Journal of the Optical Society of Korea, Vol. 1, No. 1, March 1997, pp. 10~14

# Energy transfer and photon avalanche in $Tm^{3+}$:$LaF_3$

**Yoo Mi Oh and Ki-Soo Lim**

*Department of Physics, Chungbuk National University, Cheongju 360-763, Korea*

*(Received; February 5, 1997)*

Single pulse laser excitation at 656 nm and successive pulse excitation at 635.2 and 648.4 nm produced blue emission at 480 nm by two-step upconversion process in $Tm^{3+}$:$LaF_3$. The excited-state absorption cross-section of the $^3F_4$ to $^1G_4$ transition was estimated by a looping mechanism with cross-relaxation processes. The dynamics of upconversion and the possibility of the photon avalanche by a pulse laser excitation were studied by numerical simulation with the rate equation model.

## I. INTRODUCTION

Upconversion of radiation has been observed in rare-earth or transition metal ion doped systems[1] after Auzel first reported[2] it. Typically, a large population in an excited state is created by an optical pump and upconverted emission is observed from the higher excited states that become populated through one or more energy transfer processes. This upconversion effect has recently gained much attention because of its usefulness as a pumping mechanism for an upconversion laser[3]. Under continuous pumping, the photon avalanche effect by energy transfer has been recently reported in a few systems. Some Tm systems have been reported to show upconversion[4-7] and photon avalanche effects[8-11]. Photon avalanche emission can be obtained when the pumping intensity reaches a critical value, even in the case where the first step absorption from the ground state is weak due to the fact that the pump wavelength is not resonant with an absorption line of the material. Upconversion emission in $Tm^{3+}$:$LaF_3$ was first observed with continuous excitation at 647 nm by Huang *et al*[12]. Photon avalanche in this system was recently reported with continuous excitation at 635.2 nm by Collings *et al*[13].

We have the first upconversion experiment with pulsed laser excitation and numerical simulation study for the photon avalanche process in pulsed operation mode in the $Tm^{3+}$:$LaF_3$ system.

## II. EXPERIMENT

The sample used in the experiment was a 1%$Tm^{3+}$:$LaF_3$ grown by Optovac, and was excited by a dye laser(LPD 3001) with DCM dye pumped by a XeCl excimer laser(Lamda 1000). The pulse duration was 20 ns and the repetition rate was varied from 1 to 200 Hz. The pulse energy of the DCM dye laser was 0.4 mJ in the excitation wavelength range with 20 ns pulse width. The fluorescence from the sample was focused onto a 1 m double spectrometer(JY U-1000) and was detected by a R943-02 photomultiplier tube. The signal was registered with a boxcar integrator(SR 250). and digitized for each pulse. The experiment was done at liquid nitrogen temperature.

## III. RESULTS AND DISCUSSION

The fluorescence spectrum shown in Fig. 1 was produced by laser excitation at 656 nm.

The upconversion emission bands near 360 nm, 450 nm and 480 nm are $^1D_2 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3H_5$ and $^1G_4 \rightarrow {}^3H_6$ transitions respectively, with the assignments of the $Tm^{3+}$:$LaF_3$ energy levels[14] and the spectrum reported in continuous excitation[12]. The laser excitation spectrum of the 480 nm emission with 50 Hz excitation repetition rate is represented in Fig. 2(a). The peaks at 635.2, 641.9, 647, 648.4, 650, 652, 656, 658.5 nm were reported as $^3F_4 \rightarrow {}^1G_4$ transitions in an upconversion experiment with continuous excitation[13],

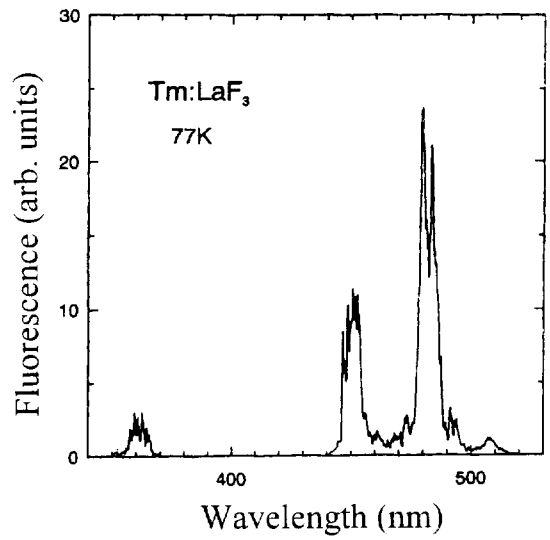


Fig 1. Fluorescence spectrum at 77 K from a 1% $Tm^{3+}$:$LaF_3$.

