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Thermally induced absorption-intensity transfer between Tl^+ bands in alkali halides

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The effects of the electron-lattice interaction in KBr:Tl have been experimentally examined by thermomodulated absorption measurements. The variation of the zeroth and first moment of the bands have been evaluated together with an analysis of the band multiplicity carried out by a computerized fitting of the experimental curves. The results obtained have been interpreted on the basis of a theoretical calculation of the moment variations and compared with the existing results.

INTRODUCTION

The splittings of the absorption bands originating from the presence of Tl^+-like ions in alkali-halide cubic matrices and the correlations between the impurity localized electronic levels, induced by the application to these phosphors of different external perturbations, have been widely investigated by means of modulation techniques.[1-5] On the contrary the band-shape behavior and the eigenfunction mixing occurring through electron-lattice interaction have been studied up to now only by normal spectroscopy measurements[6-8] or indirectly deduced from the results of experiments dealing with stress[9] or magnetic effects.[3,10] For this reason, the existing results concerning the exact number of subbands and the unambiguous mechanism of the level correlation and the oscillator-strength transfer are clearly approximate and sometimes in strong disagreement.[11,12] A striking improvement can be achieved by use of a modulation technique enhancing only electron-phonon interaction, which allows for a greater possibility of detecting the related effects. This is the case for the thermomodulation measurements that we have carried out on the Tl^+ absorption in KBr and reported in this paper along with our conclusions, which we have deduced after a comprehensive discussion of most of the results comparable with ours in the present situation.

BAND MULTIPLICITY

The first analysis of the absorption spectra of different Tl^+-like centers in various host lattices with both NaCl- and CsCl-type structure firmly established that they have an ${}^1A_{1g}(\Gamma_1^+)$ ground state and the three excited states ${}^3T_{1u}({}^3\Gamma_4^-)$, ${}^3T_{2u}({}^3\Gamma_3^-, {}^3\Gamma_5^-)$, and ${}^1T_{1u}({}^1\Gamma_4^-)$ which are mixed differently by spin-orbit and electron-lattice Hamiltonians to form the states responsible for the corresponding absorption bands. The symmetry of the ${}^1A_{1g}$ ground state is the same as the impurity center and it is consistently nondegenerate, but the excited levels have a multifold degeneracy which is more or less removed when the lattice is distorted from the equilibrium position, causing the splitting of the states.

Initially, some possible patterns of vibration-induced splitting of the absorption bands of localized optical electrons were analyzed[13] by applying the Franck-Condon approximation, and the results were used to propose an explanation of the observed triplet structure of the C band and of the apparent doublet structure of the temperature-sensitive asymmetric A band. Based upon the same assumptions, a correspondence has been established[14] between the structures present in the absorption bands arising from the transitions leaving from ${}^1A_{1g}$-state towards the excited ones and the three quantities a, b, and c defined as the coupling constants. They describe the intensity of the electron-phonon interaction with the lattice vibrational modes of one-, two-, and three-dimensions, respectively, and are expressed as follows:

$$a = \langle p_x | V_1 | p_x \rangle , \quad b = \langle p_x | V_2 | p_x \rangle , \quad c = \langle p_y | V_4 | p_z \rangle ,$$

using the current symbolism.[15]

The triplet structure of the highest-energy C band, experimentally observed[16] for the various Tl^+-like impurities contained in different alkali-halide phosphors, undoubtedly supports, through the typical $T^{1/2}$ law followed by the subsidiary-peak energy separation, the dynamical Jahn-Teller (JT) effect, which is a linear electron-lattice interaction.

The trigonal T_{2g} modes, assisted by totally symmetrical vibrations, should also account for the C-band line shape recently observed[17] for In^+ impurities on a large temperature range. The increasing asymmetry in the band with increasing temperature seemed to reveal[16,18] the existence of a quadratic interaction arising from the first-order perturbation of the quadratic electron-lattice coupling. The absorption C-band line shape, however, has been subsequently derived by the method of moments, considering the dynamic JT interaction in the excited T_{1u} electronic states to be linear in the lattice displacement. An asymmetric triplet structure has been obtained even in this linear approximation, limiting the necessity of using a quadratic approximation to get line-shape temperature-dependent variation.[19] These results are in disagreement with Jacobs's conclusions about the A and C bands where the observed asymmetry has been ascribed to the quadratic electron-lattice interaction with T_{2g}-symmetry reticular vibrations.[8,17]

