Extent to which the Jahn-Teller model can account for Tl$^+$ luminescence

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Several mechanisms have been considered for obtaining coexistence of different kinds of Jahn-Teller minima on the excited-state potential surfaces of the impurity, but no one was able to give a satisfactory interpretation of Tl$^+$ luminescence. These models are here critically reexamined, and an attempt is made for recognizing a scheme suitable to explain most of the experimental features.

The relevance of the Jahn-Teller effect (JTE) in the excited states of impurity centers with s^2 ground-state electronic configuration, such as Tl$^+$ in alkali halides, has been demonstrated for the interpretation of the optical properties of these phosphors, both in absorption and emission.[1]

As regards emission, the problem of the double A-band emission characteristic of Tl$^+$-like phosphors has been extensively studied and many efforts have been made in order to get a plausible interpretation of the complex phenomenology relative to this emission.[2]

The most widely accepted model is based on the coexistence of two kinds of Jahn-Teller minima on the $^3T_{1u}$ relaxed excited state, in the space of the normal coordinates of the $(TlX_6)^{5-}$ cluster (where X = Cl, Br, etc). These minima, accessible after optical absorption in the A band, lead to the so-called A_X and A_T emission bands.[3]

The possibility of coexistence of different kinds of minima, at different energies, has been demonstrated theoretically in a number of ways:

(i) In the framework of linear JTE, within the ϵ_g subspace of tetragonal distortions, coexistence is made allowed by strong spin-orbit mixing between the $^3T_{1u}$ and $^1T_{1u}$ states.[4,5]

(ii) By extending the analysis to the five-dimensional space of both ϵ_g and τ_{2g} (trigonal) modes, coexistence may be caused by quadratic JTE or by anharmonic terms in the potential energy.[6,7]

(iii) By considering the role of the totally symmetrical coordinate Q_1, it is found that if Q_1 varies strongly from one kind of distortion to the other, both can be minima.[8,9]

The latter mechanism has been proposed in order to explain the coexistence of tetragonal and trigonal minima in KI:Ga$^+$,[8] and hydrostatic pressure experiments on In$^+$ and Tl$^+$ phosphors[10,11]; these latter, however, can also be interpreted by scheme (i).[12] Moreover, scheme (iii) appears not to be suitable to explain Tl$^+$ luminescence, because when plausible values for the involved coupling constants are used coexistence is not found.[9] It can be said that the attempt of including all of the second-order terms [i.e., a combination of schemes (ii) and (iii)] was only partially successful in yielding coexistence; however, it showed that if the linear coupling constants to tetragonal (b) and trigonal (c) modes are nearly equal (which is the case for Tl$^+$ phosphors) a small variation of the parameters values makes it possible to obtain minima of different symmetry.[9]

On the other hand, scheme (i), which of course is in a sense limited because it does not involve trigonal modes (these modes are relevant to Tl$^+$ luminescence[13,14]), has been successfully employed to explain some properties of Tl$^+$ phosphors, such as: temperature behavior of A_T and A_X intensities,[15] hydrostatic pressure experiments,[12] negative magnetic circular polarization (MCP) of A_T emission,[16] triple decay time of A_X,[17] and absence of the slow component of A_T at low temperature $(T \lesssim 120$ K).[18]

More recently, the relevance of these level schemes for systems other than Tl$^+$ phosphors become evident. In particular, scheme (i) was used to interpret the low-temperature luminsecence spectra of complex ions like Cs$_2$SeCl$_6$.[19] In Ref. (19), however, the role of the parameter g (which is the ratio

of the exchange energy G to the spin-orbit coupling constant ζ) in determining level positions and minima depths, has been misunderstood.

Therefore, also in consideration of this fact, and that the energy-level scheme (i) is the most complete and comprehensive, under some assumptions, of schemes (ii) and (iii), it seems worthwhile to us to reconsider it in order to better clarify its attainment, limits of its validity, and to indicate possible improvements of the model for a more extensive understanding of Tl^+ phosphors and, possibly, other luminescent systems.

