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JAHN-TELLER EFFECT IN THE PARITY-FORBIDDEN TRANSITION $^2p_{1/2} \rightarrow ^2p_{3/2}$ OF Tl^0 IN KCl (*)

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Résumé. — Le profil du spectre d'absorption pour la transition $^2p_{1/2} \rightarrow ^2p_{3/2}$ de Tl^0 dans KCl a été calculé en considérant l'interaction électron-phonon. Le profil théorique est en bon accord avec le spectre expérimental. On a déterminé la valeur de la constante du couplage pour chaque mode de vibration du réseau (A_{1g} , E_g et T_{2g}).

Abstract. — The absorption spectrum at 153 K measured by Delbecq *et al.* has been quantitatively analyzed in terms of the adiabatic treatment of the lattice vibrations. In this analysis we have employed nine modes of phonons, i. e. A_{1g} , E_g , T_{2g} and T_{1u} modes. By fitting the theoretical curve to the experimental one, we have determined the values of the coupling constants. The values for E_g and T_{2g} modes are very near to those for KCl : Tl^+ , as is expected.

The lowest energy excitation of a neutral thallium atom $\{ (1s)^2 \dots (6s)^2 (6p)^1 \}$ corresponds to the transition between the spin-orbit split states of the 6p electron. Although this transition is parity-forbidden in the free space, it becomes electric-dipole allowed in solids because we have parity-breaking field due to static and/or dynamic lattice potentials.

In this paper we calculate the absorption line shape of this transition by assuming that the Tl^0 atom lies at the O_h symmetry position in the KCl lattice. In this model the parity-breaking field is provided by the odd-parity modes of the lattice vibrations, and therefore we have a remarkable temperature dependence on the oscillator strength of the transition as was observed by Delbecq *et al.* [1].

Although the measured spectrum has fine structures at low temperature, we try in this paper to analyze quantitatively only the high temperature curve. In this case we may treat the lattice vibrations adiabatically, and we introduce the interaction mode coordinates for each mode of symmetry in a similar way as in the case of KCl : Tl^+ type phosphors and the F-centers [2], [3], [4] :

$$\begin{aligned} \text{For } A_{1g}\text{-mode} &: Q_1. \\ \text{For } E_g\text{-mode} &: Q_2, Q_3. \\ \text{For } T_{2g}\text{-mode} &: Q_4, Q_5, Q_6. \\ \text{For } T_{1u}\text{-mode} &: Q_x, Q_y, Q_z. \end{aligned} \quad (1)$$

In the presence of the E_g and T_{2g} modes of the lattice distortions, all the states of $p_{1/2}$ and $p_{3/2}$ interact with each other, and we can expect the Jahn-Teller splitting of the $p_{3/2}$ level and also the mixing of $p_{1/2}$ and $p_{3/2}$. The eigenvalue equation leads to the

following cubic equation [3] (Kramers degeneracy still remains) :

$$X^3 - TX + S = 0 \quad (2)$$

where (1)

$$T = \frac{3}{4} \lambda^2 + b^2(Q_2^2 + Q_3^2) + c^2(Q_4^2 + Q_5^2 + Q_6^2) \quad (3)$$

$$\begin{aligned} S = \frac{1}{4} \lambda^3 + \frac{2}{3\sqrt{3}} b^3 Q_3(3Q_2^2 - Q_3^2) - 2c^3 Q_4 Q_5 Q_6 \\ + bc^2 \left\{ \frac{1}{\sqrt{3}} Q_3(2Q_6^2 - Q_5^2 - Q_4^2) - Q_2(Q_5^2 - Q_4^2) \right\}. \end{aligned} \quad (4)$$

Here, λ is the spin-orbit coupling constant, and b and c the coupling constants for E_g and T_{2g} mode, respectively. Let X_0 , X_1 and X_2 be the three roots of the eq. (2) in the order of the increasing energy for a given set of $\{Q_2, Q_3, Q_4, Q_5, Q_6\}$, and

$$\psi_j = (a_j x + c_j y + e_j z) \alpha + (b_j x + d_j y + f_j z) \beta, \quad (j = 0, 1, 2) \quad (5)$$

the corresponding eigenstates, where α and β are the usual spin functions and x , y and z the three p-type functions which transform like the cartesian coordinates x , y and z , respectively. Because of the time reversal symmetry, the state

$$\tilde{\psi}_j = (a_j x + c_j y + e_j z)^* \beta - (b_j x + d_j y + f_j z)^* \alpha \quad (6)$$

also belongs to the same eigenvalue X_j . From the normalization condition, we have

$$|a_j|^2 + |b_j|^2 + |c_j|^2 + |d_j|^2 + |e_j|^2 + |f_j|^2 = 1, \quad (j = 0, 1, 2). \quad (7)$$

(1) Eq. (2.6) of [6] contains a misprint in the expression for S .

