

## Characteristics of the Thallous Dimer Center in Sodium Iodide\*

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An investigation of some of the characteristics of the thallous double center (dimer) in NaI:Tl was carried out over the temperature range 15 to 300°K and for thallium concentrations of 0.08 to 1.01 mole% Tl. A measurement of the lifetime of the dimer excited state resulted in a value of 7 nsec as an upper limit. The decay time is independent of temperature and thallium concentration for the ranges investigated. A symmetry determination yielded as the dimer center a  $\langle 100 \rangle$  cube-edge direction. The radiation model of the dimer center is discussed.

### I. INTRODUCTION

WHEN NaI:Tl, at a temperature of the order of liquid nitrogen (LNT) and above, is excited in the characteristic thallium *A*, *B*, and *C* absorption bands,<sup>1</sup> an emission of approximately unit quantum efficiency at 425 nm results. It has been observed<sup>2</sup> that in crystals of relatively high thallium concentration ( $>0.1$  mole%), additional absorption bands yielding a single new emission band at 325-nm LNT result. The excitation bands (which are labeled *A'*, *B'*, and *C'*) of the 325-nm emission lie approximately 0.15 eV to the low-energy side of the corresponding absorption bands of the 425-nm emission.<sup>3</sup> In view of the study of the absorption coefficient at the peak of the absorption band as a function of thallium concentration in KI:Tl by Yuster and Delbecq,<sup>4</sup> it is assumed that the 425-nm emission in NaI:Tl is due to absorption caused by the presence of single isolated thallous ions in the crystal (monomer centers), while the 325-nm emission arises from absorption by a center which has two thallous ions as near neighbors (dimer centers). Assuming that the thallous ions are nearest cation neighbors and that all positive ion sites are equally probable to a thallous ion, one obtains for the dimer concentration

$$N_d \cong 6N_m^2/N, \quad (N_m \ll N)$$

where  $N_d$  is the number of dimer centers per  $\text{cm}^3$ ,  $N_m$  is the number of thallous ions per  $\text{cm}^3$ , and  $N$  is the number of available sites per  $\text{cm}^3$ .

It has been suggested that the dimer center plays a significant role in the NaI:Tl scintillation process by capturing excitons for which its cross section is one or two orders of magnitude greater than for the monomer center.<sup>5</sup> Its presence is expected to be of particular interest in the case of  $\alpha$ -particle scintillation, since the wake of this particle consists primarily of excitons. It appears highly likely that the "spike" emission at

345 nm in NaI:Tl crystals (0.45 mole% thallium) undergoing  $\alpha$ -particle bombardment as observed by Eby and Jentschke<sup>6</sup> arises from the thallium dimer.

Yuster and Delbecq's suggestion that the dimer center is composed of two thallous ions in nearest-neighbor positions<sup>4</sup> requires the center axis to be directed along a  $\langle 110 \rangle$  cubic-face diagonal. Uchida and Matsui<sup>7</sup> claim to have determined the symmetry axis of the dimer center in NaI:Tl to be directed along  $\langle 110 \rangle$ . However, the results of our investigation are in direct disagreement with those of Uchida and Matsui.

It is the purpose of this paper to report the results of measurements made on the thallium dimer in the crystal NaI:Tl. Lifetime and orientation measurements were carried out as a function of thallium concentration and temperature.

### II. EXPERIMENTAL TECHNIQUE

#### A. Samples and Thallium Concentration

Single crystals of NaI:Tl were supplied by the Harshaw Chemical Co. There were six groups of samples, each having a different thallium concentration. Freshly cleaved surfaces were produced for the face through which the crystal was illuminated and two faces from which luminescence was observed. Typical dimensions of a crystal are  $16 \times 13 \times 5 \text{ mm}^3$ .

The thallium concentration was determined chemically, using a spectrophotometric method based on a measurement of the absorbance of the organometallic complex formed by  $\text{TlBr}_4^-$  and methylviolet.<sup>8</sup> The results of the concentration determination indicated a range of 0.08 to 1.01 mole% Tl.

#### B. Research Cryostat

A Sulfrian-helium Dewar was used to provide the crystal with a variable temperature. The crystal was cleaved in a dry box and mounted on the cold finger of the Dewar without exposure to room air. The crystal temperature was measured with a Chromel-versus-

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<sup>1</sup> F. Seitz, *J. Chem. Phys.* **6**, 150 (1938).

<sup>2</sup> W. J. Van Sciver, thesis, Stanford University, 1955 (unpublished).

<sup>3</sup> W. J. Van Sciver, *Phys. Rev.* **120**, 1193 (1960).

<sup>4</sup> P. Yuster and C. Delbecq, *J. Chem. Phys.* **21**, 92 (1953).

<sup>5</sup> W. J. Van Sciver, *Phys. Letters* **9**, 97 (1964).

<sup>6</sup> F. Eby and W. Jentschke, *Phys. Rev.* **96**, 911 (1954).

<sup>7</sup> Y. Uchida and E. Matsui, *J. Phys. Soc. Japan* **20**, 874 (1965); E. Matsui, *ibid.* **22**, 819 (1967).

