# Optical and Thermal Electron Transfer in KCl: $Tl^+$ Crystals

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Z. Naturforsch. **33a**, 1154–1157 (1978); received January 2, 1978

The absorption spectra of $Tl_2^+$ in KCl crystals have been measured from 77 to 300 K. $Tl_2^+$ gives rise to five absorption bands peaking at 1760, 860, 680, 460 and 233 nm. These oscillator strengths have been calculated. Optical excitation in the 460 nm band destroys the $Tl_2^+$ and $Tl^{++}$ bands and produces the $Tl^0$ bands. Thermal excitation of a crystal containing only $Tl_2^+$ and $Tl^{++}$ results in the simultaneous decay of $Tl_2^+$ and $Tl^{++}$.

It is concluded that electrons released from $Tl_2^+$ by optical or thermal excitation are trapped at $Tl^+$ and $Tl^{++}$. A discussion is given on $Tl_2^{+++}$: A $Tl_2^{+++}$ which has an absorption band at 1075 nm is formed when a $(Tl^+)_2$ traps a positive hole of a nearby $Cl_2^-$, whereas it is deformed when a $Tl_2^{+++}$ traps an electron released from a $Tl_2^+$ by optical excitation in the 460 nm band.

## Introduction

$(Tl^+)_2$ as well as $Tl^+$ are known to be present in alkali halide: $Tl^+$ crystal. It has been established [1–7] that $Tl^0$ and $Tl^{++}$ are formed when an electron and positive hole, which were produced by an ionizing-radiation exposure of a KCl: $Tl^+$ crystal, are trapped by $Tl^+$. In a heavily doped crystal, $Tl_2^+$ is known to be formed when a $(Tl^+)_2$ traps an electron which was produced by the ionizing-radiation exposure or released from $Tl^0$ by optical or thermal excitation. $Tl_2^+$ gives rise to four Gaussian-shaped absorption bands with peaks at 1760, 860, 680 and 460 nm in KCl [8, 9]. Additionally, $Tl_2^{+++}$ is expected to be formed when a $(Tl^{++})_2$ traps an electron [10] or when a $(Tl^+)_2$ traps a positive hole. In contrast with many reports on the optical and thermal properties of $Tl^0$ and $Tl^{++}$, few investigators have studied the optical properties of $Tl_2^+$ and $Tl_2^{+++}$.

So far, the main interest in $Tl_2^+$ was in its correlation with $Tl^0$. There is no detailed report on correlation of $Tl_2^+$ with other color centers, e.g. $Tl^{++}$ and F. It is interesting to investigate the whereabouts of electrons released from the electron-trapped center, $Tl_2^+$, since various color centers ($Tl^0$, $Tl^{++}$, $Tl_2^{+++}$, F, $Cl_2^-$), in addition to $Tl^+$ and $(Tl^+)_2$, are present in an X-rayed crystal. In this paper we study the optical properties of the absorption bands of $Tl_2^+$ under thermal or optical excitation and discuss the transfer of electrons from $Tl_2^+$.

## Experimental Procedure and Results

The experimental techniques used have been already described [9]. Single crystals of KCl: $Tl^+$ were exposed, at 77 K, to ionizing-radiation from a Toshiba X-ray tube operated at 30 kV and 100 mA.

Figure 1 shows the absorption spectra at 77 K of a KCl: $Tl^+$ (0.05 mole% in the melt) crystal which was exposed to X-rays at 77 K and subsequently warmed to 200 K. Several absorption bands are produced during X-ray exposure: two bands of $Tl^0$ peaking at 640 and 380 nm and a band of $Cl_2^-$ peaking at 367 nm are observed, which decrease after thermal treatment; four bands of $Tl^{++}$ are observed at 364, 294, 262 and 220 nm which increase after thermal treatment. Additionally, two weak bands are observable at 460 nm (2.69 eV) and 233 nm (5.32 eV) in Figure 1. The existence of

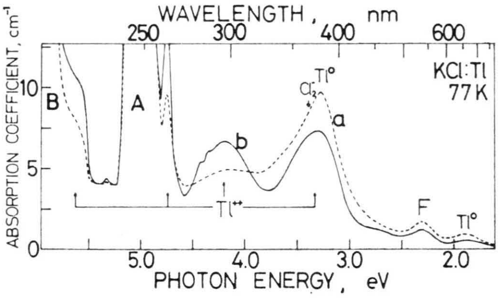

Fig. 1. Absorption spectra of a KCl: $Tl^+$ (0.05 mole% in the melt) crystal at 77 K after (a) a 30 minute exposure to X-rays at 77 K and (b) warming the crystal to 200 K for 10 minutes.