(*) A short communication of this work has been published [6].

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If we have the odd mode of the lattice distortion at the same time, the wave functions (5) and (6) will get the mixture of the functions of even-parity. Since the nearest excited state of the atom has 7s character, we consider the mixing of the s-state into ψ_1 and ψ_2 with the help of the T_{1u} mode. We neglect the mixing of the s-state into ψ_0 because X_0 is energetically more distant from the s-level than X_1 and X_2 . Treating this mixing by the second order perturbation theory, we get the perturbed wave function

$$\varphi_j = \psi_j + \delta(a_j Q_x + c_j Q_y + e_j Q_z) s\alpha + \delta(b_j Q_x + d_j Q_y + f_j Q_z) s\beta, \quad (8)$$

where δ is the coupling constant for T_{1u} mode divided by the energy separation between X_j and the s-level. The j -dependence of δ is neglected because the relevant value of $X_2 - X_1$ is small compared with the separa-

tion between $^2p_{3/2}$ - and s-levels. The transition $X_0 \rightarrow X_j$ consists of the following four processes ;

$$\begin{aligned} \uparrow\uparrow : \psi_0 &\rightarrow \varphi_j \\ \uparrow\downarrow : \psi_0 &\rightarrow \tilde{\varphi}_j \\ \downarrow\uparrow : \tilde{\psi}_0 &\rightarrow \varphi_j \\ \downarrow\downarrow : \tilde{\psi}_0 &\rightarrow \tilde{\varphi}_j \end{aligned} \quad (9)$$

where $\tilde{\varphi}_j$ is the time reversed state of φ_j . For the incident light with the polarization (l, m, n) , the matrix element for the electric dipole transition is of the form

$$(l, m, n) \begin{pmatrix} A_{11}, A_{12}, A_{13} \\ A_{21}, A_{22}, A_{23} \\ A_{31}, A_{32}, A_{33} \end{pmatrix}_{\sigma\tilde{\sigma}} \begin{pmatrix} Q_x \\ Q_y \\ Q_z \end{pmatrix}, \quad (10)$$

where σ and $\tilde{\sigma}$ distinguish the four processes (9) and

$$(A_{\mu\nu})_{\uparrow\uparrow} = M\delta \begin{pmatrix} a_0^* a_j + b_0^* b_j, & a_0^* c_j + b_0^* d_j, & a_0^* e_j + b_0^* f_j \\ c_0^* a_j + d_0^* b_j, & c_0^* c_j + d_0^* d_j, & c_0^* e_j + d_0^* f_j \\ e_0^* a_j + f_0^* b_j, & e_0^* c_j + f_0^* d_j, & e_0^* e_j + f_0^* f_j \end{pmatrix} \quad (11)$$

$$(A_{\mu\nu})_{\downarrow\uparrow} = M\delta \begin{pmatrix} a_0 b_j - b_0 a_j, & a_0 d_j - b_0 c_j, & a_0 f_j - b_0 e_j \\ c_0 b_j - d_0 a_j, & c_0 d_j - d_0 c_j, & c_0 f_j - d_0 e_j \\ e_0 b_j - f_0 a_j, & e_0 d_j - f_0 c_j, & e_0 f_j - f_0 e_j \end{pmatrix} \quad (12)$$

$$(A_{\mu\nu})_{\downarrow\downarrow} = \{ (A_{\mu\nu})_{\uparrow\uparrow} \}^* \quad (13)$$

$$(A_{\mu\nu})_{\uparrow\downarrow} = \{ (A_{\mu\nu})_{\downarrow\uparrow} \}^* \quad (14)$$

with

$$M = \langle s | ex | x \rangle. \quad (15)$$

By taking the thermal average of the absolute square of (10) over the Boltzmann distribution, we get, for each combination of σ and $\tilde{\sigma}$,

$$\frac{1}{2} kT \sum_{\mu=1}^3 |lA_{1\mu} + mA_{2\mu} + nA_{3\mu}|^2. \quad (16)$$