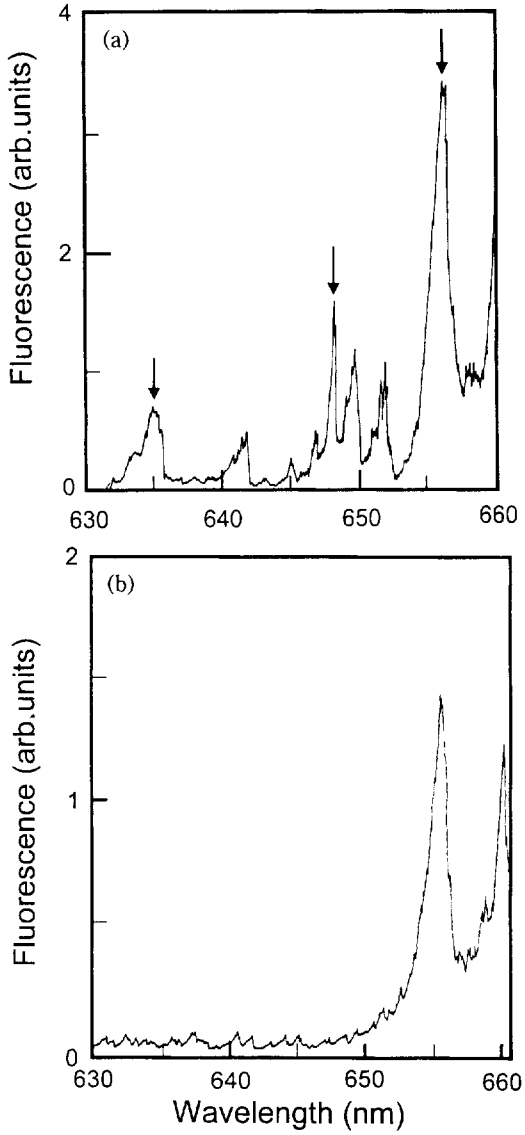


Fig. 2. Excitation spectra of $Tm^{3+}$:$LaF_3$ at 77 K associated with the emission: (a) at 480 nm and (b) at 694 nm. The arrows are indicated at 635.2, 648.4 and 656 nm.

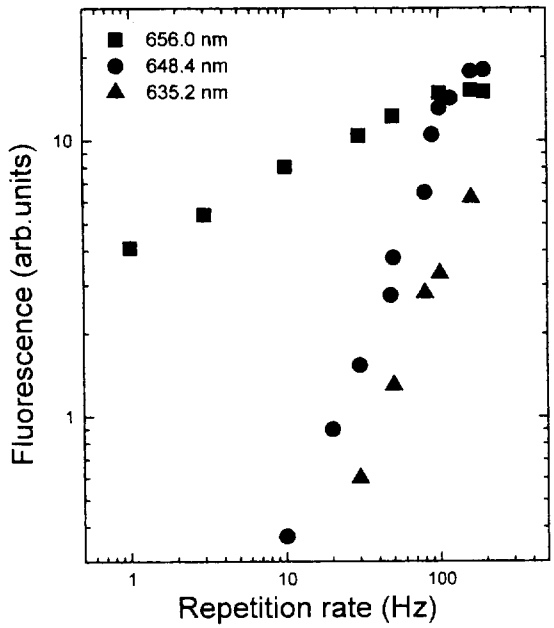


Fig. 3. Pulse repetition rate dependence of fluorescence peak intensity at 635.2, 648.4 and 656.0 nm.

where the peaks at 635.2 and 648.4 nm were reported as more than a hundred times stronger than the one at 656 nm and the peak at 660 nm was negligible. However, the peaks at 656 nm and 660 nm are much stronger than others in 50 Hz pulse excitation. This result indicates that the upconversion processes of 656 and 660 nm excitation are different from those of 635.2 and 648.4 nm excitation.