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the 233 nm band was not shown in the previous work. The intensity-ratio between the 233 nm band and the 460 nm band was little dependent on the concentration of TlCl doped in KCl. Its ratio was almost unchanged during their growth or decay. For example, (1) these bands were simultaneously enhanced after warming the crystal to a temperature between 200 and 300 K, and (2) these bands were simultaneously decreased during optical excitation in the 460 nm band of $Tl_2^+$ as seen in Figure 2b. This suggests that the 233 nm band belongs to $Tl_2^+$ as the 460 nm band.

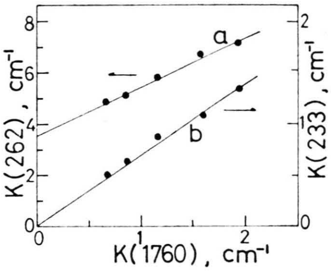

Fig. 2. Plot of the peak-heights of the 262 nm band of $Tl^{++}$ (a, scale on left) and the 233 nm band (b, scale on right) versus that of the 1760 nm band, at 77 K, in a KCl:$Tl^+$ (0.5 mole% in the melt) crystal, which was exposed to X-rays at 77 K, subsequently warmed to 280 K and then irradiated with 470 nm light at 77 K. K(262) denotes the maximum absorption coefficient of the 262 nm band.

Figure 2a plots the intensity of the 262 nm band of $Tl^{++}$ during the optical excitation in the 460 nm band. It is seen that the $Tl^{++}$ band decays with the $Tl_2^+$ band, but survives the $Tl_2^+$ band even after a 60 minute excitation. Such a simultaneous decay of $Tl_2^+$ and $Tl^{++}$ was also obtained during thermal excitation of a crystal which contains only $Tl_2^+$ and $Tl^{++}$. (It was found that $Tl_2^+$ and $Tl^{++}$ survive $Tl^0$ and $Cl_2^-$ by warming the X-rayed crystal to a temperature near 300 K. When the crystal is subsequently cooled to 77 K and then warmed to 300 K, $Tl^{++}$ decays with $Tl_2^+$ as shown in Figure 3.) Unlike the case of a crystal containing $Tl^0$ and $Cl_2^-$ as well as $Tl_2^+$ and $Tl^{++}$ at the initial stage [8], the $Tl_2^+$ and $Tl^{++}$ bands were never grown during the thermal excitation. In the thermal excitation of the $Tl^0$- and $Cl_2^-$-doped crystal, $Tl^0$ decays to release an electron which is mainly retrapped by $(Tl^+)_2$ to form $Tl_2^+$ whereas $Cl_2^-$ decays to release the hole which is mainly retrapped to form $Tl^{++}$.

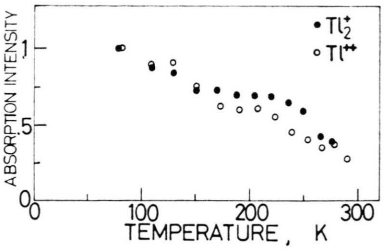

Fig. 3. Temperature dependence of the absorption intensities (band areas) of the 860 nm band (●) and the 294 nm band (○) in a KCl:$Tl^+$ (2.8 mole% in the melt) crystal which was exposed to X-rays at 77 K. The crystal was warmed to 250 K for 10 minutes after X-ray exposure and then cooled to 77 K again, and subsequently its absorption spectra were measured at various temperatures. The intensities of both bands are normalised at 77 K.

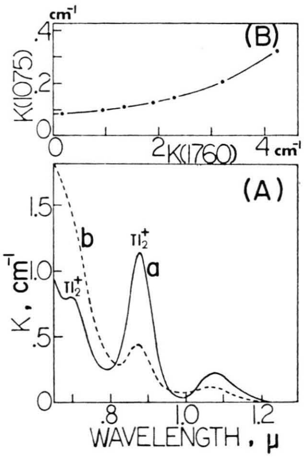

Fig. 4. (A) Absorption spectra, at 77 K, of the $Tl_2^+$ bands and the 1075 nm band in a KCl:$Tl^+$ (2.5 mole% in the melt) crystal (a) before and (b) after excitation with 470 nm light for 30 minutes. K denotes the absorption coefficient.