The undefined multiplicity of the above-mentioned structures has been the subject of recent studies[20] on heavily-lead-doped NaCl crystals. They have shown a more marked A- and B-band splitting, which agrees with the previously discussed results, thus reproposing the occurrence of the JT effect. As far as the B band is concerned, more recently a systematic experimental investigation,[6,21] supported by a theoretical analysis of its line shape, led to the conclusion that the transition responsible is the ${}^1A_{1g} \rightarrow {}^3T_{2u}$, strongly assisted by the T_{2g} modes of lattice vibration and also by A_{1g} and E_g modes which are responsible for the lifting of the degeneracy and for the smoothing of the logarithmic singularity and broadening of the line shape, respectively. The B-band asymmetry has been attributed to the mixing of the states responsible for the A and C bands into the ${}^3T_{2u}$ level. This kind of assignment is the same as previously proposed by us on the basis of different considerations.[3] The difficulty in observing distinctly, by unmodulated absorption, the JT splitting of this band has been attributed[22] to the embedding of the higher-energy subband in the C-band tail. This kind of behavior is similar to the type predicted for In^+- and Sn^{2+}-doped phosphors[23] upon varying the temperature, which causes a shift of the main peak toward higher energy and a width growth hiding the low-energy shoulder. However, at low temperatures the B band in the In^+ center has been reported doubly structured,[6] though the high-temperature-calculated curves do not exhibit any resolved structure,[24] essentially owing to the higher-energy peak intensity which is remarkably sensitive to temperature. Only for quenched crystals containing Sn^{2+}, has been reported,[25] at low temperatures, a B band quintuplet structure ascribed to the JT-split ${}^3T_{2u}$ and ${}^3E_u$ states. The discrepancy between all of these results is evident enough, and supports a doubtful understanding of the actual behavior of the electronic levels.

Computer analysis has also been used to resolve into their components the KCl:Tl absorption bands. Approximating the dynamic electron-lattice interaction by a term linear in the lattice coordinates,[26] three subsidiary bands have been proposed as giving rise to the A band at high temperatures. Two subbands were required at low temperatures, while three components were needed for the C band at all temperatures. The B band was well approximated by a temperature-dependent doublet structure. Subsequently, the observed A band has been quite accurately fitted by the sum of two Gaussian subbands over a large temperature range (4–700 K), while the temperature behavior of the subband energy parameters supported the theory attributing the observed structures to the dynamical JT effect.[27] The use of asymmetric Gaussians has recently been proposed by Jacobs *et al.*[7] to explain, in the framework of the configuration-coordinate model, the A band shape. The overlapping of two asymmetric subbands has been required to reproduce experimental curves as caused by the JT interaction with trigonal-symmetry vibrational modes. Also, for the A absorption band in KF:Tl (Ref. 28) a computer simulation has been performed of the superposition of two Gaussian subbands whose separation increased with temperature, which adds a further confirmation to the JT interaction. The model constructed in the interim, taking into account spin-orbit coupling, vibrational mixing of the excited states, and the dynamical JT effect in the perturbed $|A\rangle$ and $|C\rangle$ states[17] has yielded band-shape calculation, but failed to account for temperature-dependent peak reversal.

COUPLING CONSTANTS

It has also been attempted to estimate the values of both the individual a^2, b^2, and c^2 parameters and their linear combination $2b^2+3c^2$. The values of these interaction parameters have been recently collected for KBr:Tl, to be compared with those obtained by a computer best-fit process.[29] In the same paper a discussion of the wealth of different methods was also contained, each method being more or less directly related to the optical-absorption band shapes. In the same period there has appeared the sophisticated proposition of introducing two sets of three interaction parameters for the singlet and the triplet state, respectively,[30] in order to overcome the difficulties arising from the possible difference in the radial wave function of different states. In this case, however, the c^2 values for $|A\rangle$ and $|C\rangle$ are very close to each together,[17] so that the necessity of such a treatment will be discussed in a later paper.

THERMAL OSCILLATOR-STRENGTH TRANSFER

The exchange of absorption intensity between the three bands with varying temperature, quantitatively expressed by their zeroth-moment variations, constitutes more experimental evidence of the coupling of electronic states through the electron-lattice interaction Hamiltonian. As the temperature was increased[11] from 10 to 300 K, the integrated absorption intensity of the B band in several Tl$^+$-doped alkali halides varied according to a $\coth(h\nu_q/2kT)$ law, revealing its vibration-assisted nature. The temperature dependence of the relative absorption intensities of all the three bands showed a correlation between the B and C bands, suggesting that the $|c\rangle$ state should be the main mixing state for the occurrence of the otherwise forbidden B band. On the contrary as the temperature was raised in In$^+$-doped phosphors, the B-band intensity increased at the expense of the A-band intensity, with a total intensity that was almost constant or slightly increasing at least up to 200 K.[17,31] In conclusion the B-band intensity increased with temperature in all crystals examined, and was supplied by either the C- or the A-band.