This result is obtained for a given set of $\{Q_2, Q_3, Q_4, Q_5, Q_6\}$. For the set which is obtained by operating one of the symmetry operations of the O_h group to the original set of $\{Q\}$, we have the same set of the eigenvalues $\{X_j\}$. The eigenstates for them can be obtained by applying the same symmetry operation to ψ_j , which, in (16), is equivalent to one of the permutations of $(\pm l, \pm m, \pm n)$. Therefore the sum of (16) over all the possible sets of the equivalent distortions leads to

$$8 kT \sum_{\mu=1}^3 \sum_{\nu=1}^3 |A_{\mu\nu}|^2. \quad (17)$$

The sum of (17) over all the four processes (9) gives

$$\begin{aligned} &16 kTM^2 \delta^2 \times \\ &\times (|a_0|^2 + |b_0|^2 + |c_0|^2 + |d_0|^2 + |e_0|^2 + |f_0|^2) \\ &\times (|a_j|^2 + |b_j|^2 + |c_j|^2 + |d_j|^2 + |e_j|^2 + |f_j|^2) \end{aligned} \quad (18)$$

which, by (7), leads to

$$16 kTM^2 \delta^2. \quad (19)$$

Thus we have shown that the transition probability of $X_0 \rightarrow X_j$ depends neither on j nor on the set of $\{Q\}$.

The line shape function in the classical Franck-Condon approximation is given by (2)

$$\begin{aligned} f(E) &= N \int dQ \exp \left\{ -\frac{X_0(Q)}{kT} \right\} \times \\ &\times \tilde{N} \int d\tilde{Q} \exp \left\{ -\frac{\tilde{Q}^2}{kT} \right\} \\ &\times \frac{1}{2} \sum_{j=1}^2 | \langle j | \hat{M} | 0 \rangle |^2 \delta(X_j - X_0 - E) \end{aligned} \quad (20)$$

where $\hat{M}$ is the dipole moment operator, Q and $\tilde{Q}$

(2) There are miswritings in the expressions (2.1) ~ (2.3) of [6]. The Boltzmann factor in each expression should be corrected according to the expressions (20) and (23) of this paper. The numerical calculation in [6] was done with correct expression.

represent the whole sets of the coordinates $\{Q_2, Q_3, Q_4, Q_5, Q_6\}$ and $\{Q_x, Q_y, Q_z\}$, respectively, and

$$\frac{1}{N} = \int dQ \exp \left\{ -\frac{X_0(Q)}{kT} \right\} \quad (21)$$

$$\frac{1}{\tilde{N}} = \int d\tilde{Q} \exp \left(-\frac{\tilde{Q}^2}{kT} \right) = (\pi kT)^{3/2}. \quad (22)$$

Using the result (19), we can simplify (20) as

$$f(E) = \frac{M^2 \delta^2 kT}{3} N \int dQ \exp \left\{ -\frac{X_0(Q)}{kT} \right\} \times \frac{1}{2} \sum_{j=1}^2 \delta(X_j - X_0 - E). \quad (23)$$

The expression (23) is quite similar to that for the dipole allowed transition except for the factor $\delta^2 kT/3$ which explains the temperature dependence of the oscillator strength. For the lower temperatures T must be replaced by some effective temperature because we are in the semi-classical regime in that case. Therefore the spectrum does not vanish at 0 K.

For given values of T , b , c and λ , the integral (23) can be numerically calculated by means of Monte Carlo method with good accuracy and without much labor [3], which enables us to directly compare the theoretical and experimental line shapes, and thus to determine the values of the parameters. The selection of the trial values of the parameters has been made in the following way :

- i) T is fixed to the experimental value 153 K.
- ii) λ must be near to the atomic value 0.64 eV.
- iii) b and c must be near to the values for $\text{KCl} : \text{Ti}^+$ ($b^2 = 0.50$ eV, $c^2 = 0.48$ eV) [5]. This is because we may, in the first approximation, employ the same molecular orbitals for the description of the 6p orbitals of Ti^0 and Ti^+ .

In the first place, we have tried to get a good fit to the peak separation, and the final values are

$$\begin{aligned} \lambda &= 0.584 \text{ eV} \\ b^2 &= 0.667 \text{ eV} \\ c^2 &= 0.619 \text{ eV}. \end{aligned} \quad (24)$$

Although the over-all fit is not yet good for these values, the theoretical curve has already a good tendency : The lower energy peak is higher and narrower than the higher energy one, and there appears a plateau between the two peaks. The functional form of this plateau is $\sim (E - 3\lambda/2)^4$ [4]. If we consider the E_g mode only, this has the form $\sim |E - 3\lambda/2|$. The difference between these two functional forms comes essentially from the dimensionality of the model (E_g : two dimensions, $E_g + T_{2g}$: five dimensions). The incompleteness of the curve is that the both peaks are too narrow and the ratio of the peak heights is about twice bigger than the experimental value. This point can, however, be improved by the intro-