For our purposes it is suffficient to consider the cross sections of the $^3T^*_{1u}$ potential surfaces along the tetragonal coordinate Q_3 since the analysis for the existence of true minima in a multidimensional space has been already done for the several cases in other papers.[4-9]

Referring the energy zero[19] to W_0 [W_0 being the energy difference between the excited state $a_{1g}t_{1u}$ and the ground state a^2_{1g} electronic configuration,[2] so that, neglecting the spin-orbit and Jahn-Teller interactions, we have $E_0(^3T_{1u})=W_0-G$, $E_0(^1T_{1u})=W_0+G$], the energy levels $E(Q_3)$ are obtained by solving a third-degree secular equation; this, for the z components, can be factorized into a linear and a quadratic equation.[5] By putting $y=E/\zeta$ and $x_3=x=(-b/2\sqrt{3}\zeta)Q_3$ and have for the $^3T^*_{1u,z}$ cross section

$$y = -x - \tfrac{1}{4} - [(3x - \tfrac{1}{4} - g)^2 + \tfrac{1}{2}]^{1/2} + Ax^2 , \qquad (1)$$

where $g = G/\zeta$, $A = 12(1-\beta)\zeta/b^2$, $\beta = -a_{\epsilon\epsilon}$ is a quadratic term which accounts for the difference in curvature between the ground and the excited-state potential surfaces.[20]

For the underlying $^3A_{1u}$ state, we have

$$y = -x - \tfrac{1}{4} - g - [(3x - \tfrac{1}{4})^2 + \tfrac{1}{2}]^{1/2} + Ax^2 . \qquad (2)$$

The x and y components of the $^3T^*_{1u}$ state are degenerate along the Q_3 tetragonal axis; their cross sections are given by $y = \bar{y} + Ax^2$ where $\bar{y}$ is the lowest solution of the third-degree equation

$$\bar{y}^3 + g\bar{y}^2 - \bar{y}(12x^2 + 4gx + g^2 + \tfrac{3}{4}) - g^3 - 4xg^2$$
$$+ g(4x^2 - \tfrac{1}{4}) + 16x^3 + \tfrac{1}{4} = 0 . \qquad (3)$$

Figure 1 shows some cross sections of $^3T^*_{1u}$ and $^3A_{1u}$ potential surfaces obtained with Eqs. (1)—(3) for different values of the parameter g and for
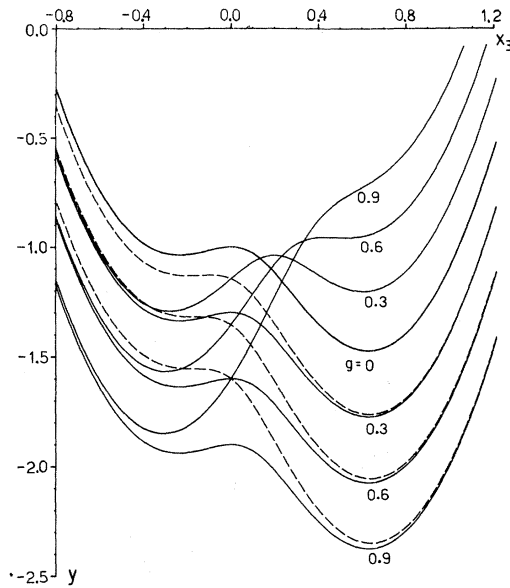

FIG. 1. Cross sections along the Q_3 axis of the $^3T^*_{1u}$ and $^3A_{1u}$ states computed for $A = 3$ and $g = 0, 0.3$, $0.6, 0.9$; the energy zero is referred to W_0 as in Ref. 19. For $g = 0$ the cross section of the $^3A_{1u}$ is coincident with $^3T^*_{1u,z}$ and $^3T^*_{1u,x(y)}$. For $g > 0$ the upper solid lines correspond to the $^3T^*_{1u,z}$, the lower solid lines to the $^3A_{1u}$, and the dashed lines to the double-degenerate $^3T^*_{1u,x(y)}$.

