation of Ag^{2+}, with the "aging time," and with the rate of warmup. As will be demonstrated in Sec. V A, these effects which have been described arise from the anisotropic tunneling between nearby Ag^0-Ag^{2+} pairs, and from the fact that the luminescence from an Ag^0-Ag^{2+} pair is polarized.

The effect of this anisotropic tunneling can also be seen in a crystal which does not contain preferentially oriented Ag^{2+}. When a crystal containing Ag^0 and Ag^{2+}, populating equally the three $\langle 100\rangle$ directions, is excited at 6 K with nonpolarized light absorbed by the Ag^0 band, the afterglow is stimulated. If the crystal remains at 6 K for an "aging time" of 3 h and is then warmed at a rate of 6 K/min, the results shown in Fig. 4 are obtained. The afterglow intensity drops slowly until about 45 K where it begins to rise through a maximum at about 55 K, and then decays.

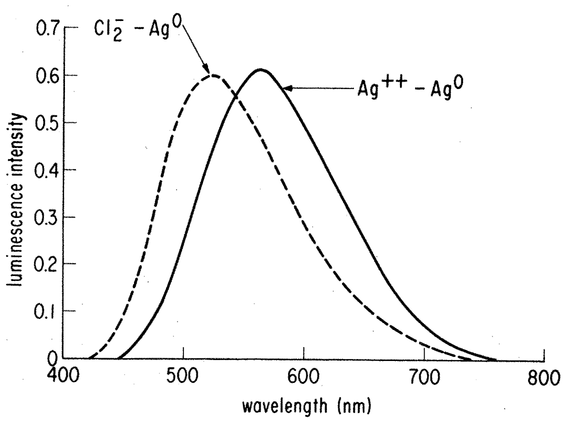

FIG. 5. Uncorrected emission spectra of the Ag^0-Cl$_2^-$ and the Ag^0-Ag^{2+} afterglows.

C. Emission spectra

The uncorrected emission spectra of the Ag^0-Cl_2^- tunnel emission afterglow and the Ag^0-Ag^{2+} tunnel emission afterglow, taken with the same equipment and under the same conditions, are shown in Fig. 5. The Ag^0-Ag^{2+} emission is clearly displaced to long wavelength and is distinct from the Ag^0-Cl_2^- emission. The full width at half-height of these two emissions is about 0.5 eV. No measureable change in the spectral characteristics has been observed from 1 min to 3 h after the generation of the afterglow.

IV. DISCUSSION

After a KCl:AgCl crystal is exposed at 77 K to γ rays a persistent afterglow is observed which has the spectral characteristics shown by the dashed curve of Fig. 5. This luminescence has previously been shown to arise from tunneling recombination between nearby pairs of Ag^0 and Cl_2^-. After an "aging time" of several hours at 77 K, this luminescence has decayed about two orders of magnitude because those pairs having the shortest lifetimes are destroyed; however, the luminescence can be regenerated by excitation with light absorbed in the 425-nm Ag^0 absorption band. Excitation in this Ag^0 absorption band produces, with high quantum yield, electrons in the conduction band:

$$Ag^0 \xrightarrow{h\nu_{425}} Ag^+ + e^- . \qquad (1)$$

These electrons are then captured by either Ag^+ or Cl_2^-:

$$e^- + Cl_2^- \rightarrow 2Cl^- , \qquad (2)$$

or

$$e^- + Ag^+ \rightarrow Ag^0 . \qquad (3)$$

Since the concentration of Ag^+ in these experiments is much greater than the concentration of Cl_2^-, reaction (3) predominates. Thus the light excitation causes a spatial redistribution of Ag^0, some of which now will be close to Cl_2^-, and results in a regeneration of the afterglow.

On the other hand, when the crystals are exposed at 77 K to γ rays, warmed to 250 K, cooled to 77 K, and then excited with light absorbed in the Ag^0 band, an afterglow is generated which has the emission spectrum shown by the solid curve in Fig. 5. This emission spectrum is different from that of the Ag^0-Cl_2^- afterglow. Warming the crystal to 170 K causes Cl_2^- to diffuse slowly through the crystal. As the temperature is raised further this diffusion rate increases and by 250 K the following reactions[5] have occurred:

$$Cl_2^- + Ag^0 \rightarrow 2Cl^- + Ag^+ + \text{luminescence} , \qquad (4)$$

$$Cl_2^- + Ag^+ \rightarrow Ag^{2+} + 2Cl^- . \qquad (5)$$

Again because the concentration of Ag^+ is much greater than that of Ag^0, reaction (5) predominates and a large fraction of the Ag^0 is preserved. Thus, after this thermal treatment, the crystal contains equal concentrations of Ag^0 and Ag^{2+} and no Cl_2^-. Excitation of Ag^0 in such a crystal at 77 K cannot yield Ag^0-Cl_2^- emission since no Cl_2^- is present; however, redistribution of Ag^0 will occur but in this case some Ag^0 will be close to Ag^{2+}. We propose that the luminescence generated results from electron-hole tunneling recombination between nearby Ag^0-Ag^{2+} pairs, similar to the case of Ag^0-Cl_2^- pairs, but the trapped hole is Ag^{2+} instead of Cl_2^-.

Osminin[2] and Osminin and Zazubovich[3] have attributed the emission generated as described in the above paragraph to a long-lived bound excited state of Ag^0. However, several of our experimental results are in disagreement with this assignment:

(i) The afterglow can only be generated when Ag^{2+} is present.

(ii) The afterglow does not have a simple exponential decay which would be characteristic of a single excited state.

(iii) The afterglow only shows polarization when Ag^{2+} has been preferentially oriented by excitation with polarized light; therefore, Ag^{2+} must be involved in the luminescence process.

Figure 1 shows a plot of afterglow intensity versus time at 6 K. The intensity and rate of decay are independent of temperature up to 40 K and only very minor changes are observed to temperatures above 77 K. Thus, the process responsible for the luminescence is not thermally activated. The three characteristics of the luminescence listed above and the additional fact that (iv) the afterglow is not the result of a thermally activated process, are consistent with the proposal that the emission results from tunneling recombination between Ag^0-Ag^{2+} pairs.

V. ANISOTROPIC TUNNELING AND POLARIZATION OF THE AFTERGLOW

A. Arguments leading to a model

In this section we address physical arguments leading to a model with which we can calculate some of the salient features of the afterglow. In order to understand some of the features of the polarization we will consider some properties of Ag^{2+} which have already been reported.[5] Ag^{2+} has the electron configuration $4d^9$. Since the Ag^{2+} ion is substituted for a K^+ ion in the lattice it is nominally surrounded by octahedral symmetry. Under these conditions the $4d$ hole level is split into a doublet and a triplet with a doublet lower in en-

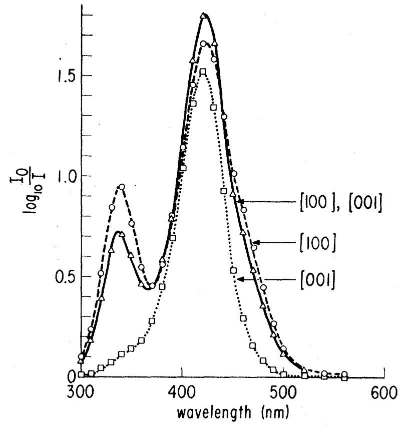

FIG. 6. Absorption spectra taken with [100]– and [001]-polarized light of a KCl:AgCl crystal containing Ag^0 and Ag^{2+} centers at 6 K. The solid curve shows spectra with randomly oriented Ag^{2+} centers. Spectra taken after the Ag^{2+} centers had been preferentially oriented by exciting at 6 K with [001] polarized 460-nm light are shown, dashed and dotted, when measured with [100] and [001] polarized light, respectively.

ergy. The degeneracy in the ground state is removed by a Jahn-Teller distortion involving a small inward displacement of four chlorines in a plane and a small outward displacement of the other two chlorines. The ESR spectra of Ag^{2+} indicate that the hole on the Ag^{2+} is primarily shared by the silver and the four chlorines which have moved inward, and to first approximation is not shared by the other two chlorines. The complex, which can be approximated by $AgCl_4^{2-}$, has tetragonal symmetry with a fourfold axis along the two chlorines which are extended along the z axis, see Fig. 2(a). Optical studies have shown that absorption bands at 340, 460, 560, and 630 nm belonging to Ag^{2+} are all quite anisotropic and are π polarized, i.e., the transitions are allowed for light with electric vector perpendicular to the fourfold axis. Under a normal distribution, equal numbers of complexes have their fourfold axis along the three ⟨100⟩ directions of the crystal. However, at 6 K, it has been shown that excitation of Ag^{2+} with polarized light can cause a redistribution of these fourfold axes so that they are almost all pointed along a single ⟨100⟩ direction. The optical anisotropy shown in Fig. 6 results from the preferential orientation of Ag^{2+} so that their fourfold axes are along [001].

