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Resonance between electronic and vibronic levels of Tm^{3+} in yttrium aluminium garnet

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Abstract. An attempt to explain some of the Tm^{3+} spectra features in YAG in terms of the splitting of the zero-photon lines due to the even part of the linear vibronic interaction Hamiltonian with a single active phonon mode in the cases of resonance or quasi-resonance between a pure electronic and vibronic level is presented. The observed features in absorption and emission spectra are discussed and the active mode is identified. The experimental splittings and intensities allow estimation of the vibronic coupling matrix elements of about 4–5 cm^{-1}.

In recent years a series of papers have been dedicated to the study of spectral characteristics of Tm^{3+} ions in garnets [1–7], which are important systems for 2 μm laser emission. In our recent paper on Tm^{3+} in YAG [7], the difficulties connected with the correct determination of an energy level diagram for Tm^{3+} in prevailing dodecahedral sites of D_2 local symmetry have been discussed. Three main experimental problems in the assignment of position and symmetry labels to the singlet Stark levels (irreducible representation Γ_i) have been mentioned: the fact that electric and magnetic dipole $\Gamma_i \rightarrow \Gamma_i$ transitions in D_2 symmetry are forbidden, the complex multisite structure and the interferences between 'pure' electronic and vibronic lines. To our knowledge the vibronic structure of Tm^{3+} in garnets has not been analysed. As mentioned in [7], our Tm^{3+} spectra in YAG present, besides phonon side bands in various spectral regions, complex features connected with photons in the cases of resonance or quasi-resonance between the energy differences of Stark levels and peaks in the phonon density. The investigation of vibronic interaction effects for Tm^{3+} ($4f^{12}$) is of basic interest since no reliable explanation for the rather strong vibronic structure for rare-earth ions at the end of the $4f^n$ series has been given up to now, as discussed in [8], a special case being Yb^{3+} ($4f^{13}$); the assignment of the electronic levels of this ion in various hosts, including YAG [9], is also difficult owing to strong phonon interferences.

Complex structures with possible phonon interferences have also been observed for the Pr^{3+} spectra in YAG [10] or GGG [11] where the emission terminated on the ground-state multiplet contains an overlap of more lines than allowed by symmetry selection rules of D_2. In YAG [10] the effect was associated with a strong interaction between electronic states and near-resonance phonons that introduce new vibronic states into the ground-state crystal field levels. The possibility of small shifts of some Stark levels owing to accidental resonances with phonon peaks, especially for the lower-lying levels of a configuration, was also suggested in [12]. In order to explain the shape of the Yb^{3+} emission lines (corresponding to the laser transition) in several apatite crystals, a near-resonance effect has been assumed in the ground-state multiplet [13].

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Such behaviour is, however, not characteristic of ground-state levels. If there is a near resonance between electronic and vibronic states (whether they belong to the same multiplet or not) due to the vibronic interaction, modified vibronic states could be obtained (depending on the strength of the vibronic coupling, the degree of resonance and the width of the phonon spectrum), and the transitions involving these states should reflect this mixing [14–16]. This problem needs attention not only in order to obtain accurate electronic energy level diagrams or to explain the discrepancies between calculated Stark splittings and experimental data in some spectral regions, but also since the lines involved in laser processes could be composites resulting from near-resonance effects (as in the case of Yb^{3+}) that should be taken into account when the laser parameters are evaluated. At the same time, such lines can assure a certain tunability for emission. The vibronic problem in the case of resonance or quasi-resonance could be solved analytically as proposed in [15] by using Davydov's [16] theory only if a very small number of states are involved. Otherwise, numerical solutions could be obtained, but many adjustable quantities are necessary.

The purpose of this paper is to attempt to explain some spectral characteristics of YAG:Tm^{3+} absorption and emission spectra in terms of near-resonance effects between 'pure' electronic and vibronic levels. A semiquantitative modelling for the case of a one-phonon vibronic state $|\phi_f, \nu = 1\rangle$ in resonance or near resonance with a zero-phonon electronic non-degenerate state $|\phi_l, \nu = 0\rangle$ is presented [15]. Schematically the problem for absorption is illustrated in figure 1(a) and for emission in figure 1(b) for the concrete experimental cases to be discussed later. The vibronic Hamiltonian V, generally written as $V = \sum_k V^k Q_k$, where k extends over the normal vibrational modes Q_k and V^k represents the electronic part, contains in this case only the resonant active phonon normal mode Q. For a non-centrosymmetric site an odd and even part of V can be defined. Since the levels involved belong to the same electronic configuration, only the even part V' of the vibronic Hamiltonian will contribute to the problem, and its matrix elements between Born–Oppenheimer states are defined as $V'_{lm} = \langle\phi_l, \nu'|V'|\phi_m, \nu\rangle$. If the two near-resonance states $|\phi_f, \nu = 1\rangle$ and $|\phi_l, \nu = 0\rangle$ are coupled by V', modified eigenstates are obtained [15, 16]:

$$\begin{aligned} |\psi_1\rangle &= \cos(\tfrac{1}{2}\tau)|\phi_l, \nu = 0\rangle + \sin(\tfrac{1}{2}\tau)|\phi_f, \nu = 1\rangle \\ |\psi_2\rangle &= -\sin(\tfrac{1}{2}\tau)|\phi_l, \nu = 0\rangle + \cos(\tfrac{1}{2}\tau)|\phi_f, \nu = 1\rangle \end{aligned} \tag{1}$$

with

$$\tan\tau = \frac{2V'_{fl}}{V'_{ll} - V'_{ff} + \delta} \qquad \delta = E_l - (E_f + \varepsilon) \tag{2}$$

δ being the degree of resonance, E_m the zero-phonon energies and ε the phonon energy of the active mode Q. The diagonal matrix elements of the vibronic operator are null in this case and the separation between the energies of the two new states is enhanced by the vibronic coupling to

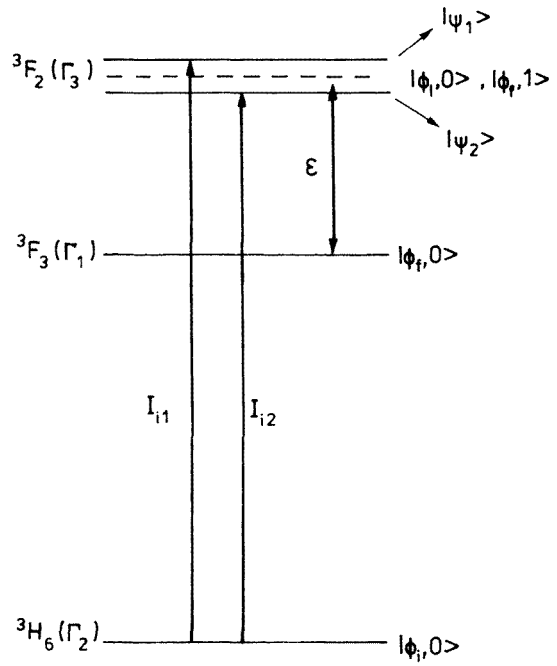
$$\Delta E = (\delta^2 + 4V'^2_{lf})^{1/2}. \tag{3}$$

The transition probabilities between a zero-phonon state $|\phi_i, \nu = 0\rangle$ and these new vibronic states $|\psi_j\rangle$ $(j = 1, 2)$ are proportional to $|\langle\phi_i, \nu = 0|\boldsymbol{\mu}|\psi_j\rangle|^2$ where $\boldsymbol{\mu}$ is the sum of forced electric dipole, the dynamic coupling and magnetic dipole operators [15].

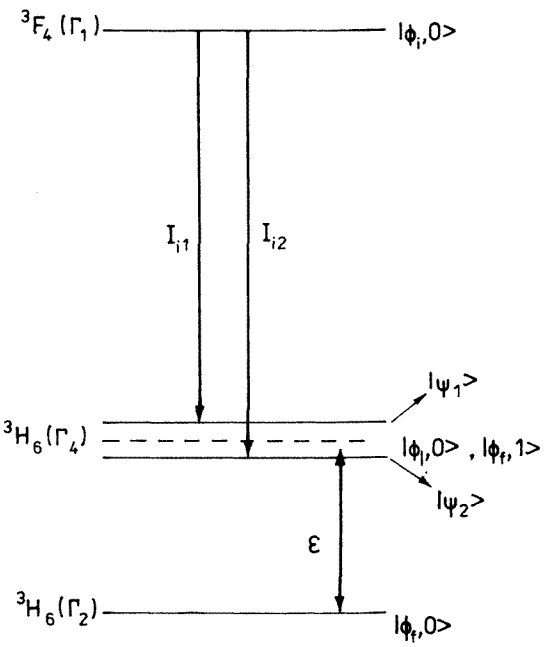
Thus, the intensities of the two vibronic lines are

