

## Geometrical structure of $(\text{Tl}^+)_2$ luminescent center in alkali halides: Presence of $D_{2h}$ and $D_{4h}$ dimer centers

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Absorption, emission, and excitation spectra of the  $(\text{Tl}^+)_2$  center in KI, KBr, and KCl have been investigated and compared with the excitation spectrum of the  $(\text{Au}^-)_2$  center with  $D_{2h}$  symmetry in KCl. Dichroism produced in the  $\text{Tl}_2^+$  absorption band after bleaching with polarized light has also been investigated in  $\gamma$ -ray-irradiated  $\text{KCl}:\text{Tl}^+$ . From these results and from the magnetic-circular-dichroism measurements, it is shown that the  $(\text{Tl}^+)_2$  absorption bands observed thus far arise from a  $D_{2h}$ -symmetry  $(\text{Tl}^+)_2$  center. An additional absorption band called  $A'$ , which has been found at a position close to the peak position of the  $A$  band, produces an emission band which is different from the previously observed  $(\text{Tl}^+)_2$  emission bands. From a systematic investigation of the separation between the  $A'$  and  $A$  bands in various alkali halides, it is shown that the  $A'$  band arises from a  $D_{4h}$ -symmetry  $(\text{Tl}^+)_2$  center.

### I. INTRODUCTION

In alkali halide crystals containing  $\text{Tl}^+$  concentrations of less than  $10^{-3}$  mol %,  $\text{Tl}^+$  monomer center is formed when a  $\text{Tl}^+$  ion is substituted for an alkali ion far from other  $\text{Tl}^+$  ions as shown in Fig. 1(a), giving rise to absorption bands labeled  $A$ ,  $B$ ,  $C$ , and  $D$ .<sup>1</sup> As the  $\text{Tl}^+$  concentration is increased, another center called  $\text{Tl}^+$  dimer, i.e.,  $(\text{Tl}^+)_2$ , is formed when two  $\text{Tl}^+$  ions occupy nearby cation sites. Two geometrical structures are possible for the dimer center: one is a dimer with  $D_{2h}$  symmetry, where two  $\text{Tl}^+$  ions are at the nearest cation sites in a  $[110]$  direction [Fig. 1(b)], the other is a dimer with  $D_{4h}$  symmetry where two  $\text{Tl}^+$  ions are at the second-nearest cation sites in a  $[100]$  direction [Fig. 1(c)]. Since the population is proportional to the square of the  $\text{Tl}^+$  concentration for both dimer centers,<sup>2</sup> one can easily identify the  $(\text{Tl}^+)_2$  absorption band by measuring the concentration dependence of its intensity. Since the first observation of  $(\text{Tl}^+)_2$  absorption bands in KI in 1953,<sup>3</sup> considerable work has been reported on the optical properties of  $\text{Tl}^+$  dimer center in various alkali halides, e.g., in KCl,<sup>2,4-6</sup> KBr,<sup>2,5,7,8</sup> KI,<sup>2,4,5,7-10</sup> NaI,<sup>11-14</sup> RbI,<sup>4,15</sup> and CsI.<sup>4</sup>

So far, many investigators have devoted their attention to determining whether the  $(\text{Tl}^+)_2$  center has a  $D_{2h}$  symmetry or  $D_{4h}$  symmetry. Unfortunately, conflicting assignments have been suggested; one group suggests the  $D_{2h}$  dimer,<sup>2,7,10,11,15</sup> the other the  $D_{4h}$  dimer.<sup>4,5,9,13,16</sup> These assignments have been suggested mainly from the azimuthal dependence of polarized luminescence measured with the use of a so-called "straight-through" optical arrangement, where one detects the luminescence emitted from the same direction as the propagation of exciting light.<sup>17</sup> The group supporting the  $D_{4h}$  dimer has simply come to this conclusion from the experimental result that the degree of polarization (DOP) takes a minimum in the  $[110]$  direction and a maximum in the  $[100]$  direction,<sup>4,16</sup> although a  $D_{2h}$ -dimer model is able to explain the result

also (see Fig. 5 of Ref. 7).

The method that uses the polarized luminescence, which has been known to be useful in determining the symmetry of color centers,<sup>17</sup> seems to be unsuitable to establish the  $(\text{Tl}^+)_2$  geometry for the following reasons. Firstly, the azimuthal dependence observed thus far has not agreed with any model quantitatively, especially regarding the value of DOP at its maximum and minimum. Secondly, the absorption bands of the dimer center are located close to those of the monomer center, and they overlap each other, which is also true for the emission bands in some crystals.<sup>2,14</sup> Therefore, since the monomer luminescence is polarized by the Jahn-Teller effect,<sup>18</sup> the observed polarization of luminescence produced by excitation in the  $(\text{Tl}^+)_2$  absorption bands involves inevitably an effect of polarization or depolarization by the monomer center, which makes it difficult to estimate the exact DOP of dimer luminescence. Thirdly, the "straight-through" measurement is technically not so easy because, for example, an accurate orientation must always be chosen for the crystal axes and for the electric vectors of exciting light and luminescence, sometimes resulting in a discrepancy of

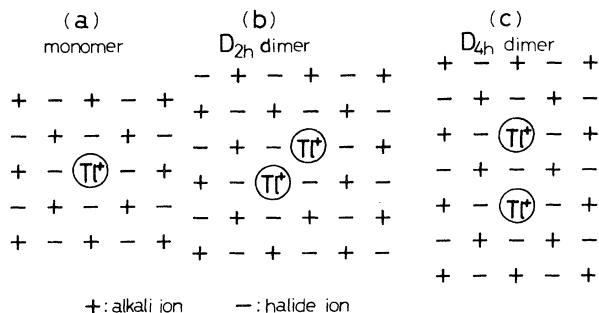


FIG. 1. (a) Geometrical structure of  $\text{Tl}^+$  monomer and [(b) and (c)]  $\text{Tl}^+$  dimer centers in alkali halides.