Fig. 2(b) shows the laser excitation spectrum of the emission at 694 nm, originating from the $^3F_3$ level. It is representative of the first absorption step. From this spectrum we know the peaks at the 656 and 660 nm show strong ground state absorption and 635.2 and 648.4 nm have negligible ground state absorption. It explains that despite the fact that there are no absorption lines from the ground state at 635.2 or 648.4 nm, a weak absorption towards the vibronic sideband of the $^3F_2$ level exists at these wavelengths and is responsible for the feeding of the $^3H_4$ and $^3F_4$ levels by subsequent laser pulses after deexcitation from $^3F_2$. For example, at 50 Hz repetition rate, the duration between two laser pulses is 20 ms and there is only one level excited by a first pulse which can still be populated when a second pulse comes. It is the $^3F_4$ level whose lifetime is 20 ms at 77 K so that 37% of the ions in the level are still excited. A second pulse can excite the ions at the $^3F_4$ level to the $^1G_4$ level, since the excitation spectrum of the blue emission is in the range of $^3F_4 \rightarrow {}^1G_4$ transition.

The dependence of the upconversion emission at 480 nm on the pump repetition rate is shown in Fig. 3 for three different excitation wavelengths, 635.2 , 648.4, 656 nm. The fact that the emission intensity can be recorded at 656 nm even at very low repetition rate excludes that it occurs via absorption of two photons belonging to two consecutive laser pulses, because the lifetimes of the $^3H_4$ level and $^3F_4$ level which are 2 ms and 20 ms respectively are much shorter than the duration between two pulses at low repetition rate. The possible explanation is the absorption of two photons from the same laser pulse. We find also that the 656 nm and 660 nm correspond to the transitions from the lowest subband of $^3H_6$ to the sublevels of $^3F_2$. Fast nonradiative relaxation from $^3F_2$ to $^3H_4$ follows in less than the 20 ns pulse duration. The second transition from $^3H_4$ to $^1D_2$ at 656 nm needs phonon assistance. Finally, we can observe blue emission from $^1G_4$ following $^1D_2 \rightarrow {}^1G_4$

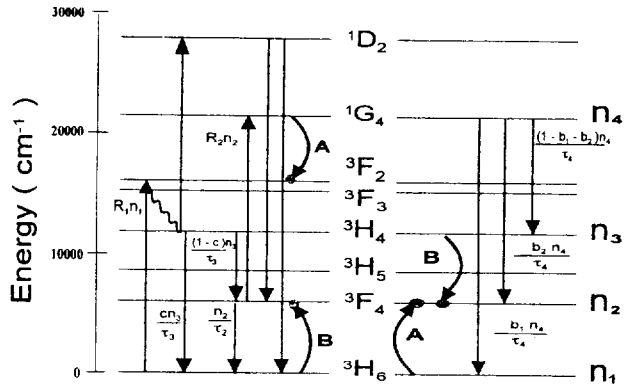


Fig. 4. Multiplet energy level structure showing the upconversion processes in $Tm^{3+}$:$LaF_3$. A single pulse can excite the ions to the $^1D_2$ level. Wavy line and curved arrows indicate nonradiative decay and cross-relaxation processes respectively. A and B represent two cross-relaxation channels.

nonradiative relaxation. The small change of the emission at 656 nm excitation with increasing of the pump repetition rate may be due to the small accumulation at $^3H_4$ level.

Now, we have to take into account the two cross-relaxation energy transfer processes which were found in the continuous experiment[13]. One process is that two ions in the $^1G_4$ and $^3H_6$ levels move to the $^3F_3$ and $^3F_4$ levels. The other process produces two ions in $^3F_4$ levels from the ones in $^3H_6$ and $^3H_4$ levels. These processes are indicated by curved arrows in Fig. 4. By these two processes one ion in the $^1G_4$ level can produce three ions in the $^3F_4$ level if cross-relaxation rate is much larger than radiative relaxation rate. Because the repetition rate of our pulse laser was limited to 200 Hz, we could not find the photon avalanche which was found in $^1G_4 \rightarrow {}^3H_6$ transition for continuous excitation. Instead, we investigated the possibility of the photon avalanche at high repetition pumping rate by numerical simulation. For this purpose, the rate equations were used for the populations in four levels, $n_1(^3H_6)$, $n_2(^3F_4)$, $n_3(^3H_5)$, and $n_4(^1G_4)$.