<sup>8</sup> *Standard Methods of Chemical Analysis*, edited by N. H. Furman (D. Van Nostrand, Inc., Princeton, N. J., 1962), p. 1053.

constantan thermocouple. With liquid helium in the Dewar, the temperature of the crystal was measured to be 13°K.

A crystal holder of silver (99.999% pure) was mounted to the cooling block of the cryostat by screws with a thin layer (0.020 in.) of pure indium in between to insure good thermal contact. The crystal was held against the silver crystal holder by a thin copper plate with spring loading screws. A strip of pure indium was placed between the silver holder and the crystal to facilitate thermal contact.

### C. Lifetime Measurement

The experimental arrangement is shown in Fig. 1. The crystal is illuminated with light from a low-pressure hydrogen discharge lamp. The illumination is a pulse of light whose time duration at half-maximum height from leading to trailing edge of the pulse waveform is typically 20–25 nsec. The light pulses were produced at a rate of 60 per sec.

An Engis monochromator with a focal length of 250 mm and an aperture ratio of  $f/4.4$  was used as the excitation monochromator. The grating had 1200 lines/mm and was blazed at 200 nm, giving a linear dispersion of 3.3 nm/mm. The monochromator slits were set to give a bandpass of 2.5 nm. This value of the bandpass was used as a compromise between good signal-to-noise ratio of the observed luminescence (broad bandpass) and discrimination of excitation between monomer and dimer bands (narrow bandpass). The monochromator wavelength setting was adjusted to produce maximum dimer emission intensity.

A LiF lens was used to focus an image of the exit slit of the exciting monochromator onto the crystal. A quartz lens produced nearly parallel rays from the emission of the crystal. The detector of the luminescence was placed at right angles to the illumination direction, so that scattered light entering the detector was minimized. The detector was an RCA type C70117

photomultiplier. Discrimination between monomer and dimer emission was accomplished by inserting two Corning filters (Nos. 0-54 and 7-54) between the quartz lens and the phototube face. The filters allowed transmission of light from 300 to approximately 380 nm, with a 65% transmission at 325 nm (center of dimer luminescence).

To obtain the measurement of the dimer decay time, the exciting monochromator was set at the wavelength of a dimer absorption band. The  $B'$  absorption band (257 nm) was used for most of the measurements since it provides greater wavelength separation between exciting and emitted light and thus minimizes the detection of scattered light. The phototube output was terminated by a 50- $\Omega$  resistance at the input of a Tektronix type 581A oscilloscope with a type 82 pre-amplifier. The triggering pulse to the oscilloscope was provided from the output of a RCA type 7200 photomultiplier which viewed the hydrogen lamp directly. The luminescence pulse was displayed as an oscilloscope trace. A time exposure involving 150–200 traces was taken.

Without changing any other parameter, the wavelength setting of the exciting monochromator is changed to a value of 320 nm. At this point of its spectrum the crystal is transparent and does not exhibit luminescence. Scattered light causes an oscilloscope trace. A shift of the leading edge of the pulse of about 4 nsec toward earlier time was observed for the scattered pulse compared to the luminescence pulse. Independent measurements indicated that the pulse shape of the exciting light (scattered light) is independent of wavelength in the region 200 to 350 nm. The scattered light pulse is also photographed, using many oscilloscope traces, on the same film frame as the luminescence pulse. Hence, now displayed on the photograph is the dimer luminescence pulse (trailing) along with a pulse that is essentially the excitation pulse (leading) which excited the luminescence. This is shown in Fig. 2.

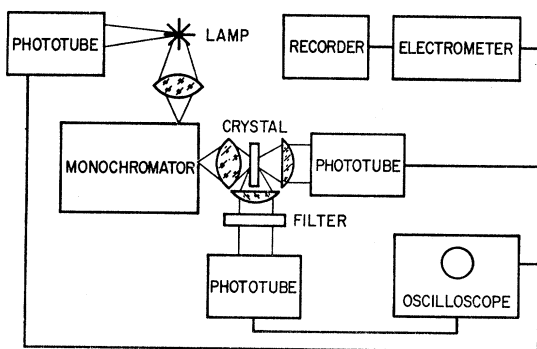


FIG. 1. Schematic arrangement of the apparatus for the lifetime determination. The luminescence pulses are observed at right angles to the illumination direction while transmission spectra of the sample are taken in the straight-through direction.

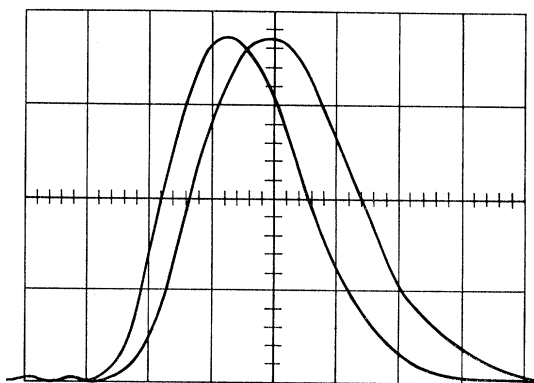


FIG. 2. Superimposed excitation (leading) and dimer luminescent pulses (trailing). Time scale:  $10^{-8}$  sec/cm.

