

ENERGY TRANSFER PHENOMENA
IN Tb³⁺-ACTIVATED GADOLINIUM TANTALATE (GdTaO₄)

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ABSTRACT

The energy transfer phenomena in GdTaO₄ activated with Tb³⁺ have been investigated. It is shown that the ratio of the ⁵D₃ and ⁵D₄ emission intensities of Tb³⁺ depends strongly on the excitation wavelength. The Tb³⁺ ⁵D₃ level is populated by direct excitation into the Tb³⁺ 4f⁸ levels, by energy transfer from the Gd³⁺ ⁶P level or by energy transfer from the intrinsic tantalate group via the Gd³⁺ ⁶P level. The Tb³⁺ ⁵D₄ level is populated by direct excitation into the 4f⁷5d state, by energy transfer from the Gd³⁺ ⁶I level, or by cross-relaxation from the ⁵D₃ level. Direct relaxation from ⁵D₃ to ⁵D₄ is found to be improbable. The ⁶I → ⁶P relaxation of the excited Gd³⁺ ion is slow in comparison with the competing energy transfer processes.

Introduction

Compounds with the fergusonite structure have the general formula Ln(Nb,Ta)O₄ and can be considered as distorted scheelites (1,2). Some years ago Blasse and Brill reported extensively on the luminescence phenomena in compounds with this structure (3,4). Also Brixner paid attention to this type of compounds (5,6). It has been shown that next to the fergusonite modification (M-type) another modification is possible which is structurally related (M'-type) (2,7).

The M-type GdTaO₄ proved to be a reasonably efficient host for

luminescence when activated with Bi^{3+} , Eu^{3+} or Tb^{3+} (ref.3). The host lattice itself does not luminesce at room temperature. This has been explained by energy transfer from the tantalate group to the surrounding Gd^{3+} ions followed by concentration quenching of the Gd^{3+} emission. This is possible because the host-lattice emission is in the u.v. and overlaps the energy levels of the Gd^{3+} ion. However, when the host is activated with a suitable ion, the energy can be transferred to this ion. Emission occurs subsequently from the activator.

In this paper we want to report in more detail on the luminescence properties of the M-type GdTaO_4 activated with terbium. The luminescence of the M' modification described by Wolten (2) was recently reported superficially by Brixner and Chen (7). The latter authors showed that Tb^{3+} -activated GdTaO_4 is an excellent X-ray phosphor. In this paper mainly the energy transfer phenomena in $\text{GdTaO}_4\text{-Tb}^{3+}$ are reported. They appear to be rather complicated.

Experimental

Samples were prepared by usual solid-state techniques. Starting materials were Gd_2O_3 (99.999 %), Ta_2O_5 (99.9 %) and Tb_4O_7 (99.999 %). The mixtures were fired thrice at temperatures in between 1250 and 1400 °C. The terbium concentration was 0, 0.2 and 2 mol %. A second sample with 0.2 mol % Tb^{3+} was prepared in a different way. First the rare earth oxides were dissolved in concentrated HCl. With a NaOH solution $(\text{Gd,Tb})(\text{OH})_3$ was precipitated and fired twice at 500 °C to obtain $(\text{Gd,Tb})_2\text{O}_3$. This was mixed with Ta_2O_5 and fired as described above. Samples were checked by X-ray powder diffraction using $\text{CuK}\alpha$ radiation and by Raman spectroscopy. The Raman spectra were compared with those given by Brixner and Chen (7).

Luminescence spectra were measured down to liquid helium temperature on a Perkin-Elmer spectrofluorometer (MPF 3L) equipped with a Xenon lamp as described in (8) and at room temperature on a Perkin-Elmer spectrofluorometer (MPF 4) equipped with an X-ray source with a maximum voltage of 100 kV.

Results

The fergusonite GdTaO_4 does not luminesce at room temperature. At liquid helium temperature (LHeT) a luminescence was observed originating from Gd^{3+} ions and two different tantalate groups. For excitation below 235 nm we observed a.o. a weak emission band around 335 nm. This band was also observed in the case of YTaO_4 (ref.3) and is ascribed to the intrinsic tantalate emission. In GdTaO_4 at LHeT its emission intensity is about 25 % of the total emission intensity. The Gd^{3+} emission contributes about 50 %, and another tantalate emission 25 %. This other emission band peaks at 440 nm and has an excitation band around 265 nm. Like in tungstates

(9,10,11), titanates, niobates and other tantalates (4,12) this band must be due to a defect tantalate group. A similar band was reported for YTaO₄ (3). The excitation spectrum of the 440 nm emission band contains also the Gd³⁺ lines around 277 nm. This points to energy transfer from Gd³⁺ to the defect tantalate group.