$$I_{i2} = \sin^2(\tfrac{1}{2}\tau)I^{zp}_{il} \qquad I_{i1} = \cos^2(\tfrac{1}{2}\tau)I^{zp}_{il} \tag{4}$$

where $I^{zp}_{il} \sim |\langle\phi_i, \nu = 0|\boldsymbol{\mu}|\phi_l, \nu = 0\rangle|^2$ is the intensity of zero-phonon line in the absence of resonance, with $I_{i1} + I_{i2} = I^{zp}_{il}$. Therefore, owing to vibronic interaction the electronic line is split into two vibronic lines that share the intensity in proportions dependent both on the



(a)



(b)

Figure 1. Schematic presentation of the effect of splitting of a zero-phonon line due to resonance or quasi-resonance between an electronic and one phonon (of energy ε) vibronic level: (a) absorption; (b) emission. On the left-hand sides of the figures the Tm^{3+} levels in YAG involved in such a process are given.

strength of the vibronic coupling and on the degree of resonance. If $|2V'_{fl}/\delta| \ll 1$, which corresponds to small coupling or non-resonance, the vibronic line intensity I_{i2} becomes very small compared with the zero-phonon line intensity while, if $|2V'_{fl}/\delta| > 1$, the intensities of the two lines could be comparable. In this treatment the phonon band dispersion was neglected. The estimates in [15] give matrix elements V'_{lf} for rare earths in the range 0.5–5 cm^{-1}.

The absorption and emission spectra at various temperatures from 10 to 300 K of several Tm (0.1 to 5 at.%)-doped YAG crystals, recorded with experimental set-ups described in our previous papers [2, 7], have been analysed. Spectral features that could be connected with resonant effects have been observed in several absorption transitions such as $^3H_6 \rightarrow {}^3F_2$ or $^3H_6 \rightarrow {}^3H_4$ and in the emission from different multiplets $^1G_4$, $^3H_4$ or $^3F_4$ to the ground-state $^3H_6$ multiplet.

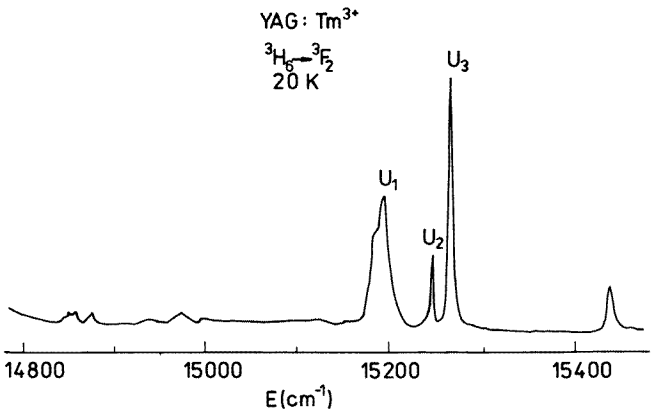


Figure 2. Transmission spectra corresponding to $^3H_6 \rightarrow {}^3F_2$ Tm^{3+} transitions in YAG.

Since one of the most peculiar features has been observed in the transmission spectra corresponding to the $^3H_6 \rightarrow {}^3F_2$ region (at low temperatures), we shall reproduce it in figure 2 (part of figure 4 of [7]). For Stark levels the notation in [1] is used. The $^3H_6 \rightarrow {}^3F_2$ spectrum at low temperatures presents a peculiar behaviour; a rather broad and split line U_1 (with a similar hot band structure at 27 cm^{-1} at 77 K) is followed by two much sharper lines, U_2 and U_3. In the first assignment [1] the $^3H_6(1) \rightarrow {}^3F_2(1)$ transition was connected with the line U_2; however, from the analysis of the data on Tm^{3+} in other garnets such as YSAG, YSGG and GSGG [3–5] we arrived at the conclusion that at least one Stark level should be located at lower energies, i.e. in the region of the broad split line U_1. The crystal-field calculations for Tm^{3+} in YAG [7] confirmed this assumption and the second line of the doublet U_1 (figure 2) has been tentatively connected with phonon contributions. This line is unlikely to be a Van Vleck vibronic line connected with a forbidden $^3H_6 \rightarrow {}^3F_3$ transition since it appears in the hot band structure at 27 cm^{-1} too (the upper part of figure 4 of [7]) and the two lowest Stark levels of $^3H_6$ have different symmetry labels (Z_1–Γ_2 and Z_2–Γ_1). Other phonon effects such as side bands associated with the intense zero-phonon lines correponding to $^3H_6 \rightarrow {}^3F_3$ transitions have relatively low intensities (as can be observed at low energies in figure 2). Therefore, the observed split line U_1 (which could be decomposed into two components separated by about 9 cm^{-1}, of half-width about 10 cm^{-1} and relative intensities about 1:1.5) could be connected to a near-resonance effect as discussed above, since the first Stark electronic level of $^3F_2$ (U_1–Γ_3 at about 15 190 cm^{-1}) is close to a