$A = 3$ which is quite a plausible value for this parameter.[4,19,21]

The same results can, of course, be obtained by assuming for the energy zero a different value. By referring it to $W_0 - G$ we get more simplified expressions for the energy levels and a more compact graphical presentation.[4,5,21] For the $^3T^*_{1u,z}$ we have, directly from Eq. (1),

$$y + g = -x - \tfrac{1}{4} + g$$
$$- [(3x - \tfrac{1}{4} - g)^2 + \tfrac{1}{2}]^{1/2} + Ax^2 . \qquad (4)$$

This relation, for $g = 0$, corresponds to the $^3A_{1u}$ level which, in this case, is independent of g.

The cross sections of $^3T^*_{1u,x}$ and $^3T^*_{1u,y}$ components are given by $y + g = \bar{y} + Ax^2$ where $\bar{y}$ is given now by the lowest solution of the equation[4,5]

$$\bar{y}^3 - 2g\bar{y}^2 - \bar{y}(12x^2 + 4gx + \tfrac{3}{4})$$
$$+ g(16x^2 + \tfrac{1}{2}) + 16x^3 + \tfrac{1}{4} = 0 . \qquad (5)$$

Figure 2 shows the cross sections of the $^3T^*_{1u}$ and $^3A_{1u}$ potential surfaces obtained with Eqs. (4) and (5) and for the same parameter values as in Fig. 1. By comparison of the two figures the advantage of
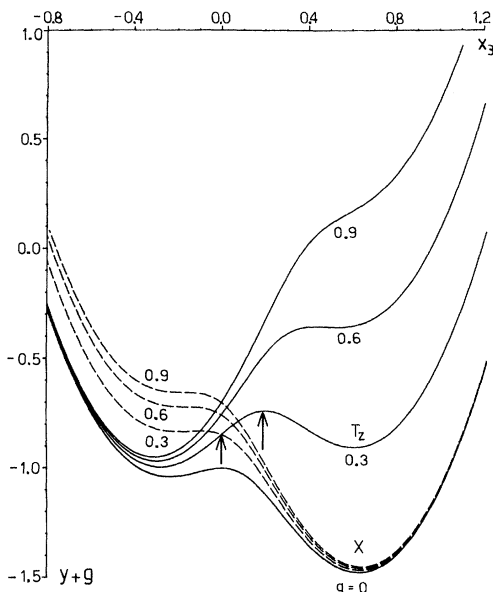
FIG. 2. Same as Fig. 1 but with the energy zero referred to W_0-G which allows for a more compact presentation. For $g=0$ we have the cross section of the $^3A_{1u}$ whose position is, in this case, independent on g. The two arrows indicate the excitation point for $x_3=0$ and the same point shifted $(x_3>0)$.

referring the energy zero to W_0-G becomes evident, since in this case the $^3A_{1u}$ level $(g=0)$ has a fixed position. In the following we shall refer to Fig. 2 for discussing the interpretation possibilities of the model.

The two kinds of coexisting minima on the $^3T_{1u}^*$ state are, in this case [scheme (i)], three tetragonal minima T_x, T_y, and T_z, and three couples of rhombic, nearly tetragonal X minima, each with underlying trap minimum on the $^3A_{1u}$ state. For sufficiently high values of g, the upper tetragonal minima tend to disappear. This limiting value of $g(\sim 0.6$ for $A=3)$ depends on the parameter A and increases with decreasing A.[4,5] The upper-lying tetragonal minima are directly caused by the mixing with the singlet $^1T_{1u}$. When this effect is neglected $(g\to\infty)$ we have only one kind of minima (X in Fig. 2).

In this approximation $(g\to\infty)$ schemes (ii) and (iii) have also been obtained[6,7,9]: They lead to cross sections similar to those in Fig. 2 for the tetragonal Q_3, as well as for the trigonal Q_ζ coordinate where the trigonal minima are situated, provided that some substitutions are made [in case (iii) $b\to\tilde{b}=b+b_{a\epsilon}Q_1$, $c\to\tilde{c}=c+c_{a\tau}Q_1$].[6,7,9] So, in a sense, scheme (i) is the most complete and it is comprehensive of the other two.

