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Basic model for energy transfer in nanocrystals

First Version (V1)

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Abbreviations and Acronyms

Dx.y	Deliverable <i>x.y</i> (<i>x, y</i> are two numbers)
ETU	Energy transfer upconversion
FIBIRYCIS	Fundacion para la Investigacion Biomedica del Hospital Universitario Ramon Y Cajal
LIR	Luminescence intensity ratio
NIR	Near infrared
РМТ	Photomultiplier tube
RELIC	Rare Earth Level and Intensity Calculation (open-source software)
UAVR	Universidade de Aveiro
UB	University of Belgrade
UU	Utrecht University
VINCA	Vinča institute
WP	Work package(s)
WPAS	Instytut Niskich Temperatur I Badan Strukturalnych Im. Wlodzimierza Trzebiatowskiego Polskiej Akademii Nauk



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D3.1 Basic model for energy transfer in nanocrystals

1. Organization of the report

Work package 3 (WP3) is entitled: "Modelling energy transfer processes for temperature sensing". The report has been mainly created by Utrecht University (UU) as the lead beneficiary of the WP3 along with other partners:

- Fundacion para la Investigacion Biomedica del Hospital Universitario Ramon Y Cajal (FIBIRYCIS)
- Universidade de Aveiro (UAVR)
- Institute za nuklearne nauke Vinča (VINCA)

According to the final project proposal, deliverable 3.1 should contain a microscopic model of the energy transfer and luminescent processes to both understand the luminescence dynamics and also to optimize the luminescence efficiency. Moreover, objective 2 of the *nanoTBTech* project aims at a complete understanding of the physical mechanisms governing the performance of self-monitored nanothermometers. Thus, besides a first basic model of energy transfer including the interaction between single ions and vibrations, also some general foundations of luminescence thermometry were focussed on that allow clear predictions on the limitations and validity regimes of their usage for temperature calibration.

This report is structured as follows. First, the general theoretical framework of the capabilities and limitations of single centre luminescent nanothermometers will be elaborated. In particular, the role of non-radiative transitions as energy transfer processes between the ion and phonons are discussed. Finally, the extension to two-centre luminescent nanothermometers and temperature-dependent energy transfer processes are presented. In particular, the achievable relative thermal sensitivities and temperature resolution of both mechanisms are critically compared. Future work will involve validation of the models developed and extension and refinement of the models outlined in this first deliverable on modelling.



2. Elaborated model for single ion luminescent nanothermometers

2.1. Optimized temperature sensing with the Boltzmann distribution

2.1.1. Foundations of the Boltzmann distribution

The concept of a luminescent thermometer relies on the detection of an optical signal that shows a specific and sensitive temperature dependence. The desirable way of temperature sensing consists in a linear calibration between the detected response signal and the correlated temperature. In its most commonly applied realization, the luminescence intensity ratio (LIR) of two emission bands arising from thermally coupled excited states is employed. That detection principle is favourable since an intensity ratio is not readily affected by any absolute intensity uncertainty and, in addition, also the thermal sensitivity is enhanced. Several very good overviews are given in literature [1-4].

In the simplest case of a single luminescent ion, thermal equilibrium with a surrounding heat bath (such as the embedding host compound of the luminescent entity) implies that the population of the various excited states should obey a canonical Boltzmann distribution. Let $|1\rangle$ and $|2\rangle$ be the two thermally coupled excited states with degeneracies g_1 and g_2 , respectively, that luminescence is detected from. Then, the population ratio of the two states in thermodynamic equilibrium reads

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \exp\left(-\frac{E_2 - E_1}{k_{\rm B}T}\right) = \frac{g_2}{g_1} \exp\left(-\frac{\Delta E_{21}}{k_{\rm B}T}\right)$$
(1)

A reliable and sensitive measure for the population ratio is the detected luminescence intensity from any excited state $|i\rangle$ to a ground state $|f\rangle$ due to the proportionality [5]

$$I_{if} \propto r_{if} \beta_{if} k_{if} \omega_{if} N_i \tag{2}$$

with r_{if} as the detector sensitivity at the emission resonance ω_{if} (emission energy $E_{if} = \hbar \omega_{if}$), $\beta_{if} \le 1$ as the emission branching ratio and k_{if} as the related radiative decay rate. Thus, the basic calibration law for single ion luminescence thermometry based on the detection on the ratio of two emission intensities is given by

$$R(T) = \frac{I_{20}}{I_{10}} = \frac{r_{20}A_{20}\omega_{20}N_2}{r_{10}A_{10}\omega_{10}N_1} = \frac{r_{20}\beta_{20}\tau_{10}\omega_{20}N_2}{r_{10}\beta_{10}\tau_{20}\omega_{10}N_1} = C\frac{g_2}{g_1}\exp\left(-\frac{\Delta E_{21}}{k_{\rm B}T}\right).$$
(3)

Both the constants *C* and ΔE_{21} have a clear physical interpretation that can be derived from experimentand also predicted theoretically. Thus, any temperature calibration of the thermodynamic Boltzmann law (3) is independently verifiable by means of theory.

2.1.2. Optimum performance range of the Boltzmann distribution

Usage of the Boltzmann distribution for temperature sensing is not equally effective for every temperature range in terms of temperature accuracy. Within D3.1, we could derive that the optimum condition for globally maximum absolute thermal response for all positive absolute temperatures *T*, i.e.

$$S_{a} = \frac{\mathrm{d}R}{\mathrm{d}T}\Big|_{T=T_{0}} \to \mathrm{max.},\tag{4}$$



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is fulfilled, if the energy difference obeys the condition

$$\Delta E_{\rm opt} = 2k_{\rm B}T_0 \tag{5}$$

for a temperature $T_0 > 0$ aimed to be detected.

In practice, it might be difficult to exactly match this optimum condition. A way to independently judge a Boltzmann thermometer in terms of its performance for any desirable temperature may be given as follows. If the energy difference is scaled in thermal energies, $\Delta E = nk_{\rm B}T$, with *n* defined by that identity, a reasonable measure for the performance of any luminescent thermometer using the Boltzmann distribution as the underlying operation principle is given by a *performance function P*(*n*),

$$P(n) := \frac{S_{a}(T)|_{T=\frac{1\Delta E}{nk_{B}}}}{S_{a}(T)|_{T=T_{0}=\frac{1\Delta E}{2k_{B}}}} = \frac{1}{4}n^{2}\exp(2-n) = \frac{\exp(2)}{2}\gamma(3,1),$$
(6)

where $\gamma(3,1)$ denotes the Erlang distribution with shape parameter 3 and rate parameter 1. This gives the performance function of any Boltzmann thermometer a definite probabilistic interpretation, which we have elaborated in detail in a manuscript to be published but is beyond the scope of this summarizing report. The main conclusions out of the probabilistic interpretation of eq. (6) are that besides the maximum (or, alternatively interpreted, the modus) located at n = 2 (*cf.* eq. (5)), the expectation value is given by

$$\Delta E_{\rm mean} = 3k_{\rm B}T_0 \tag{7}$$

A plot of the performance function of a Boltzmann-based thermometer scaled in values of n is depicted in Figure 1. It illustrates that the condition for optimum performance is not very strict, but allows for appreciable deviation from the optimum condition (5) without significant reduction in absolute thermal response of the Boltzmann distribution towards small temperature changes. On the other hand, it shows, however, that not every energy difference is similarly well suited for temperature sensing by luminescence thermometry dependent on the temperature range of interest.



Figure 1. Plot of the performance function P(n) of any luminescent thermometer operating with a Boltzmann distribution according to eq. (6). *n* is the dimensionless measure for the energy gap ΔE in terms of thermal energies, $k_{\rm B}T$. Both the optimum and mean energy difference for temperature sensing at a desired temperature range T_0 are indicated (see eqs. (5) and (7)).