This experimental result matches the theoretical one achieved by means of the calculated eigenfunctions of the first excited state of Tl$^+$ in the O_h crystalline field of KCl.[26] The C- and A-band oscillator strength has been found to be almost constant over a wide temperature range, but the C-band oscillator strength began to decrease at very high temperatures together with a rapid increase of the B-band oscillator strength.

Experimentally, however, the area under the A band decreased by about 10% on progressive warming,[27] though the individual components behaved differently. In fact, the area under the lower-energy subband grew toward a maximum up to 150 K while the higher-energy component intensity decreased in the same manner. This behavior reversed only at very high temperatures. Their relative amplitudes are independent of thallium concentration which when increased causes the corresponding growth of the third component at long wavelengths.[32] The band area as a whole, showed a net temperature-dependent decrease, in agreement with the 5% oscillator-strength decrease first observed by Wagner.[33] This variation, however, was uncompensated because the C-band variation approximated quite well the B-band increase, so that the area over all three bands revealed a net decrease. This conclusion, conflicting the spectroscopy stability principle, also refers both to Fukuda's[34] results carried out by a systematic investigation of this type of phosphors, and to the recent spectroscopy studies[28] in KF:Tl, where only B-band absorption increases with temperature, A and C bands having temperature-independent oscillator strengths. However, the above-mentioned principle is verified in Pb^{2+}-doped crystals, where the absorption band areas in total hardly vary with temperature. When high concentrations of impurity ions were dissolved in the host crystal, the A-band intensity fell upon cooling the sample, either from supplying intensity to a higher-energy band or from a reduced transition probability.[20]

All the mentioned investigations, moreover, are strongly limited by the overlapping of the different bands which increasingly occurs when the temperature reaches relatively high values. In the above-mentioned experimental and theoretical situation a remarkable contribution has been provided by the thermomodulated Tl$^+$-induced absorption measurements carried out throughout the temperature range 88–300 K. Our results allow for the determination of the multiplicity of each absorption band and exhibit a well-defined correlation which makes clearer the interaction between impurity states via electron-lattice interaction.

THERMOMODULATED ABSORPTION

The variations induced on some Tl$^+$-absorption bands by applying a thermal perturbation, enhanced by means of a modulation technique, have been briefly reported in previous limited investigations.[35,36] The comprehensive analysis here presented, which allows for understanding of electronic levels behavior under thermal interaction with lattice vibrations, has been carried out by means of the experimental apparatus reported in Fig. 1. Light from a low-pressure hydrogen-flow lamp powered by a dc regulated supply, was focused on the entrance slit of a Schöffel prism monochromator whose resulting monochromatic light crossed the sample. The crystal, $10\times2.5\times0.6$ mm^3, supported by a large copper finger to avoid spurious signals due to sample vibrations and to ensure a good thermal contact, was mounted in a cryostat suitable to cover the investigated temperature range. The temperature of the sample was changed using an indirect modulation technique due to its insulating nature. A current square wave crossed a Ni substrate evaporated upon a face of the crystal pressed to the sample holder by two spring electrodes. A blank reference crystal was also glued near the sample to take into account the effect of the thermomodulation upon the bulk of the host crystal. The light transmitted by the sample was refocused on a HTV R136 pho-

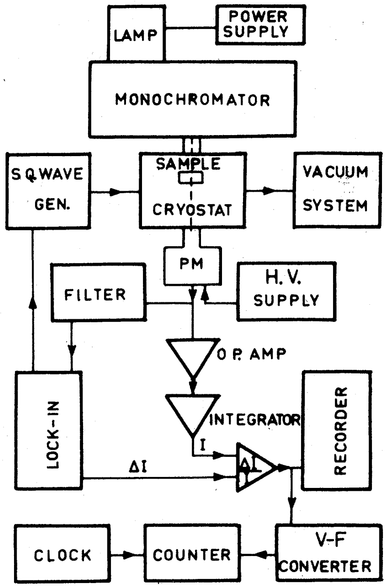

FIG. 1. Experimental setup.