GdTaO₄ activated with terbium is an efficient green phosphor under u.v. and X-ray excitation. The quantum efficiency is found to be about 80 % by comparison with standard phosphors. For the samples prepared by solid-state techniques, the emission consists mainly of the Tb³⁺ ⁵D₄ emission for low (0.2 % Tb³⁺) as well as for higher concentration (2 % Tb³⁺) (figure 1). For the M' modification Brixner and Chen (7) have reported the same observation. This is remarkable, because at low concentration the Tb³⁺ emission consists usually of mainly ⁵D₃ emission which is quenched for higher concentrations by cross-relaxation resulting in more ⁵D₄ emission (13). An explanation for the low ⁵D₃/⁵D₄ ratio in the low concentrated sample can be clustering of the Tb³⁺ ions due to incomplete reaction, so that cross-relaxation can take place even at low concentrations. To investigate this, a second sample with 0.2 % Tb³⁺ was prepared in such a way that a better distribution of the Tb³⁺ ions was reached (see Experimental). Indeed we observed a higher ⁵D₃/⁵D₄ ratio. This ratio depends on the excitation wavelength (table 1).

TABLE 1

Intensity Ratios of the ⁵D₃ and ⁵D₄ Emission in Gd_{0.998}Tb_{0.002}TaO₄ at LHeT as a Function of Excitation

Excitation			⁵ D ₃ / ⁵ D ₄ intensity ratio
Tb ³⁺	4f ⁸	(352 nm)	3.2
Tb ³⁺	4f ⁷ 5d	(270 nm)	0.5
Gd ³⁺	6p	(312 nm)	1.2
TaO ₄		(230 nm)	0.8

Since the intrinsic tantalate absorption is situated at very high energy, it is possible to excite the Gd³⁺ ions selectively in the ⁶I level (~ 277 nm). Unfortunately the defect tantalate group is also excited by

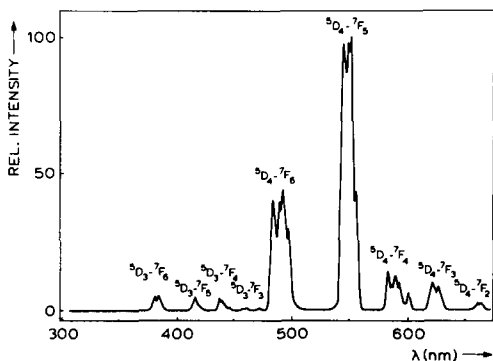


FIG. 1

Emission spectrum of $M\text{-Gd}_{0.98}\text{Tb}_{0.02}\text{TaO}_4$ at room temperature. The excitation wavelength is 274 nm.

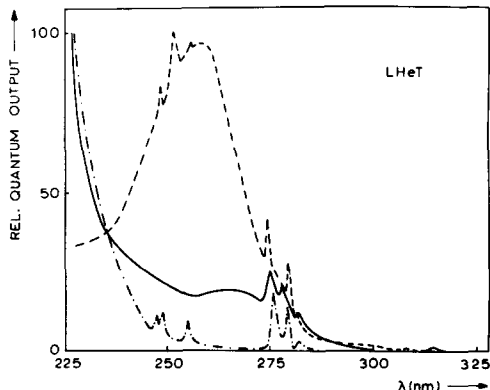


FIG. 2

Excitation spectra of the Gd^{3+} emission ($\lambda_{em} = 313 \text{ nm}$, - - -), the defect tantalate group emission ($\lambda_{em} = 420 \text{ nm}$, —) and the Tb^{3+} emission ($\lambda_{em} = 544 \text{ nm}$, - · -) of $M\text{-Gd}_{0.998}\text{Tb}_{0.002}\text{TaO}_4$ at LHeT.