experimental results between investigators. For example: (1) Trinkler and Zolovkina<sup>19</sup> observed a maximum DOP of  $\sim 0.08$  at  $45^\circ$  (i.e., in the  $[110]$  direction) for 440-nm emission produced by excitation with 283-nm light in  $\text{KI}:\text{Ti}^+$ , whereas Ohata *et al.*<sup>10</sup> observed a minimum DOP of  $\sim -0.07$  at  $45^\circ$  for the same emission by excitation with 284.5-nm light; (2) Tsuboi and Jacobs<sup>7</sup> observed a minimum polarization DOP of 0 at  $45^\circ$  for 426-nm emission by excitation with 250-nm light in  $\text{KI}:\text{Ti}^+$  in agreement with Zazubovich's result,<sup>4</sup> whereas Ohata *et al.* observed a maximum at  $45^\circ$  for the same emission by excitation with 249.5-nm light. Lastly, the dimer luminescence is finally produced after passing through several processes, e.g., (1) radiationless transitions among excited states and a relaxed excited state of  $(\text{Ti}^+)_2$  and (2) energy transfer between monomer and dimer centers.<sup>12,20</sup> These processes give rise to depolarization of luminescence, which makes it difficult to determine the geometry accurately since the theory of the depolarization mechanism has not been established yet.

It is desirable, in order to determine the  $(\text{Ti}^+)_2$  geometry, to investigate the characteristics of the absorption spectrum rather than investigate the DOP of luminescence, because the absorption spectrum reflects the geometry more directly than the polarization of luminescence. In this paper we use two methods to determine the  $(\text{Ti}^+)_2$  geometry. One is to find all the  $(\text{Ti}^+)_2$  absorption bands, not only by the absorption spectrum but by the excitation spectrum, and to compare them with the  $(\text{Au}^-)_2$  absorption bands in alkali halides. The  $(\text{Au}^-)_2$  has the same electronic structure as  $(\text{Ti}^+)_2$  and has been established to have a  $D_{2h}$  symmetry,<sup>21,22</sup> therefore the comparison with the  $(\text{Au}^-)_2$  data is expected to be useful for our purpose. The other method is to elucidate the  $(\text{Ti}^+)_2$  structure from the geometrical structure of the  $\text{Ti}_2^+$  center which is formed when  $(\text{Ti}^+)_2$  captures an electron.<sup>23-25</sup>

## II. EXPERIMENTAL PROCEDURE

Single crystals of KI, KBr, and KCl containing various  $\text{Ti}^+$  concentrations ( $10^{-4}$ – $10^{-1}$  mol %) were grown by the Kyropoulos or Stockbarger method. Absorption spectra were measured with a Shimadzu model MPS-50L spectrophotometer. A Shimadzu model QV-50 quartz-prism monochromator in conjunction with a 500-W Xe lamp was adopted to produce exciting light. The crystal luminescence emitted at right angles to the exciting beam was passed through another Shimadzu model QV-50 monochromator and detected with a RCA model 1P28 photomultiplier. Excitation spectra were measured by setting the emission monochromator at the wavelength of interest and scanning the excitation monochromator. Care was taken to narrow the slits of the excitation monochromator (band pass of less than 1 nm) to obtain sufficient resolution in the spectra.

The measurements of optical bleaching of the  $\text{Ti}_2^+$  band in KCl were carried out as follows. A heavily  $\text{Ti}^+$ -doped crystal was irradiated with  $\gamma$  rays at 77 K at the Institute for Chemical Research of Kyoto University. To enhance the  $\text{Ti}_2^+$  absorption bands, the irradiated crys-

tal was warmed to about 200 K and cooled to 77 K again. Optical bleaching was done using the previously described excitation monochromator and attached Xe lamp. A Glan prism was used to polarize the measuring and bleaching light. Absorption measurements were done at 77 K.

## III. EXPERIMENTAL RESULTS

### A. Absorption bands due to $(\text{Ti}^+)_2$

Figure 2(b) shows the absorption spectrum of a  $\text{KI}:\text{Ti}^+$  (0.045 mol %) crystal at 15 K. Two  $(\text{Ti}^+)_2$  absorption bands are observed on the low-energy side of the *A* band, and two bands on the low-energy side of the *B* band. Optical excitation in any of these  $(\text{Ti}^+)_2$  bands is known to produce a single emission band peaking at 412 nm at 15 K.<sup>2</sup> The excitation spectrum for the 412-nm emission is shown in Fig. 2(a), where the observed peaks are labeled  $A_1$ ,  $A_2$ ,  $A_3$ ,  $B_1$ ,  $C_1$ ,  $C_2$ ,  $C_3$ , and  $D_1$ . The labeling was made taking into account our previous assignment for the  $(\text{Ti}^+)_2$  bands,<sup>2,8</sup> i.e.,  $X_i$  ( $X=A,B,C,D$ ;  $i=1,2,3$ ) means the  $(\text{Ti}^+)_2$  band associated with the *X* band of the monomer center. In addition to the  $A_1$ ,  $A_2$ ,  $B_1$ , and  $C_1$  bands found in the absorption spectrum, two weak bands ( $A_3$  and  $C_2$ ) are found in the *A*- and *B*-band regions, and a relatively strong band ( $C_3$ ) is found at the tail of the *C* band. These bands, which are hidden under the strong monomer bands in the absorption spectrum, are attributable to the  $(\text{Ti}^+)_2$  center since they were confirmed to produce the 412-nm  $(\text{Ti}^+)_2$  emission band by excitation in these bands as was the case of the  $A_1$ ,  $A_2$ ,  $B_1$ , and  $C_1$  bands.