### D. Orientation Measurement

According to Yuster and Delbecq<sup>4</sup> the separation between the dimer doublet in KI:Tl at liquid-helium temperature (LHeT) is approximately 3 nm. Hence the bandpass of the exciting monochromator was adjusted to 1.2 nm to discriminate between the two bands in the dimer doublet of NaI:Tl. The experimental arrangement is shown in Fig. 3. A high-intensity deuterium lamp (model D-102-S) obtained from the G. Gates Co. provided a continuum of nearly uniform intensity per wavelength interval in the region of interest for excitation. The deuterium arc was imaged at the entrance slits of the excitation monochromator through a pair of LiF collimating lenses. A lock-in amplifier (PAR model HR-8) was employed in the detector circuit and the light was "chopped" by electrically modulating the high voltage placed across the deuterium lamp by means of the internal oscillator of the lock-in amplifier.

The light emerging from the excitation monochromator is rendered nearly plane polarized by a Polacoat ultraviolet filter (polarizer) placed between the exit slit of the monochromator and the LiF lens which images the exit slit onto the crystal. The Polacoat filter has a major disadvantage in that it is not a perfect polarizer. However, its transmission intensity was large enough to allow the dimer luminescence to be monitored. A second Polacoat filter (analyzer) was placed between two quartz collimating lenses which imaged the sample onto the entrance slits of the emission monochromator.

The emission monochromator was a Bausch and Lomb high-intensity grating instrument of the non-collimated optical system type, providing a diverging exit beam of  $f/3.5$ . The grating has 1200 lines/mm and was blazed at 220 nm. The reciprocal linear dispersion is 7.4 nm/mm. The slits were set to an equivalent separation of 2 mm, which results in a bandpass of 14.8 nm. A EMI type 9502-S photomultiplier viewed the light from the exit slit of the emission monochromator and was positioned so that the diverging light beam covered

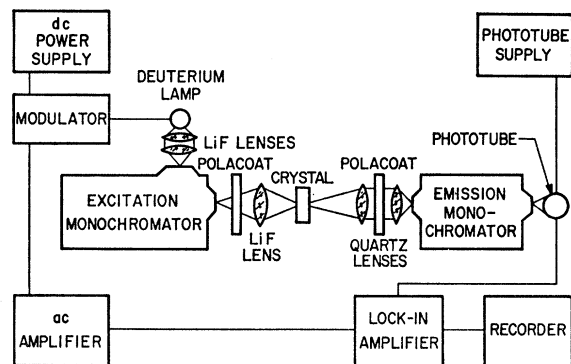


FIG. 3. Schematic arrangement of apparatus for studying the polarization effect of the luminescence. The detector system can be moved to view the emission at right angles to the illumination direction.

the photocathode area. The phototube output was terminated with a 100-k $\Omega$  resistance and placed across the input of the lock-in amplifier. The output of the lock-in amplifier drove a Varian Associates model G-14 recorder.

The detector system could be rotated to view the crystal emission in the illumination direction. Luminescent spectra were extremely difficult to obtain in the straight-through direction because of the relatively large amount of incident light passing through the crystal and entering the detector. The intensity level of the luminescence is at least three orders of magnitude lower than that of the unabsorbed "background" light. Only the higher-energy dimer doublet ( $B'$  band) could be observed in the straight-through direction (LNT). Figure 4 shows the dimer luminescence observed above a much larger scattered light "tail." This scattered light did not permit observation of the luminescence for the  $A'$  band (transmission of crystal is high on both

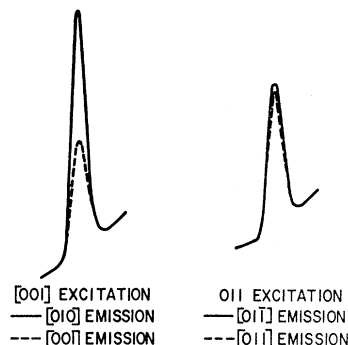


FIG. 4. Polarization spectra for the  $B'$  band in the straight-ahead direction at LNT. The band is centered at 256 nm and superimposed upon a large scattered light component.

sides of the absorption band) at LNT or for any band at LHeT (scattered light "tail" increased due to temperature narrowing of the absorption bands).

The data were taken in the form of photoexcitation emission spectra. The emission monochromator was set for passage of the dimer luminescence at 325 nm, while the wavelength drive of the excitation monochromator was swept over the spectral region of interest. The polarizer and analyzer axes were set to positions of interest. A set of data consists of spectra with a single polarizer position and two analyzer positions, the axes of the polarizer and analyzer being parallel and crossed. Spectra of the polarization effect for the  $B'$  dimer doublet taken at 77°K as a function of the polarizer axis position in the straight-through direction are shown in Fig. 4.

Spectra of the polarization effect taken in the perpendicular direction at 77°K as a function of the polarizer axis direction for both the  $A'$  and  $B'$  dimer band are shown in Fig. 5. Figure 6 shows the polarization effect of the  $A'$  band at 13°K, where the doublet is partially resolved.