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Besides the absolute thermal response, another figure of merit of any general thermometer is its *relative thermal sensitivity*, S_r . It reflects the relative response of a signal reacting on a temperature change relative to the value of the signal at the initial temperature. The advantage of this quantity is that it readily allows to compare differently operating thermometers in terms of their thermal response. For a Boltzmann thermometer, it can be specifically calculated as

$$S_{\rm r}(T) := \left| \frac{1}{R} \frac{{\rm d}R}{{\rm d}T} \right| = \frac{\Delta E}{k_{\rm B}T^2} \cdot 100\% = \frac{n}{T} \cdot 100\%$$
 (8)

The relative thermal sensitivity gains its importance by its impact on the temperature accuracy of a thermometer,

$$\delta T(T) := \left| \frac{1}{S_{\rm r}} \frac{\mathrm{d}R}{R} \right| = \frac{T}{n} \cdot \frac{\left| \frac{\mathrm{d}R}{R} \right| \%}{100\%},\tag{9}$$

where $\left|\frac{dR}{R}\right|$ is experimentally determined by the relative luminescence intensity accuracy (for a photomultiplier tube (PMT), it can be assessed by a Poisson distribution, for instance). Given the capabilities of modern light detection devices, a good practical relative sensitivity is $S_r > 1 \% \cdot K^{-1}$ to allow for temperature accuracies below 0.1 K. If combined with the previous discussion on a strong absolute response of any Boltzmann thermometer, we could conclude the following fundamental issues for any single ion luminescent thermometer with that operating principle:

- a) Single ion Boltzmann thermometers are particularly sensitive for cryogenic temperatures. In there, both maximized absolute thermal response in conjunction with high relative thermal sensitivities $S_r \gg 1 \% \cdot K^{-1}$ can be fulfilled. This agrees with all separate experimental findings reported in literature so far.
- **b)** At physiological temperatures (T = 310 K or 37 °C), the lower boundary limit $S_r > 1 \% \cdot K^{-1}$ is not compatible anymore with the demand for an optimum energy difference according to eq. (5). Only for yet larger energy differences in the range of the expectation value (7), the thermal sensitivity can still be kept at around $1\% \cdot K^{-1}$.
- c) For temperatures higher than 420 K (~ 150 °C), the thermal response performance drops below 50% and the relative sensitivity S_r below $1\% \cdot K^{-1}$. Thus, it may be concluded that single ion Boltzmann thermometers are not very sensitive thermometers for high temperatures based on their operating principle.

Some relative sensitivity curves illustrating these conclusions are depicted in Figure 2. Physiological temperatures are already close to the limit of desirable relative sensitivity ($S_r = 1\% \cdot K^{-1}$) by usage of the Boltzmann distribution. Thus, other operating principles such as temperature-dependent energy transfer processes between several ions are more promising to circumvent the limitations of thermal equilibrium. All previously presented fundamental results are part of a manuscript in its final stage and parts thereof were also presented at several conferences in form of oral presentations or posters.





Figure 2. (a) Plot of the temperature dependence of relative thermal sensitivities S_r for different energy gaps (scaled in *n*) matching an appreciable absolute thermal response according to the performance function P(n). **(b)** Corresponding theoretical minimum temperature uncertainties δT assuming a relative intensity uncertainty of 0.1%. The dashed lines indicate the desired threshold values for *in vivo* applications within *nanoTBTech*.

2.2. Critical validation of approximations of the Boltzmann distribution in the field of *in vivo* thermometry

Especially in *in vivo* nanothermometry, only small temperature changes are probed. In many publications in this field, it is in fact found that not the conventional Boltzmann-type temperature calibration (plot of $\ln(I_{20}/I_{10})$ vs. 1/T), but a simple linear calibration of the intensity ratio I_{20}/I_{10} vs. temperature *T* is performed instead [3],[6]-[11]. Throughout this deliverable, we also critically validated this type of temperature calibration and compared it to the validity regime of the Boltzmann distribution.

Suppose a small temperature range ΔT around a desirable temperature $T_0 \gg \Delta T$ is aimed to be probed. If $k_{\rm B}(T_0 + \Delta T) = k_{\rm B}T < \Delta E$, the Boltzmann distribution can be expanded around T_0 . Let $n = \frac{\Delta E}{k_{\rm B}T_0}$, then it is

$$R(T) = C \frac{g_2}{g_1} \exp\left(-\frac{\Delta E}{k_{\rm B}T}\right) = C \frac{g_2}{g_1} \exp(-n) \left[(1-n) + n\frac{T}{T_0}\right] + \mathcal{O}\left(\left(\frac{\Delta T}{T_0}\right)^2\right)$$
(10)

up to first order. In particular, the approximation (10) predicts a positive slope if the intensity ratio itself is plotted versus temperature, in agreement with all observations reported so far. If an intermediate temperature T_0 is selected (e.g. 310 K) around which temperatures are aimed to be measured with a single ion luminescent thermometer, eq. (10) provides a general formula to easily calculate a linear approximation of the Boltzmann distribution that can be independently tested with respect to experimental data.

In application, it is also necessary to consider the error made with this approximation to account for the temperature accuracy. Since the model function is known, the relative error can be explicitly calculated and is given by

$$\left|\frac{\Delta(T)}{R(T)}\right| \cdot 100\% = \left|1 - \left[(1-n) + n\frac{T}{T_0}\right] \exp\left[-n\left(1 - \frac{T_0}{T}\right)\right]\right| \cdot 100\%$$
(11)





Figure 3. Plots of relative errors connected to a Taylor expansion of the Boltzmann distribution law in a temperature range close to the physiological temperature range for energy gaps of (a) $\Delta E = 100 \text{ cm}^{-1}$ (Stark states of $4f^n$ electronic levels), (b) $\Delta E = 432 \text{ cm}^{-1}$ (optimum for physiological temperature sensing) and (c) $\Delta E = 1000 \text{ cm}^{-1}$. The physiological temperature window and maximum relative error made therein is indicated. Note the different scales of relative errors.

with *n* and T_0 as defined before. Some examples of the stability of the linearization of the Boltzmann distribution around physiological temperatures ($T_0 = 310.15$ K) are plotted in Figure 3. In particular, it is also intuitive that the linearization is most accurate for a matching with the optimum response condition (5) and thus, the relative error becomes minimal for n = 2.

Finally, it was aimed to compare the two types of temperature calibration with respect to the relative luminescence intensity uncertainties that have an impact on the temperature accuracy. The relative error in a Boltzmann plot ($\ln R(T)$ vs. 1/T) may be assessed by

$$\left|\frac{\mathrm{d}\ln R(T)}{\ln R(T)}\right| = \frac{1}{|\ln R(T)|} \left|\frac{\mathrm{d}R(T)}{R(T)}\right| = \frac{1}{|\ln R(T)|} \left|\frac{\mathrm{d}I_{10}(T)}{I_{10}(T)} + \frac{\mathrm{d}I_{20}(T)}{I_{20}(T)}\right|$$
(12)

The experimental relative error in R(T) or, alternatively, upon plotting R(T) directly versus the temperature is only smaller than the one in a Boltzmann-type plot if $|\ln R(T)| < 1$. This is only the case if $\Delta E < k_{\rm B}T$. It can then be concluded that for temperature calibration at physiological temperatures ($k_{\rm B}T \sim 216 \text{ cm}^{-1}$) with, e.g. Stark levels of the lanthanides exhibiting energy differences in the range of around 100 cm⁻¹, a plot of R(T) vs. T is more robust towards relative intensity



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uncertainties given by $\left|\frac{dR(T)}{R(T)}\right|$ than a conventional Boltzmann plot with appreciably low relative errors (see Figure 3.(a)). In contrast, a Boltzmann-type calibration (ln I_{20}/I_{10} vs. 1/T) is readily feasible for energy differences $\Delta E > k_B T$. A special case is given for n = 2 (see Figure 3.(b)). If temperatures in a close environment around a given temperature T_0 are aimed to be detected, a linearization of the Boltzmann distribution (see eq. (10)) leads to almost vanishing relative errors in that environment. However, any experimental intensity uncertainty does yet lead to only half a relative error in a Boltzmann plot compared to a calibration of R(T) vs. T. For larger n, the relative error in a linearization quickly becomes non-negligible anymore and usage of the accurate Boltzmann distribution is strongly recommended for stronger temperature accuracies (see Figure 3.(c)).