Figure 3 shows the absorption and excitation spectra of a  $\text{KBr}:\text{Ti}^+$  (0.15 mol %) crystal at 15 K. Optical excitation in the  $(\text{Ti}^+)_2$  band produces an emission band peaking at 443 or 312 nm at 15 K, depending on the absorption band excited. For example, a low-energy component ( $A_1$ ) of the doublet-structured absorption band, which ap-

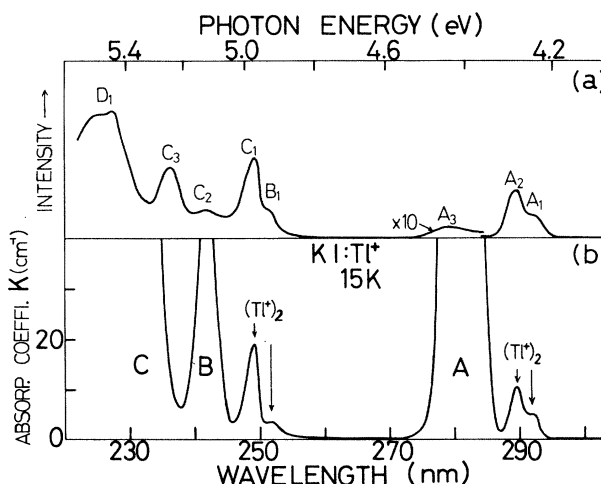


FIG. 2. (a) Excitation spectrum for 412-nm emission and (b) absorption spectrum of a  $\text{KI}:\text{Ti}^+$  (0.045 mol %) crystal at 15 K.

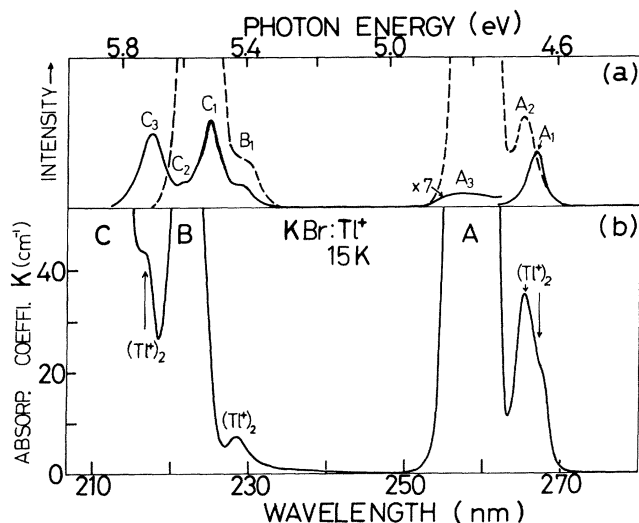


FIG. 3. (a) Excitation spectra for 443-nm emission (solid curve) and for 312-nm emission (dotted curve) and (b) absorption spectrum of a KBr:Ti<sup>+</sup> (0.15 mol %) crystal at 15 K.

peaks on the tail of the *A* band, produces the 443-nm emission band, whereas a high-energy component (*A*<sub>2</sub>) produces the 312-nm emission band. The *A*<sub>3</sub>, *C*<sub>1</sub>, and *C*<sub>2</sub> bands, which are hidden under the strong monomer bands, are found by the excitation spectrum for the 443-nm emission. Unlike the case of KI, the *C*<sub>3</sub> band happens to be observed in the absorption spectrum. Similarities are seen in the excitation spectra for KI and KBr; a weak band (*A*<sub>3</sub>) appears at the high-energy tail of the doublet-structured *A*<sub>1</sub>-*A*<sub>2</sub> band, a weak band (*C*<sub>2</sub>) appears between the *C*<sub>1</sub> and *C*<sub>3</sub> bands, and the *C*<sub>1</sub>, *C*<sub>2</sub>, and *C*<sub>3</sub> bands appear in the *B*-band region on the low-energy tail of the *C* band.

In KCl:Ti<sup>+</sup> it is known that an emission band peaking at 475 nm is attributable to the (Ti<sup>+</sup>)<sub>2</sub> center.<sup>2,4,26</sup> Figure 4 shows the excitation spectrum for the 475-nm emission at 77 K together with the absorption spectrum of a KCl:Ti<sup>+</sup> (0.1 mol % in the melt) crystal for comparison.

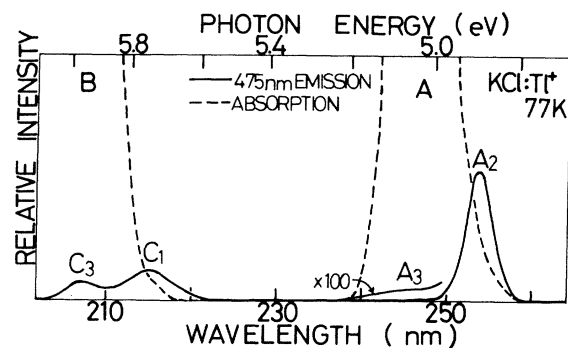


FIG. 4. Excitation spectrum from 475-nm emission (solid curve) and absorption spectrum (dotted curve) of KCl:Ti<sup>+</sup> (0.1 mol % in the melt) at 77 K.