$$\frac{dn_1}{dt} = -R_1 n_1 + \frac{n_4 b_1}{\tau_4} + \frac{n_3 c}{\tau_3} + \frac{n_2}{\tau_2} - \eta_a n_1 n_4 - \eta_b n_1 n_3 \quad (1)$$

$$\frac{dn_2}{dt} = -R_2 n_2 - \frac{n_2}{\tau_2} + \frac{n_4 b_2}{\tau_4} + \frac{n_3(1-c)}{\tau_3} + \eta_a n_1 n_4 + 2\eta_b n_1 n_3 \quad (2)$$

$$\frac{dn_3}{dt} = +R_1 n_1 - \frac{n_3}{\tau_3} + \frac{n_4(1-b_1-b_2)}{\tau_4} + \eta_a n_1 n_4 - \eta_b n_1 n_3 \quad (3)$$

$$\frac{dn_4}{dt} = +R_2 n_2 - \frac{n_4}{\tau_4} - \eta_a n_1 n_4 \quad (4)$$

$$1 = n_1 + n_2 + n_3 + n_4. \quad (5)$$

where $\tau_2$, $\tau_3$, and $\tau_4$ are the lifetimes of $^3F_4$, $^3H_4$, and $^1G_4$, which are 20 ms, 2 ms, 0.9 ms respectively; $\eta_a$ and $\eta_b$ are the rates of the two cross-relaxation processes in Fig. 4, which are known to be about 1000 $s^{-1}$. The branching ratios of $b_1$, $b_2$, and c are 0.45, 0.43, and 0.83 respectively. The total ion density of $Tm^{3+}$ ions was normalized and the actual density in 1% $Tm^{3+}$:$LaF_3$ is $2\times10^{20}cm^{-3}$. However, $R_1$, the ground state pump rate from $^3H_6$ to $^3F_2$, and $R_2$, the excited state pump rate from $^3F_4$ to $^1G_4$, are not known except that their ratio $R_1/R_2$ is 0.002[13]. $R_1$ and $R_2$ are represented by $I\sigma_g$ and $I\sigma_e$ respectively, where I is the pump intensity and $\sigma_g$ and $\sigma_e$ are the ground state and excited state absorption cross sections respectively. $\sigma_g$ and $\sigma_e$ are not known. We failed to measure $\sigma_g$ because the absorption is very weak due to the phonon-assisted transition. We could estimate $\sigma_e$ by the looping mechanism[15].

When we excite the ions at 648.4 or 635.2 nm, there is a looping mechanism originating from the $^3F_4$ level, which is very similar to the mechanism in $Tm^{3+}$:$Gd_3Ga_5O_{12}$[15]. If the population in the $^3F_4$ level whose lifetime is $\tau_2$ is $n_2(0)$ just after the first laser pulse with repetition rate $f$, it will be $n_2(0)e^{-1/f\tau_2}$ or $n_2(1)$, just before the second pulse. If the pulse interval is much larger than the life time of the $^3H_4$ level, which is the case in our experiments, the new population just before the third pulse will be

$$n_2(2) = n_2(1)[1 + \exp(-\phi\sigma_e/A - 1/f\tau_2) + m(1-\exp(-\phi\sigma_e/A))]\exp[-1/f\tau_2 \quad (6)$$

where $\phi$ is the number of photons in a single laser pulse, $\sigma_e$ is the excited state absorption for the $^3F_4 \rightarrow {}^1G_4$ transition, and A is the cross-section of the pump beam at the sample. The first term is the residual population from each pulse without any contribution from previous pulses. The second term is the residual contribution from the previous population after upconverted transition to the $^1G_4$ level. The last term is the contribution from the $^1G_4$ level which produces m electrons in the $^3F_4$ level from one electron in its level. The radiative relaxation rate[12] and cross-relaxation rate [13] from $^1G_4$ level are both about 1000 $s^{-1}$. In addition, about 40% of the radiative relaxation rate from $^1G_4$ is for the transition of the $^1G_4$ to $^3H_5$ or $^3F_4$ level. Therefore, one half of the population in the $^1G_4$ level relax to the $^3H_4$ level by energy transfer producing the same number of ions in the $^3F_4$ level, while about 20% of the population in the $^1G_4$ level relax to the $^3H_4$ level radiatively. In the $^3H_4$ level, about 70% of the population relax to the $^3H_6$ level by energy transfer producing the same number of ions in the $^3F_4$ level. Most of the rest

