

Energy Transfer by Resonance in KCl/Ag, Pb Single Crystals

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Decay curves of fluorescences from Ag^+ and Pb^{++} in KCl single crystals have been observed by the pulse method. The time constant of the former becomes smaller with coexistence of Pb^{++} . This effect has been analyzed by the resonance theory of energy transfer. The dipole-dipole interaction between Ag^+ and Pb^{++} promotes the relaxation of excited Ag^+ s. By examining the decay curves in detail, it is concluded that some Ag^+ s aggregate with one Pb^{++} as the neighbour and a possibility of derivation of informations on the aggregation of Ag^+ with Pb^{++} in KCl single crystals is obtained.

1. Introduction

In solids as well as in liquids which contain two kinds of activators, there are two types of energy transfer between both activators with no movement of charge carriers. One is a cascade process which involves a real emission and reabsorption of photons. The other is a nonradiative transfer of energy by resonance between absorbers and emitters. In both processes, necessary conditions are as follows. Both centers have emissive configurations when they are excited after their own absorption of light and the emission band of the first center overlaps appreciably with the absorption band of the second center. The first process is recognized trivial and the second one has been discussed theoretically by Dexter.¹⁾

The process of nonradiative energy transfer has been applied widely in the practical application of luminescent materials, being called as the sensitization, and many studies have been carried out on this process. All the measurements, however, were carried out in static manners, and it has not been clarified definitely whether the emission from the emitter is really due to the resonance process or the cascade process.

In order to confirm the resonance process actually, it will be desired to observe the process as a transient phenomenon, because it is dependent on time essentially. In the luminescence system in which the absorption and emission of light take place in the same center, the decay of the emission obeys the usual exponential law. If an excited center transfers some of its energy by the non-radiative resonance, the decay constant should become smaller, because the new type of

relaxation is added to the normal radiative relaxation. Accordingly, to verify the resonance transfer of energy, it is the nearest way to observe the decay process transiently.

2. Some Optical Characteristics of KCl/Ag and KCl/Pb

As informations concerning luminescences of KCl/Ag and KCl/Pb are necessary for the study of the energy transfer in KCl/Ag, Pb, some of the characteristic properties of both single crystals²⁾ are mentioned in the following.

Fig. 1 shows the excitation as well as

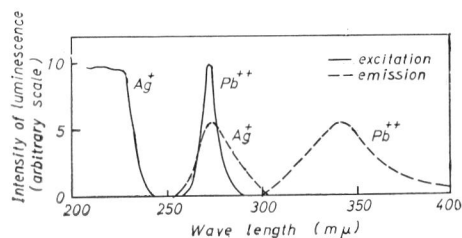


Fig. 1. The excitation and emission bands of KCl/Ag and KCl/Pb single crystals at room temperature.

emission spectra of KCl/Ag and KCl/Pb single crystals at room temperature. As the emission band of Ag^+ overlaps with the excitation band of Pb^{++} at $2730\text{\AA}$, in the case of KCl/Ag, Pb the energy transfer from Ag^+ to Pb^{++} may be possible by the resonance process mentioned before under the excitation at $2250\text{\AA}$. In other words, by the excitation of Ag^+ at $2250\text{\AA}$ the emission from Pb^{++} will appear at $3400\text{\AA}$ through the nonradiative process.

The oscillator strength of the absorption due to Ag^+ has a rather small value as 0.003

at its first peak and the one due to Pb^{++} 0.07, so the dipole-dipole interaction between both ions may be so small that the phenomena which should be caught will lie in a time duration of micro-second.

3. Experimental Procedures

In order to observe decay curves of luminescences, it is the best method to excite activators of materials with repeating pulsed lights of very short duration, displaying the decay curves on a cathode ray tube. In the present measurements, pulsed ultra-violet light from a hydrogen discharge tube operated at 3000 volts was made monochromatic (2250Å) through a quartz monochromator. The half width of the pulsed light was about $40\text{m}\mu$ sec.

The emission was detected by a photo-multiplier of 1P-28 type which was pulsed rectangularly in duration of 15μ sec at 2000 volts in synchronism with the pulsed lights so as to include the emission within the duration.

Single crystals were prepared by the usual Kylopoulos method and concentrations of Ag^+ and Pb^{++} were analyzed chemically. The concentration of Ag^+ was kept at $3\sim 5 \times 10^{18}/\text{cm}^3$ and that of Pb^{++} was varied from 10^{17} to $10^{19}/\text{cm}^3$.

All measurements were carried out only at room temperature.

4. Experimental Results

In Fig. 2 the decay curves of the emission of KCl/Ag and KCl/Pb displayed on the CRT are shown. They were of a perfectly exponential type and their time constants were 13.6 and 0.47μ sec respectively, which were suitable to the magnitudes of the oscillator strength mentioned in Section 2.