However, for a complete description of the experimental facts, we also have to take into account trigonal modes. An attempt to do this has been made, in order to interpret negative MCP, by extending the analysis to the bidimensional Q_2Q_6 space, and making the plausible assumption of nearly-equal coupling to tetragonal and trigonal modes $(b\sim c)$.[16,22] In this hypothesis, relaxation from rhombic X points (which are not necessarily minima) to orthorhombic or trigonal points (which could be minima) can easily take place,[9] as required by the symmetry properties of the A_X emission.[13,14]

Therefore, from the above analysis it seems to us that scheme (i), when suitably modified to include trigonal modes, could be the most appropriate for interpreting the luminescence properties of Tl^+ phosphors. There are, however, some points that should be better clarified before such a conclusion can be drawn:

(a) It is not clear why the system, after absorption at low temperature, relaxes preferentially into the tetragonal T minima, the lower-lying X minima being populated only by nonradiative transitions[15];

(b) Using values of G as deduced from absorption data, the energy separation δ between tetragonal minima T and rhombic points X $(\delta\simeq 2G\sim 2000$ cm$^{-1})$ appears to be too large for interpreting the temperature dependence of the emission intensities for $T\gtrsim 100$ K (Refs. 21 and 23) and the degree of MCP of the A_T emission in the case of KI:Tl$^+$ $(\delta\sim 1000$ cm$^{-1})$, KCl:Tl$^+$ $(\delta\sim 300$ cm$^{-1})$ and, especially, in KBr:Tl$^+$ $(\delta\sim 100$ cm$^{-1})$.[16,24] In addition, we have to consider that the electric field-induced structure in the emission of KCl:Tl$^+$ could be easily explained by the existence of different potential minima whose energy separation is about 800 cm^{-1}.[25]

Both difficulties can be overcome by the following considerations. The A absorption transition, which is spin-orbit allowed, tends to shift its point of arrival on the excited state from $x_3=0$ (which corresponds to the minimum of the ground state) towards a point where $x_3>0$; this is so because the percentage of singlet in the wave function (and consequently the electronic contribution to the oscillator strength) increases with x_3. The displacement will also depend on the overlap of the vibrational wave functions of the ground and excited states and it is not easily evaluated. If this shift corresponds to a point of arrival placed near or beyond the maximum on the potential surface (see arrows in Fig. 2, item a) is explained. The plausi-

bility of this hypothesis can be tested assuming that the shift of the point of arrival is comparable with the amplitude of the low-temperature vibrational-motion in the ground state. This quantity is estimated as $(\hbar\omega/2A\zeta)^{1/2}$ and with the parameter values here adopted (see also Ref. 15) turns out to be ~ 0.1 which is of the right order of magnitude. Another consequence of this fact is that the value of G as deduced by peak absorption-band values is surely overestimated, because

the energy of the shifted point of arrival corresponds, for $x_3 = 0$, to a potential curve with a higher value of g. This effect can, at least partially, explain item (b).

After these considerations we think we have indicated a way for getting over these difficulties and to reach a better understanding of this problem. However, due to its intrinsic complexity, we feel that this topic is not at all exhausted.

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[3] In this paper and in previous ones by us and other authors, the spin-orbit states arising from the electronic configuration sp in cubic symmetry (O_h) are denoted, in order of decreasing energy, as: $^1T_{1u}$; $^3T_{2u}$; ^3E_u; $^3T_{1u}$; $^3A_{1u}$. A more proper indication for these states should take into account the Bethe notation that is (in the same order): Γ_4^- ($^1T_{1u}$); Γ_5^- ($^3T_{1u}$), Γ_3^- ($^3T_{1u}$); Γ_4^- ($^3T_{1u}$); Γ_1^- ($^3T_{1u}$). See for instance A. Fukuda, Phys. Rev. B 1, 4161 (1970).

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