### E. Calibration of the Apparatus

Calibration of the apparatus was carried out to determine what amount of the observed polarization effect was contributed by the measuring system. A LiF plate set at Brewster's angle was used to test the individual components of the system. The reflected light exhibited 100% polarization in the wavelength region 250 to 325 nm as tested by a Glan prism. The anisotropy of the Polacoat filters was measured by observing the modulation in phototube output when the Polacoat is rotated between a phototube and the Brewster's plate.

According to Yakovlev,<sup>9</sup> the grating of a monochromator has a marked effect upon the intensity of polarized light as a function of the angle of incidence. Unpolarized light is introduced to the entrance slits of the monochromator and a Glan prism is placed between the exit slits and a photomultiplier. Upon rotation of the Glan prism the phototube output modulation gives

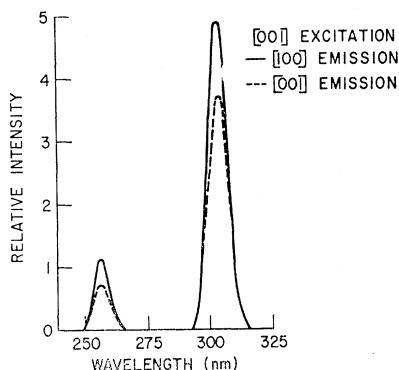


FIG. 5. Polarization spectra of the  $A'$  and  $B'$  bands taken in the perpendicular direction at LNT.

the polarization effect of the grating as a function of wavelength (angle of incidence of light on grating).

No asymmetry could be detected for either the deuterium lamp or the photomultiplier tube used in the measurement. It was further noticed that this null effect was observed independently of whether the photomultiplier has an end window (light at normal incidence to photocathode), as the RCA type C70117, or an arrangement of the RCA type 7200 (light incident at an angle of  $42^\circ$  to the photocathode).

## III. RESULTS AND DISCUSSION

### A. Lifetime Measurements

The procedure used to evaluate the decay time of the dimer luminescence is the same as previously used to report the measured decay time of sodium salicylate.<sup>10</sup>

<sup>9</sup> E. A. Yakovlev, Opt. i Spektroskopiya **19**, 417 (1965) [English transl.: Opt. Spectry. (USSR) **19**, 233 (1965)].

<sup>10</sup> G. K. Herb and W. J. Van Sciver, Rev. Sci. Instr. **36**, 1650 (1965).

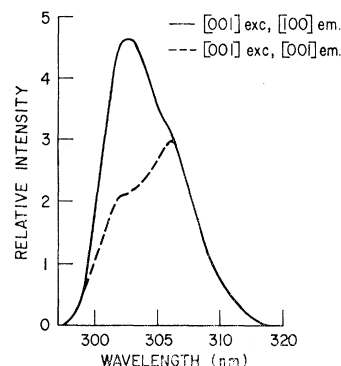


FIG. 6. Polarization spectra of the  $A'$  band taken at LHeT showing the partially resolved dimer doublet structure. The band pass of the apparatus was 1.2 nm.

The decay time is determined by comparison of the experimental luminescence pulse to calculated pulses which are predicted by a computer under the following assumptions: (1) The luminescence decay is a single exponential. (2) The computer is given an excitation pulse shape as a function of time in tabular form. (3) The computer is given a number of assumed values of the luminescence decay constant  $\tau$ .

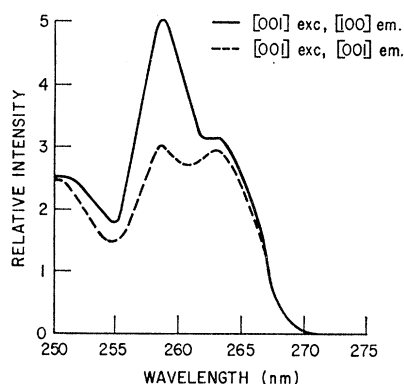
Comparison of the experimental luminescence pulse to the predicted computer pulses for various values of  $\tau$  did not yield a definitive lower limit for the decay time. The measurement indicated a value of 4–5 nsec for the decay lower limit, whereas an unambiguous value of  $\tau = 7$  nsec can be given for the upper limit. To assign a definitive lower limit for  $\tau$  a faster lamp is needed.

When the experimental pulse was compared to a computer predicted pulse whose  $\tau$  was equal to 6 nsec, a rather good match was observed. This indicated that the assumption of the luminescence decay being predominantly a single exponential ( $I = I_0 e^{-t/\tau}$ ) was valid.

The dimer decay time was found to be independent of thallium concentration for the range of concentrations studied. The dimer decay time was also found not to change with temperature. This study was conducted in the temperature range 13 to 170°K. Above 170°K the dimer luminescence intensity was not large enough to allow measurement. The decay time was not found to be different when the dimer luminescence was excited via the  $A'$  absorption band. Excitation in the  $C'$  band did not yield measurable dimer luminescence even for the highest thalliated crystal.