In the cases of KCl/Ag, Pb, the emission from Ag^+ as well as Pb^{++} will appear under the excitation of Ag^+ , because some part of the energy is transferred from Ag^+ to Pb^{++} by the dipole-dipole interaction or by the process of the cascade type. In order to observe the relaxation of Ag^+ itself, it is sufficient to catch only the emission from Ag^+ . However, almost all of the emission from Ag^+ will be reabsorbed by Pb^{++} in the cases of higher concentration of Pb^{++} , being converted into the emission of Pb^{++} . Because of the very small time constant of the decay

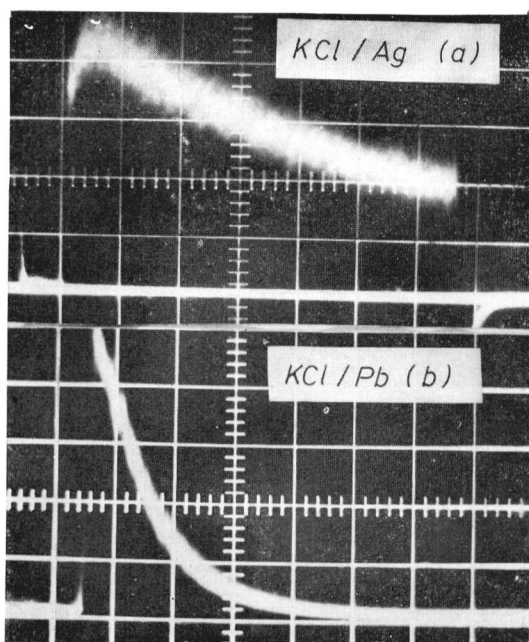


Fig. 2. The decay curves of the emissions of KCl/Ag (a) and KCl/Pb (b). The larger divisions are 2μ sec in (a) and 0.2μ sec in (b).

curve of the intrinsic emission of Pb^{++} , the reabsorption process does not modify appreciably the shape of the decay curve corresponding to the relaxation of Ag^+ , even if the converted emission from Pb^{++} is detected. Furthermore, as mentioned afterwards, the manner of the relaxation of the transferred energy by the resonance is the same as that of the relaxation of Ag^+ . Then it is no essential matter whether filters are used to catch only the emission from Ag^+ or Pb^{++} . In the present measurements, a filter for the emission of Pb^{++} was used.

Some examples of the decay curves of KCl/Ag, Pb are shown in Fig. 3. In contrast to the case of KCl/Ag, the initial part of the decay curve drops rapidly, especially in the case of the higher concentration of Pb^{++} , while in the region of the tail part of the curve the time constant is about the same as that of KCl/Ag. The slope at the initial part of the curve increases with the concentration of Pb^{++} . In the cases of the very high concentration of Pb^{++} , the time constant of the tail part also reduces to $10\sim 9\mu$ sec. At any rate, the fact that the relaxation of the excited Ag^+ was promoted under co-existence of Pb^{++} can be found.

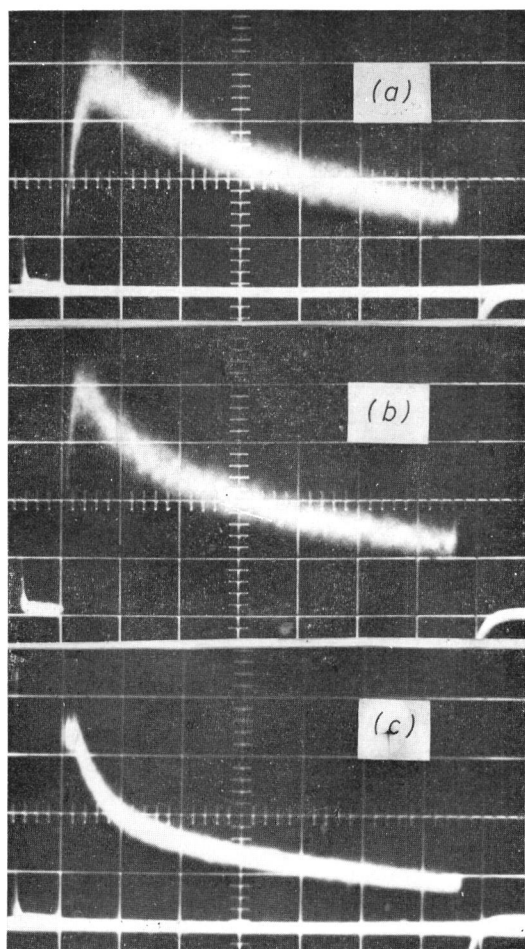


Fig. 3. The decay curves of KCl/Ag, Pb under the excitation at 2200 Å. The larger division is 2μ sec. Pb^{++} concentrations are $8.5 \times 10^{17}/\text{cm}^3$ (a), $2.2 \times 10^{18}/\text{cm}^3$ (b) and $3.8 \times 10^{18}/\text{cm}^3$ (c).