2.3. Tuning of the Boltzmann distribution with excited state dynamics – Energy transfer mechanism between single ions and phonons

2.3.1. Non-radiative transitions by energy transfer between electric/magnetic dipole transitions and vibrational overtones

Linear temperature calibration with a Boltzmann distribution in single ion luminescence thermometry only works if thermal equilibrium between the probed excited states is always sustained in the considered temperature range. This means that the non-radiative rates governing equilibration between the excited states must be much higher than the radiative decay rates back to a common ground state. A fundamental consideration of the thermal exchange between the two excited states in a single ion luminescent thermometer involves the absorption and emission of phonons. It is then possible to derive the Boltzmann distribution as the governing population law in thermodynamic equilibrium by the second quantization picture in conjunction with an energy transfer consideration. A very thorough derivation and careful review of the different models on non-radiative rates was incorporated into the manuscript about to be submitted within the context of D3.1. For this report, only the most important results will be summarized that indicate how the final generalized model on excited state dynamics evolves.

We regard an effective phonon mode with energy $\hbar \omega_{eff} \leq \hbar \omega_{max}$ limited by the cut-off energy $\hbar \omega_{max}$ in the phonon density of states of a considered host compound. The thermal average phonon occupation number is then given by the Bose-Einstein factor

$$\langle n_{\rm eff} \rangle = \frac{1}{\exp\left(\frac{\hbar\omega_{\rm eff}}{k_{\rm B}T}\right) - 1}$$
 (13)

For two excited states that are not shifted in the configurational coordinate space such as the electronic levels within the $4f^n$ configuration of the lanthanides, the Franck-Condon factors impose an additional selection rule, as then the vibrational overlap integral between two vibrational states $|m\rangle$ and $|n\rangle$ is given by

$$S_{mn} = \langle m | n \rangle \approx \delta_{mn} \tag{14}$$

with δ_{mn} as the Kronecker symbol. In that special case, non-radiative transitions are governed by multi-phonon processes within a second quantization picture. The non-radiative absorption rate $k_{nr}^{abs}(T)$ is [12],[13],[14]



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$$k_{\rm nr}^{\rm abs}(T) = k_{\rm nr}(0) \langle n_{\rm eff} \rangle^p \tag{15}$$

with

$$p = \left|\frac{\Delta E}{\hbar\omega_{\rm eff}}\right| \ge \left|\frac{\Delta E}{\hbar\omega_{\rm max}}\right| \tag{16}$$

as the round-off integer number (ensured by the floor function $\lfloor x \rfloor$) of phonons required to bridge the energy gap ΔE between the two thermally coupled excited states. In contrast, the non-radiative emission rate is given by

$$k_{\rm nr}^{\rm em}(T) = k_{\rm nr}(0)(1 + \langle n_{\rm eff} \rangle)^p \tag{17}$$

where the additional term of 1 accounts for the spontaneous emission of phonons. Even the radiative decay rates have a small temperature dependence, which stems from the thermally induced emission and absorption of phonons,

$$k_{\rm r}(T) = k_{\rm r}(0)(1 + 2\langle n_{\rm eff} \rangle)$$
(18)

The intrinsic non-radiative transition rate $k_{nr}(0)$ is difficult to calculate from first principles. For electronic levels of the shielded $4f^n$ configuration of lanthanides, however, a so-called phenomenological energy gap law has been proven to be valid experimentally and could even be derived theoretically and improved by many models [12]-[15],

$$k_{\rm nr}(0) = \mathcal{O}(\exp[-(p-2)])$$
 (19)

More advanced effective theories exist that give agreement in at least the same order of magnitude and derive the non-radiative rate in a similar manner to radiative ones by means of effective electronic structure theories [16],[17],[18],[19],[20]. In this sense, it is possible to give substantial credit to the magnitude and type of non-radiative transition in an analogous way to radiative transitions. As will become clear in the next section, an appreciable and accurate knowledge on the intrinsic non-radiative rate in the limit of 0 K is relevant to derive clear guidelines for a design of a luminescent thermometer towards Boltzmann behaviour.

A particularly successful attempt, which is also related to the final goal of this deliverable, is the identification of a non-radiative transition as an energy transfer between the transition dipole moment and a vibrational overtone of the considered phonon in resonance to the energy gap ΔE [21]-[24]. Since vibrational overtones of phonons are connected to substantially weaker transition dipole moments, the qualitative decrease of the non-radiative transition rate with larger energy gaps becomes intuitively clear. Moreover, any vibrational transition is predominantly electric dipole in nature and Dexter-type exchange effects between electrons and vibrational modes can be safely ruled out. Thus, two main mechanistic possibilities arise for the description of non-radiative transitions within the framework of a Förster-type energy transfer:

a) <u>Electric dipole-electric dipole coupling</u>: If the non-radiative transition has a dominant electric transition dipole moment, it can couple to any resonant vibrational overtone and the corresponding transition dipole moment. The master formula for the non-radiative transition described with this mechanism is given by



$$k_{\rm nr}(0) = \frac{\kappa^2}{8\pi\hbar\epsilon_0^2 n^4 |\boldsymbol{r} - \boldsymbol{r}_{\rm vib}|^6} |\boldsymbol{\mu}_{\rm el}|^2 |\boldsymbol{\mu}_{\rm vib}|^2 \rho(E)$$
(20)

In there, \hbar is Planck's reduced constant, ε_0 the vacuum permittivity and κ^2 considers the relative orientation of the electric transition dipole moment μ_{el} and the vibrational dipole moment μ_{vib} . In most dielectric host compounds, it is a fair approximation to take its angle average, $\langle \kappa^2 \rangle = \frac{2}{3}$. n is the refractive index of the host medium and $\rho(E)$ is the density of available states for the energy transfer and ensures the resonance condition by consideration of the spectral overlap between the lanthanide emission and absorption spectrum of the respective vibrational mode. Finally, $R = |\mathbf{r} - \mathbf{r}_{vib}|$ is the distance between the two mutually coupling dipole moments. After several rearrangements to the spectroscopic observables, eq. (20) can be converted to the more practical formula [22],[25],[26]

$$k_{\rm nr}^{\rm ed}(0) = \frac{9000\kappa^2 |\chi(n)|^2 \ln 10}{128\pi^5 \varepsilon_0^2 n^4 N_{\rm A}} \frac{\int d\lambda \,\lambda^4 F_{\rm em}(\lambda)\varepsilon_{\rm vib}(\lambda)}{\int d\lambda F_{\rm em}(\lambda)} \frac{k_r^{\rm ed}(0)}{|r - r_{\rm vib}|^6} \equiv \left(\frac{R_0^{\rm ed}}{R}\right)^6 k_{\rm nr}^{\rm ed}(0)$$
(21)

where $|\chi(n)|^2$ is a local electric field correction dependent on the refractive index, N_A is Avogadro's constant, $F_{em}(\lambda)$ the emission line shape and $\varepsilon_{vib}(\lambda)$ is the extinction coefficient deduced from the absorption spectrum of the vibrational (overtone) mode coupled to. Besides the peculiar R^{-6} dependence, special attention should be paid to the proportionality to the radiative rate $k_{nr}^{ed}(0)$. This allows to use the same selection rules on electric dipole transitions to evaluate non-radiative transitions. In the special case of $4f^n$ -based electronic levels of the trivalent lanthanides, these can thus be evaluated by means of the phenomenological Judd-Ofelt theory. Specifically, the radiative transition rate is proportional to the electric dipole line strength S_{ED} , which is given by

$$S_{\rm ED} = \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle 4f^n[\gamma LS]J| |U^{(\lambda)}| |4f^n[\gamma' L'S']J'\rangle|^2$$
(22)

with the Ω_{λ} as the three phenomenological Judd-Ofelt parameters (in the order of 10^{-20} cm^2) and the $|\langle 4f^n[\gamma LS]J||U^{(\lambda)}||4f^n[\gamma'L'S']J'\rangle|^2$ as the absolute values of the reduced matrix elements of the irreducible unit tensor forms of rank λ in the intermediate coupling scheme (as indicated by the squared brackets). These can be gathered from literature [27] or nowadays even easily calculated with the open-source software RELIC by Hehlen, Brik and Krämer [28]. This mechanism provides a very useful interpretation since it readily allows to set radiative and non-radiative rates on an equal footing that obey similar selection rules. If the number of vibrational overtones is not too high, the resulting non-radiative transition rates can cover ranges between 10^{12} s^{-1} down to 10^4 s^{-1} .