It has also been shown that this Ag^{2+} anisotropy will persist if the crystal is kept at sufficiently low temperatures. However, if the crystal is warmed to 50 K the anisotropy is soon lost since the thermal energy causes the fourfold axis of the Jahn-Teller distortion to hop among the three possible ⟨100⟩ directions. The center of gravity of the hole stays on the Ag^{2+} but the bonds of the four chlorines that share the hole are broken causing the square planar complex to hop among the orientations A, B, and C of Fig. 2.

After most of the Ag^{2+} have been aligned into orientation A, the crystal is excited with light absorbed by Ag^0 to produce an afterglow. Using a photomultiplier and analyzing prism to observe the light emitted in the y direction, we observe that the component with electric vector along x, I_x is greater than that along z, I_z. In fact, $I_x/I_z = 1.6$ so that $P = 0.23$. P stays constant at about 0.23 with some minor oscillations [as shown in Fig. 1(b)] over periods of several hours. These oscillations in P with time as well as the undulations observed in the decay curves are very likely influenced by the discreteness of the lattice. As the decay time increases the separation of those Ag^0-Ag^{2+} pairs of importance in the luminescence process increases. These distances are properties of shells of positive ion sites surrounding the central Ag^{2+} and because of the discreteness of the lattice the number of sites per unit length does not vary smoothly as a function of separation.

If the temperature of the crystal is raised, P behaves as is shown in Fig. 3(b). When the crystal reaches 50 K, the disorientation temperature of the Ag^{2+} complex, P changes sign and shows a much greater negative polarization on reversal than the original positive polarization. This negative polarization eventually goes to zero after several hours. The magnitude of the reversal depends upon the degree of preferential orientation of Ag^{2+}, the length of time the crystal is allowed to stand at 6 K, and the rate of warming past 50 K.

We believe that the results which we have reported can be understood if we argue along the following lines.

(i) The luminescence arises from tunneling between nearby pairs of Ag^0-Ag^{2+}.

(ii) The tunneling is anisotropic and the anisotropy is determined by the symmetry properties of Ag^0 and Ag^{2+}. Consider the anisotropic Ag^{2+} in orientation A of Fig. 2; since the hole spends very little time along the z axis, an Ag^0 on this z axis will have a low probability for tunneling while an Ag^0 along the x or y axis at the same distance from Ag^{2+} will have a much higher tunneling probability because the hole spends much more time along the x and y axes.

(iii) The electric vector of the emitted light lies along the line joining the Ag^0 and Ag^{2+} which undergo tunneling recombination. The polarization of the luminescence emitted when an Ag^0-Ag^{2+} pair react cannot be determined simply by the properties of a state, or states, of Ag^{2+} or Ag^+, since, if this were the case, the absolute value of the polarization upon reversal (Fig. 3) could never be larger than the initial polarization with the Ag^{2+} preferentially oriented.

As a crystal containing Ag^{2+} in the A orientation "ages," tunneling is taking place much more rapidly, for pairs of a given separation, with Ag^0 along x and y than along z. Thus, with time the initial distribution of Ag^0 around Ag^{2+} changes to one in which there is a much higher concentration of pairs at a given distance along z than along x or y. Upon warming the crystal to 50 K where the Ag^{2+} can hop to orientation C, it finds Ag^0 which have high tunneling probabilities and which yield luminescence with electric vector predominantly along the z axis thus giving the observed large reversal of P. An analogous situation holds if the complex hops to orientation B. The increase in the strength of the reversal of P with "aging time" at 6 K is also accounted for.

Whether the Ag^{2+} complexes are oriented with polarized light or whether they are randomly oriented, the anisotropic tunneling described above occurs. Thus, warming a randomly oriented sample which has been "aging" at 6 K causes a burst of luminescence, when the Ag^{2+} change orientation, and results in the curve shown in Fig. 4. Glow peaks usually encountered arise from thermal activation and release of an electron or hole from a trap and subsequent radiative electron-hole recombination; however, this glow peak does not originate from such a process but from the anisotropic tunneling that has preserved some close pairs with a tunneling probability which is initially low but becomes high when the nearby Ag^{2+} reorients. The extended tail on the high-temperature side of the peak does not arise from a temperature dependence of the tunneling process but from the new distribution of tunneling lifetimes involving an increased number of pairs with lifetimes less than or equal to the "aging time." If the tunneling process were isotropic there would be no glow peak at all.