vibronic level of $^3F_3$ (V_6–Γ_1) + 463 cm^{-1} with V_6 at 14 720 cm^{-1}. The observed splitting and the relative intensities of the two components of U_1 could be consistently described by equations (3) and (4) by taking $V'_{lf} \simeq$ 4–4.5 cm^{-1} and $\delta =$ 1.5–2 cm^{-1}. The parameter V'_{lf} estimated here is consistent with the estimates in [15]; no other phonon [18] is close enough to resonance to produce a line I_{i2} of sizeable intensity.

A second region where phonon interferences could be suspected in absorption is the $^3H_6 \rightarrow {}^3H_4$ transition; at least four Stark levels lie in the range 12 900–13 200 cm^{-1}, i.e. at 300–500 cm^{-1} from the lowest Stark level of the $^3H_4$ multiplet. At the same time, there are several phonons that could be in near resonance with these crystal-field splittings. The absorption spectrum (given in figure 3 of [7]) shows a complex structure, with more lines than expected for electronic allowed transitions. Some of these lines could originate from vibronic quasi-resonance effects, with possible involvement of several phonons, but so far we have not been able to give a consistent assignment of the observed structure.

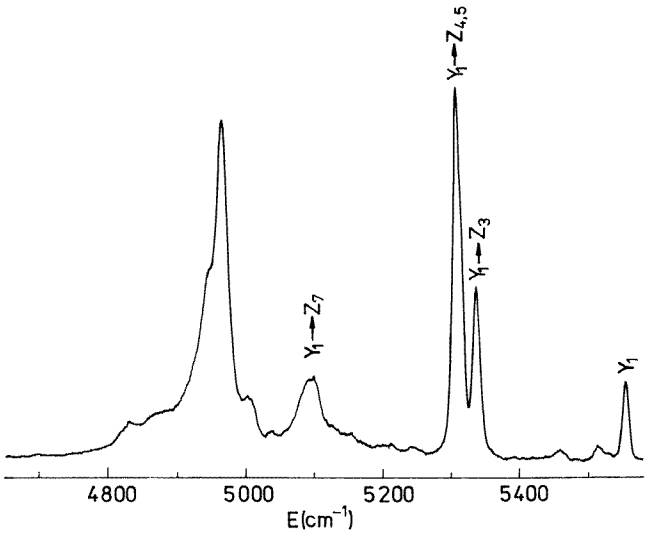


Figure 3. Emission spectrum from $^3F_4$(Y_1–Γ_1) to $^3H_6$ at 77 K.

The presence of additional lines that could be connected with phonon effects was also observed in the emission spectra from $^1G_4$, $^3H_4$, $^3F_4$ to the ground-state $^3H_6$ multiplet. If the lines corresponding to the transitions to the $^3H_6$ Stark levels situated up to about 300 cm^{-1} (Z_1–Z_5) are rather intense and sharp, those terminated on levels situated in the 300–800 cm^{-1} range are broad and contain more lines than allowed by symmetry. This is illustrated in figure 3 where the $^3F_4 \rightarrow {}^3H_6$ emission spectrum at 77 K is presented. According to our discussion, the shape of the $^3F_4(Y_1) \rightarrow {}^3H_6(Z_7)$ line (with a splitting of about 8 cm^{-1}) could be the result of coupling between the vibronic level $^3H_6(Z_1)$+463 cm^{-1} and the 'pure' electronic level $^3H_6(Z_7)$ placed around 460 cm^{-1}. The observed splitting and the relative intensities of the two components could be explained by taking $V'_{lf} \simeq 4$ cm^{-1} and $\delta \simeq 0.5$ cm^{-1}. The phonon effects connected with emission from $^3F_4$ at lower energies are very complex and could not be analysed so far, although they involve the range of the laser transition. The resonant splitting of $^3H_6(Z_7)$ level can also explain the shape of $^1G_4(A_1) \rightarrow {}^3H_6(Z_7)$ line (figure 2 of [7]). In the examples discussed, the phonon energy is in the 460 cm^{-1} range. According to the recent assignments [18] this could