### B. Orientation Measurement

In Fig. 5 we report typical polarized excitation spectra for the dimer emission excited in the  $A'$  and  $B'$  bands at 77°K, and in Figs. 6 and 7 the  $A'$  and  $B'$  band spectra taken at 13°K. We note immediately from these latter spectra that both bands ( $A'$  and  $B'$ ) are actually doublets and, most importantly, that the two components of the doublets show different polarization

FIG. 7. Same as Fig. 6 but for  $B'$  band.

characteristics. In particular, the high-energy components (henceforth called  $A_H'$  and  $B_H'$ ) present a large negative degree of polarization (dp). At LNT, where the two components in each band overlap completely, the dp of the emission will be some weighted average of the dp proper of each component. Since they show different polarization characteristics, the net effect of the overlapping will be a depolarization of the emission.

In order to deduce the orientation of the dimer center from polarized excitation spectra, one must make some assumptions concerning the nature and characteristics of the absorbing and emitting states. A successful technique is that employed by van Doorn<sup>11</sup> in his investigations of the  $M$  center.

We assume that the centers can be treated as simple dipoles with axial symmetry. Then some simple radiation models are introduced and degrees of polarization are calculated on this basis for various assumed center axis orientations. The radiation models have been called A, B, C, and D.<sup>11</sup> Model A stands for absorption and emission of light polarized along the center axis. Model B stands for absorption perpendicular and emission parallel to the center axis. Model C stands for absorption along the axis and emission perpendicular to it. Finally, model D stands for absorption and emission perpendicular to the axis. The dp for various center orientations calculated using these models, for

TABLE I. Ideal and corrected degrees of polarization for excitation at 257 nm ( $B'$  band) for detection perpendicular to exciting beam. ("Corrected" values are those that result when apparatus anisotropy is introduced into the dp calculation.)

Dimer orientation	Excitation	Radiation model					
		A		B,C		D	
		Ideal	Cor-rected	Ideal	Cor-rected	Ideal	Cor-rected
$\langle 100 \rangle$	[001]	1.00	0.74	-1.00	-0.64	0.33	0.10
	[010]	0	-0.76	0	0.14	0	0.07
$\langle 110 \rangle$	[001]	0.33	0.13	-0.20	-0.23	0.09	-0.04
	[010]	0	0.07	0	0.11	0	0.10

<sup>11</sup> C. Z. Van Doorn, Philips Res. Rept. Suppl. 4, 39 (1962).

TABLE II. Ideal and corrected dp for excitation at 257 nm ( $B'$  band), for detection in the direction of the exciting beam.

Dimer orientation	Excitation	Radiation model					
		A		B,C		D	
		Ideal	Cor-rected	Ideal	Cor-rected	Ideal	Cor-rected
$\langle 100 \rangle$	[001]	1.00	0.56	-1.00	-0.63	0.33	0.10
	[010]	1.00	0.63	-1.00	-0.56	0.33	0.29
$\langle 110 \rangle$	[001]	0.33	0.10	-0.20	-0.22	0.09	-0.05
	[010]	0.33	0.29	-0.20	-0.02	0.09	0.16

the electric vector of the exciting light in the [001] and [010] directions are shown in Tables I-III, where dp is defined as

$$P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}).$$

Here  $I_{\parallel}$  and  $I_{\perp}$  are the luminescence intensities detected with the analyzer axis parallel and perpendicular to the polarizer axis, respectively.

These results hold for a perfectly symmetric experimental situation in which the apparatus introduces neither spurious polarization or depolarization of the light; also one must have perfect polarizers. Since neither of these conditions was satisfied for our apparatus, we have calculated the theoretical degrees of polarization (labeled "corrected") which we should expect in our experimental situation. The results are also shown in Tables I-III. Note that the apparatus has quite a large effect on the ideal values.

At 13°K, where the two components of the doublets are partially resolved, we note that the high-energy component has a large negative degree of polarization for [001] excitation. This indicates that only models B or C are likely to describe this transition. The large value of the dp which is -0.35 for the  $A'$  component indicates that a  $\langle 100 \rangle$  orientation is more likely than a  $\langle 110 \rangle$  orientation.

For a  $\langle 100 \rangle$  orientation, the symmetry of the dimer center is  $D_{4h}$ . This means that the energy level scheme proposed by Yuster and Delbecq<sup>4</sup> on the basis of  $C_{2v}$  symmetry must be modified somewhat. The higher symmetry means that the threefold degeneracy of the monomer excited states will not be lifted completely, since in  $D_{4h}$  symmetry the  $x$  and  $y$  directions are equivalent. The new energy level scheme is depicted schematically in Fig. 8.

TABLE III. Ideal and corrected degrees of polarization for excitation at 305 nm ( $A'$  band) for detection perpendicular to the exciting beam.

Dimer orientation	Excitation	Radiation model					
		A		B,C		D	
		Ideal	Cor-rected	Ideal	Cor-rected	Ideal	Cor-rected
$\langle 100 \rangle$	[001]	1.00	0.74	-1.00	-0.57	0.33	0.11
	[010]	0	-0.74	0	0.17	0	0.04
$\langle 110 \rangle$	[001]	0.33	0.11	-0.20	-0.23	0.09	-0.03
	[010]	0	0.05	0	0.12	0	0.09

TABLE IV. Selection rules for electronic transitions for polarized exciting light, in  $D_{4h}$  symmetry.