At 77 K one can produce the same tunneling recombination luminescence with roughly the same decay characteristics as that produced at 6 K, Fig. 1(a). Since no anisotopy can be produced in the Ag^{2+} distribution at 77 K no polarization in the luminescence can be produced. Yet for a crystal containing oriented Ag^{2+}, as shown in Fig. 2(a), when the temperature is raised from 6 to 77 K a reversed polarization persists which decays to zero in several hours. The reason that a polarization is evident at 77 K in this case is related to the change in angular distribution, produced by anisotropic tunneling, which cannot be immediately reversed by rapidly raising the temperature, i.e., temperature has very little or no effect on the tunneling rates, and the lifetimes which give the anisotropy are less than or comparable to the "aging" period.

Further proof that anisotropic tunneling is playing an important role can be seen in the lifetime of some components of the luminescence on reversal. After an "aging time" of a minute or two we are measuring lifetime components of about minutes; while after several hours the lifetimes are of the order of hours. On the other hand, I_z, immediately after reversal, shows some lifetime components of the order of minutes even though the crystal had been "aging" for several hours. This indicates that some close Ag^0 along the z direction had very low tunneling probabilities per minute before reorientation took place.

Above the disorientation temperature of 50 K the fourfold axis of the Ag^{2+} complex hops rather rapidly among the A, B, and C orientations of Fig. 2. Thus, in the reversal experiment described in Fig. 3, above 50 K at any given time there are equal populations among the three directions. If all of the complexes could be forced into only the B or only the C orientation, a larger reversal would be expected. In fact the largest reversal should occur if all the Ag^{2+} were put into the C orientation because the x component would be the weakest in this case. We have attempted to produce the reversal by excitation with light of proper polarization to change the orientation of Ag^{2+}. Very intense light of wavelength 630 nm has been found to produce the desired reorientation in times of the order of 1 min. However, in order to observe the maximum reversal, it is important that the anisotropic distribution produced by tunneling not be disturbed by liberating electrons into the conduction band with the exciting light. We have been able to produce the expected reversal by optically changing the orientation from A to B or A to C. However, we have not been able to obtain the high degree of reversal expected because even at 630 nm the Ag^0 has some slight absorption; this excitation produces electrons in the conduction band which are captured by Ag^+ to produce new Ag^0, thus changing the distribution of Ag^0 about Ag^{2+}. and attenuating the degree of reversal.

B. Calculation of the properties of the afterglow

In order to calculate some of the properties of the Ag^0-Ag^{2+} afterglow, it is first necessary to consider the distribution of Ag^0 and Ag^{2+} centers in the crystal. During the growth of the KCl:AgCl crystal from the melt we assume that the Ag^+ ions are distributed at random among the positive ion lattice sites. We also assume that subsequent treatments cause no preferential migration of the Ag^+ ions, so that electrons and holes are distributed among a small fraction of these randomly distributed Ag^+ ions to form Ag^0 and Ag^{2+}, respectively.

The afterglow is initiated by optical excitation of Ag^0 which puts free electrons into the conduction band. Those electrons then recombine with Ag^{2+}, influenced by the long-range Coulomb attraction, or with the more numerous Ag^+, to which the electron is bound by a short-range potential. Since Ag^{2+} has a larger capture cross section than Ag^+ has for a slow free electron, it is relatively unlikely that an electron will be captured by an Ag^+ if an Ag^{2+} is nearby. Accordingly, at the end of the excitation of the Ag^0, $t=0$, we expect the relative probability of finding an Ag^0 at a site $\vec{\rho}_i$ from any given Ag^{2+} to be small for small ρ and to increase and approach a constant as ρ increases. We shall describe the distribution by $N_0(\vec{\rho}_i)=\bar{N}_0(1-e^{-(\rho_i/A)^2})$; in these experiments $\bar{N}_0$ is approximately 10^{-5} and is equal to the fraction of positive ion sites occupied by Ag^0. Between the "aging time" of 1 and 1000 min the total number of Ag^0 and Ag^{2+} in the crystal decreases by one-half to 1% during the decay of the afterglow; therefore, the average concentrations of these species can be considered to be constant and since $\bar{N}_0$ is so small we do not have to consider the possibility that two or more Ag^0 are approximately equally close "nearest" neighbors to a given Ag^{2+}. We shall take our unit of length to be the nearest-neighbor separation in KCl, $a=3.145$ Å, and shall arbitrarily choose $A=8a$. A larger value than this makes no difference in our calculated results. A smaller value influences the results for long observation times, that is, the intensity of luminescence falls off faster at long times and the polarization decreases at long times.