duction of a slight broadening due to the A_{1g} mode. The theoretical background for this effect is given as follows : The p-type molecular orbitals for ${}^2p_{1/2}$ and ${}^2p_{3/2}$ can be slightly different from one another in the higher order approximation because the mixing coefficient for the neighboring orbital depends on the energy separation between the levels of the neighboring orbital and ${}^2p_{1/2}$ or ${}^2p_{3/2}$. If we have such a difference in the molecular orbitals, we get slightly different energy shifts for ${}^2p_{1/2}$ and ${}^2p_{3/2}$ in the presence of the A_{1g} mode lattice distortion. If we define the difference in their energy shifts by aQ_1 , the final expression of the line shape function is

$$g(E) = (\pi kT)^{-1/2} \int dQ_1 \exp \left(-\frac{Q_1^2}{kT} \right) f(E - aQ_1). \quad (25)$$

Applying this convolution to the curve obtained above, we finally get an over-all good fit to the experimental curve as in figure 1. The value of the parameter a is

$$a^2 = 0.055 \text{ eV}, \quad (26)$$

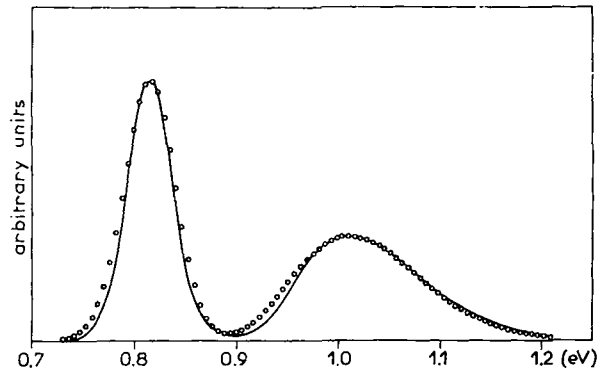


FIG. 1. — Line shape function ($\sim$ absorption constant/photon energy) at 153 K. Solid line : experiment. Points : theory.

which is really small compared with the values in (24). Although the introduction of the difference in the molecular orbitals for ${}^2p_{1/2}$ and ${}^2p_{3/2}$ states should in principle be accompanied with the change in the eigenvalue eq. (2), (3) and (4), we can expect that this effect is small because a^2 is by an order of magnitude smaller than λ , b^2 and c^2 .

We have also tried to analyze the curve at 77 K, but the fitting is not so good as at 153 K. This is mainly because the area of the two well-separated peaks of the experimental curve are different by about 10 %.

Furthermore we have to use an effective temperature of about 100 K. Therefore the difference in the area might indicate some quantal nature of the system at this temperature.

Summary. — The parity-forbidden transition ${}^2p_{1/2} \rightarrow {}^2p_{3/2}$ in $\text{KCl} : \text{Ti}^0$ at high temperature can be quantitatively described in terms of the interplay of

the spin-orbit and electron-phonon interactions. The role of each mode of the lattice vibration is quite distinct: T_{1u} mode makes the transition electric dipole allowed and give the temperature dependence of the oscillator strength, E_g and T_{2g} modes give the Jahn-Teller splitting in the ${}^2p_{3/2}$ level and mix ${}^2p_{1/2}$ and ${}^2p_{3/2}$ levels, which leads to the occurrence of the two peaks, the narrower and higher nature of the lower energy peak and the existence of the plateau between

the peaks, and A_{1g} mode makes a slight contribution as the line broadening.

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DISCUSSION

W. HAYES. — Do you have any suggestions to explain the failure of various laboratories to detect EPR on the ground state of Ti^0 ?

K. CHO. — Since the mixing of ${}^2p_{3/2}$ states into the ground ${}^2p_{1/2}$ states through even parity lattice vibrations is quite appreciable, one might have a very short spin-lattice relaxation time which prevents us from observing the EPR signal easily.

P. W. M. JACOBS. — From the temperature dependence of the splitting of the A band (resolved as two asymmetric gaussians) in $KCl : Ti^+$ we found C^2 to be about 1.1 eV, considering only interactions of T_{2g} symmetry. Do you think that this was due to our neglect of E_g modes ?

K. CHO. — Yes. Actually both modes contribute to the splitting almost equally according to my analysis of $KCl : Ti^+$ including all symmetry modes of vibrations.

P. W. M. JACOBS. — What about the temperature-dependence ? Were you equally successful in calculating the band shape at lower temperatures ?

K. CHO. — The trial to fit the curve at 77 K was not so successful as at 153 K. This is mainly because the measured curve has different area for each peak by about 5 ~ 10 %. Further more we had to use an effective temperature of about 100 K instead of 77 K. These facts seem to indicate that some quantal nature appears already at 77 K. The curve at 5 K is not yet analysed.