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Luminescence polarization of dimer centers in KI:Tl$^+$ crystals: Analysis of experimental data and structure of dimers

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An analysis of experimental results on luminescence polarization has been performed for dimer centers of D_{2h} symmetry in KI:Tl$^+$. The results obtained by theoretical calculations of the polarization degrees associated with the excitation and emission transitions allow us to assign the molecular orbitals of thallium dimer centers involved in the emission processes and to determine a possible sequence of the relaxed excited electronic states versus the energy.

I. INTRODUCTION

It is known[1-4] that ns^2 impurities in alkali-halide crystals give rise to single (monomers) A^+ and paired (dimers) $(A^+)_2$ centers.

It is well established that dimers have absorption bands called A', B', and C' related to A, B, and C monomer absorption bands, respectively,[2] and that excitation into these bands results in light emission.[3]

The attribution of the allowed electronic transitions involved in absorption, and more so in emission is still a debated question.[2,3,5-10] Moreover, the structural symmetry of dimers is a controversial point that needs further study also in the light of recent interesting results[11] (see Ref. 9 and references therein).

In a recent paper[10] we have found a good agreement between theoretical calculations and experimental results for the absorption states of thallium dimers $(\mathrm{Tl}^+)_2$ in potassium iodide. We have been able to identify the absorption states and their electronic symmetry.

Following these results we try, in this paper, to obtain a detailed description of the luminescence processes, analyzing all experimental results on luminescence and on its polarization reported so far for KI:Tl$^+$. In this way we find a possible assignment of the molecular orbitals of thallium-ion dimer centers in KI involved in the absorption and emission processes. These results, as far as the absorption processes are concerned, confirm our theoretical expectations.

II. EXPERIMENTAL RESULTS AND THEORETICAL PROCEDURE

A. Experimental data

The experimental data available on the polarized luminescence of thallium dimers in KI are reported in Fig. 1 (Ref. 11) and Fig. 2 (Ref. 6) for $T = 80$ K and in Fig. 3 (Ref. 8) for $T = 10$ K. Other results at 80 K, reported in Refs. 4 and 12, are in agreement with Figs. 1 and 2.

The analysis of these data shows that by raising the temperature from 10 to 80 K, the polarization degree decreases strongly while its polarity changes. Moreover, it has been shown that for a fixed excitation wavelength ($\lambda = 295$ nm) the polarization degree changes from negative to positive at about $T = 140$ K (Ref. 11) for zero azimuthal angle. This complex behavior suggest that (1) electronic states with different symmetry are involved in the luminescence processes and (2) different nonradiative processes can take place in these states when the temperature increases. The most meaningful results of the polarization behavior are summarized in Table I.

B. Theoretical considerations

In order to understand the whole behavior of the luminescence polarization of thallium dimers it is convenient to compare experimental and calculated polarization degree for the azimuthal angles $\theta = 0°$ and 45°. Theoretical calculations are performed on dimers of D_{2h} symmetry. This choice will be justified in the next section.

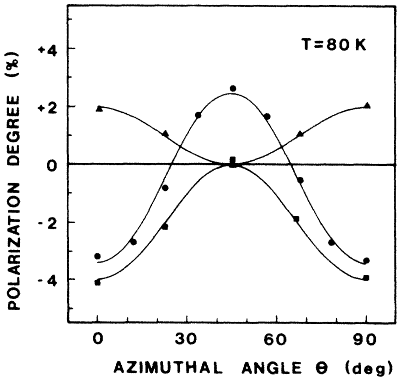

FIG. 1. Azimuthal dependence of polarization degree P measured at 80 K for 402-nm emission and $\lambda_{\mathrm{exc}} = 290$ nm (▲), $\lambda_{\mathrm{exc}} = 293$ nm (●), $\lambda_{\mathrm{exc}} = 295$ nm (■) by Benci *et al.* (Ref. 11).

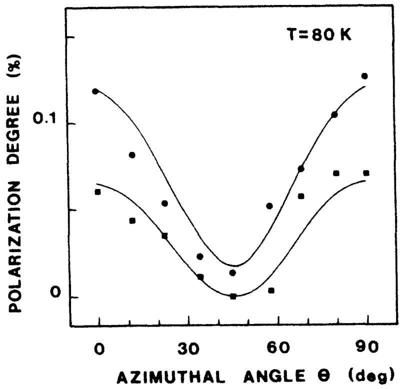

FIG. 2. Azimuthal dependence of polarization degree measured at 80 K for 405-nm emission and $\lambda_{exc}=250$ nm (●), $\lambda_{exc}=291$ nm (■) by Tsuboi and Jacobs (Ref. 6).