tomultiplier and monitored by a digital voltmeter. The ac portion of the output signal, proportional to the change ΔI induced by the temperature modulation ($\Delta T \simeq 0.2$ K), was determined using a PAR HR8 lock-in amplifier in the internal mode tuned to the temperature modulation frequency (1.6 Hz). The ac signal ΔI then was used as one of the inputs to an analog dividing element. The dc channel consisted of an operational amplifier followed by another amplifier which was used as an integrator determining the time constant for the dc signal. The signal was then fed to the second input of the analog divider whose output $\Delta I/I$ was registered on a (x, t) recorder. The $\Delta I/I$ signal after a voltage-to-frequency conversion was also monitored by an electronic counter that, used in the totalizing mode with a start-stop clock, allowed us to obtain directly the average value of the signal at prefixed time intervals. The amplified reference voltage from the coherent amplifier biased the Ni heater by means of the current square wave generator.

The behavior of the thermal-induced variation of the absorption coefficient $\Delta\alpha$ over all three band energy ranges is similar throughout the investigated temperature interval. We have therefore reported in Figs. 2 and 3 the typical energy dependence of $\Delta\alpha$ at liquid-nitrogen (LNT) and room temperature (RT). Both spectra show the same peaks which suggests the existence of a common mechanism affecting the Tl^+ energy states. A first quantitative examination shows that the area under the three absorption bands is conserved, though the *A*-band absorption intensity suffers a net decrease at all temperatures. It is compensated by, within experimental accuracy, the growth of the *B*- and *C*-band oscillator strength, most of the increase roughly occurring in the *B* absorption range. The observed positive *B*-area change, by itself, does not completely compensate the *A*-band decrease, the small increase of the *C* oscillator strength having to be considered, in agreement with spectroscopic stability. These experimental results support the existence of a well-defined correlation between the states responsible for the absorption bands: in agreement with the theoretical consideration about singlet and triplet nature of Tl^+ states,[37] the oscillator strength of the *B* band seems directly related to that of the *A* band at each temperature. However, the overlapping between the *B* and *C* bands, growing as temperature increases, makes this first analysis approximate. Moreover, most of the thermal effect seems to occur beyond the *A*-band peak in the asymmetric-tail energy range,

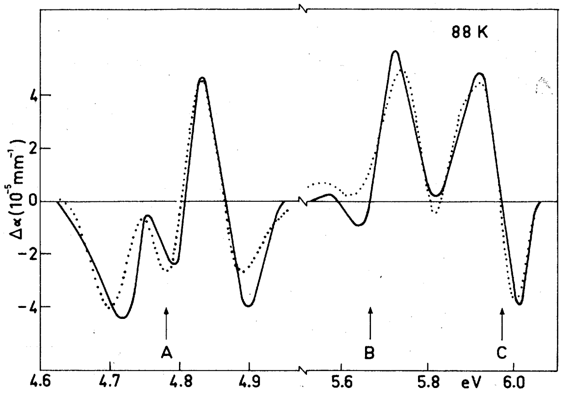

FIG. 2. Variation of the absorption coefficient (solid) for KBr:Tl at liquid-nitrogen temperature, compared with the theoretical best fit (dotted).

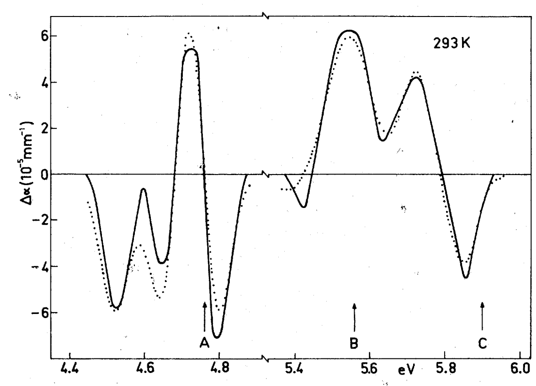

FIG. 3. Variation of the absorption coefficient (solid) for KBr:Tl at room temperature, compared with the theoretical best fit (dotted).

but the number of components making up each nonelementary absorption band cannot be deduced by the simple observation of the curves in Figs. 2 and 3.