b) <u>Magnetic dipole-electric dipole coupling</u>: Particularly, transitions between many of the thermally coupled excited states of the lanthanide ions are characterized by quantum numbers $\Delta L = \Delta S = 0$ and $\Delta J = \pm 1$. These transitions are mostly electric dipole-forbidden in Judd-Ofelt theory even in the intermediate coupling scheme and magnetic dipole-allowed instead. A well-known example is already known for transitions among the 4f¹³5d¹-based electronic levels of Yb²⁺ [29]. Given a purely magnetic transition dipole moment for the non-radiative transition, already Dexter indicated the possibility of a magnetic-dipole-electric



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dipole type of energy transfer. The notation is somewhat misleading as the electric transition dipole moment μ_{vib} of the fundamental or overtone vibration acts in an indirect manner. The vibrational motion of the surrounding nuclei in a host compound corresponds to a time-dependent electric dipole moment, which in the ideal case gives rise to a harmonic variation of the electric dipole moment. This situation corresponds to a Hertz dipole antenna. The corresponding emitted electric and magnetic field components can be derived from the Liénard-Wiechert potentials known from electrodynamics within in the near field limit (i.e. $R = |\mathbf{r} - \mathbf{r}_{vib}|$ is much smaller than the wavelength of the phonons in the range of μ m) [30]. Let \mathbf{k} be the wavevector of the vibrational mode considered. In the near-field limit $|\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_{vib})| \ll 1$, the corresponding real part of the locally induced magnetic field is

$$\operatorname{Re}(\boldsymbol{B}(t,\boldsymbol{r})) = \frac{\mu_0}{4\pi} \frac{\dot{\boldsymbol{\mu}}_{\operatorname{vib}}(t)}{R^2} \times \frac{(\boldsymbol{r} - \boldsymbol{r}_{\operatorname{vib}})}{R}$$
(23)

with $\dot{\mu}_{\rm vib}(t)$ as the time-dependent change in the vibrational electric dipole moment due to the oscillation of the surrounding lattice. It is this magnetic field that the magnetic transition dipole moment of the non-radiative transition couples to. Notably, however, the magnitude of this magnetic field compared to the emitted electric field in the near field is only very weak. Due to the explicit form of the induced magnetic field, cubic symmetries necessarily lead to a vanishing interaction matrix element with the magnetic transition dipole moment as first indicated by Chua, Reid and Tanner [31].

Finally, the explicit formula for the non-radiative transition rate $k_{nr}^{md}(0)$ is quite complicated, but at least the following effective law can be given (*cf.* eq. (21))

$$k_{\rm nr}^{\rm md}(0) = \left(\frac{R_0^{\rm md}}{R}\right)^4 k_{\rm r}^{\rm md}(0)$$
(24)

where R_0^{md} contains information about the coupling between the induced magnetic field due to the collective motion of the nuclei and the peculiar longer-range R^{-4} dependence similarly derives from application of Fermi's Golden rule for the evaluation of transition matrix elements. The analogous proportionality of the non-radiative transition rate to the radiative transition rate $k_r^{\text{md}}(0)$ again allows to qualitatively assess a dominance of this mechanism by regarding the corresponding magnetic dipole line strength. For trivalent lanthanides, it is given by

$$S_{\rm MD} = \left(\frac{\mu_{\rm B}}{e\hbar}\right)^2 |\langle 4f^n[\gamma LS]J||\boldsymbol{L} + g_s \boldsymbol{S}||4f^n[\gamma' L'S']J'\rangle|^2$$
(25)

In there, $\mu_{\rm B} = \frac{e\hbar}{2m_{\rm e}}$ is Bohr's magneton and *e* the elementary charge. *L* and *S* denote the orbital and spin angular momentum, respectively, and $g_s \approx 2.0023...$ is the electron g_s factor. Like for the electric dipole line strength, the reduced matrix elements $|\langle 4f^n[\gamma LS]J||L + g_s S||4f^n[\gamma'L'S']J'\rangle|^2$ defined in intermediate coupling scheme are well recorded[27] and also accessible in e.g. RELIC [28].

Despite the longer-range dependence compared to electric dipole-electric dipole energy transfer mechanisms (R^{-4} vs. R^{-6}), already Dexter was able to estimate that non-radiative transitions rates with an underlying magnetic dipole-electric dipole energy transfer mechanism should be reduced by a factor of 10⁸ compared to the electric dipole-electric dipole-electric dipole coupling mechanism[32]. Thus, $k_{nr}^{md}(0)$ will be in the range of around 10³ – 10⁴ s⁻¹ even



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if a fundamental vibrational mode can bridge the energy gap ΔE between the thermally coupled excited states.

2.3.2. Control over Boltzmann behavior in single ion luminescent thermometers – Accurate excited state dynamics and guidelines for an optimum luminescent thermometer

Within deliverable D3.1, we were able to establish a more general model including all microscopic processes during the thermal equilibration of the two excited states to be used for luminescence thermometry. Especially due to the foundations laid down in the last section, it becomes clear that dependent on the phonon energies of the host compound and also the selection rules for a non-radiative transition compared to those for the radiative emission transitions, the non-radiative and radiative transition rates may become similar in magnitude. In that case, the validity of the Boltzmann distribution as governing temperature calibration law is not given anymore. It is mandatory to know the impacts on these features in order to avoid such a failure within the physiological temperature window.

Consideration of the relevant rate equations and the steady state dynamics allow for the following general excited state dynamics model developed based on first foundations established for Eu³⁺ at UU [33]. For a single ion with two thermally coupled excited states, the steady state kinetics including the impact of multiphonon absorption or relaxation affords

$$R(T) = \frac{I_{20}}{I_{10}} = C \frac{N_2}{N_1} = C \cdot \frac{k_{1r}(0)(2\langle n_{\text{eff}} \rangle + 1)\beta_{32} + k_{\text{nr}}(0)g_2(\beta_{31} + \beta_{32})\langle n_{\text{eff}} \rangle^p}{k_{2r}(0)(2\langle n_{\text{eff}} \rangle + 1)\beta_{31} + k_{\text{nr}}(0)g_1(\beta_{31} + \beta_{32})(1 + \langle n_{\text{eff}} \rangle)^p}$$
(26)

where the factors $0 \le \beta_{ij} \le 1$ denote so-called feeding ratios from any excited state |3). Model (26) does contain the Boltzmann distribution as the limit of dominant non-radiative terms,

$$\frac{I_{20}}{I_{10}} \to C \exp\left(-\frac{\hbar\omega_{\rm eff}}{k_{\rm B}T}\right) \frac{g_2}{g_1} \exp\left(-\frac{(p-1)\hbar\omega_{\rm eff}}{k_{\rm B}T}\right) = C \frac{g_2}{g_1} \exp\left(-\frac{\Delta E_{21}}{k_{\rm B}T}\right),\tag{27}$$

which can be easily shown using the identity

$$\frac{\langle n_{\rm eff} \rangle}{1 + \langle n_{\rm eff} \rangle} = \exp\left(-\frac{\hbar\omega_{\rm eff}}{k_{\rm B}T}\right) \tag{28}$$