Peaks are observed at 253.8, 215.5, and 207 nm in the excitation spectrum, and additionally a considerably weaker band at the high-energy tail of the 253.8-nm band. From the comparison with the data of KI and KBr, these bands can be labeled *A*<sub>2</sub>, *C*<sub>1</sub>, *C*<sub>3</sub>, and *A*<sub>3</sub> as shown in Fig. 4. The 253.8-nm band observed as a single band at 77 K is believed to exhibit a doublet structure composed of *A*<sub>1</sub> and *A*<sub>2</sub> bands (the *A*<sub>2</sub> is about twice the *A*<sub>1</sub> in intensity) at low temperatures as we have observed at 77 and 15 K for the *A*<sub>1</sub> and *A*<sub>2</sub> bands of KI and KBr. We tried to find the structure at 15 K in both the absorption and excitation spectra, but we were not successful, presumably because (1) the 253.8-nm band is too close to the strong *A* band to be resolved from the *A* band clearly in the absorption spectrum, and (2) the 475-nm emission disappears at low temperatures.<sup>27</sup>

In Table I are summarized the peak positions of the (Ti<sup>+</sup>)<sub>2</sub> bands in KI, KBr, and KCl, together with the separation between the *A*<sub>1</sub> and *A*<sub>3</sub> bands and between the *C*<sub>1</sub> and *C*<sub>3</sub> bands. The present investigation has revealed the presence of two weak *A*<sub>3</sub> and *C*<sub>2</sub> bands, which was missed in the previous investigation,<sup>7</sup> and moreover revealed that both bands arise from the same (Ti<sup>+</sup>)<sub>2</sub> center that is responsible for the *A*<sub>1</sub>, *A*<sub>2</sub>, *B*<sub>1</sub>, *C*<sub>1</sub>, and *C*<sub>3</sub> bands.

TABLE I. Peak position (in eV) of absorption bands due to (Ti<sup>+</sup>)<sub>2</sub> center in KI, KBr, and KCl and due to the (Au<sup>-</sup>)<sub>2</sub> center in KCl.

	KI:(Ti <sup>+</sup> ) <sub>2</sub>	KBr:(Ti <sup>+</sup> ) <sub>2</sub>	KCl:(Ti <sup>+</sup> ) <sub>2</sub>	KCl:(Au <sup>-</sup> ) <sub>2</sub>
Band				
<i>A</i> <sub>1</sub>	4.238	4.648		3.96
<i>A</i> <sub>2</sub>	4.281	4.664	4.88 <sup>a</sup>	4.07
<i>A</i> <sub>3</sub>	4.46 <sup>a</sup>	~4.82 <sup>a</sup>		~4.28
<i>B</i> <sub>1</sub>	4.915	5.426		
<i>C</i> <sub>1</sub>	4.989	5.51 <sup>a</sup>	5.76 <sup>a</sup>	5.08
<i>C</i> <sub>2</sub>	5.123 <sup>a</sup>	~5.56 <sup>a</sup>		5.27
<i>C</i> <sub>3</sub>	5.253 <sup>a</sup>	5.71	~5.96 <sup>a</sup>	5.44
Separation				
<i>A</i> <sub>1</sub> - <i>A</i> <sub>3</sub>	0.23	0.18		0.32
<i>C</i> <sub>1</sub> - <i>C</i> <sub>3</sub>	0.27	0.20	~0.20	0.36

<sup>a</sup>Obtained from excitation spectrum.

TABLE II. Anisotropy produced by bleaching with polarized light.  $[\Delta(\text{OD})]_{100}$ : Decrement of optical density (OD) measured with light polarized along [100].

OD parallel to	Bleached with [100] light		Bleached with [110] light	
	[100]	[010]	[110]	[1 $\bar{1}$ 0]
Center oriented parallel to				
[100]	decrease of (OD) <sub>100</sub>	$[\Delta(\text{OD})]_{010}=0$	$[\Delta(\text{OD})]_{110}=[\Delta(\text{OD})]_{1\bar{1}0}$	
[110]	$[\Delta(\text{OD})]_{100}=2[\Delta(\text{OD})]_{010}$		$[\Delta(\text{OD})]_{110}=5[\Delta(\text{OD})]_{1\bar{1}0}$	
[111]	$[\Delta(\text{OD})]_{100}=[\Delta(\text{OD})]_{010}$		decrease of (OD) <sub>110</sub>	$[\Delta(\text{OD})]_{1\bar{1}0}=0$
$\text{Ti}_2^+$ (experiment)	$[\Delta(\text{OD})]_{100}=2.02[\Delta(\text{OD})]_{010}$		$[\Delta(\text{OD})]_{110}=2.73[\Delta(\text{OD})]_{1\bar{1}0}$	

### B. Dichroism of $\text{Ti}_2^+$ center

The  $\text{Ti}_2^+$  center is produced in heavily  $\text{Ti}^+$ -doped alkali halide crystals which were irradiated with  $\gamma$  or x rays,<sup>23-25,28,29</sup> giving rise to five absorption bands at 233, 460, 680, 860, and 1760 nm in KCl.<sup>25</sup> These  $\text{Ti}_2^+$  bands were found to be bleached by optical irradiation into the 460-nm band at 77 K or by thermal treatment.<sup>25</sup> Here we investigate the dichroism produced in the absorption bands after bleaching with polarized light to determine the symmetry of  $\text{Ti}_2^+$ . Data on the anisotropic bleaching of the 460-nm  $\text{Ti}_2^+$  band are shown in Figs. 5 and 6. The  $\gamma$ -ray irradiation and optical bleaching were made at 77 K. Figure 5 was measured with light polarized along [100] and [010] after irradiation with 460-nm light polarized along [100], whereas Fig. 6 was measured with light polarized along [110] and [1 $\bar{1}$ 0] after irradiation with 460-nm light polarized along [110]. It is seen in the 460-nm band that the decrement of absorption intensity mea-

sured with light polarized along [100],  $\Delta(\text{OD})_{100}$ , is about twice of  $\Delta(\text{OD})_{010}$ , whereas  $\Delta(\text{OD})_{110}=2.73\Delta(\text{OD})_{1\bar{1}0}$ . The same was also obtained in the other  $\text{Ti}_2^+$  bands.