In order to define unquestionably the multiplicity of these bands and to determine quantitatively the amount of their zeroth-moment variations (proportional to the changes of the areas lying under them), we performed a computerized analysis of the thermomodulated-absorption spectra. These spectra have been fitted to the sum of n terms of the type

$$\Delta\alpha_i = \exp\left[-\frac{1}{2}\left(\frac{E-E_i}{\Gamma_i}\right)^2\right] \times\left(\Delta k_i + \frac{k_i(E-E_i)\Delta E_i}{\Gamma_i^2} + \frac{k_i(E-E_i)^2\Delta\Gamma_i}{\Gamma_i^3}\right), \tag{1}$$

each one representing the differential of a symmetric Gaussian band

$$G = K\ \exp\{-\tfrac{1}{2}[(E-E_0)/\Gamma]^2\}, \tag{2}$$

where the absorption intensity K, energy peak position E_0 and half width at half height Γ are considered temperature dependent.

The best fits have been reported by dotted lines in Figs. 2 and 3 superimposed on the relative experimental curves. The satisfactory agreement allows us to state that the most suitable number of subbands G_i is three for the A and C absorption and one for the B band. This therefore seems to be the splitting effect of the dynamical JT interaction, which removes the degeneracy of the ${}^3T_{1u}$, ${}^1T_{1u}$, and ${}^3T_{2u}$ states originating the threefold-structured A and C bands and a single B band, respectively. The composition occurs in such a way that the A band appears asymmetrically low-energy tailed, while the B band is hidden by the C absorption with increasing temperature and a consequent shape alteration.

To calculate the amount of the zero-order moment variation[38] for the B and C bands separately, we have theoretically reconstructed the thermomodulated-absorption curves for each of them, their composition giving the experimental curves here reported. In such a way we are able to determine that the oscillator-strength variations of the different transitions originating the absorption bands as being caused by the electron-lattice coupling through the T_{2g} modes of vibrations, assisted by A_{1g}- and E_g symmetry potentially active modes. The normalized zeroth-, first-, and second-moment variations have been reported in Table I at LNT and RT together with the temperature coefficients relative to a 0.2 K thermomodulation. At all temperatures the strong A-band oscillator strength decrease is compensated by a net B-band increase, which is also temperature sensitive, the C band weakly growing in intensity. The first moment of the B and C bands exhibits the same temperature dependence opposite to that one of the A band, while A- and B-band second-moment variations have a sign opposite to the one of the C band. The above results are not in agreement with all those previously examined, some of which report a different correlation between the levels[11] of the impurity as a function of temperature. Apart from the superiority of modulated-spectroscopy over normal-spectroscopy techniques, the difference may be attributed to the different physical conditions which characterize the measurements: the temperature dependence of the several parameters of each band necessarily must be investigated over a large temperature interval, which causes thermal expansion[7] and variation of the atomic parameters, while thermomodulation does not.

To understand the mechanism underlying these results, we have analyzed the behavior of the single subbands and reported in Table II the structural variations suffered by each component due to

TABLE I. Normalized band moment variations and temperature coefficients of the absorption bands in KBr:Tl at LNT and RT.

				LNT		
Band	$\Delta M_0/M_0$	$\Delta M_1/M_1$	$\Delta M_2/M_2$	$(1/M_0)\Delta M_0/\Delta T$ (K^{-1})	$(1/M_1)\Delta M_1/\Delta T$ (K^{-1})	$(1/M_2)\Delta M_2/\Delta T$ (K^{-1})
A	-1.4×10^{-4}	-0.3×10^{-5}	0.5×10^{-3}	-6.8×10^{-4}	-1.6×10^{-5}	2.5×10^{-3}
B	1.0×10^{-4}	0.1×10^{-5}	-0.2×10^{-3}	5.2×10^{-4}	0.7×10^{-5}	-0.9×10^{-3}
C	0.6×10^{-4}	0.2×10^{-5}	-0.3×10^{-3}	2.9×10^{-4}	0.9×10^{-5}	-1.6×10^{-3}
				RT		
Band	$\Delta M_0/M_0$	$\Delta M_1/M_1$	$\Delta M_2/M_2$	$(1/M_0)\Delta M_0/\Delta T$ (K^{-1})	$(1/M_1)\Delta M_1/\Delta T$ (K^{-1})	$(1/M_2)\Delta M_2/\Delta T$ (K^{-1})
A	-1.4×10^{-4}	-3.2×10^{-6}	10.2×10^{-4}	-6.8×10^{-4}	-1.6×10^{-5}	5.1×10^{-3}
B	1.1×10^{-4}	2.6×10^{-6}	6.2×10^{-4}	5.2×10^{-4}	1.3×10^{-5}	3.1×10^{-3}
C	0.1×10^{-4}	0.6×10^{-6}	-0.6×10^{-4}	0.6×10^{-4}	0.3×10^{-5}	-0.3×10^{-3}

TABLE II. Band parameter variations of the absorption bands in KBr:Tl at LNT and RT, as obtained from the theoretical best fits of the experimental curves.