While eq. (26) is in principle exact under the assumption that the two thermally coupled excited levels are well enough isolated from other electronic levels, practical single ion thermometry is yet desirably performed in the Boltzmann range as this allows linear calibration. Thus, it is mandatory to know the control parameters for dominant non-radiative transition rates. This allows for clear guidelines for an optimized single ion luminescent thermometer.

a) <u>Phonon number p</u>: An obvious control parameter would be an increase of the number of required phonons *p* to bridge the energy gap due to the exponential dependence of the non-radiative transitions thereon. However, this control parameter becomes only effective if $\langle n_{eff} \rangle \gtrsim 1.50$. According to eq. (13), this condition requires $\hbar \omega_{eff} \lesssim 0.51 k_{\rm B}T$. The minimum optical phonon energy in inorganic compounds is in the range of 120 cm⁻¹ (e.g. iodides), while most stable host compounds that are well processable in nanocrystalline form exhibit phonon energies larger than 350 cm⁻¹. Accordingly, control over the non-radiative transition rates by this pathway would only be effective for high temperature thermometry (T > 1000 K) in most host compounds. In contrast, Boltzmann thermometry at those temperatures is not very



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accurate anymore (see section 2.1.2). An additional problem with keeping the phonon energy low then is that the intrinsic non-radiative transition rate $k_{nr}(0)$ decreases approximately exponentially with higher *p* (see eq. (19)).

b) Intrinsic non-radiative transition rate $k_{nr}(0)$: The intrinsic non-radiative transition rate can be indirectly tuned by the phonon number p and should then be kept small (p = 1, 2) for maximization. More importantly, within the framework of the energy transfer model between the non-radiative transition dipole moment and vibrations, non-radiative transitions can also be divided into the type of multipole transition. Electric dipole-allowed non-radiative transitions are much faster ($10^{12} - 10^4 \text{ s}^{-1}$) than the corresponding magnetic dipole-allowed transitions ($10^3 - 10^4 \text{ s}^{-1}$) given the same number of required phonons to bridge the energy gap between the excited states. Accordingly, electric dipole-allowed non-radiative transitions are favourable. For lanthanide ions with $4f^n$ electronic levels, non-radiative transitions can be easily characterized by their tabulated reduced electric or magnetic dipole matrix elements, respectively (see eqs. (22) and (25)).

If the phonon number p is 1 or 2, it is even possible to give an explicit criterion for the necessary magnitude of the non-radiative transition rate with respect to the radiative rates from the thermally coupled states in order to tune a luminescent thermometer to Boltzmann behavior at a desired temperature T_{probe} . The derivation of this formula is contained in detail in the manuscript about to be submitted, thus, only the final result will be given,

$$k_{\rm nr}(0) > \left[\frac{\exp\left(\frac{p\hbar\omega_{\rm eff}}{k_{\rm B}T_{\rm probe}}\right)}{g_2\left(1+\frac{\beta_{31}}{\beta_{32}}\right)}k_{\rm 1r}(0) - \frac{1}{g_1\left(1+\frac{\beta_{32}}{\beta_{31}}\right)}k_{\rm 2r}(0)\right]\Theta(k_{\rm nr}(0)),\tag{29}$$

with p = 1, 2 and $\Theta(k_{nr}(0))$ as the Heaviside step function ensuring that the non-radiative transition rate remains positive.

In the special case of lanthanides and $4f^n$ -based levels, the radiative decay rates are typically in the order of $10^3 - 10^4 \text{ s}^{-1}$. Thus, especially non-radiative transition rates that have a strong magnetic dipole character are critical for a desirable Boltzmann-type behaviour over a wide temperature range and may even lead to substantial deviations according to eq. (26).

Out of these considerations, two general guidelines for practical single ion luminescent thermometers can be stated:

- **1.** The two excited levels should be connected by a non-radiative transition rate with dominant electric dipole character to allow for an efficient energy transfer to the phonons governing the non-radiative transition. In particular, the non-radiative transition rate should be larger than $10^5 \, \text{s}^{-1}$ to ensure Boltzmann behaviour within the physiological temperature range (*T* = 310.15 K).
- **2.** The energy gap should be chosen such that the number of necessary phonons to bridge the gap does not exceed 2 ($p \le 2$).



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2.3.3. Matching of the validity regime of the Boltzmann distribution with optimum performance range

Within *nanoTBTech*, it is aimed for sensitive luminescent thermometers operating in the near infrared (NIR) biological windows I, II and III that allow to measure physiological temperatures. If a single ion luminescent thermometer is employed for that purpose, the previous optimum and energy transfer models allow for clear statements on the choice of activator and host compound. We will demonstrate that for lanthanides with their rich 4f^{*n*} electronic structure, for which the excited state dynamical model (26) applies.

According to section 2.1, a combined optimized absolute thermal response (P(n) > 0.50) with a relative thermal sensitivity $S_r \ge 1 \% \cdot K^{-1}$ makes an energy difference of $\Delta E = 3.1k_BT_0 - 3.3k_BT_0 = 670 \text{ cm}^{-1} - 720 \text{ cm}^{-1}$ a suitable choice ($T_0 = 310.15 \text{ K}$). Any higher energy difference leads to quick losses in absolute thermal response. The corresponding emission transitions from the two selected excited states are recommended to have large branching ratios. In the special case of lanthanides, an analysis of the reduced matrix elements then allows for a choice of a host compound with suitable Judd-Ofelt parameters to enhance the intensities of the desired emission transitions.

In order to tune the excited state dynamics towards Boltzmann behaviour at especially physiological temperatures, it is feasible to design the non-radiative transition rate, $k_{nr}(0)$, such that it matches condition (29). With a temperatures T_{probe} well below physiological temperatures such as $T_{probe} = 150$ K to safely ensure a Boltzmann behaviour at physiological temperatures, the non-radiative transition rate should be in the order of $10^6 - 10^7$ s⁻¹ for lanthanides. Thus, the two thermally coupled excited states should best be coupled by an electric dipole-allowed non-radiative transition. Finally, the two excited levels should be well isolated in order to avoid spoiling quenching pathways to lower excited levels or also thermalization into higher excited levels. This also typically imposes to keep the host phonon energy small such that fluorides may be a good option due to their air stability and processability in nanocrystalline form.

2.3.4. Suggestions for trivalent lanthanide ions operating as single ion thermometers for *in vivo* applications

For the trivalent lanthanides, two basic practical options are possible for that purpose within a singleion thermometer. The simplest approach consists in an excitation in biological window I and detection of two emission transitions in biological windows II and III, which fulfil the previous guidelines. The only trivalent lanthanide ions with directly excitable electronic levels in biological windows I or II would be **Pr**³⁺ (${}^{3}F_{3} - {}^{3}F_{4}$, $\Delta E \approx 450$ cm⁻¹), **Nd**³⁺ (${}^{4}F_{3/2} - {}^{4}F_{5/2}$, $\Delta E \approx 1000$ cm⁻¹), **Dy**³⁺ (${}^{6}F_{5/2} - {}^{6}F_{3/2,1/2}$, $\Delta E \approx 750$ cm⁻¹) and **Tm**³⁺ (${}^{3}F_{3} - {}^{3}F_{2}$, $\Delta E \approx 650$ cm⁻¹). The basic energy level schemes are depicted in **Figure 4**. Except of Nd³⁺, there is also an additional electronic level around 1500 – 2000 cm⁻¹ below the indicated electronic levels present in each of the mentioned lanthanide ions that could act as potential quenching level by multi-phonon relaxation. For that reason, a low-phonon host such as a fluoride is mandatory. In addition, nanostructures of these compounds will have to be shelled in order to avoid quenching by surface ligands with higher energy vibrations. The phonon number *p* for these hosts is then in the range of *p* = 1 – 2. Finally, all the non-radiative transitions between the mentioned electronic levels obey the selection rules $\Delta L = \Delta S = 0$, $\Delta J = \pm 1$ and thus have a





Figure 4. Promising lanthanide ions and their corresponding energy gaps of interest for both excitation and single ion luminescence thermometry within the biological windows. For details concerning each lanthanide ion, see text.

strong magnetic dipole-allowed character with almost zero electric-dipole allowed character according to the reduced matrix elements. An experimental verification of this theoretical prediction is also currently on-going and will be incorporated in a future report.