this wavelength. For excitation into the ^6I level of the Gd^{3+} ion we observe at room temperature no Gd^{3+} emission from the ^6P level in $\text{Gd}_{0.98}\text{Tb}_{0.02}\text{TaO}_4$ and only a very small amount (less than 1 % of the total emission) in the sample with 0.2 % Tb^{3+} . At LHeT the Gd^{3+} emission intensity has increased, but the terbium emission remains dominating for $\text{Gd}_{0.98}\text{Tb}_{0.02}\text{TaO}_4$ (10 % Gd^{3+} and 90 % Tb^{3+} emission at 8 K). In the case of the sample with 0.2 % Tb^{3+} , this excitation at LHeT yields, in addition to the Tb^{3+} emission, the defect tantalate emission band. For excitation into the intrinsic tantalate group of $\text{Gd}_{0.998}\text{Tb}_{0.002}\text{TaO}_4$ at LHeT the emission consists of 15 % intrinsic tantalate group emission, 20 % defect tantalate group emission, 40 % Gd^{3+} emission and 25 % Tb^{3+} emission.

The excitation spectra of the luminescence of $\text{Gd}_{0.998}\text{Tb}_{0.002}\text{TaO}_4$ at LHeT are shown in figure 2. The emission wavelengths are 313, 420 and 544 nm, corresponding to the Gd^{3+} emission, the defect tantalate group emission and the $\text{Tb}^{3+} \ ^5\text{D}_4$ emission, respectively. The excitation spectrum of the Tb^{3+} emission agrees with the results reported by Blasse and Brill at room temperature (figure 2): (i) sharp lines between 320 and 380 nm, not shown in figure 2, corresponding to transitions within the 4f shell of Tb^{3+} ; (ii) sharp lines around 255, 277 and 310 nm corresponding to transitions within the 4f shell of Gd^{3+} . These indicate energy transfer from Gd^{3+} to Tb^{3+} as observed in other host lattices too (14,15); (iii) a broad band at 260 nm belonging to the Tb^{3+} centre; (iv) a broad band corresponding to host lattice excitation. According to ref.(3) this band peaks at 210 nm. We could not determine the exact position of the band, because our spectrofluorometer is equipped with a Xenon lamp. This band indicates energy transfer from the TaO_4 groups to Tb^{3+} .

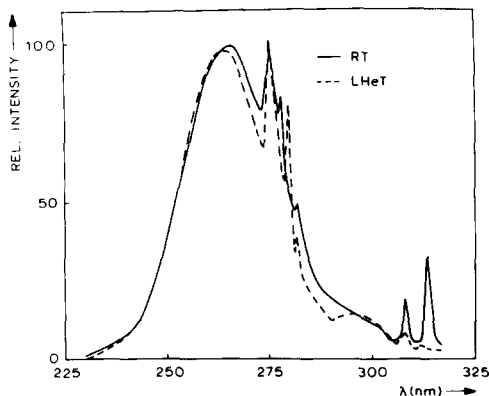


FIG. 3

Uncorrected excitation spectra of the Tb^{3+} emission ($\lambda_{em} = 544$ nm) at room temperature (—) and at LHeT (---). Note the weak broad band peaking at 295 nm and the different intensity ratios between the $Gd^{3+} 8S \rightarrow 6P$ and the $Gd^{3+} 8S \rightarrow 6I$ peaks at these two temperatures.

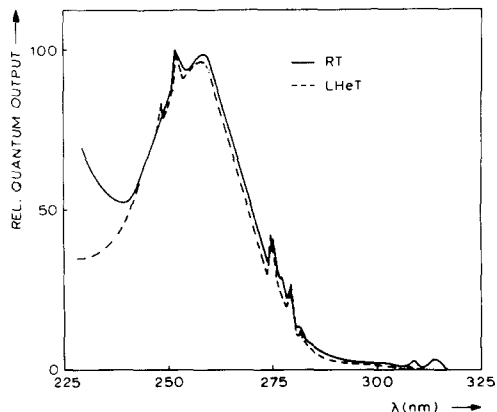


FIG. 4

Excitation spectra of the Tb^{3+} emission ($\lambda_{em} = 544$ nm) at room temperature (—) and at LHeT (---).

A comparison of these excitation spectra with those at room temperature reveals the following. At LHeT the broad band at 260 nm is somewhat narrower and another broad band with low intensity can be seen at about 295 nm. This is more clear in the uncorrected spectra (figure 3). Note further at LHeT (a) the reduction of the intensities of the $Gd^{3+} 8S \rightarrow 6P$ excitation peaks at 310 nm relative to the $Gd^{3+} 8S \rightarrow 6I$ excitation peaks at 277 nm and (b) the decrease of the broad band below 230 nm (figure 4).