Parameter	Band A_1	A_2	A_3	B	C_1	C_2	C_3
LNT							
ΔK (mm^{-1})	3.6×10^{-6}	-551.8×10^{-6}	523.7×10^{-6}	4.0×10^{-6}	-348×10^{-6}	808×10^{-6}	-296.5×10^{-6}
ΔE_0 (meV)	1.03	-0.12	0.0176	-3.85	-2.28	0.096	0.131
$\Delta\Gamma$ (meV)	-0.863	0.262	0.22	0.526	-0.53	0.180	-0.019
RT							
ΔK (mm^{-1})	-58.95×10^{-6}	64.02×10^{-6}	-59.02×10^{-6}	52.9×10^{-6}	429.7×10^{-6}	-284.9×10^{-6}	409.4×10^{-6}
ΔE_0 (meV)	-2.17×10^{-2}	3.3×10^{-2}	-0.19×10^{-2}	-1.2×10^{-2}	5.35×10^{-2}	0.2×10^{-2}	-0.52×10^{-2}
$\Delta\Gamma$ (meV)	-0.43×10^{-2}	-2.9×10^{-2}	0.09×10^{-2}	-1.7×10^{-2}	1.38×10^{-2}	-2.56×10^{-2}	0.55×10^{-2}

the thermal effects. As one can see, the different subbands composing each absorption band do not behave in the same way, this result being consistent with the proposal of Braner and Halperin[27] based on computer analysis. Although the quantitative values reported for the different parameters are affected by the uncertainty due to the large number of parameters involved in the fitting operation, the effects upon the Tl$^+$ bands as a function of temperature may therefore be ascribed to the different behavior of the subbands, which together give rise to the reported macroscopic dependences.

The most-striking coupling underlined by our results is the one occurring between the levels responsible for the A and B band via electron-lattice interaction. To investigate the role of the JT or linear electron-lattice Hamiltonian, we have theoretically reproduced the zeroth- and first-moment variation caused by thermal perturbation by using the method of moments developed by Henry, Schnatterly, and Slichter.[38] The linear electron-lattice interaction Hamiltonian H_{el} may be represented, for a Tl$^+$-like ion embedded in a host lattice with cubic symmetry O_h, by the second term of the expression

$$V(\vec{r},\vec{R}) = V(\vec{r},\vec{R}_0) + \sum_i \left(\frac{\partial V}{\partial R_i}\right)_{\vec{R}_{i0}} (R_i - R_{i0})$$

around the equilibrium positions $\vec{R}_{i0}$ of the ions; $\vec{r}$ refers to electron coordinates.[26] The unperturbed wave functions we refer to are eigenfunctions of the Hamiltonian which includes static O_h crystal-field, exchange, and spin-orbit interactions:

$$\begin{aligned} |a^i\rangle &= -\nu\,|{}^1T^{\,i}_{1u}\rangle + \mu\,|{}^3T^{\,i}_{1u}\rangle\,, \\ |b^i\rangle &= |{}^3T^{\,i}_{2u}\rangle\,, \quad |{}^3E^{\,i}_{u}\rangle\,, \\ |c^i\rangle &= \mu\,|{}^1T^{\,i}_{1u}\rangle + \nu\,|{}^3T^{\,i}_{1u}\rangle\,, \end{aligned} \tag{3}$$

are responsible for the sharp absorption lines broadened and split by the thermal interaction in the multifold-structured absorption bands A, B, and C, respectively. Here the superscript i refers to the three states corresponding to the quantum number $m_j = 1, 0, -1$, while μ and ν are the spin-orbit mixing coefficients. In perturbation-theory framework the eigenfunction of the state $|R\rangle$ responsible for any one of the three bands may be written to the first order in H_{el}:

$$|R\rangle = |r\rangle + \sum_{n\neq r} \frac{\langle n\,|H_{el}\,|r\rangle}{E_r - E_n}\,|n\rangle\,, \tag{4}$$

$|r\rangle$ and $|n\rangle$ representing any of the eigenfunctions in Eq. (3), $|R\rangle$ the corresponding perturbed one, and E_r the relative energy.