5. Discussion

As the decay curves of KCl/Ag and KCl/Pb are of the exponential type, the absorption and emission occur in the same center respectively. Accordingly, the number n of the excited Ag^+ is shown as

$$dn/dt = -P_s n. \quad (1)$$

P_s is the probability of its own emission process. If some part of the energy is transferred to Pb^{++} s by the dipole-dipole interaction, the decay must obey the following equation, because the other process of relaxation is added,

$$dn/dt = -(P_s + P_t)n. \quad (2)$$

Here, P_t is the probability of the energy transfer by the dipole-dipole interaction. In

the case of the energy transfer of the cascade type, however, the manner of the relaxation does not change itself, because the process of reabsorption is independent of the process of the initial emission.

By integrating Eq. (2), we obtain as the equation which is proportional to the intensity of the emission

$$\begin{aligned} dn/dt = & -P_s n_0 \exp [-(P_s + P_t)t] \\ & -P_t n_0 \exp [-(P_s + P_t)t]. \end{aligned} \quad (3)$$

n_0 is the initial number of the excited Ag^+ after the absorption of one pulse of light. The first term of Eq. (3) means the relaxation of Ag^+ by emitting photons directly from the ion and the second term means that by transferring its energy to Pb^{++} s.

In the present measurement, the density of photon absorbed by Ag^+ within one pulse of the incident light is so smaller than the density of Pb^{++} and the time constant of the decay curve of the intrinsic emission of Pb^{++} is so small that the transferred energy will be emitted as photon from Pb^{++} in the appreciably same manner as the relaxation shown by the second term of Eq. (3).

As $1/P_s$ and $1/(P_s + P_t)$ are the time constants of the decay curves of KCl/Ag and KCl/Ag, Pb, we can easily obtain the value of P_t . However, as shown in Fig. 4, the decay curve of KCl/Ag, Pb is not of an exponential type, but seems to be composed of two kinds of the exponential decay curve. In the cases of not very high concentration of Pb^{++} , the

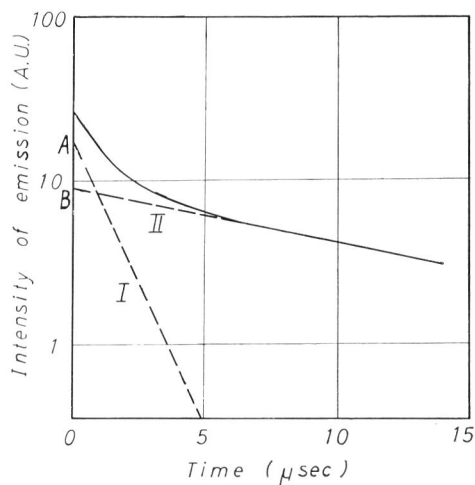


Fig. 4. The decay curve of KCl/Ag, Pb. Pb^{++} concentration is $3.8 \times 10^{18}/\text{cm}^3$. The curve is separated into I and II.

tail parts of the decay curves show the same time constant as KCl/Ag, so the present decay curve can be separated into two exponential curves: the one has the shorter time constant and the other the same time constant as that of KCl/Ag.

Table I shows these results. The former time constant is nearly independent of Pb^{++} concentration, being approximately constant at 1.3μ sec.

Table I. The concentration dependence of the time constant of the decay curve I.

Pb ⁺⁺ concentration (1/cm ³)	Time constant (μ sec)
3.8×10^{18}	1.3
3.0 "	1.3
2.2 "	1.3
1.0 "	1.6
8.5×10^{17}	1.2
6.2 "	1.3
5 "	1.3

The above results may be explained by the following model. Although Ag^+ s and Pb^{++} s distribute randomly in the host crystal, if there are some kinds of interaction between both of them, some Ag^+ s aggregate with one Pb^{++} as the neighbour; while the other Ag^+ s are surrounded by randomly distributed Pb^{++} s. The former Ag^+ will transfer its energy to its neighbouring Pb^{++} with a larger probability P_n and the latter Ag^+ to the randomly distributed Pb^{++} s with a smaller probability P_d , because the probability of the energy transfer by the dipole-dipole interaction is inversely proportional to the sixth power of the distance between both ions.¹⁾

Accordingly, the relaxation curve in the present case may be shown as

$$dn/dt = -(P_s + P_n)n_{0n}\exp[-(P_s + P_n)t] - (P_s + P_d)n_{0d}\exp[-(P_s + P_d)t], \quad (4)$$

where n_{0n} and n_{0d} are the initial numbers of both kinds of the excited Ag^+ respectively. The first term means the curve I and the second the curve II in Fig. 4. P_d in the first term is neglected, because P_d is very much smaller than P_n in the present case. $1/P_s$ and $1/(P_s + P_n)$ are 13.6 and 1.3μ sec respectively, $1/P_n$ is obtained as 1.4μ sec. On the other hand, in the case of very high concentration of Pb^{++} such as about $1 \times 10^{19}/\text{cm}^3$,

the time constant of the curve II is $9 \sim 10\mu$ sec, resulting in that $1/P_d$ is $27 \sim 38\mu$ sec.