The dimer orientation axes are shown in Fig. 4. Absorption or emission transition moments parallel or perpendicular to the dimer axes are called Σ and Π, respectively. The two Π transitions will be Π_2 if parallel to the twofold axis or Π_4 when parallel to the fourfold axis of the crystal.

In order to obtain the polarization degree P we first calculate the polarization degree P_i linked to the pure absorption transitions Σ, Π_2, or Π_4. Then, when more than one absorption transition is involved P is calculated[13] by means of the following relationship:

$$P=\frac{\sum_i \alpha_i P_i I_i}{\sum_i \alpha_i I_i}, \quad i=\Sigma,\Pi_2,\Pi_4 \tag{1}$$

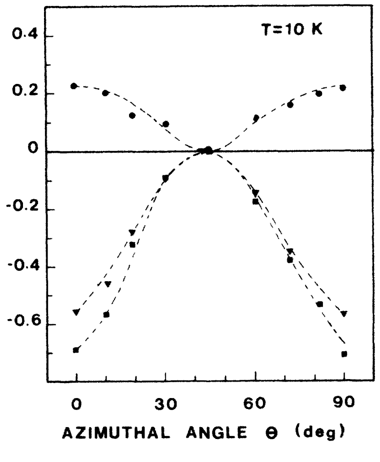

FIG. 3. Azimuthal dependence of polarization degree measured at 10 K for 412-nm emission and $\lambda_{exc}=293$ nm (●), $\lambda_{exc}=289$ nm (▲), $\lambda_{exc}=249.5$ nm (■) obtained by Ohata *et al.* (Ref. 8).

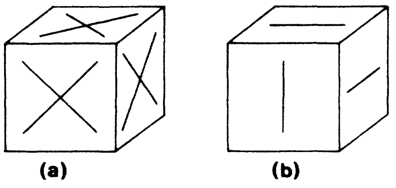

FIG. 4. Dimer orientation in the alkali-halide crystals (a) D_{2h} symmetry, (b) D_{4h} symmetry.

where P_i, I_i, and α_i are, respectively, polarization degrees, emitted intensities, and absorption fractions associated with the Σ,Π_2,Π_4 excitation transitions.

The model we used in order to calculate P_i and I_i is based on the following assumptions: (1) the light emission comes from the excited relaxed triplet states ${}^3\Sigma_u^+$, ${}^3\Pi_{2u}^+$, ${}^3\Pi_{4u}^+$ following the level scheme discussed in Ref. 10; (2) the ratios between the radiative electronic transition probabilities are those calculated for the absorption bands, i.e., $A_\Sigma:A_{\Pi_2}:A_{\Pi_4}=4:1:1$;[10] (3) the equilibrium population ratios of the relaxed triplet states, at a fixed temperature, are the same for different excitation wavelengths, in agreement with the experimental results reported in Refs. 5 and 8. They show a steady emission band at about 412 nm for different excitation wavelengths at low temperature.

If we define

$$a=\frac{N_\Sigma}{N_{\Pi_2}}, \quad b=\frac{N_{\Pi_4}}{N_{\Pi_2}},$$

where N_Σ, N_{Π_2}, and N_{Π_4} are the equilibrium populations of the emitting states, we obtain the results reported in Table II for the pure absorption transitions. In Table II the reported intensities are normalized to the absorption intensity for each transition.

If the light absorption takes place at wavelengths for which an overlap between absorption bands with different symmetry occurs, the final polarization degree can be calculated by means of expression (1). When the absorption takes place, for example, on bands having Π_2 and Π_4 symmetry, one obtains

$$\begin{aligned} P(\theta=0^\circ)&=\frac{(4a+1-2b)(3\alpha-2)}{2(4a+1+2b)+\alpha(4a+1-2b)}, \\ P(\theta=45^\circ)&=\frac{2\alpha(1-4a)}{2(4a+1+2b)+\alpha(4a+1-2b)}, \end{aligned} \tag{2}$$

where α and $1-\alpha$ are, respectively, the absorption fractions connected with the Π_2 and Π_4 transitions.

In a similar way any other combinations can be obtained.

III. DISCUSSION AND CONCLUSIONS

We have supposed the presence in the crystal of only one type of center, a dimer with D_{2h} symmetry. Such a

TABLE I. Experimental results of luminescence polarization degree for azimuthal angle values $\theta=0°$ and 45° at 10 and 80 K for different excitation ($\lambda_{\rm exc}$) and emission ($\lambda_{\rm em}$) wavelengths.