The change of the zeroth-order moment M_{0r} due to the electron-lattice perturbation can therefore be obtained from the first-order wave functions (4) according to the expression

$$\frac{\Delta M_{0r}}{M_{0r}} = \sum_i \frac{|\langle 0|P_\eta|R^i\rangle|^2 - |\langle 0|P_\eta|r^i\rangle|^2}{M_{0r}}\,, \tag{5}$$

where $|0\rangle$ indicates the undegenerate ground state and P_η is the electric-dipole-moment operator for η polarization. Taking into account that the only nonvanishing matrix elements of the electric-dipole-moment operator for η polarization, P_η, are

$$\langle 0\,|P_x|x\rangle = \langle 0\,|P_y|y\rangle = \langle 0\,|P_z|z\rangle\,,$$

we have evaluated the relative variations of the zeroth moments induced by the coupling between the levels through the electron-lattice interaction, directly related to temperature. They are for A, B, and C band, respectively,

$$\frac{\Delta M_{0a}}{M_{0a}} = \left(\frac{\mu}{\nu}\,\frac{\langle c|H_{el}|a\rangle}{E_a - E_c} - 1\right)^2 - 1\,,$$

$$\frac{\Delta M_{0b}}{M_{0b}} = \left(\frac{\nu}{\mu}\,\frac{\langle a|H_{el}|b\rangle}{\langle c|H_{el}|b\rangle}\,\frac{E_c - E_b}{E_b - E_a} + 1\right) \times \left(\frac{\nu}{\mu}\,\frac{\langle b|H_{el}|a\rangle}{\langle b|H_{el}|c\rangle}\,\frac{E_c - E_b}{E_b - E_a} + 1\right) - 1\,, \tag{6}$$

$$\frac{\Delta M_{0c}}{M_{0c}} = \left(\frac{\nu}{\mu}\,\frac{\langle a|H_{el}|c\rangle}{E_a - E_c} + 1\right)^2 - 1\,,$$

which give a good qualitative account of the experimental observations. In fact, substituting in (6) the values of the parameters reported in Ref. 15, we obtain a decrease of the A-band zeroth moment and a positive variation of the B- and C-band areas, thereby reproducing the experimental behavior. On this basis we can interpret the actual mechanism occurring when electronic state eigenfunctions are vibronically mixed, which causes a B-band intensity increase at the expense of the A-band oscillator strength, also supplying the small growth of the C band.

The perturbative expression of the first-moment variation reported[38] for a transition between a ground state $|0\rangle$ and a well-resolved excited state $|r\rangle$ is

$$\Delta M_{1\eta} = M_{0r}^{-1} A'_{Vm} \sum_{rr'} \langle m|\langle 0|P_\eta^+|r\rangle\langle r|H_{el}|r'\rangle \times \langle r'|P_\eta|0\rangle|m\rangle\,, \tag{7}$$

where $|m\rangle$ stands for the spin states and A'_{Vm} is the thermal average over ground-state spin polarizations. A straightforward calculation of expression (7) that we carried out by substituting the eigenfunctions (3) relative to the Tl^+ center in O_h symmetry environment has given the values for the first-moment changes of the A, B, and C bands, respectively. As a function of the coupling constants and of the symmetry coordinates for the totally symmetric (Q_1) and trigonal modes (Q_4, Q_5, Q_6) of lattice vibrations the first-moment changes are

$$\Delta M_{1a} = 3aQ_1 + 2c(\nu^2 - \tfrac{1}{2}\mu^2)Q\,,$$

$$\Delta M_{1b} = 3aQ_1 + cQ\,, \tag{8}$$

$$\Delta M_{1c} = 3aQ_1 + 2c(\mu^2 - \tfrac{1}{2}\nu^2)Q\,,$$

where we have used the elements of the matrix which describes the electron-lattice interaction reported by Tsuboi *et al.*[6] setting $Q = Q_4 + Q_5 + Q_6$. Substitution in the expressions (2) of the numerical values of the parameters reported in the literature[15,29] also allows for qualitative reproduction of the sign of the band first-moment changes we have experimentally observed and reported in Table I.

In conclusion we wish to emphasize that the thermomodulation results presented here allow for a positive definition of the numerous questionable situations we state initially. The interpretation we have suggested fits well in the framework that by a systematic investigation[5,29,39,40] we are attempting to build up, namely, Tl^+-like impurity behavior strongly affected by electron-lattice interaction.