As KCl has the f.c.c. crystal symmetry, we can calculate the site number of the positive ions which has equal distance from a certain positive ion, as well as the product of the number and the reciprocal of the sixth power of the distance. The ratio of the value of this product for the first 12 nearest neighbours to that of the summation of the products in the region of the 25 nearest neighbours is about 1 : 1.45. Assuming that both optical transition moments of Ag^+ and Pb^{++} have the spherical symmetry, the ratio $P_n : P_d$ is $1 \times 1/12 : 1.45 \times n/N$. n is the concentration of Pb^{++} and N is that of K^+ in the host KCl crystal.

The calculated value of P_n/P_d is about three times larger than the observed value of it. As the crystal becomes a little opaque in the case of very high concentration of Pb^{++} , the real concentration cannot be decided. Then the above agreement seems rather well.

As for the absolute value of the probability of the energy transfer between the neighbouring ions, we can estimate it by the Dexter's calculation¹⁾ in which several values are introduced from the experimental results; such as the absorption cross section of Pb^{++} , relaxation time of Ag^+ , distance between both ions, refractive index of the host crystal and overlapping constant of the emission band of Ag^+ with the absorption band of Pb^{++} . The order of magnitude of the calculated probability is $10^9/\text{sec}$ in contrast with the above observed value of $10^6/\text{sec}$. The discrepancy may be ascribed to the polarization of the optical transition moments of both ions as well as the difference of their orientations.

Eq. (4) tells us that if we divide the initial values A and B of the decay curves I and II in Fig. 4 with each relaxation probability, we can obtain n_{0n} and n_{0d} which are proportional to the concentrations of both type of Ag^+ . In other words, the proportion of Ag^+ aggregated with Pb^{++} to the other type of Ag^+ might be obtained. However, in the procedure of these analyses cares must be taken to know the amount of reabsorption of the emission from Ag^+ by Pb^{++} . For instance, in the case of Pb^{++} concentration $3.8 \times 10^{18}/\text{cm}^3$ where the reabsorption is almost perfect, the amount of Ag^+ aggregated with

Pb⁺⁺ is about 10%.

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Interaction of Low Energy Electrons with Insulating Crystals

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The absorption coefficients for slow electrons on sodium chloride have been measured. New techniques developed for these measurements utilizing 0.2 to 12 eV beams with a dispersion of 0.2 eV and currents less than 2×10^{-14} amperes are outlined. The data show that strong electron-crystal interactions occur at impacting energies equivalent to F and V_3 center optical absorption bands. With these centers to orient the energy scale, the onset of secondary emission provides an estimate of the energy required for a band to band transition. The NaCl data are similar to and compared with previous measurements on KCl, KCl:K, and KBr:K. The divergency between the band gap energy E_g in NaCl as measured by various techniques is considered and it is concluded that the most probable value for E_g is 9.6 ± 0.2 eV.

I. Introduction

When electrons impinge on an insulating crystal they may undergo interactions with energetically available levels of the crystal and its imperfections. These interactions have been observed by several investigators. Hilsch¹⁾ studied the change of the electron reflection coefficient of KCl near the band gap. Jacobs *et al.*²⁾ observed changes in target current of KCl evaporated film targets as a function of electron impacting energy. The secondary electron emission from cleaved alkali halide crystals produced by electrons impacting with energies greater than 3.5 eV has been studied by Fridrikhov and Goryacheva.³⁾ Cook and Fredericks⁴⁾ produced evidence strongly suggesting that the apparent conflict among these results arose from differences in target structure (film or single crystal) and experimental conditions (amount of target charging and

energy dispersion of incident electron beam). Further, they demonstrated how unique electron interaction data can be obtained and that such data show a direct correspondence between photon absorption and electron interactions.⁵⁾

This experiment provides an additional technique to measure band gaps in insulating crystals. The results of such measurements on sodium chloride are reported in this paper and compared with similar measurements on other alkali halides.

II. Experimental

The electron beam was supplied by a symmetrical acceleration-deceleration device. The beam's minimum energy dispersion corresponded to a cathode temperature ranging from 750° to 1000°K, (0.1 eV or less). The mean beam energy at the target chamber entrance could be determined to within 0.03 eV. Construction details and operation are described elsewhere.^{6), 4)}

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