The upper part of Table II presents a summary of the expected change that is introduced in an absorption band in a NaCl-type crystal by bleaching with polarized light, if the band results from centers whose dipole moments are parallel to [100], [110], or [111].<sup>30</sup> The lower part of Table II presents a summary of our experimental results on the  $\text{Ti}_2^+$  band. The table indicates that the dipole moment of  $\text{Ti}_2^+$  center in KCl is parallel not to [100] but preferably to [110], although  $\Delta(\text{OD})_{110}$  did not become exactly 5 times of  $\Delta(\text{OD})_{1\bar{1}0}$ , presumably by a small error of crystal orientation. This suggests that the geometrical structure of  $\text{Ti}_2^+$  has a  $D_{2h}$  symmetry. This is consistent with the recent results of electron spin resonance (ESR) due to the  $\text{Ti}_2^+$  center in KCl, which indicate that two  $\text{Ti}^+$  ions of  $\text{Ti}_2^+$  are at the nearest-neighbor cation sites.<sup>29</sup>

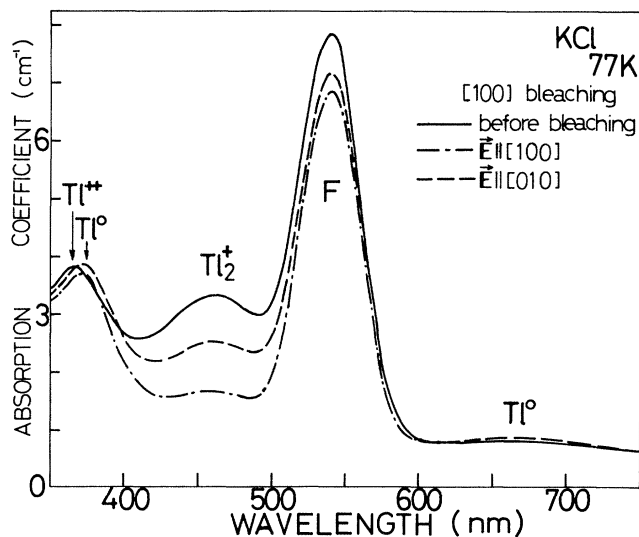


FIG. 5. Absorption spectrum measured at 77 K of a KCl: $\text{Ti}^+$  (0.15 mol % in the melt) crystal exposed to  $\gamma$  rays at 77 K for 4 h and irradiated with 460-nm light polarized along [100] at 77 K for 1 h. Curves show the spectra measured before the 460-nm light irradiation and measured with light polarized along [100] and [010] after irradiation.

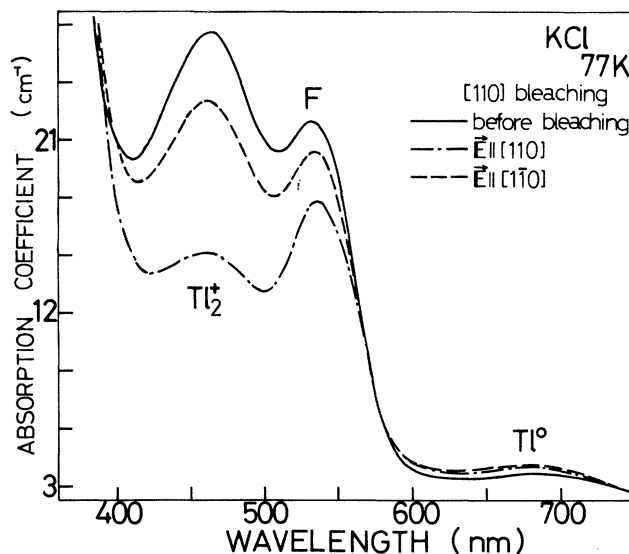


FIG. 6. Absorption spectra measured at 77 K of a KCl: $\text{Ti}^+$  (0.3 mol % in the melt) crystal exposed to  $\gamma$  rays at 77 K for 4 h and irradiated with 460-nm light polarized along [110] at 77 K for 1.5 h. Curves show the spectra measured before the 460-nm light irradiation and measured with light polarized along [110] and [1 $\bar{1}$ 0] after irradiation.

## IV. DISCUSSION

A. Presence of  $D_{2h}$  dimer

We have observed the  $A_1$ ,  $A_2$ ,  $A_3$ ,  $B_1$ ,  $C_1$ ,  $C_2$ , and  $C_3$  bands of  $(\text{Tl}^+)_2$  in KI, KBr, and KCl by the absorption or excitation spectrum. The  $A_1$ - $C_3$  band spectrum is quite similar among KI, KBr, and KCl; for example, (1) the  $A_1$  and  $A_2$  bands are located close to each other, giving a doublet-structured band where the  $A_2$  band is about twice the  $A_1$  band in intensity, and (2) the  $C_3$  band is lower in peak height than the  $C_1$  band. This allows us to draw a conclusion that the same  $(\text{Tl}^+)_2$  center gives rise to these bands in all the KI, KBr, and KCl crystals. In the following, we discuss which of the  $D_{2h}$  and  $D_{4h}$ -dimer centers is responsible for these bands.