The luminescence arises from a radiative two-center transition of the extra electron on Ag^0, and involves the overlap of this wave function with that of the Ag^{2+} $4d$ hole. The former is a $5s$-like function, and the latter has the symmetry of $|(x^2-y^2)/\rho^2\rangle$ for an Ag^{2+} in orientation A of Fig. 2. One does not really know the radial parts of these functions. Neither electron nor hole is bound by Coulomb attraction, nor is either potential even approximately a square well; thus, there is no assurance that a simple exponential radial dependence is correct. However, it has long been considered the only reasonable and feasible approximation,[6] and we adopt it. Thus, we shall picture the Ag^{2+} hole wave function as $[(x^2-y^2)/\rho^2]U_v(\vec{\rho})\exp(-k_1\rho)$ measured about its origin, and the Ag^0 electron wave function as $U_c(\vec{\rho}-\vec{\rho}_i)\exp(-k_2|\vec{\rho}-\vec{\rho}_i|)$ around its origin at $\vec{\rho}_i$. Here U_v and U_c are the periodic parts of the Bloch functions of the valence and conduction bands of KCl. This approach is common in the effective mass approximation in semiconductors, and has been used successfully, though less justifiably in a formal sense, in alkali halides. Thus, the dipole matrix element is that between the valence and conduction band, independent of direction in the cubic KCl crystal, and the coefficient is that of the product of the envelope functions along the line joining the two centers. The intensity of the μ component of the luminescence from an Ag^0 atom at $\vec{\rho}_i$ is proportional to

$$\left(\frac{\mu_i}{\rho_i}\right)^2 W(\vec{\rho}_i)\propto\left(\frac{\mu_i}{\rho_i}\right)^2\left(\frac{x_i^2-y_i^2}{\rho_i^2}\right)^2 e^{-K\rho_i}, \tag{6}$$

where $W(\vec{\rho}_i)$ is the transition probability for tunneling recombination with the Ag^{2+} in orientation A of Fig. 2, $\mu=x$, y, or z, and K depends on k_1 and k_2.

The probability that a pair separated by $\vec{\rho}_i$ at $t=0$ would still exist at time t is

$$\exp\left[-Ct\left(\frac{x_i^2-y_i^2}{\rho_i^2}\right)^2 e^{-K\rho_i}\right].$$

Here C is a proportionality constant having the dimensions of t^{-1} and includes such factors as the normalization of the wave functions, the transition moment between U_v and U_c, and other crystal parameters. We do not know C, and shall treat it merely as a normalization constant for the time scale. Henceforth, we shall treat Ct as a dimensionless time parameter, and call it $\hat{t}$. Similarly we do not know the value of K in our units of a^{-1}. We expect it to represent the longest range of the radial components of the wave functions of the electron and hole. A value of 3 seems reasonable in terms of the bleaching distance attainable in a few hours. Calculations with greater and smaller values have been carried out with no significant differences.

Finally, we write the total intensity of the μ-polarized component of the luminescence as

$$I_\mu(t)=B\sum_i(\mu_i/\rho_i)^2\bar{N}_0(1-e^{-(\rho_i/8)^2})\left(\frac{x_i^2-y_i^2}{\rho_i^2}\right)^2 e^{-3\rho_i} \times\exp\left[-\hat{t}\left(\frac{x_i^2-y_i^2}{\rho_i^2}\right)^2 e^{-3\rho_i}\right], \tag{7}$$

where B is a constant and the sum runs over all the neighboring positive-ion lattice sites able to contribute in the greatest time of interest. In practice, the circumstance that the concentrations of Ag^0 and Ag^{2+} decrease by about $\frac{1}{2}$% to 1% during experiments of several hours duration serves to fix the distance scale. That is, no significant bleaching can occur beyond $10a$, or more than 1% of the Ag^0 and Ag^{2+} would disappear, but in