Temp.	Wavelengths		$P(0°)$	$P(45°)$
10 K	$\lambda_{\rm exc}=249.5$ nm[a]		-0.70	0
	$\lambda_{\rm exc}=289$ nm[a]	$\lambda_{\rm em}=412$ nm	-0.57	0
	$\lambda_{\rm exc}=293$ nm[a]		$+0.23$	0
80 K	$\lambda_{\rm exc}=250$ nm[b]	$\lambda_{\rm em}=405$ nm[b]	$+0.12$	$+0.02$
	$\lambda_{\rm exc}=290$ nm[c]	$\lambda_{\rm em}=402$ nm[c]	$+0.02$	0
	$\lambda_{\rm exc}=291$ nm[b]	$\lambda_{\rm em}=405$ nm[b]	$+0.06$	0
	$\lambda_{\rm exc}=293$ nm[c]	$\lambda_{\rm em}=402$ nm[c]	-0.035	$+0.025$
	$\lambda_{\rm exc}=295$ nm[c]	$\lambda_{\rm em}=402$ nm[c]	-0.04	0

[a] Reference 8.
[b] Reference 6.
[c] Reference 11.

hypothesis seems to be acceptable because many experimental results[9,11,14] have shown that the excitations used and the emission wavelengths observed are connected with the same center. Furthermore, the separation energy of the absorption bands and their oscillator strengths agree quite well with the calculated values in the D_{2h} model.[1,3,10] The qualitative suggestion one can obtain from the measurements of emission polarization[6,8,11] and of magnetic circular dichroism[9,14] at the reported wavelengths support the presence of $(\mathrm{Tl}^+)_2$ centers with D_{2h} symmetry. However, at first we did not exclude the presence of dimers of D_{4h} symmetry, but the calculations performed with this model do not explain the experimental data, in particular those obtained by us[11] with excitation at $\lambda_{\rm exc}=293$ nm and by Tsuboi and Jacobs[6] at $\lambda_{\rm exc}=250$ nm for $\theta=45°$ at 80 K. As a consequence, following the hypothesis of dimer centers with D_{2h} symmetry and the theoretical calculations discussed in Sec. II, we can determine the equilibrium population ratios for the different excitation wavelengths at 10 and 80 K using the polarization experimental results reported in Table I. When more than one absorption band is involved, we are able to determine their absorption fractions by means of expressions (2) or similar. The results we found are summarized in Table III.

Our analysis starts from the results obtained with $\lambda_{\rm exc}=250$ nm (C_z' absorption band) and with $\lambda_{\rm exc}=289$ nm at 10 K and $\lambda_{\rm exc}=290$ nm at 80 K. The dimer states we are exciting are ${}^1\Sigma_u^+$ and ${}^3\Sigma_u^+$, respectively. The ${}^1\Sigma_u^+$ symmetry of the C_z' band of dimers is well known and generally accepted. This band does not have any overlap with other bands, so the parameters obtained in this case by means of the relationship of Table II are a reference point in our analysis.

The different values of the parameters obtained for excitation at 250 nm and at about 290 nm, carry the existing difference between the experimental polarization degrees, possibly due to the monomer emission contribution owing to the closeness of the A absorption band of the monomer with the dimer absorption bands, more important at 290 nm than at 250 nm.

These results show that by increasing the temperature the population of ${}^3\Sigma_u^+$ and ${}^3\Pi_{2u}^+$ excited relaxed states increases with respect to that of ${}^3\Pi_{4u}^+$ state.

Using expressions (2) for a $\lambda_{\rm exc}=290$ nm we have considered the possibility of a simultaneous transition to ${}^3\Sigma_u^+$,

TABLE II. Polarization degrees at $\theta=0°$ and 45° and emission intensities calculated for the reported absorption transitions.

Azimuthal angle	Absorption transitions ${}^1\Sigma_u^+$ or ${}^3\Sigma_u^+$	${}^3\Pi_{2u}^+$	${}^3\Pi_{4u}^+$
$\theta=0°$	$P_\Sigma=\dfrac{4a+1-b}{12a+3+2b}$	$P_{\Pi_2}=\dfrac{4a+1-2b}{12a+3+2b}$	$P_{\Pi_4}=\dfrac{2b-4a-1}{3a+1+2b}$
	$I_\Sigma=\dfrac{12a+3+2b}{2(a+b+1)}$	$I_{\Pi_2}=\dfrac{12a+3+2b}{2(a+b+1)}$	$I_{\Pi_4}=\dfrac{4a+1+2b}{a+b+1}$
$\theta=45°$	$P_\Sigma=\dfrac{2(4a-1)}{12a+3+2b}$	$P_{\Pi_2}=\dfrac{2(1-4a)}{12a+3+2b}$	$P_{\Pi_4}=0$
	$I_\Sigma=\dfrac{12a+3+2b}{2(a+b+1)}$	$I_{\Pi_2}=\dfrac{12a+3+2b}{2(a+b+1)}$	$I_{\Pi_4}=\dfrac{4a+1+2b}{a+b+1}$