In the excitation spectrum of the Gd^{3+} emission we found the sharp lines corresponding to transitions within the 4f shell of Gd^{3+} and the broad band corresponding to the host lattice absorption. In the excitation spectrum of the defect tantalate group emission we observed the same bands as for the Gd^{3+} emission and an additional excitation band at 265 nm which is due to excitation into the defect tantalate group itself. The latter assignment is based upon a comparison with data for the unactivated $GdTaO_4$.

Discussion

The emission from the intrinsic tantalate group in the fergusonite $GdTaO_4$ is weak. This has been discussed earlier (3): the emission of the tantalate group has a maximum at 335 nm and overlaps the $6P_{7/2}$, $6P_{5/2}$ and $6P_{3/2}$ energy levels of the Gd^{3+} ion. Energy transfer from the tantalate

group to the Gd^{3+} ions is therefore possible. Since some tantalate emission is still observed, the critical distance for this transfer, R_c , is about equal to the shortest $Ta^{5+}-Gd^{3+}$ distance, viz. 3.5 Å (refs. 1,2). The value of R_c can be calculated as described elsewhere (16). We take for the spectral overlap our experimental value, viz. $\sim 1 \text{ eV}^{-1}$, and for the absorption cross-section of the Gd^{3+} ion $10^{-22} \text{ cm}^2 \text{ eV}$ (16). This yields $R_c \sim 3.5 \text{ Å}$. This value is based on electric dipole-dipole interaction and is in good agreement with experiment.

The excitation energy on the Gd^{3+} sublattice is assumed to be mobile, so that concentration quenching occurs at room temperature. Only at low enough temperatures ($T < 30 \text{ K}$) there is Gd^{3+} emission. Following known models (17) we assume that this emission arises from Gd^{3+} traps, i.e. Gd^{3+} ions with energy levels at slightly lower energy than those of the intrinsic Gd^{3+} ions. This can be due to a slight distortion of the surroundings. With the present instrumentation it is not possible to prove this. The excitation spectrum of the Gd^{3+} emission proves the occurrence of energy transfer from the tantalate group to Gd^{3+} (figure 2). At higher temperatures the traps are emptied and the energy migrates through the Gd^{3+} sublattice. The energy can be transferred to incorporated ions (e.g. Tb^{3+} ions) or to "killer" sites or can be emitted radiatively by the Gd^{3+} ions.

At low temperatures the defect tantalate group (indicated as TaO_4^*) can compete with the Tb^{3+} ion for the migrating excitation energy in $GdTaO_4$ with only 0.2 % Tb^{3+} . In the sample with 2 % Tb^{3+} nearly all the energy goes to the Tb^{3+} ions and no TaO_4^* emission is observed. Direct excitation of the TaO_4^* group to observe the TaO_4^* emission in this sample is not possible because of the strong absorption of the Tb^{3+} centre which has an allowed transition in the same spectral region.

Blasse and Brill (3) ascribed the broad band at 260 nm in the excitation spectrum of the Tb^{3+} emission to a charge-transfer transition in which an electron is transferred from Tb^{3+} to the tantalate group. There is, however, one important difference between their results and ours, viz. we observe another broad band on the long wavelength side at 295 nm. Therefore we prefer to ascribe these bands to the 4f-5d transition of the Tb^{3+} ion. The band at 260 nm is then due to the spin-allowed transition to the 7D level and the weak band at 295 nm to the spin-forbidden transition to the 9D level. The separation between the 9D and 7D levels of about 4700 cm^{-1} corresponds to the separation between these two terms reported by Ryan and Jørgensen (18) for $TbCl_6^{3-}$ and $TbBr_6^{3-}$. Their reported intensity ratio of the spin-allowed and the spin-forbidden transition of 50 is also practically the same as in our case.