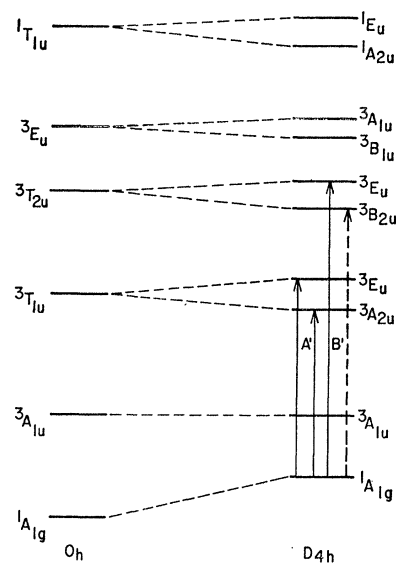
Excitation	$z$	$(x,y)$
$A'$ band $A_{1g} \rightarrow E_u$	Forbidden	Allowed
	Allowed	Forbidden
$B'$ band $A_{1g} \rightarrow E_u$	Forbidden	Allowed
	Forbidden	Forbidden

The monomer levels are split into doublets, in which one component ( $E_u$ ) is doubly degenerate, and the other ( $A_{2u}$  or  $B_{2u}$ ) is singly degenerate. Using group-theoretical techniques, we derive the selection rules for electronic transitions from the ground state to the various excited states. They are depicted in Table IV. Transitions are allowed only to the  $E_u$  and  $A_{2u}$  levels; furthermore, we are restricted in the possible models for the various transitions. The  $A_{1g} \rightarrow E_u$  transition can only be either model B or D, and the  $A_{1g} \rightarrow A_{2u}$  transition can only be either model A or C.

We identify the  $A'$  band with the low-energy doublet, and the  $B'$  band with the next higher-energy doublet. However, the  $A_{1g} \rightarrow B_{2u}$  transition is forbidden. Experiment shows that the  $B_L'$  component is less intense than the  $B_H'$  component ( $L$  and  $H$  subscripts refer to the low- and high-energy component, respectively). This indicates that the  $A_{1g} \rightarrow E_u$  transition (allowed) corresponds to the high-energy component of the doublet for the  $B'$  band. By analogy we make the same assignment for the high-energy component of the  $A'$  band. This assignment also implies that the high-energy components of each dimer band are described by model B, because of their dp.

The low-energy components are associated with the singly degenerate levels. The  $A_{1g} \rightarrow A_{2u}$  transition will be described by model A. For the electronically forbidden  $A_{1g} \rightarrow B_{2u}$  transition, we make the assumption that it is vibronically allowed. Since it shows the same polarization properties as the  $A_{1g} \rightarrow A_{2u}$  transition, we assign it model A. A qualitative investigation of the possible vibronic coupling schemes responsible for this transition shows that indeed one should expect absorption according to models A or C (absorption parallel to the axis direction).

In order to check the predictions made assuming a  $\langle 100 \rangle$  orientation and a BA radiation model (B for the high-energy components and A for the low energy ones) with the experimental data in the most clear-cut way, we should be able to resolve the doublets completely. The  $B'$  band at LHeT is resolved for all practical purposes, since the low-energy component is small with respect to the high-energy component. On the other hand, for the  $B'$  band the situation is complicated by the fact that excitation in this region at temperatures below about 50°K causes also 330-nm emission, which has been found to be positively polarized. Now, when the emission monochromator is centered for the dimer emission at 320 nm, its bandpass is such that a good

FIG. 8. Schematic energy-level diagram showing the dimer transitions in  $D_{4h}$  symmetry.

portion of the 330-nm emission passes through. The net effect is that of depolarizing the dimer emission, and in a manner which is not easily corrected. We are therefore left with the analysis of the  $A'$  band. The  $A'$  band doublet could not be resolved even at the lowest temperature we could attain (Fig. 6) using the best resolution compatible with a workable signal-to-noise ratio. It is probable that at the large Tl concentrations necessary to study dimer centers, the  $A'$  band cannot be resolved because of the intrinsic bandwidth. Because of this situation we have chosen not to eliminate the effects of overlap by subtracting away the contributions that seemed due to overlap in the experimental curves, since the subtraction technique would in our case lead to large errors, intrinsic in the operational definition of the dp and in the noise level at which we had to operate. Instead, we have measured the dp by taking the total area enveloped, respectively, by the curves for  $I_{||}$  and  $I_{\perp}$ . This is equivalent to assuming complete overlap of the two components of the doublet in calculating the dp. In order to calculate the dp for the case of complete overlap, it is necessary to know the ratio of the oscillator strengths of the two components of the band. Since the pertinent data for NaI:Tl are not in the literature, as far as we know, we have used the corresponding data of Yuster and Delbecq<sup>4</sup> for KI:Tl at LHeT. The value for the ratio of the oscillator strengths (low-energy component over high-energy component) is 0.6. Using this value, we have calculated the expected dp for [001] excitation for the  $A'$  band doublet, for both  $\langle 100 \rangle$  and  $\langle 110 \rangle$  orientations and assuming not only radiation model BA, but also model CD. The results are depicted in Table V, together with the experimental value. We see that the predictions for  $\langle 100 \rangle$  orientation agree with experiment. However, no

TABLE V. Degrees of polarization for the  $A'$  band doublet assuming complete overlap. [001] excitation and perpendicular detection.