The other strategy consists of usage of an energy transfer upconversion (ETU) process with a sensitizer excitable in the NIR range and detection of the emission of higher excited levels with the previously described characteristics for optimum Boltzmann thermometry. A strongly absorbing and emitting sensitizer for this purpose is Yb³⁺ (4f¹³, λ_{abs} = 940 – 1000 nm). Desirably, any other lanthanide ion to be used for single-ion thermometry should neither emit nor absorb strongly in that region in order to avoid any overlapping transitions that limit the accuracy of temperature measurement. For that purpose, especially Pr^{3+} (${}^{3}P_{0} - {}^{3}P_{1}$, ${}^{1}I_{6}$, $\Delta E \approx 500$ cm⁻¹), Nd^{3+} (${}^{4}G_{7/2} - {}^{4}G_{9/2}$, $\Delta E \approx 450$ cm⁻¹) or Er^{3+} $({}^{4}S_{3/2} - {}^{2}H_{11/2}, \Delta E = 700 \text{ cm}^{-1})$ are suited as they also show appreciable emission branching ratios to higher ground states in fluorides. Transitions to higher ground states are necessary to match the desired emission wavelengths in the biological windows for *in vivo* imaging. Along the series of the suggested lanthanide ions sensitized by Yb³⁺, Er³⁺ is particularly promising due to its energy difference and the electric dipole-allowed nature of the non-radiative transition between the ${}^{2}H_{11/2}$ and ⁴S_{3/2} level. Moreover, the Er³⁺-Yb³⁺ couple is a *de facto* standard in the field of photoluminescence upconversion when doped in hexagonal β -NaYF₄ [34] and has even been proven to work efficiently for luminescence thermometry [35]. Another promising compound that even supersedes the upconversion efficiency of β -NaYF₄ is the compound KYb_{1.98}Er_{0.02}F₇, in which energy clustering takes place [36]. Both fluorides are also easily shelled, and their synthesis optimized for monodisperse nanocrystals.



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Figure 5. Promising lanthanide ions and their corresponding energy gaps of interest accessible via ETU with Yb³⁺ as a NIR sensitizer and single ion luminescence thermometry of the acceptors within the biological windows. For details concerning each lanthanide ion, see text.

2.4. Experimental evidence of energy transfer model predictions for single ion thermometers

2.4.1. Nd³⁺: ${}^{4}F_{5/2} - {}^{4}F_{3/2}$ gap for *in vivo* thermometry

The Vinča institute (VINCA) sent nanocrystalline powders of La_{1-x}Nd_xPO₄ (x = 0.02, 0.05, 0.10, 0.25, 1.00) and also LiLa_{1-x}Nd_x(PO₃)₄ (x = 0.02, 0.05, 0.10, 0.25, 0.50, 1.00) to UU for characterization, photoluminescence and also luminescence thermometry in the biological windows. Most of the results on the synthesis and characterization are already presented in the corresponding reports on the deliverables D1.1 and D1.3 and the reader is referred to those reports for an overview of their structural and optical properties. Within this report, we will focus on the thermometry results of the 2 mol%-activated nanopowders as they can be best approximated as single ion luminescent thermometers and the energy transfer between non-radiative transition dipole moments and phonons can be investigated.

Both phosphate-based host compounds have a cut-off phonon energy of around 1100 cm⁻¹ and thus, only p = 1 phonon is sufficient to bridge the energy gap between the ${}^{4}F_{3/2}$ and ${}^{4}F_{5/2}$ levels of Nd³⁺ ($\Delta E = 1000 \text{ cm}^{-1}$). Nd³⁺ is a very attractive lanthanide ion for the purpose of *in vivo* thermometry because all its strong emission transitions ${}^{4}F_{3/2, 5/2} \rightarrow {}^{4}I_{J}$ (J = 9/2, 11/2, 13/2) are located in the







Figure 6. (a) Simulation of temperature dependent intensity ratios for Nd³⁺ according to eq. (25) assuming a non-radiative magnetic dipole-allowed transition ($k_{nr}(0) = 1 \cdot 10^4 \text{ s}^{-1}$). Different values for p were tested. **(b)** Selected temperature-dependent luminescence spectra in biological window I for La_{0.98}Nd_{0.02}PO₄ nanocrystals indicating the successive thermal population of the higher-lying ${}^{4}F_{5/2}$ level. **(c)** Boltzmann-type plot of the intensity ratio of the ${}^{4}F_{5/2} \rightarrow {}^{4}I_{9/2}$ and ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ emission transitions versus reciprocal temperature. Note the similarity of the evolution of data points (black) with the simulated curve for p = 1. The fitting curve is indicated in red. The Boltzmann behavior only emerges above around 400 K.

biological windows I and II of the NIR spectral range. In contrast, however, according to the previous details of our established model, the energy gap is already so large that the absolute thermal response is rather low (P(n) = 0.386, see eq. (6)). Moreover, the non-radiative transition ${}^{4}F_{5/2} \leftrightarrow {}^{4}F_{3/2}$ has an appreciable magnetic dipole contribution as $(\frac{1}{\hbar} \langle || L + g_s S || \rangle)^2 = 9.645$ [27],[28]. In contrast, the corresponding electric dipole-based reduced matrix elements are comparingly lower (($\langle || U^{(2)} || \rangle$)² = 0.0795, ($\langle || U^{(4)} || \rangle$)² = 0.0523, ($\langle || U^{(6)} || \rangle$)² = 0) [27],[28], which means that the non-radiative transition rate should be highly reduced and the impact of the radiative decay rates according to model (25) becomes significant instead. In fact, both in La_{0.98}Nd_{0.02}PO₄ and LiLa_{0.98}Nd_{0.02}(PO₃)₄, the experimentally gathered thermometric data in biological window I compared to simulations assuming a strong non-radiative magnetic dipole-type transitions clearly indicate the validity of this interpretation. Figure 6 exemplarily depicts the similarity between theoretical predictions and experimental results for LaPO₄: 2% Nd³⁺ (also to be found in the report on deliverable D1.3). In

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particular, the results also show that even with a host compound with higher energetic phonons, Nd³⁺ only allows for Boltzmann thermometry above around 100 °C (373 K). Thus, despite the suitable emission wavelengths, the ${}^{4}F_{5/2} - {}^{4}F_{3/2}$ gap is not applicable for single ion thermometry in the physiological temperature regime. Other techniques such as a two-ion thermometry with another lanthanide ion might be more promising. Also, the effect of cross relaxation will have to be investigated in more detail to additionally extend the Boltzmann regime even over the physiological temperature regime. Finally, the possibility for *in vivo* thermometry with the ${}^{4}G_{7/2} - {}^{4}G_{5/2}$ gap will have to be investigated. Due to the validity of the intermediate coupling scheme for trivalent lanthanides, a non-radiative transition within that gap has a stronger electric dipole character, which would be beneficial for its thermometry performance.