One of the most remarkable results of this study is the reduction of the intensities of the $Gd^{3+} \text{ } ^8S \rightarrow \text{ } ^6P$ excitation peaks upon cooling from room temperature to liquid helium temperature (figure 3). This suggests that $Gd^{3+} \rightarrow Tb^{3+}$ transfer at LHeT is less efficient for excitation into the 6P than into the 6I level of the Gd^{3+} ion. If the 6I level would relax rapidly to 6P , such an observation cannot be explained. The nonradiative relaxation rate ($^6I \rightarrow \text{ } ^6P$) can be estimated with the exponential energy gap law, modified recently by Van Dijk and Schuurmans (19):

$$k_{nr} = \beta_{el} \exp[-(\Delta E_o - 2 \hbar \omega_{max})\alpha] \quad (1)$$

where α and β_{el} are constants, ΔE_o is the electronic energy gap between the $4f^n$ levels involved and ω_{max} the highest frequency mode of the host lattice. With $\alpha = 4.5 \cdot 10^{-3}$ cm, $\beta_{el} = 5 \cdot 10^7$ s⁻¹, $\Delta E_o = 2500$ cm⁻¹ and $\hbar \omega_{max} = 825$ cm⁻¹, the nonradiative rate for the ⁶I - ⁶P transition in GdTaO₄ has a value of $k_{nr} = 10^6$ s⁻¹. This means that either the tantalate group vibration cannot act as a promoting mode for the ⁶I → ⁶P relaxation or the Gd³⁺(⁶I) → Gd³⁺(⁶I) or Tb³⁺ transfer probabilities are higher than 10⁶ s⁻¹.

Transfer from the ⁶P level of Gd³⁺ to Tb³⁺ at LHeT cannot take place to the 5d level of Tb³⁺. For the ⁶I level this is possible for all temperatures. This suggests that excitation into the ⁶I level is followed by migration among the Gd³⁺ ions in the ⁶I level followed by transfer to the 5d state of Tb³⁺. The latter step is very efficient in view of the allowed character of the 4f → 5d transition in Tb³⁺. For excitation into the ⁶P level the same holds, but the last step (to Tb³⁺) is now considerably less efficient and cannot compete with the Gd³⁺ traps. Similar observations were made in gadolinium-zirconates (20).

In view of the high efficiency of the Tb³⁺ emission upon tantalate or Gd³⁺ excitation at not too low temperatures, we conclude that the transfer to Tb³⁺ dominates the other processes. If the migration on the Gd³⁺ sublattice is of the fast diffusion type (21), the probability of a single-step Gd³⁺ → Tb³⁺ transfer is estimated to be > 10⁷ s⁻¹. Here we assume that the radiative decay time of Gd³⁺ is 10³ s⁻¹, the Tb³⁺ concentration 0.2 % and the ratio of the Gd³⁺ and Tb³⁺ emission intensities < 0.05. However, compared with the Gd³⁺ → Gd³⁺ transfer probability of 10⁷ s⁻¹ found in Y_{1-x}Gd_xAl₃B₄O₁₂ (ref. 22), this high value makes a fast diffusion model in our case not very probable. The situation of fast diffusion was observed in GdMgB₅O₁₀-Tb³⁺, where a value for P(Gd³⁺ → Tb³⁺) of only 4 × 10⁶ s⁻¹ has been found (16). The shortest Gd³⁺ - Gd³⁺ distance in this borate is the same as in the tantalate, viz. about 4 Å. Note, finally, that the probability of all these rates exceeds the calculated ⁶I → ⁶P nonradiative decay in the Gd³⁺ ion.

Terbium emission can originate from both the ⁵D₃ and the ⁵D₄ level. At low Tb³⁺ concentrations one expects ⁵D₃ emission because of the large energy gap between the ⁵D₃ and ⁵D₄ level of about 5500 cm⁻¹. In our samples the highest vibrational frequency does not exceed 825 cm⁻¹, so that excitation of more than six phonons is necessary to decay nonradiatively from the ⁵D₃ to the ⁵D₄ level. With eq.(1) and $\Delta E = 5500$ cm⁻¹ and $\hbar \omega_{max} = 825$ cm⁻¹, we find for the nonradiative rate of the ⁵D₃ → ⁵D₄ transition of Tb³⁺ in GdTaO₄ $k_{nr} = 1.5$ s⁻¹. This makes this process impossible so that for the isolated Tb³⁺ ion only ⁵D₃ emission is expected. When the Tb³⁺ concentration is increased, i.e. when the mean Tb³⁺ - Tb³⁺ distance becomes shorter, cross-relaxation becomes possible. So only at higher Tb³⁺ concentrations the ⁵D₃ emission can be quenched in favour of more ⁵D₄ emission.