Dimer orientation	Radiation model		Experimental
	BA	CD	
$\langle 100 \rangle$	-0.24	-0.18	-0.20
$\langle 110 \rangle$	-0.14	-0.11	

clear distinction between radiation models BA and CD can be made from these data. In order to check whether we had indeed made all the proper corrections for the imperfections of our apparatus, and to try to assign a radiation model unambiguously, we repeated some of the orientation measurements using different excitation and emission monochromators, and, most importantly, a Brewster plate reflector as the excitation polarizer. Hence, we have now essentially a perfectly plane polarized light exciting the crystal. The results (Table VI) confirm a  $\langle 100 \rangle$  orientation and a BA radiation model.

Having established an orientation and radiation model for the dimer center using the data taken at 13°K, we turn to the interpretation of the data at 77°K. At this temperature, nothing should be changed as far as the  $A'$  band is concerned. Now we have indeed complete overlap experimentally, and so the analysis of the data should proceed in the same way as for the low-temperature data. In fact, no new information can be gained.

The situation is different for the  $B'$  band. Here, there is reason to believe that the  $B_L'$  oscillator strength will not be the same at 77°K as it was at 13°K. Therefore, we cannot apply the techniques used for the  $A'$  band. However, we can reverse the process. Assuming that the results obtained from the study of the  $A'$  band apply to the  $B'$  band as well, we can get a value for the oscillator strength ratio (at LNT) for the two components of the  $B'$  band by determining the theoretical dp as a function of this ratio, and then choosing that value of the ratio which brings the theoretical value of the dp in agreement with the experimental one. At this temperature, we need not worry about the interference from the 330-nm emission, since this disappears for temperatures greater than 50°K. The experimental dp for the  $B'$  band at LNT are depicted in Table VII; the best fit with the experimental values can be obtained by

TABLE VI. Degrees of polarization for the  $A'$  band doublet assuming complete overlap. [001] excitation and perpendicular detection. The exciting polarizer for these bands is a Brewster plate reflector.

Dimer orientation	Radiation model		Experimental
	BA	CD	
$\langle 100 \rangle$	-0.21	-0.13	-0.19
$\langle 110 \rangle$	-0.09	-0.07	

assigning the value 0.4 to the oscillator strength ratio.<sup>12</sup> Comparing this with the value obtained at LHeT by Yuster and Delbecq<sup>4</sup> (0.2), we see that the oscillator strength for the  $B_L'$  component has increased with increased temperature. This fact tends to confirm the assumption that the  $B_L'$  component is a vibronically allowed transition.

#### IV. CONCLUSION

The main results of this investigation are that the Tl dimer center in NaI:Tl has a decay time for its characteristic emission which is extremely short, with an established upper limit of 7 nsec. The center has a  $\langle 100 \rangle$  orientation and the BA radiation model fits the polarization data. The latter result is satisfying in that the B model, which is doubly degenerate in excitation, applies to the higher-energy component which has approximately twice the oscillator strength of the low-energy component to which the nondegenerate A model applies.

Our result concerning the orientation is in agreement with a similar result obtained for Ga dimer centers in alkali halides by Mabuchi *et al.*<sup>13</sup> It is, however, in

TABLE VII. Experimental and predicted dp for the  $B'$  band, assuming complete overlap with an oscillator strength ratio of 0.4.

Excitation	Predicted dp	Experimental dp	
[001]	-0.34	-0.35	Straight-through detection
[010]	-0.16	-0.20	
[001]	-0.36	-0.26	Perpendicular detection
[010]	+0.12	+0.14	

complete disagreement with the conclusions reached by Uchida and Matsui,<sup>7</sup> who claim the symmetry axis of the dimer center in NaI:Tl is  $\langle 110 \rangle$ . The crucial point seems to be that they base their assignment of the orientation on a luminescence in the monomer region, excited by the low-energy component of the  $A'$  band. They show that this luminescence is not the same as monomer luminescence, and conclude that it must be dimer luminescence. We also have observed this luminescence, which is excited also by excitation in the  $B'$  band, but a careful analysis, which will be included in a further report, indicates that this luminescence, although not strictly a monomer emission, is not a dimer emission either. It is then obvious that if the luminescence is not really a genuine dimer emission, the assignment of the dimer orientation on its basis may be misleading.

The other main result concerns the decay time of the 325-nm dimer luminescence; the fact that it is so short

<sup>12</sup> It is worthwhile to note how, even assuming  $f=0$ , a  $\langle 110 \rangle$  orientation would lead to values of the dp that are much too small for the case of straight-through detection.