2.4.2. Tm³⁺: ${}^{3}F_{2} - {}^{3}F_{3}$ gap for *in vivo* thermometry

The ${}^{3}H_{6} \rightarrow {}^{3}F_{3}$ absorption transition at 690 nm has a high cross section and would allow for intense ${}^{3}F_{2,3} \rightarrow {}^{3}F_{4}$ emission transitions between 1050 nm to 1150 nm in biological window II. The most problematic issue with Tm³⁺ is the lower lying ${}^{3}H_{4}$ level separated by around 1600 cm⁻¹. Although fluorides have sufficiently low phonon energies to diminish that non-radiative relaxation pathway, the radiative decay times of both the ${}^{3}F_{2}$ and ${}^{3}F_{3}$ are very long (~ 1 ms) as deduced by a very accurate Judd-Ofelt calculation by Walsh *et al.* in LiYF₄ [37]. Due to this peculiarity of the electronic structure of Tm³⁺, non-radiative relaxation to the ${}^{3}H_{4}$ level is still efficient even in hosts with phonon energies as low as in fluorides. This feature has been also been verified at UU in microcrystalline β -NaGdF₄: 0.5% Tm³⁺ and no emission from the ${}^{3}F_{2}$ and ${}^{3}F_{3}$ levels could be observed. Thus, although quite suited for single-ion Boltzmann thermometry, the specialties in the electronic structure of Tm³⁺ finally do not make it readily suited for *in vivo* single ion thermometry.

2.4.3. $Pr^{3+}: {}^{3}P_{0} - {}^{3}P_{1}, {}^{1}I_{6}$ gap for *in vivo* thermometry

The initially proposed ${}^{3}F_{3} - {}^{3}F_{4}$ gap of Pr^{3+} already lies deep in the NIR range with absorption wavelengths from the ${}^{3}H_{4}$ ground level at around 1450 nm – 1500 nm. In turn, any other emission transition with appreciable shift is located in ranges where the photomultiplier tube becomes very inefficient (${}^{3}F_{3,4} \rightarrow {}^{3}H_{5}$ transition: $\lambda_{em} > 1900$ nm). Thus, the next obvious choice, which has also been already investigated even in β -NaYF₄:Pr³⁺ nanocrystals in the visible range [38], is single ion thermometry with the ${}^{3}P_{0} - {}^{3}P_{1}$, ${}^{1}I_{6}$ gap. Unfortunately, direct absorption with Pr^{3+} as a single ion requires excitation from the ³H₄ ground level to the ³P₂ level at 440 nm – 450 nm in the blue range. Nonetheless, the ${}^{3}P_{1}$, ${}^{1}I_{6} \rightarrow {}^{1}G_{4}$ or ${}^{3}P_{0} \rightarrow {}^{1}G_{4}$ emission transitions are located between 850 nm to 920 nm in biological window I. These emission transitions have most appreciable intensities if the host provides a large Judd-Ofelt parameter Ω_4 . The UU demonstrated the working principle both in LaF₃: 0.5% Pr³⁺ (strong Ω_6 host compound, see Figure 7.(a)) and an even more accurate performance in β -NaLaF₄: 0.1% Pr³⁺ (strong Ω_4 host compound, see Figure 7.(b)). In the special case of Pr³⁺, the doping concentrations should be kept low because of the strong liability towards the cross-relaxation process [Pr1, Pr2]: $[{}^{3}P_{0}, {}^{3}H_{4}] \rightarrow [{}^{1}G_{4}, {}^{1}G_{4}]$. Finally, the non-radiative transition between the ${}^{3}P_{0}$ and ${}^{3}P_{1}$ levels also has a slight magnetic dipole contribution $\left(\left(\frac{1}{\hbar}\langle \|\boldsymbol{L} + g_s\boldsymbol{S}\|\rangle\right)^2 = 1.994\right)$ [27],[28], while the transition between the ${}^{3}P_{0}$ and both the ${}^{3}P_{1}$ and ${}^{1}I_{6}$ level has essentially no electric dipole contribution. Future studies will focus on an energy transfer upconversion process including Yb³⁺ in order to excite Pr^{3+} into the ${}^{3}P_{0}$ level by means of two ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transitions with an energy of around 10200 cm⁻¹



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Figure 7. Temperature-dependent photoluminescence spectra of (a) LaF₃: 0.5% Pr³⁺ and (b) β -NaLaF₄: 0.1% Pr³⁺ microcrystals in the NIR range depicting the ³P₁, ¹I₆ \rightarrow ¹G₄ and ³P₀ \rightarrow ¹G₄ emission transitions. (b) and (d) depict the respective Boltzmann plots of the intensity ratio of the two emission transitions.

each. One possible disadvantage is the partial overlap between the ${}^{3}P_{1}$, ${}^{1}I_{6} \rightarrow {}^{1}G_{4}$ or ${}^{3}P_{0} \rightarrow {}^{1}G_{4}$ emission transitions with the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ emission transition of Yb³⁺.

2.4.4. $Er^{3+}: {}^{4}S_{3/2} - {}^{2}H_{11/2}$ gap for *in vivo* thermometry

Single ion luminescence nanothermometry with the ${}^{4}S_{3/2} - {}^{2}H_{11/2}$ gap of Er^{3+} excited by energy transfer upconversion from Yb³⁺ has been proven to work with the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ emission transitions between 500 nm and 570 nm in catalysis applications [35],[39],[40]. Due to the electric dipole nature of the non-radiative transition between the ${}^{2}H_{11/2}$ and ${}^{4}S_{3/2}$ level, the Boltzmann distribution as temperature calibration law is valid over a wide temperature range (~ 200 K to 700 K). Moreover, the energy gap of around 715 cm⁻¹ is perfectly suited to match the optimum conditions for a single ion luminescent thermometer operating in the physiological temperature range. A proof of principle for an operation in biological window I has at least been reported in a barium – strontium niobate glass ceramic by means of the ${}^{2}H_{11/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{13/2}$ transition between 775 nm and 900 nm [41]. Future works on fluorides will be conducted to additionally strengthen the idea. Emission



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transitions to higher ${}^{4}I_{J}$ (J = 11/2, 9/2) levels located in the biological window II are also possible, but typically have very low branching ratios ($\beta_{ij} \sim 2\% - 3\%$) only [42].



3. General conclusions and perspectives/future works

3.1. Conclusions

Single ion luminescent (nano)thermometers were thoroughly theoretically characterized within this deliverable. The optimum conditions for a sensitive luminescent thermometer with a Boltzmann equilibrium as the underlying operation principle were derived. It turns out that the maximum absolute response of a Boltzmann thermometer supposed to detect a temperature T_0 is achieved for an energy gap of $\Delta E = 2k_B T_0$. However, deviations from this optimum condition are possible without appreciable loss in thermal response of the thermometer. Next to the thermal response, the relative thermal sensitivity S_r is an important figure of merit for a luminescent thermometer. It was shown that Boltzmann thermometers show very high relative sensitivities at cryogenic temperatures, but only achieve relative sensitivities in the range of $1\% \cdot K^{-1}$ at physiological temperatures when combined with a demand for high thermal response. It could also be shown that single ion Boltzmann thermometers become ineffective above around 420 K. In the context of *nanoTBTech*, the most suitable energy difference to provide a compromise between high thermal response and relative thermal sensitivity $S_r > 1\% \cdot K^{-1}$ would be in the range of 670 cm^{-1} to 720 cm^{-1} . All previous results are generally applicable to any single ion luminescent thermometer operating with a Boltzmann distribution, irrespective of the type of transitions employed.

In addition to these general properties of the Boltzmann distribution, also potential linearization schemes typically encountered in *in vivo* thermometry were carefully evaluated. The relative errors connected to this linearization were calculated and discussed. It was also shown that thermometry with Stark levels of the lanthanides may even be better performed in that way since it is more robust towards measured intensity uncertainties compared to the Boltzmann-type calibration then. The benchmark criterion for a decision between Boltzmann-type and linear calibration is simply given by the relative size between the probed energy gap ΔE and the detected thermal energy $k_{\rm B}T_0$. If $\Delta E < k_{\rm B}T_0$, a linearization is even favourable over a Boltzmann-type calibration. Together with the desire for a high relative thermal sensitivity S_r , this technique is only feasible for cryogenic temperature measurements.