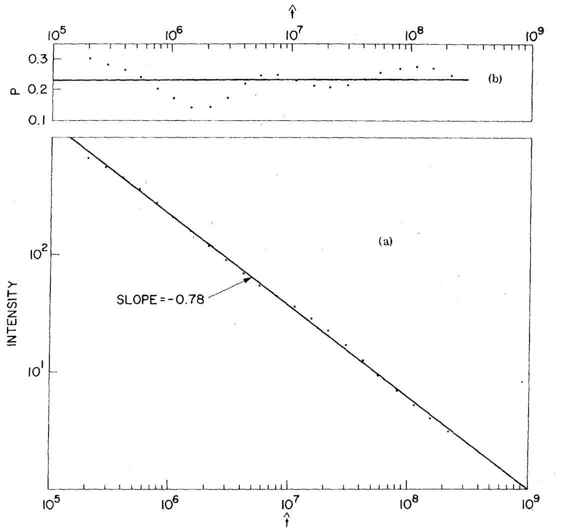

FIG. 7. (a) Calculated intensity according to Eq. (7), in arbitrary units, of tunneling luminescence between Ag^0 and Ag^{2+} as a function of $\hat{t}$. (b) The degree of polarization for Ag^{2+} as oriented in Fig. 2(a) as a function of $\hat{t}$ on the same scale.

order to account for about $\frac{1}{2}\%$ bleaching the distance must be at least $6a$.

The introduction of additional powers of ρ in $W_\mu(\vec{\rho}_i)$ [Eq. (6)] were found to have no significant effect; that is, one can write the radial dependence as $e^{-3\rho}$, $\rho^2 e^{-3\rho}$, or $\rho^{-2}e^{-3\rho}$ without noticeable effect on the results. It is customary to omit factors of powers of ρ in favor of the dominance of the exponential function for large separations, and we do so here.

We have performed the sum in Eq. (7) out to values of $|\rho_i|$ (typically 10 or 12) such that additional terms contribute no more than 0.1% to the total. In Fig. 7(a) is shown the calculated total intensity of the afterglow from a sample with randomly oriented Ag^{2+} as a function of $\hat{t}$, and in Fig. 7(b) is shown the degree of polarization on the same $\hat{t}$ scale. Shorter and longer times correspond, respectively, to smaller and larger recombination distances ρ_i. The resemblance of the curves of Fig. 7 to the experimental results of Fig. 1 is substantial. The deviations are also noticeable, that is, the oscillations in the calculated degree of polarization are more pronounced than the observed ones, and the calculated decay of intensity with time is somewhat less rapid (slope $= -0.78$) than is observed (slope$= -0.91$). Curves similar to those of Fig. 7 have been obtained for smaller and larger values of K, of course with different reduced time scales.

The initial distribution may not be adequately described by the function $1-e^{-(\rho_i/8)^2}$. As stated earlier, if the number 8 were increased the shapes of the calculated curves would be almost unchanged for the range of $\hat{t}$ exhibited here. Figure 8(a) and 8(b) show the calculated results for the case where the initial distribution of Ag^0 with respect to Ag^{2+} is random, i.e., the number 8 is replaced by zero. The slope of -0.89 calculated for this case is in better agreement with the experimental value of -0.91, but the average value of the degree of polarization and the magnitude of the oscillations are in worse agreement.

The magnitude of the undulations observed in the decay of the luminescense intensity with time, Fig. 1(a), are very similar to those of the calculated results, Figs. 7(a) and 8(a). However, as seen above, the experimentally observed oscillations in P with time, Fig. 1(b), are much smaller than those obtained in the calculations, Figs. 7(b) and 8(b). It seemed possible that taking into account the zero-point motion of the lattice might reduce the oscillations in the calculated P. Consider an Ag^0-Ag^{2+} pair separated by (b,b,c) with the Ag^{2+} fourfold axis along z; if the ions are located *exactly* on the lattice sites, tunneling recombination would *never* occur according to our model, since $x^2-y^2=0$. However, if zero-point motion should bring the Ag^0 to a relative position $(b+\Delta,\ b-\Delta,\ c)$, then the tunneling probability would not be zero. We have estimated the effect of zero-point motion for $\Delta=0.1a$ on I_x and I_z as a function of $\hat{t}$