(B) Plots of the peak-height of the 1075 nm band versus that of the 1760 nm band of $Tl_2^+$ in the above crystal during the excitation in the 460 nm band of $Tl_2^+$. K(1760) means the maximum absorption coefficient of the 1760 nm band.

Figure 4A shows the absorption spectra, taken at 77 K, of an exposed KCl:$Tl^+$ (2.5 mole% in the melt) crystal which was warmed to near 300 K, then cooled to 77 K again and subsequently excited in the 460 nm band of $Tl_2^+$. A new absorption band is observable at 1075 nm in addition to the bands of $Tl_2^+$, $Tl^{++}$ and $Tl^0$. The 1075 nm band is enhanced after the thermal treatment which was undertaken to destroy $Cl_2^-$ and $Tl^0$. This band is not observed clearly in a lightly doped crystal (less than 0.05 mole% TlCl), but observed in a heavily doped crystal (more than 0.5 mole%). The more TlCl the crystal contains, the bigger the 1075 nm band becomes. The 1075 nm band does not belong to $Tl_2^+$, since the intensity-ratio among the 1075 nm band and the $Tl_2^+$ bands was not constant for crystals with different concentrations of TlCl. When the X-rayed crystal is excited in the 460 nm band, the 1075 nm band decays with the $Tl_2^+$ and $Tl^{++}$ bands but seems to survive the $Tl_2^+$ bands, as shown in Figure 4B.

## Discussion

From the experimental result that the optical bleaching of $Tl_2^+$ in a KCl:Tl$^+$ (less than 0.1 mole%) crystal results not only in the growth of $Tl^0$ but also in the decay of $Tl^{++}$, and from the result that the thermal excitation of a crystal containing only $Tl_2^+$ and $Tl^{++}$ results in the simultaneous decay of $Tl_2^+$ and $Tl^{++}$, it is believed that such an optical or thermal treatment does not dissociate $Tl_2^+$ into $Tl^0$ and $Tl^+$ but releases an electron from a $Tl_2^+$, which is then retrapped at a site of $Tl^+$ or $Tl^{++}$ to form a $Tl^0$ or to decay a $Tl^{++}$, respectively. A growth of the $Tl^0$ bands, however, was not observed clearly in the thermal excitation. This will be explained as follows: the electrons released from $Tl_2^+$ are partially trapped at $Tl^+$ to form $Tl^0$, whereas $Tl^0$ thermally decays at a higher temperature than 77 K to release the electron [1, 8] which is subsequently retrapped at $(Tl^+)_2$ or $Tl^{++}$ to form $Tl_2^+$ or to deform $Tl^{++}$, respectively.

The electrons released from $Tl_2^+$ are expected to be partially trapped at negative ion vacancies to form additional F centers. The number of such electrons, however, was too small to give a growth of the F band as seen in Fig. 5. The F-band intensity, which was obtained by subtracting the nearby 460 nm band from the spectra, was little changed by the optical bleaching of $Tl_2^+$. Thus, it is concluded that the electrons from $Tl_2^+$ are trapped mainly at $Tl^+$ and $Tl^{++}$ in a KCl:Tl$^+$ (less than 0.1 mole%) crystal.

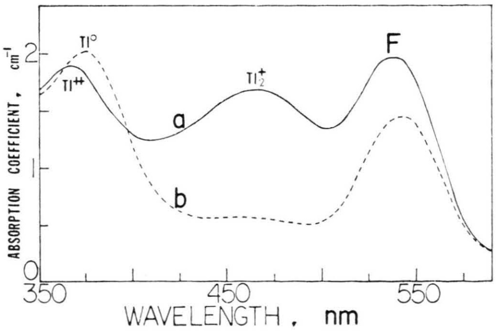

Fig. 5. Absorption spectra, at 77 K, of a KCl:Tl$^+$ (0.5 mole-% in the melt) crystal (a) before and (b) after excitation in the 460 nm band of $Tl_2^+$ for 30 minutes.

Now, let us calculate the oscillator strengths of the absorption bands of $Tl_2^+$. In the optical bleaching of $Tl_2^+$, in the first approximation, the decreased concentration of $Tl_2^+$ is given by the sum of the increased concentration of $Tl^0$ and the decreased concentration of $Tl^{++}$ as mentioned above. The concentrations of $Tl^0$ and $Tl^{++}$ are estimated easily since their oscillator strengths have been calculated by Delbecq et al. [1]. The estimated oscillator strengths of the $Tl_2^+$ bands are summarized in Table 1. The formula [12]

$$N f = 0.87 \times 10^{17} \frac{n}{(n^2+2)^2} k W$$

was used to calculate the oscillator strengths $f$, where $N$, $n$, $k$ and $W$ mean concentration (in cm$^{-3}$), index of refraction, peak-height (in cm$^{-1}$) of an absorption band, and its half-width (in eV), respectively. The $n$-value was derived from the extrapolation of the data given by Gyulai [13] and Tomiki [14].