A spectrum showing the positions of absorption bands due to  $(\text{Au}^-)_2$  was first obtained in KCl by Yoshikawa *et al.*<sup>21</sup> The similar spectrum was also obtained by us, as shown in Fig. 7.<sup>31</sup> Six bands are observed: Three of them are associated with the  $A$  band of  $\text{Au}^-$  monomer, and the others are associated with the  $C$  band. These are labeled  $A_1$ ,  $A_2$ ,  $\dots$ ,  $C_3$  (see Fig. 7) as in the case of the  $(\text{Tl}^+)_2$  bands, and different from the labeling by Yoshikawa *et al.* When comparing the  $(\text{Au}^-)_2$  spectrum with the  $(\text{Tl}^+)_2$  spectrum of KI, KBr, or KCl, we find a similarity between them: (1) The  $A_1$  band is superimposed on the  $A_2$  band, and its intensity is about a half of the  $A_2$  band, (2) a weak and broad  $A_3$  band is present at the high-energy tail of the  $A_2$  band, (3) a weak  $C_2$  band is present between the strong  $C_1$  and  $C_3$  bands, and (4) the separation between the  $A_1$  and  $A_3$  bands is almost equal to the  $C_1$ - $C_3$  separation as seen in Table I. The  $(\text{Au}^-)_2$  center responsible for the bands shown in Fig. 7 has been experimentally and theoretically established to have a  $D_{2h}$  symmetry as in the case of the  $(\text{Ag}^-)_2$  center.<sup>21,22,32,33</sup> Therefore, since  $(\text{Au}^-)_2$  has the same electronic structure as  $(\text{Tl}^+)_2$ , we can suggest that the  $(\text{Tl}^+)_2$  bands shown in Figs. 2-4 arise from the dimer center with  $D_{2h}$  symmetry.

As mentioned in Sec. IIIB, the  $\text{Tl}_2^+$  absorption band has been concluded to have a transition moment parallel to the [110] direction from the results of dichroism. Moreover we have observed that the growth and decay of

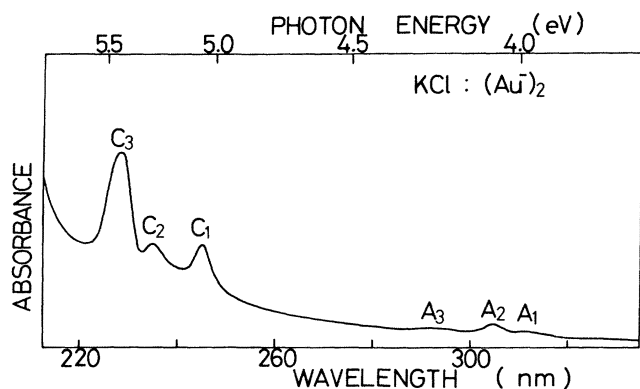


FIG. 7. A spectrum showing the  $(\text{Au}^-)_2$  absorption bands in KCl at 50 K.

the  $\text{Tl}_2^+$  band parallels the decay and growth of the  $A_2$  or  $C_1$  band of  $(\text{Tl}^+)_2$ , respectively.<sup>24</sup> These facts suggest that the  $(\text{Tl}^+)_2$  center in question can capture an electron to change into  $\text{Tl}_2^+$  and therefore it has the same  $D_{2h}$  symmetry as  $\text{Tl}_2^+$ , since moving of heavy Tl by the trapping is not expected.

The same suggestion is also obtained from the following experimental results. Firstly, our previous data of magnetic circular dichroism (MCD) on the  $A_1$ ,  $A_2$ , and  $C_1$  absorption bands are consistent with the  $D_{2h}$ -symmetry model for the  $(\text{Tl}^+)_2$  center in KI and KBr.<sup>8</sup> Secondly, unlike the case of KI, the 443-nm  $(\text{Tl}^+)_2$  emission band of KBr is located far from the emission bands of the monomer center. In this case, the polarized luminescence may be used to suggest the symmetry of  $(\text{Tl}^+)_2$  center as was done for the  $(\text{Ag}^-)_2$  and  $(\text{Au}^-)_2$  centers, because the effect of monomer luminescence is avoidable. The DOP was observed to take a maximum (with a positive DOP value) in the [110] direction and a minimum in the [100] direction in the azimuthal dependence of polarized luminescence.<sup>7</sup> The azimuthal dependence showing a maximum in the [110] direction with such a positive value is expected from the  $D_{2h}$  dimer but not from the  $D_{4h}$  dimer (see Fig. 5 of Ref. 7). The above result is consistent with our previous one, which was obtained from an analysis using the method of *independent systems approach*.<sup>2</sup>

B. Presence of  $D_{4h}$  dimer

In the preceding section we experimentally came to a conclusion that the  $D_{2h}$ -symmetry  $(\text{Tl}^+)_2$  center is present in alkali halides. The presence of such a dimer center has been confirmed by a calculation of the  $\text{Tl}^+$ - $\text{Tl}^+$  binding energy.<sup>34</sup> On the other hand, Ermoshkin *et al.*<sup>5</sup> have suggested that a calculation of stability energy and bond orders that the  $D_{4h}$  dimer is more preferable in KCl and KI than the  $D_{2h}$  dimer. Moreover, according to Ermoshkin,<sup>35</sup> a calculation of the electronic structure of  $(\text{Tl}^+)_2$  in KCl, KBr, and KI suggests that the  $D_{4h}$  dimer is much more probable in KCl than in KI, whereas both  $D_{4h}$ - and  $D_{2h}$ -dimer centers are admitted in KI.

Is the prediction for the presence of the  $D_{4h}$  dimer by such theoretical calculations inconsistent with our result? The answer is "no." The statements mentioned in Sec. IV A simply allow us to draw a conclusion that *the  $(\text{Tl}^+)_2$  center which gives rise to the  $A_1, A_2, \dots, C_3$  bands has a  $D_{2h}$  symmetry.* We believe that two kinds of dimer centers are present in alkali halides since the  $\text{Tl}^+$ - $\text{Tl}^+$  binding in alkali halides has not been theoretically suggested to be impossible for either center and since there is no reason that a  $\text{Tl}^+$  ion is allowed to occupy neither the nearest-neighbor cation site of another  $\text{Tl}^+$  ion nor the next-nearest cation site. We believe that the  $D_{4h}$  dimer gives rise to absorption and emission bands different from the  $D_{2h}$  dimer because of the difference in geometry, and moreover that previously observed  $(\text{Tl}^+)_2$  bands due to the  $D_{2h}$  dimer happened to be easily observed in the absorption spectrum.