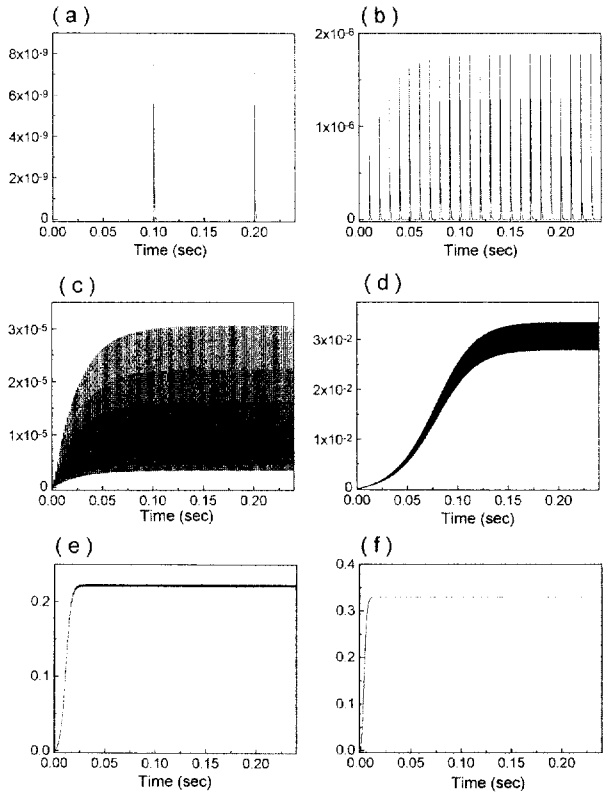


Fig. 5. Time evolution of the population in the $^1G_4$ level under 635.2 nm excitation at (a) 10, (b) $10^2$, (c) $10^3$, (d) $10^4$, (e) $10^5$ and (f) $10^6$ Hz repetition rates. The values on the vertical axis are the normalized population density in the $^1G_4$ level.

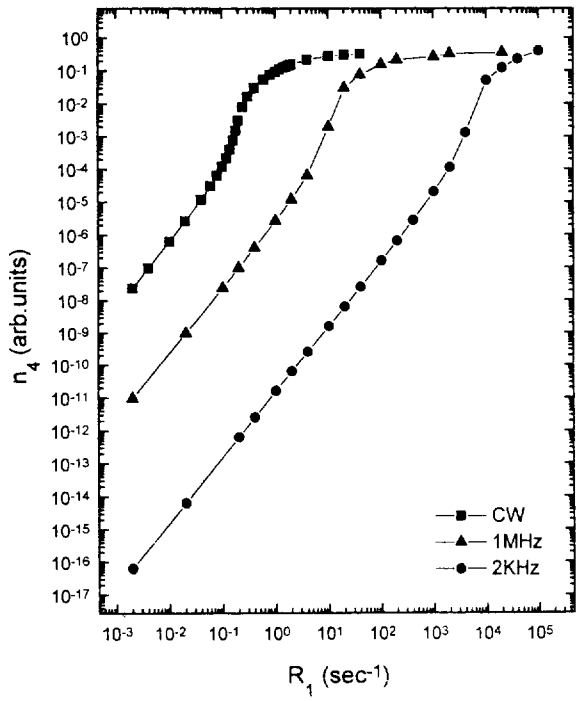


Fig. 6. Steady state population of the $^1G_4$ level versus laser pump rate for continuous wave and two different pump repetition rates,.

of population in $^3F_4$ level relax to $^3H_6$ radiatively. So, we can say that two ions in the $^1G_4$ level will give about three ions in the $^3F_4$ level with m = 1.5. Now, the relation for the *k*-th pulse can be written as

$$n_2(k) = n_2(1) + G\, n_2(k-1)$$
$$= n_2(1)\,\frac{1-G^k}{1-G} \qquad (7)$$
$$G = [\exp(-\phi\sigma_e/A) + 1.5\,[\{1-\exp(-\phi\sigma_e/A)\}]\exp[-1/f\tau_2]$$
$$= B\,\exp(-1/f\tau_2)$$

The steady state value of the $^1F_4$ population becomes

$$n_2^{(s)} = \frac{n_2(1)}{1-B\exp(-1/f\tau_2)} \qquad (8)$$

We fitted the data in Fig. 3 with Eq. (8) to get the excited state absorption crossection $\sigma_e$, assuming the emission intensity is proportional to $n_2^{(s)}$. From the results of the fit for 648.4 and 635.2 nm, a value of $1.4\times10^{-19}$ $cm^2$ was obtained for $\sigma_e$ in both cases. Now, we can estimate $\sigma_g$ as $2.8\times10^{-22}$ $cm^2$ from a numerical simulation of the $\sigma_e$ value.