be the symmetric bend mode $\nu_2(T_{1u})$ with energy of 463 cm^{-1} and the largest oscillator strength in the infrared YAG spectra and of linewidth about 10 cm^{-1}. On the basis of the symmetry of the electronic levels given in figure 1 and the selection rules of D_2, one could tentatively assign this phonon Γ_3 symmetry. Other phonon peaks of YAG [17, 18] have energies shifted at least ± 20 cm^{-1} from it; so they are expected to have small influences in the cases analysed.

Thus it is very likely that quasiresonant vibronic splitting is the explanation of the structure observed in several lines of Tm^{3+} in YAG. The splitting and the relative intensities of the two components enable an estimate to be made of the matrix elements of the vibronic interaction V'_{lf} and of the off-resonance parameter δ. The results could be influenced by several sources of errors: the measurement of the splitting and the relative intensities of the two components (usually one of the components shows up as a shoulder to the other), the phonon energy and its spectral width (different values are given in the literature [18, 19]) and the energy of the 'pure' electronic unsplit level, whose position can be obtained by parametric crystal-field calculations with its inherent errors. The vibronic interaction matrix elements V'_{lf} given here lie in the range of the theoretically estimated values of 0.5–5 cm^{-1} [15]. Important for near-resonance effects is the existence of some value for the vibronic coupling and the degree of resonance. The electron–phonon coupling for YAG:Tm^{3+} is confirmed by the vibronic side bands that we have observed in various spectral ranges. The splitting of the U_1 line of the $^3H_6 \rightarrow {}^3F_2$ transition in YAG is absent in the case of Tm^{3+} in GGG (figure 4), where no resonance exists between the similar Stark components and the phonon spectrum.

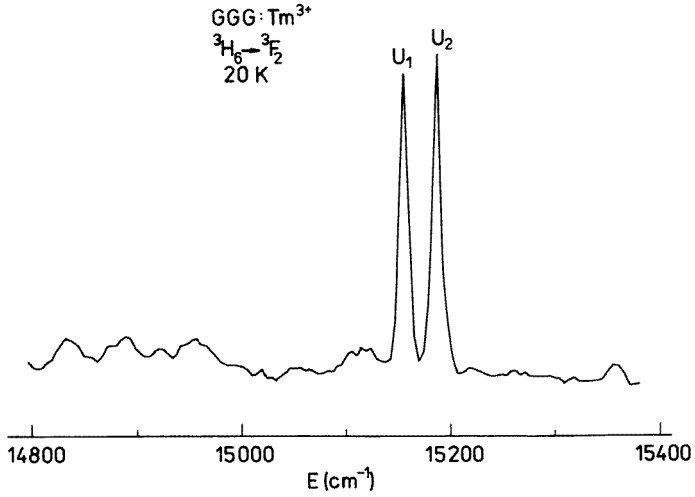


Figure 4. Transmission spectra corresponding to $^3H_6 \rightarrow {}^3F_2$ Tm^{3+} transitions in GGG.

In conclusion, several characteristics of the near-resonance effect between one 'pure' electronic and a one-phonon vibronic level can be pointed out.

(i) The effect has been observed for symmetry-allowed electronic transitions.

(ii) The lines influenced by the process show up as an unresolved doublet placed in the spectral region where the 'pure' electronic transition should lie, one of the components generally having a lower intensity.

(iii) The two components are broader than the zero-phonon electronic lines, the

broadening being related to the width of the phonon spectrum.

(iv) The effect has been observed in the ground-state as well as in excited-state multiplets.

(v) Depending on the splitting between the electronic multiplets it can also appear as an intermultiplet effect.

Some of the features of Tm^{3+} lines in YAG have been explained in the framework of a simple theory of near-resonance effects between one electronic and one vibronic level, based only on the vibronic coupling strength; a more complete description would impose consideration of the phonon density and dispersion. From the complexity of the spectra, in some multiplets, it is very likely that quasi-resonance effects involving more electronic and phonon states could take place. Besides the basic interest, the consideration of the electronic–vibronic effects at resonance could be of value in correctly estimating the laser characteristics for transitions influenced by this process.

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