In our two samples prepared by solid state reaction of the oxides hardly any difference was observed in the ⁵D₃/⁵D₄ ratio of the Tb³⁺

emission. Because the starting products reacted very slowly with each other, we supposed that clustering of the Tb^{3+} ions could be a reason for this observation. In that case cross-relaxation can occur even at low Tb^{3+} concentrations. A second sample with 0.2 % Tb^{3+} was prepared by first dissolving the two rare earth oxides in HCl. After precipitation and firing, the Tb^{3+} ions will be distributed more statistically over the Gd^{3+} sublattice.

Table 1 shows the dependence of the ratio of the 5D_3 and 5D_4 emission intensities on the excitation wavelength for this sample. Direct excitation into one of the $4f^8$ levels just above the 5D_3 level gives the highest ${}^5D_3/{}^5D_4$ ratio. The excited Tb^{3+} ion relaxes fast to the 5D_3 level, from where it can further relax to the 5D_4 level or decay radiatively to the ground state. As discussed above, the second process will be more probable in the diluted system and this is also observed. It is possible to estimate the ${}^5D_3/{}^5D_4$ intensity ratio in the following way. The critical distance for cross-relaxation is about 13 Å (ref.23) as observed in the garnet structure. A sphere with a 13 Å radius around Tb^{3+} has a volume of about 9200 Å³. Since there is 75 Å³ per Gd site (1,2), this sphere corresponds to about 122 Gd sites. The probability that all these sites are occupied by Gd^{3+} ions, i.e. the probability for 5D_3 emission, amounts to $0.998^{122} \approx 78\%$. This simple model predicts about four times more 5D_3 emission than 5D_4 emission. This is in reasonable agreement with our results (table 1 for excitation with 352 nm). For $Gd_{0.98}Tb_{0.02}TaO_4$ this calculation yields a ${}^5D_3/{}^5D_4$ ratio of about 0.1 which agrees also with experiment.

Excitation into the 4f-5d band of Tb^{3+} results in mainly 5D_4 emission. In that case the excited ion relaxes directly from the $4f^75d$ state to the 5D_4 level. The 6P level of Gd^{3+} has a reasonable overlap with the $4f^8$ levels of Tb^{3+} , but also an overlap, although it is poor, with the Tb^{3+}

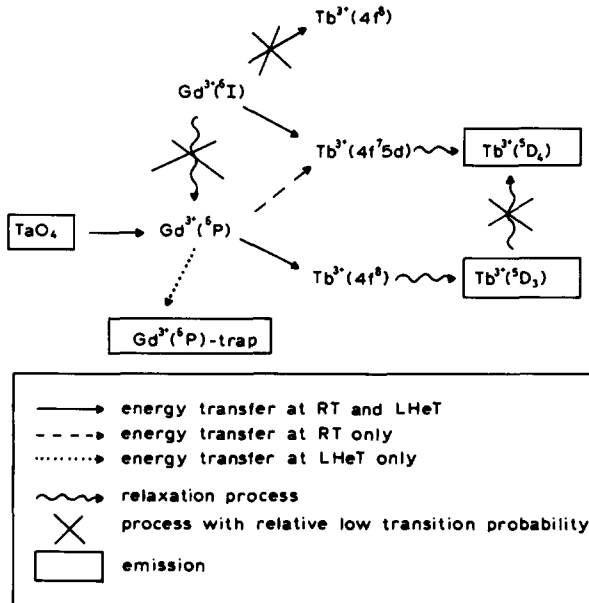


FIG. 5

Scheme representing the energy transfer and relaxation processes in $GdTaO_4:Tb^{3+}$. The meaning of the symbols is explained in the box.

4f-5d band. For excitation into this level or into the intrinsic tantalate group which transfers its energy to the Gd³⁺ 6P level, we expect more ⁵D₄ emission than for excitation into one of the Tb³⁺ 4f⁸ levels. This is indeed observed (table 1). With increasing temperatures the overlap of the 6P level with the 4f-5d band increases and the ⁵D₃/⁵D₄ ratio decreases. X-ray excitation results in the same spectrum as observed for excitation into the 4f-5d band. This means that the last steps in the mechanism of X-ray excitation have to be excitation or relaxation of the Gd³⁺ ion to the ⁶I level followed by energy transfer to the Tb³⁺(4f-5d) band.

To summarize all the energy and relaxation processes which take place in M-type GdTaO₄ doped with Tb³⁺, we have put them together in one scheme. This scheme is represented in fig. 5. The defect tantalate group has been omitted for simplicity.

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