An emission band peaking at 380 nm has been observed in KCl: $\text{Tl}^+$  together with the 475-nm  $(\text{Tl}^+)_2$  emission band.<sup>6,36</sup> Its excitation band has a peak at 252.5 nm,

which is different from the excitation band peak at 253.8 nm for the 475-nm emission.<sup>6</sup> The 380-nm emission has been confirmed to arise not from the  $\text{Tl}^+$ -monomer center but from a  $\text{Tl}^+$ -aggregate center. It may be attributable to  $(\text{Tl}^+)_2$  since it appears even in a relatively lightly doped crystal such as  $\text{KCl:0.0009 wt \% Tl}^+$ , as was observed by Johnson and Williams.<sup>36</sup> The 252.5-nm band is not observed in the absorption spectrum because it is superimposed on the large  $A$  band. Similarly, an emission band peaking at 400 nm was recently found in  $\text{KBr:Tl}^+$  together with the 443-nm  $(\text{Tl}^+)_2$  emission band by us; its excitation band has a peak at 262 nm. On the other hand, Ohata *et al.* observed an additional  $(\text{Tl}^+)_2$  emission band peaking at 450 nm in  $\text{KI:Tl}^+$ ; its excitation band has a peak at 284.5 nm.<sup>10</sup> Such a new excitation band, which is called  $A'$  hereafter, is located closer to the  $A$  band than the main band of the  $D_{2h}$  dimer,  $A_2$  band. The similar  $A'$  band is also found in the data from  $\text{RbI}$  and  $\text{NaI}$ .<sup>14,15</sup> The center responsible for the  $A'$  band was found to give rise to absorption bands in the  $B$ - $C$ -band region too, just as in the case of the  $D_{2h}$  dimer. The emission band produced by the  $A'$ -band excitation is closer to the monomer emission band than the so-called "dimerlike" emission band<sup>2</sup> due to the  $D_{2h}$  dimer. For example, in  $\text{KCl}$  the 380-nm emission is energetically closer to the 300-nm monomer emission than the 475-nm emission, and in  $\text{KBr}$  the 400-nm emission is closer to the 363-nm monomer emission than the 443-nm emission.

The positions of the  $A'$  band in various alkali halides are summarized in Table III, together with the  $A_2$  band. We see the following results from Table III. (1) The  $A$ - $A_2$  separation is almost the same among  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{KI}$ , and  $\text{RbI}$ , and (2) the  $A$ - $A'$  separation is almost the same among three iodides  $\text{KI}$ ,  $\text{RbI}$ , and  $\text{NaI}$ , whereas it is different among  $\text{KCl}$ ,  $\text{KBr}$ , and  $\text{KI}$ , i.e., it decreases from  $\text{KCl}$  to  $\text{KBr}$  to  $\text{KI}$ . If we are allowed to speak generally, the  $A_2$ -band position measured from the  $A$  band depends on nei-

ther alkali ion (except  $\text{NaI}$ ) nor halide ion of the crystal, whereas the  $A'$ -band position depends not on the alkali ion, but on the halide ion.

When no covalency exists between two  $\text{Tl}^+$  ions of the dimer center, the electronic states of the  $\text{Tl}^+$  dimer can be approximated by those of a  $\text{Tl}^+$ -monomer center perturbed by another  $\text{Tl}^+$  ion, i.e., perturbed by a  $C_{2v}$  or  $C_{4v}$  crystal field for the  $D_{2h}$  or  $D_{4h}$  dimer, respectively. In this case the energy-level splitting is expected to be much smaller in the  $D_{4h}$  dimer than in the  $D_{2h}$  dimer since the  $\text{Tl}^+$ - $\text{Tl}^+$  distance is larger in the former than in the latter, indicating that the position of the  $D_{4h}$ -dimer band is nearer the monomer band in absorption and emission spectra than the  $D_{2h}$ -dimer band, and moreover that the separation between the  $D_{4h}$ -dimer band and monomer band decreases with increasing  $\text{Tl}^+$ - $\text{Tl}^+$  distance. When covalency exists between the  $\text{Tl}^+$  ions, on the other hand, the  $D_{4h}$ -dimer band position depends on the halide ion of the crystal but not on the alkali ion because the  $D_{4h}$  dimer has a halide ion between two  $\text{Tl}^+$  ions, whereas the  $D_{2h}$ -dimer band position depends little on the halide ion because the two  $\text{Tl}^+$  ions of the  $D_{2h}$  dimer contact each other directly (see Fig. 1).

From the comparison of such an expectation for the  $D_{2h}$ - and  $D_{4h}$ -dimer centers with the experimental results shown in Table III, we can suggest that the  $D_{4h}$  dimers are responsible for the  $A'$  band, whereas the  $D_{2h}$  dimer correlates with the  $A_2$  band. Therefore, one can understand that the absorption spectrum of a highly  $\text{Tl}^+$ -doped crystal, which induces strong and broad monomer bands, has never allowed us to find the  $D_{4h}$ -dimer bands, unlike the case of  $D_{2h}$ -dimer bands which are relatively far from the monomer bands.

Is the covalency between two  $\text{Tl}^+$  ions of a dimer center strong or not? In the case of  $(\text{Au}^-)_2$ , Yoshikawa *et al.* found that the  $(\text{Au}^-)_2$  bands disappear when a  $\text{KCl}:(\text{Au}^-)_2$  crystal is heated at about 400°C for a few

TABLE III. Peak position (in eV) of main absorption bands due to  $D_{2h}$ -dimer,  $D_{4h}$ -dimer, and monomer centers observed in the  $A$ -band region in  $\text{Tl}^+$ -doped alkali halides, and distance (in Å) between two  $\text{Tl}^+$  ions in  $D_{2h}$ -dimer and  $D_{4h}$ -dimer centers.