The time evolution of the population $n_4$ is shown in Fig. 5 using Eq. (1-5) for various repetition rates with 20 ns pulse width and 2000 $s^{-1}$ ground state pump rate. It shows the blue upconversion emission intensity. At very low repetition rate, the population is almost independent of the number of laser shots. In the middle range of frequencies, the shape of the time evolution is what we expect in Eq. (7) due to the looping mechanism, and the population is at the steady state value after about 100 ms. Finally, at high repetition rate, the abrupt increase of the population indicates the photon avalanche process.

The dependence of the steady state population of $^1G_4$ on the laser pump rate in Fig. 6 shows the blue upconversion intensity as a function of laser pump intensity. It is a quadratic dependence at low pump rate and shows a dramatic increase of the emission intensity above some critical pump rate in high repetition rate or continuous excitation. In the experiment, the maximum pulse repetition rate was 200 Hz and no photon avalanche effect can be found even at high pump rates. However, in case of 1 MHz, the photon avalanche effect will be found with relatively low pump rates. We can see why the photon avalanche was reported only in the continuous excitation case, although we could see the avalanche effect with a pulse excitation source if the laser had a high repetition rate.

## IV. CONCLUSIONS

We have studied the two-step upconversion processes and generation of the photon avalanche in $Tm^{3+}$:$LaF_3$ in pulse excitation. Selective excitation methods separated two different two-step excitations and the excited state absorption cross section was estimated. Numerical simulation showed the possibility of photon avalanche in high repetition mode. An experiment with a mode-locked dye laser would verify the analysis with the rate-equation model.

## VI. Acknowledgments

The authors wish to thank A. Nakamura and Y. L. Lee for some measurements. This work was supported by KOSEF 961-0206-059-2 and BSRI 96-2435.

## REFERENCES

[1] B. Di Bartolo, *Optical Properties of Excited States in Solids* (Plenum Press, New York, 1992).
[2] F. Auzel, Phys. Rev. **B 13**, 2809 (1976)
[3] R. M. Macfarlane, J. Phys. **IV 4**, 289 (1994).
[4] B. P. Scott, F. Zhao, R. S. F. Chang and N. Djeu, Opt. Lett. **18**, 113 (1993).
[5] T. Hebert, R. Wannemacher, R. M. Macfarlane, and W. Lenth, Appl, Phys, Lett. **60**, 2592 (1992).
[6] M. Dulick, G. E. Faulkner, N. J. Cockroft, and D.C. Nguyen, J. Lumin. **48/49**, 517 (1991).
[7] S. Tanabe, K. Tamai, K. Hirao, and N. Soga, Phys. Rev. **B 47**, 2507 (1993).
[8] A. W. Kueny, W. E. Case and M. E. Koch, J. Opt. Soc. Am. **B 10**, 1834 (1993).
[9] H. Ni and S. C. Rand, Opt. Lett. **16**, 1424 (1991).
[10] V. Francois, F. Pelle, P. Goldner, D. Simkin, J. Lumin. **65**, 57 (1995).
[11] W. Lenth and R. M. Mactarlane, J. Lumin. **45**, 346 (1990).
[12] S. Huang, S. T. Lai, L. Lou, W. Jia, and W. M. Yen, Phys. Rev. **B 24**, 59 (1981).
[13] B. C. Collings and A. J. Silversmith, J. Lumin. **62**, 271 (1994).
[14] W. T. Carnall, P. R. Fields, T. Morrison, and R. Sarup, J. Chem. Phys. **52**, 4054 (1970).
[15] A. Brenier, C. Garapon, C. Madej, C. Pedrini, G. Boulton, J. Phys. **IV 4**. 431 (1994).