Table I. Characteristics of the absorption bands of the $Tl_2^+$ center at 77 K.

| Peak-position | Half-width | Oscillator strength |
|---|---|---|
| 233 nm | 0.08 eV | 0.06 |
| 460 | ~ 0.64 | 0.36 |
| 680 | 0.16 | 0.002 |
| 860 | 0.14 | 0.007 |
| 1760 | 0.14 | 0.021 |

We shall calculate the number of electrons which are released from $Tl_2^+$ and trapped by $Tl^+$ and by $Tl^{++}$. One can estimate it from the change of the absorption intensites of the $Tl^0$ and $Tl^{++}$ bands by the optical bleaching of the $Tl_2^+$ bands. An estimate was obtained after excitation in the 460 nm band in a KCl:Tl$^+$ (about 0.1 mole%) crystal for 25 minutes. The result was that the number of electrons trapped by $Tl^+$ is $3.5 \times 10^{15}/cm^3$, whereas that trapped by $Tl^{++}$ $9.6 \times 10^{15}/cm^3$. It is noted that the latter is larger than the former. This seems reasonable, since the divalent ion of $Tl^{++}$ probably exerts a more attractive Coulomb force on the electrons in alkali halide lattice than the monovalent ion of $Tl^+$ does.

It is likely that the new 1075 nm band arises from $Tl_2^{+++}$ which is formed when a $(Tl^+)_2$ traps the hole released from nearby $Cl_2^-$. $Tl_2^{+++}$ decays into $(Tl^+)_2$ by recombination with the electron released from $Tl_2^+$ *. A photoionization of $(Tl^+)_2$ will also produce $Tl_2^{+++}$. Our previous measurement showed that $(Tl^+)_2$ has the absorption bands at 254, 215 and 207 nm. None of the excitation in these bands, however, produced the 1075 nm band. It is expected that $(Tl^+)_2$ possesses another higher excited state in the vacuum ultraviolet region. The corresponding optical excitation would give photoionization although we have not found it yet.

## *Summary*

The principal results of this work are the following:

a) A new absorption band peaking at 233 nm is attributable to $Tl_2^+$.
b) By the optical and thermal excitations of a KCl:$Tl^+$ (less than 0.1 mole%) crystal, electrons are released from the $Tl_2^+$ centers and are mobile in the crystal.
c) Most of the electrons, which are released from $Tl_2^+$, are trapped at $Tl^+$ and $Tl^{++}$, resulting in the formation of $Tl^0$ and in the annihilation of $Tl^{++}$, respectively.
d) In a heavily doped KCl:$Tl^+$ (more than 0.5 mole%) crystal, part of the electrons released from $Tl_2^+$ are trapped at $Tl_2^{+++}$ which has an absorption band at 1075 nm.

## *Acknowledgements*

The author would like to thank Professor Donald S. McClure for useful discussions. He also wishes to thank Miss. Y. Matsusaka for assistance at the initial stage of this work.

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* Earlier work [11], which involves ESR measurement of $\gamma$-rayed KCl:$Tl^+$ (more than 5 mole% in the melt) crystals using an X-band spectrometer working at 9.22 GHz, showed that four new ESR-signals with equal intensity (centered at 5.88, 6.27, 7.08 and 7.57 kG) are observed on the tails of two ESR-signals due to $Tl^{++}$ ion[15] (centered at 6.08 and 7.32 kG). The intensity of the new signals were smaller than that of the $Tl^{++}$ signals: the former was about 0.06 of the latter. Each of the new lines showed the same superhyperfine structure as the central $Tl^{++}$ lines. It is believed that the four satellite signals arise from $Tl_2^{+++}$, because the behaviors of the ESR signals are similar to those of the 1075 nm band, and because their hyperfine and superhyperfine structures can be explained using the spin Hamiltonian for a $Tl^{++}$ ion which is accompanied with six first-nearest-neighbor $Cl^-$ ions and with a second-nearest-neighbor $Tl^+$ ion in KCl lattice. Toyotomi and Onaka[10] also observed the same four satellite signals.

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