TABLE III. Calculated parameters by fitting the experimental polarization degrees for azimuthal angles $\theta=0^\circ$ and 45° obtained at different excitation wavelengths and temperatures for D_{2h} $(\mathrm{Tl}^+)_2$ dimers in KI.

T (K)	λ_{exc} (nm)	$a=N_\Sigma/N_{\Pi_2}$	$b=N_{\Pi_4}/N_{\Pi_2}$	N_Σ (%)	N_{Π_2} (%)	N_{Π_4} (%)	Absorption (symmetry)
10	250	0.25	10.3	2	9	89	1 $({}^1\Sigma_u^+)$
	289	0.25	6.3	4	13	83	1 $({}^3\Sigma_u^+)$
	293	0.25	4.13	4	19	77	0.5 $({}^3\Pi_{2u}^+ \cong {}^3\Pi_{4u}^+)$
80	250	0.27	0.59	14	54	32	1 $({}^1\Sigma_u^+)$
	290	0.25	0.77	12	49	38	1 $({}^3\Sigma_u^+)$
	293	0.25	0.73	13	51	36	0.5 $({}^3\Pi_{2u}^+ \cong {}^3\Pi_{4u}^+)$
	295	0.25	0.77	10	51	39	0.5 $({}^3\Pi_{2u}^+ \simeq {}^3\Pi_{4u}^+)$

${}^3\Pi_{2u}^+$, and ${}^3\Pi_{4u}^+$ states with the following absorption conditions $\mathscr{A}_{\mathrm{abs}}$:

$$\mathscr{A}_{\mathrm{abs}}(\Pi_2)=\mathscr{A}_{\mathrm{abs}}(\Pi_4)=\alpha \text{ and } \mathscr{A}_{\mathrm{abs}}(\Sigma)=1-2\alpha\ . \qquad (3)$$

The experimental results of polarization degree, on the assumption that the equilibrium population ratios do not depend on the excitation wavelength, give a value of $\alpha=0$, confirming that the 290-nm band can be assigned to a ${}^3\Sigma_u^+$ absorption transition only. Moreover, the possibility of Σ,Π_2 or Σ,Π_4 absorption combinations can be excluded for a 290-nm band. In fact the a and b parameters values calculated at 10 and 80 K for these combinations are in agreement with the population ratios obtained for $\lambda_{\mathrm{exc}}=250$ nm only when the Σ absorption fraction is equal to 1.

For $\lambda_{\mathrm{exc}}=293$ nm, the experimental results are consistent with the assumption that the absorption transitions are Π_2 and Π_4. The behaviors of a and b parameters versus α (fraction of Π_2 absorption) obtained with expressions (2), both at 10 and 80 K, give α values ranging between 0.1 and 0.5. This means that the Π_4 absorption is prevalent over the Π_2 absorption. However, a value of $\alpha=0.45$ is necessary in order to obtain the same equilibrium population ratios as calculated for the emission at $\lambda_{\mathrm{exc}}=290$ nm and at fixed temperature. This value of α means that Π_2 and Π_4 states are nearly degenerate.

The assumption that the absorption at $\lambda=293$ nm can be Σ, Π_2, and Π_4 with the absorption conditions (3) can be excluded since the suitable value of $\alpha\simeq0.5$ corresponds to zero Σ absorption. Moreover, the hypothesis of Σ,Π_2 absorption cannot explain the experimental results at 10 K, meanwhile a Σ,Π_4 absorption cannot be theoretically excluded owing to the same behavior foreseen for the azimuthal dependence of degree of polarization of $\Pi_2\rightarrow\Pi_2$ and $\Sigma\rightarrow\Sigma$ transitions, and also of $\Sigma\leftrightarrow\Pi_4$ and $\Pi_2\leftrightarrow\Pi_4$ transitions.[6] However, the Π_2,Π_4 combination seems more suitable than the last since it is rather difficult to believe that at $\lambda_{\mathrm{exc}}=293$ nm the Π_2 level is not involved in the absorption. In fact the Π_2 and Π_4 states are nearly degenerate in absorption[10] and the 290 nm transition is well explained by a pure Σ transition. Therefore, if we exclude a Σ absorption at $\lambda_{\mathrm{exc}}=293$ nm, we are justified to consider a Π_2,Π_4 combination for the absorption at $\lambda_{\mathrm{exc}}=295$ nm. On this assumption the experimental results give at 80 K, $a=0.25$ and $b=0.77$ for $\alpha\leq0.45$. This means that the Π_4 absorption is prevailing.