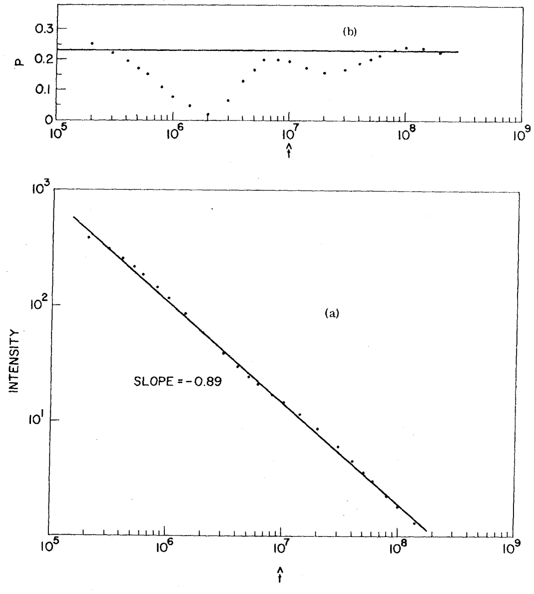

FIG. 8. (a) Calculated intensity, in arbitrary units, of tunneling luminescence between Ag^0 and Ag^{2+} as a function of $\hat{t}$ assuming a random distribution of Ag^0 about Ag^{2+}. (b) The degree of polarization as a function of $\hat{t}$.

for Ag^0 located at the sites which could have an appreciable effect. We find that taking the zero-point motion into account in this manner does result in a reduction in the oscillations in P but only by a very small percentage and cannot account for the discrepancy between experiment and theory.

We turn now to a consideration of the reversal of the polarization of the afterglow when the crystal is warmed and the Ag^{2+} can disorient (see Fig. 3). A realistic calculation is difficult during the warm-up period when the degree of orientation of the Ag^{2+} is changing rapidly. Instead, we have calculated the distribution after a period of "aging," $\hat{t}_0$, and then assumed that the Ag^{2+} are instantaneously disoriented, and calculated the values for I_x and I_z after that instant. That is, we calculate

$$I_\mu(\hat{t}') = \sum_i \left(\frac{\mu_i}{\rho_i}\right)^2 N_i(\hat{t}_0)\overline{W}_i \exp(-\hat{t}'\overline{W}_i)\,, \tag{8}$$

where

$$N_i(\hat{t}_0) = \overline{N}_0(1 - e^{-(\rho_i/8)^2}) \times \exp\left[-\hat{t}_0\left(\frac{x_i^2 - y_i^2}{\rho_i^2}\right)^2 e^{-3\rho_i}\right]\,, \tag{9}$$

$$\hat{t}' = \hat{t} - \hat{t}_0\,, \tag{10}$$

$$\mu = x,\ y,\ \text{or}\ z\,, \tag{11}$$

and

$$\overline{W}_i = \frac{1}{3}\left[\left(\frac{x_i^2 - y_i^2}{\rho_i^2}\right)^2 + \left(\frac{y_i^2 - z_i^2}{\rho_i^2}\right)^2 + \left(\frac{z_i^2 - x_i^2}{\rho_i^2}\right)^2\right] e^{-3\rho_i}\,. \tag{12}$$

The calculated results, Fig. 9, show a discontinuous jump in both I_z and I_x at $\hat{t}' = 0$ ($\hat{t}_0$ is taken to be 8.1×10^7) followed by a rapid drop as electrons on the very close and now favorably located (high tunneling probability) Ag^0 atoms tunnel to Ag^{2+} ions. Both I_x and I_z increase at $\hat{t}' = 0$, the latter increasing more because of the greater region now having become newly available to favorable tunneling conditions.

The fact that I_x increases upon disorientation [Fig. 3(a)] is particularly significant, and demonstrates the azimuthal dependence of the tunneling probability. For example, with the Ag^{2+} oriented as in Fig. 2(a), consider any recombination probability that depends only on the polar angle measured from the fourfold axis, z, of the preferentially oriented Ag^{2+}, and let I_z be less than $I_x(=I_y)$. Any reorientation must enhance I_z and must inevitably *reduce* I_x and I_y. But it is observed (see Fig. 3) that I_x *increases* upon reorientation, hence, there must be an additional angular dependence such that the newly oriented Ag^{2+} ions can find favorably located Ag^0 atoms such that I_x and I_y increase. This is a natural result of our model, e.g., Ag^0 located at $(\pm m, \pm m, l)$ sites will not have recombined with Ag^{2+} in the original orientation for any l, but many of them readily can in the new orientation, thereby increasing both I_z and I_x (or I_y) as observed.