ACKNOWLEDGMENTS

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[1] V. Grasso, P. Perillo, and G. Vermiglio, Phys. Rev. B 4, 3731 (1971).

[2] V. Grasso, P. Perillo, and G. Vermiglio, Solid State Commun. 11, 563 (1972).

[3] C. Bagnato, V. Grasso, P. Perillo, and G. Vermiglio, Nuovo Cimento B 26, 263 (1975).

[4] D. Bimberg, W. Dultz, and W. Gebhardt, Phys. Status Solidi 31, 661 (1969).

[5] W. Dultz and W. Gebhardt, Solid State Commun. 7, 1153 (1969).

[6] T. Tsuboi, Y. Nakai, K. Oyama, and P. W. M. Jacobs, Phys. Rev. B 8, 1698 (1973).

[7] P. W. M. Jacobs and S. A. Thorsley, Cryst. Lattice Defects 5, 51 (1974).

[8] T. Tsuboi, K. Oyama, and P. W. M. Jacobs, Can. J. Phys. 53, 192 (1975).

[9] W. Dultz, Phys. Status Solidi B 48, 571 (1971).

[10] K. Cho, J. Phys. Soc. Jpn. 27, 646 (1969).

[11] T. Tsuboi and R. Kato, J. Phys. Soc. Jpn. 27, 1192 (1969).

[12] R. Laiho, Ann. Acad. Sci. Fenn. A1 6, 1 (1971).

[13] Y. Toyozawa and M. Inoue, J. Phys. Soc. Jpn. 21, 1663 (1966).

[14] K. Cho, J. Phys. Soc. Jpn. 25, 1372 (1968).

[15] A. Honma, Sci. Light (Tokyo) 16, 212 (1967); J. Phys. Soc. Jpn. 24, 1082 (1968).

[16] A. Fukuda, J. Phys. Soc. Jpn. 27, 96 (1969).

[17] P. W. M. Jacobs and K. Oyama, J. Phys. C 8, 851 (1975); 8, 865 (1975).

[18] A. Honma, Sci. Light 18, 33 (1969).

[19] R. Sati, S. Wang, and M. Inoue, Can. J. Phys. 50, 1370 (1972).

[20] S. B. S. Sastry, V. Viswanathan, and C. Ramasastry, Phys. Status Solidi B 55, K21 (1973).

[21] D. Bimberg, W. Dultz, and K. Fussgaenger, Phys. Lett. A 25, 766 (1967).

[22] S. Asano and Y. Tomishima, Surf. Sci. 4, 1 (1973).

[23] A. Honma, J. Phys. Soc. Jpn. 36, 1708 (1974).

[24] A. Matsushima and A. Fukuda, Phys. Status Solidi B 66, 663 (1974).

[25] T. Tsuboi, K. Oyama, and P. W. M. Jacobs, J. Phys. C 7, 221 (1974).

[26] A. M. Lemos, M. C. Stauber, and J. F. Marion, Phys. Rev. B 2, 4161 (1970).

[27] A. A. Braner and A. Halperin, Phys. Rev. B 4, 543 (1971).

[28] U. Mayer, D. Schimid, and H. Scidel, Phys. Status Solidi B 70, 269 (1975).

[29] U. Giorgianni, G. Mondio, P. Perillo, G. Saitta, and G. Vermiglio, Physica B 79, 175 (1975).

[30] A. Honma, J. Phys. Soc. Jpn. 35, 1115 (1973).

[31] A. Fukuda, J. Luminesc. 112, 376 (1970).

[32] D. A. Patterson, Phys. Rev. 119, 962 (1960).

[33] W. Wagner, Z. Phys. 181, 143 (1964).

[34] A. Fukuda, Sci. Light 13, 64 (1964).

[35] U. Giorgianni, P. Perillo, G. Saitta, and G. Vermiglio, Solid State Commun. 17, 895 (1975).

[36] U. Giorgianni, G. Mondio, G. Saitta, and G. Vermiglio, Phys. Lett. A 54, 45 (1975).

[37] A. M. Lemos and C. Krolik, Phys. Rev. B 7, 1608 (1973).

[38] C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137, A583 (1965).

[39] U. Giorgianni, G. Mondio, G. Saitta, and G. Vermiglio, Phys. Status Solidi B 74, 317 (1976).

[40] U. Giorgianni, G. Mondio, G. Saitta, and G. Vermiglio, Physica B 81, 311 (1976).