In a previous calculation[10] of the $(\mathrm{Tl}^+)_2$ dimers absorption in KI, we were not able to establish the sequence in energy of the ${}^3\Pi_2$ and ${}^3\Pi_4$ levels, since the two levels are nearly degenerate. The present analysis of the polarization results shown in Table I allow us to resolve this point. We can say that the state ${}^3\Pi_4$ is lower in energy than the ${}^3\Pi_2$. In fact, as previously observed, the calculated equilibrium population ratios after a Σ absorption ($\lambda_{\mathrm{exc}}=250$ nm and $\lambda_{\mathrm{exc}}=290$ nm), show that the emission from the Σ and Π_2 states increases by increasing the temperature. The same behavior has been found also for the other excitation wavelengths (see Table III). A reasonable explanation of this behavior can be that the relative population of the higher states increases owing to the phonon interaction with the electronic relaxed states, so the emitting levels can be ${}^3\Pi_{4u}^+$, ${}^3\Pi_{2u}^+$, and ${}^3\Sigma_u^+$ in order of increasing energy. This behavior can be due, on the other hand, to different increase of radiationless transitions from the emitting levels. Measurements of luminescence lifetime can clarify this point. However, it is possible to support

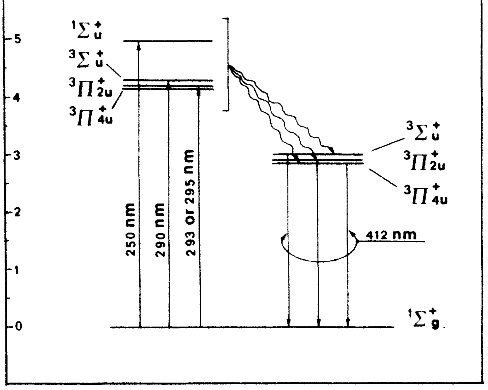

FIG. 5. Energy-level diagram showing the transitions involved in both absorption and emission of D_{2h} thallium dimers in potassium iodide.

the proposed energy order of the D_{2h} dimer triplet states by a second point. This is the behavior of the luminescence polarization degree at $\theta=0°$ for temperature higher than 80 K.[11] In fact, for $\lambda_{\text{exc}}=295$ nm (and also for $\lambda_{\text{exc}}>295$ nm at temperature higher than about 200 K) the polarization P $(\theta=0°)$ assumes positive values at $T\geq 140$ K. Following the proposed levels sequence, this behavior can be explained by the fact that at high temperature the population of Σ and Π_2 states can increase so that an increasing contribution of $\Pi_2\rightarrow\Pi_2$ and $\Pi_2\rightarrow\Sigma$ transitions[6] occurs. This interpretation, which does not involve a Σ absorption for $\lambda_{\text{exc}}\geq 300$ nm,[11] can be acceptable. Moreover, let us emphasize that this experimental result cannot be explained in the D_{4h} dimer configuration, unless we take into consideration a Σ absorption also for low excitation energy. The energy-level diagram summarizing both the absorption and emission processes for D_{2h} thallium dimers in KI, as discussed before, is shown in Fig. 5.

In conclusion, the experimental results of the luminescence polarization of thallium dimer centers in KI can be explained by means of one type of dimer center with D_{2h} symmetry. This is supported by a model that details both the absorption and emission processes and is able to fit the experimental data by means of parameters having a clear physical meaning. In particular, the increasing energy sequence of the relaxed excited electronic triplet levels is found to be $^3\Pi_4$, $^3\Pi_2$, and $^3\Sigma$, while the $^3\Pi_{4u}^+$ and $^3\Pi_{2u}^+$ levels (A_1 absorption band) overlap also at low temperature (10 K). Moreover, the A_2 absorption band is well characterized by means of a pure $^3\Sigma_u^+$ transition.

Detailed measurements of polarization degree and lifetime of luminescence versus the temperature for many excitation wavelengths can allow us to evaluate the soundness of the proposed model.

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