	KCl	KBr	KI	RbI	NaI
$A_2$ ( $D_{2h}$ dimer)	4.885 eV	4.664	4.281	4.33 <sup>a</sup>	4.067 <sup>b</sup>
$A'$ ( $D_{2h}$ dimer) <sup>c</sup>	4.910	4.732	4.358 <sup>d</sup>	4.39 <sup>a</sup>	4.22 <sup>e</sup>
$A$ (monomer)	5.020	4.802	4.400	4.44	4.263 <sup>b</sup>
Separation					
$A$ - $A_2$	0.135	0.138	0.119	0.11	0.196
$A$ - $A'$	0.110	0.070	0.042	0.05	0.04
$\text{Tl}^+$ - $\text{Tl}^+$ distance					
$D_{2h}$ dimer	4.44 Å	4.67	4.98	5.18	4.57
$D_{4h}$ dimer	6.28	6.59	7.05	7.33	6.46

<sup>a</sup>From Ref. 15.

<sup>b</sup>From Ref. 11.

<sup>c</sup>Obtained from excitation spectrum.

<sup>d</sup>From Ref. 10.

<sup>e</sup>From Ref. 14.

minutes.<sup>21</sup> We found, even when a  $\text{KCl}:(\text{Au}^-)_2$  crystal is kept at room temperature, the  $(\text{Au}^-)_2$  center is dissolved and changed to two  $\text{Au}^-$  monomer centers as time goes by, indicating the  $\text{Au}^-$ - $\text{Au}^-$  binding of the  $(\text{Au}^-)_2$  center is not so strong. On the other hand, the  $(\text{Tl}^+)_2$  center in an alkali halide crystal was found to be thermally stable. The  $(\text{Tl}^+)_2$  absorption bands never disappeared after such a thermal treatment or after holding the crystal at room temperature for a long time. We carried out an experiment of taking the absorption spectrum of a  $\text{KI}:\text{Tl}^+$  thin film. The film was evaporated on a LiF plate with the use of a heavily doped  $\text{KI}:\text{Tl}^+$  crystal. We first expected that  $(\text{Tl}^+)_2$  centers would be dissolved during the evaporation and only the  $\text{Tl}^+$ -monomer bands would be observed if the  $\text{Tl}^+$ - $\text{Tl}^+$  covalency is weak. The  $(\text{Tl}^+)_2$  bands, however, were found in the evaporated film as shown in Fig. 8. Moreover, the intensity ratio between the dimer and monomer bands were almost the same between the thin film and single crystal.<sup>37</sup> These facts indicate that, unlike the case of  $(\text{Au}^-)_2$ , the  $\text{Tl}^+$ - $\text{Tl}^+$  binding of  $(\text{Tl}^+)_2$  is not so weak.

## V. CONCLUSION

Firstly, we have noted that both the  $D_{2h}$ -symmetry  $(\text{Tl}^+)_2$  and  $D_{4h}$ -symmetry  $(\text{Tl}^+)_2$  centers are present together in an alkali halide crystal, giving rise to the absorption and emission bands that are different from each other. Secondly, we have found that all the  $A_1$ ,  $A_2$ ,  $A_3$ ,  $B_1$ ,  $C_1$ ,  $C_2$ , and  $C_3$  bands originated from the  $D_{2h}$ -dimer center. This was obtained from (1) the resemblance of the  $(\text{Tl}^+)_2$  absorption or excitation spectrum to the spectrum due to the  $(\text{Au}^-)_2$  center with  $D_{2h}$  symmetry, (2) the presence of  $D_{2h}$ -symmetry  $\text{Tl}_2^+$  centers, (3) the MCD measurements, and (4) the azimuthal dependence of polarized  $(\text{Tl}^+)_2$  luminescence in KBr. Thirdly, we have suggested that the absorption band  $A'$  originates from the  $D_{4h}$ -dimer

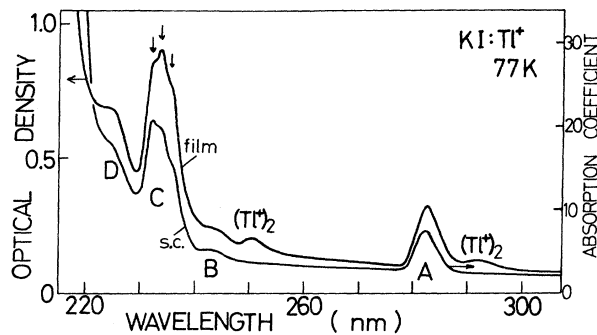


FIG. 8. Absorption spectrum of a  $\text{KI}:\text{Tl}^+$  thin film (scale on left), measured at 77 K, deposited on a Hawshaw LiF plate at 300 K. Original material to be evaporated was a fragment of  $\text{KI}:\text{Tl}^+$  (0.4 mol % in the melt) single crystal. Lower spectrum (labeled s.c. scale on right) is an absorption spectrum of a  $\text{KI}:\text{Tl}^+$  (0.001 mol %) single crystal with thickness of 0.47 nm, which is shown for comparison. Three arrows on the C band show the fine structure of the C band, which is induced by the Jahn-Teller effect.

center. In conclusion, we have abandoned the idea that either the  $D_{2h}$ -symmetry  $\text{Tl}^+$  dimer or the  $D_{4h}$ -symmetry  $\text{Tl}^+$  dimer is uniquely present in alkali halides, the idea which was implicitly believed by many investigators.

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