The initial burst of luminescence shown by these curves at $\hat{t}' = 0$ may appear to be too large, however this burst is very short lived so the area, proportional to the number of photons emitted, is small. The more rapid the warming of the crystal,

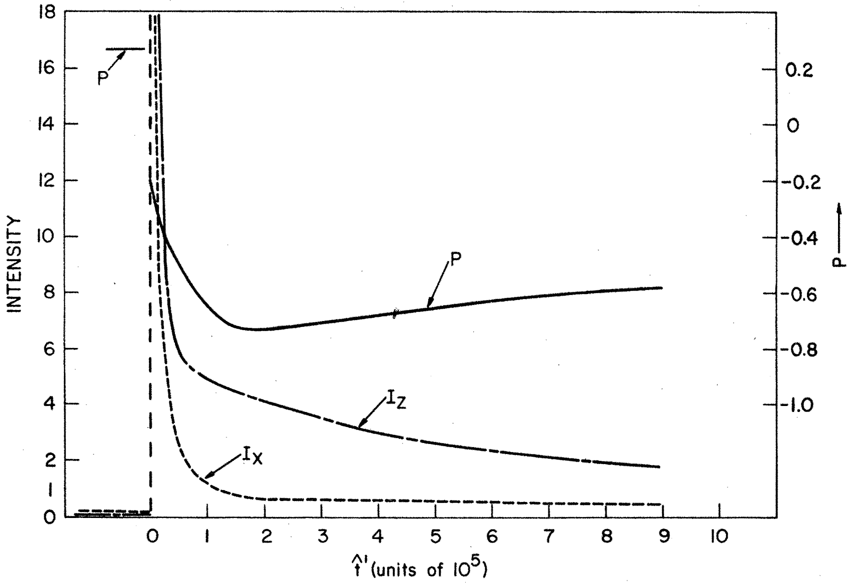

FIG. 9. Calculated intensities, I_x and I_z, and degree of polarization P at values of $\hat{t}'$ near the assumed instantaneous randomization of the orientation of Ag^{2+}.

the closer the experimental conditions approach this description of the instantaneous disorientation of the Ag^{2+} ions and the closer the experimental results approach the calculated results.

An identical calculation with $\hat{t}_0$ chosen to be 2.7 times larger shows very similar results, but with a substantially greater percent increase in I_x and I_z when the Ag^{2+} are disoriented. This is to be expected in the model, and is observed experimentally. When $\hat{t}_0$ is increased both I_x and I_z decrease; however, the number of pairs located at unfavorable angles does not decrease as fast and therefore have a larger impact on reorientation.

VI. CONDITIONS FOR LARGE REVERSAL OF *P*

Anisotropic tunneling and a reversal of P on warming have also been observed in the Ag^0-Cl_2^- system. The polarization of the afterglow in this case is almost twice as great as that of Ag^0-Ag^{2+} but the reversal is far less. We believe that the tunneling is very anisotropic in the Ag^0-Cl_2^- case but that the reversal is limited by the mechanism of reorientation which is different in the two cases. Ag^{2+} reorients by changing its configuration by 90° because the fourfold axes are along cube edges. In the case of Cl_2^- its axis lies along a $\langle 110 \rangle$ direction. Experiments show that on reorientation the axis of Cl_2^- changes by 60° per jump.[7] Thus, it takes at least two jumps to change the orientation by 90°. A 60° jump yields luminescence with equal I_x and I_z components. In this case z is along the molecular axis of the preferentially orientated Cl_2^- which we assume to be [101], x is along $[10\bar{1}]$ and y is along [010]. The molecular axis of the preferentially oriented Cl_2^- is along z, and the tunneling probability per unit time for a given separation is highest for an Ag^0 along the molecular axis. Only when the total jump is 90° is the I_x component larger than the I_z component; therefore, the anisotropy contributed by these Cl_2^- is reduced by the four times as numerous Cl_2^- which have jumped through 60° and contribute no anisotropy. In addition when Cl_2^- reorients it moves one lattice spacing and thus changes the Ag^0 distribution around it with each jump while the center of gravity of Ag^{2+} does not move. Thus, Ag^{2+} is an especially good system to obtain a very large polarization reversal.

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