<sup>13</sup> T. Mabuchi, A. Fukuda, and R. Onaka, *Sci. Light* (Tokyo) **15**, 79 (1966).

indicates that the emitting state is atomic, or molecular, in character. Hence it has relatively small interaction with the surrounding lattice. This fact may indicate that there is a covalent type of bonding between the two  $Tl^+$  ions that make up the dimer center. The short lifetime and small Stokes shift indicate that the wave function of this center remains relatively closely confined to the immediate vicinity of the dimer center, in contrast to that of the monomer center. This is analogous to the short lifetime of the  $M$  center (two  $F$  centers) as opposed to the relatively long lifetime of  $F$ -center luminescence as reported by Swank and Brown<sup>14</sup> and discussed by Fowler.<sup>15</sup>

<sup>14</sup> R. A. Swank and F. C. Brown, *Phys. Rev.* **130**, 34 (1963).

<sup>15</sup> W. Beall Fowler, *Phys. Rev.* **135**, A1725 (1964).

A basic consequence of the  $\langle 100 \rangle$  orientation of the dimer center is the fact that the two  $Tl^+$  ions are not in nearest-neighbor positions. As of now, it is not possible to answer the question of what is in between them; but, whatever it is, it is felt that it plays an essential role in the mechanism by which dimers are formed and held together.

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## Lattice Sidebands of Vibrational Spectra and Their Pressure Dependence

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Vibrational spectra of solids which show the general form  $\nu_{\text{int}} \pm \nu_{\text{ext}}$  are discussed, and the information that they contain about the lattice modes of the solid is considered. Small polyatomic impurity ions isolated in alkali halides are responsible for most of the spectra considered. The importance of torsional motion of the impurity ion is shown, and a directional selection of  $\nu_{\text{ext}}$  controlled by the  $\nu_{\text{int}}$  transition moment is suggested. The pressure dependence of some of these spectra, up to 50 kbar at 100°K, is presented and discussed in terms of the host-lattice dispersion curves. For instance, it is shown that there is no acoustic-to-optic energy gap in the high-pressure CsCl-type structures of KBr, KI, RbBr, and RbI. Some of the wider applications of this type of spectrum are also indicated.

#### INTRODUCTION

VIBRATIONAL spectra which have the general form  $\nu_{\text{int}} \pm \nu_{\text{ext}}$  have been reported for several different systems, e.g., iodoform,<sup>1</sup> brucite,<sup>2</sup> polyatomic impurity ions in alkali halides,<sup>3-6</sup> impurity molecules in solidified rare-gas matrices.<sup>7</sup>  $\nu_{\text{int}}$  is a frequency which

<sup>1</sup> R. M. Hexter and H. Cheung, *J. Chem. Phys.* **24**, 1187 (1956).

<sup>2</sup> R. M. Hexter, *J. Opt. Soc. Am.* **48**, 770 (1958).

<sup>3</sup> J. C. Decius, J. L. Jacobson, W. F. Sherman, and G. R. Wilkinson, *J. Chem. Phys.* **43**, 2180 (1965).

<sup>4</sup> R. Metselaar and J. van der Elsken, *Phys. Rev. Letters* **16**, 349 (1966).

<sup>5</sup> M. A. Cundill and W. F. Sherman, *Phys. Rev. Letters* **16**, 570 (1966).

<sup>6</sup> C. K. Chau, M. V. Klein, and B. Wedding, *Phys. Rev. Letters* **17**, 521 (1966).

<sup>7</sup> B. Vodar, in Fourth High-Pressure Research Meeting, Eindhoven, 1966 (unpublished). Although there are many references available in the published literature which give spectra of impurities isolated in rare-gas matrices [e.g., L. F. Keyser and G. W. Robinson, *J. Chem. Phys.* **44**, 3225 (1966); D. E. Mann, N. Acquista, and D. White, *ibid.* **44**, 3453 (1966)], there do not seem to be any examples which show a very strong  $Q$  branch accompanied by sum and difference binary combinations with the host crystal lattice vibrations. We understand, however, that this type of spectrum has been observed in Professor B. Vodar's laboratory, Bellevue, France.

can be identified with a specific molecular group and which occurs at an energy only slightly displaced from that at which it would be found in an isolated molecule.  $\nu_{\text{ext}}$  are frequencies associated with the movement of one molecule with respect to its neighbors, and represent a selection of the available energies of the lattice vibrations of the crystal at the point at which it is sampled. In iodoform, for example, if the C-H stretching frequency is used as  $\nu_{\text{int}}$  and the radiation passed through the crystal such that its  $E$  vector is perpendicular to the C-H bonds, all of which align in the crystal, then the sharp C-H absorption is itself seen only very weakly (only seen at all because of convergence of the beam, crystal imperfections, etc.), and broad wings are seen extending between 20 and 50  $\text{cm}^{-1}$  on each side. By cooling the crystal to liquid-helium temperature the low-energy wing can be completely suppressed. In principle, any strongly active band should show this kind of side structure, but the best examples are certainly those where complete longitudinal alignment of the  $\nu_{\text{int}}$  transition moment renders it virtually non-absorbing and allows the usually broad  $\pm \nu_{\text{ext}}$  bands to