Finally, the microscopic mechanism governing the validity range of the Boltzmann distribution was investigated by means of an established general excited state dynamical model of the two thermally coupled excited states. The non-radiative transitions can be very accurately modelled and interpreted by means of a Förster-type energy transfer between the non-radiative transition dipole moment and a vibrational fundamental or overtone. While it is intuitively clear how an electric non-radiative transition dipole moment couples to a vibrational mode, we also gave an interpretation for the coupling of a corresponding magnetic dipole moment by means of classical electrodynamics. It has also been indicated that electric dipole-allowed non-radiative transitions give rise to higher transition rates.

The presented excited state dynamical model is predominantly applicable to intraconfigurational transitions such as the $4f^n \leftrightarrow 4f^n$ transitions of the lanthanide ions in its current form. Nonetheless, some very general guidelines for the design and tuning of the non-radiative transitions can be given. Most importantly, the phonon energy of the host compound should be chosen such that only 1 to 2 phonons are required to bridge the energy gap between the two thermally excited states. Especially



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fluorides are suited for that purpose. Next to that, the non-radiative transition should best have an appreciable electric dipole-allowed character to make it dominant compared to the radiative decay rates. In contrast, most of the thermometrically interesting excited levels of the lanthanides matching the optimum performance conditions for a Boltzmann distribution rather have a strong magnetic dipole character. Several of the predicted lanthanide ions have already been tested and validated or refused for practical *in vivo* thermometry. While Tm^{3+} will not work due to intrinsic electronic features despite the matching boundary conditions for optimum thermometry, Pr^{3+} has already been shown to work in principle as a single ion luminescent thermometer operating in biological window I. Nd³⁺ can operate in biological windows I and II, but the large energy gap between the $^{4}F_{5/2}$ and $^{4}F_{3/2}$ excited levels together with the strong magnetic dipole-type non-radiative transition does not make Nd³⁺ sensitive as a single ion thermometer within the physiological temperature range and, in fact, does already lead to a failure of the Boltzmann equilibrium in that range. Especially Dy³⁺ and Er³⁺ are still promising, however, and will have to be tested for this purpose still.

3.2. Perspectives and future works

Although the single ion luminescence thermometry model provides very extensive conclusions and guidelines, two important generalizations are necessary to yet achieve higher thermal sensitivities and more flexibility in the choice of luminescent thermometers. As has already been indicated throughout this report, single ion thermometers operating in the physiological temperature range are always limited in their relative thermal sensitivity intrinsically. One possibility to extend the energy transfer model is to use two ions and a phonon instead of only one ion. An artificially created energy gap between two excited states of two separate ions changes the mechanism as now the energy transfer is predominantly governed by the coupling of the transition dipole moments of the slightly off-resonant transitions. A thermally excited back energy transfer to the ion with the slightly higher excited level gives rise to a similarly operating luminescent thermometer with higher relative thermal sensitivities. The insights from the current energy transfer model will be useful to extend the model to two ions. Moreover, it is aimed to give an optimized range for an additional parameter then: the dopant concentration.

The other possibility consists in the consideration of a different type of non-radiative transition also allowing for an offset of the electronic states within the configurational coordinate space. Then, the Franck-Condon selection rule (14) does not apply anymore and non-radiative transitions are described by a crossover mechanism (as established by, e.g. Struck and Fonger [43]) instead, which leads to a quenching of a broad-band emission transition such as in many transition metal ions. The main challenge for this mechanism is, however, to find a potential candidate for intense broad-band emission in the biological windows. In addition, also the effect of a third excited level is interesting to be investigated as these levels can also lead to deviations from the simple Boltzmann distribution.

Finally, also the other deliverables are continued to be worked on. Besides the optimization of luminescent thermometers, it is also important to consider heat and light propagation theoretically. While light propagation and attenuation is relevant to properly account for a final temperature accuracy, knowledge on heat propagation is important to account for a two-dimensional spatial resolution within the body. This addresses the question about the temperature sensing accuracy of a luminescent thermometer at a certain small distance from its position. Those aspects are of uttermost



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importance for thermal bioimaging with aid of luminescent thermometers. Thus, theoretical models describing these effects will also be developed in future. Apart from that, also manuscripts and close collaboration with the other partners of the consortium will be continued.



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References

- 1 Brites, C.D.S., Lima, P.P., Silva, N.J.O., Millán, A., Amaral, V.S., Palacio, F., Carlos, L.D. (2012) Thermometry at the nanoscale. *Nanoscale*, **4** (16), 4799–4829.
- 2 Jaque, D. and Vetrone, F. (2012) Luminescence nanothermometry. *Nanoscale*, **4** (15), 4301–4326.
- del Rosal, B., Ximendes, E., Rocha, U., Jaque, D. (2017) In Vivo Luminescence Nanothermometry: from Materials to Applications. *Adv. Opt. Mater.*, **5** (1), 1600508.
- 4 Brites, C.D.S., Balabhadra, S., Carlos, L.D. (2019) Lanthanide-Based Thermometers: At the Cutting-Edge of Luminescence Thermometry. *Adv. Opt. Mater.*, **7** (5), 1801239.
- 5 Wade, S.A., Collins, S.F., Baxter, G.W. (2003) Fluorescence intensity ratio technique for optical fiber point temperature sensing. *J. Appl. Phys.*, **94** (8), 4743–4756.
- 6 Rocha, U., Jacinto da Silva, C., Ferreira Silva, W., Guedes, I., Benayas, A., Martínez Maestro, L., Acosta Elias, M., Bovero, E., van Veggel, F.C.J.M., García Solé, J.A., Jaque, D. (2013) Subtissue thermal sensing based on neodymium-doped LaF₃ nanoparticles. *ACS Nano*, **7** (2), 1188–1199.
- 7 Rocha, U., Jacinto, C., Kumar, K.U., López, F.J., Bravo, D., Solé, J.G., Jaque, D. (2016) Real-time deep-tissue thermal sensing with sub-degree resolution by thermally improved Nd³⁺:LaF₃ multifunctional nanoparticles. *J. Lumin.*, **175**, 149–157.
- Ximendes, E.C., Santos, W.Q., Rocha, U., Kagola, U.K., Sanz-Rodríguez, F., Fernández, N., Gouveia-Neto, A.d.S., Bravo, D., Domingo, A.M., del Rosal, B., Brites, C.D.S., Carlos, L.D., Jaque, D., Jacinto, C. (2016) Unveiling in Vivo Subcutaneous Thermal Dynamics by Infrared Luminescent Nanothermometers. *Nano Lett.*, **16** (3), 1695–1703.
- 9 Ximendes, E.C., Rocha, U., del Rosal, B., Vaquero, A., Sanz-Rodríguez, F., Monge, L., Ren, F., Vetrone, F., Ma, D., García-Solé, J., Jacinto, C., Jaque, D., Fernández, N. (2017) In Vivo Ischemia Detection by Luminescent Nanothermometers. *Adv. Healthc. Mater.*, **6** (4), 1601195.
- 10 Ximendes, E.C., Rocha, U., Sales, T.O., Fernández, N., Sanz-Rodríguez, F., Martín, I.R., Jacinto, C., Jaque, D. (2017) In Vivo Subcutaneous Thermal Video Recording by Supersensitive Infrared Nanothermometers. *Adv. Funct. Mater.*, **27** (38), 1702249.
- 11 Ximendes, E.C., Pereira, A.F., Rocha, U., Silva, W.F., Jaque, D., Jacinto, C. (2019) Thulium doped LaF₃ for nanothermometry operating over 1000 nm. *Nanoscale*, **11** (18), 8864–8869.
- 12 Riseberg, L.A. and Moos, H.W. (1967) Multiphonon Orbit-Lattice Relaxation in LaBr₃, LaCl₃, and LaF₃. *Phys. Rev. Lett.*, **19** (25), 1423–1426.
- 13 Riseberg, L.A. and Moos, H.W. (1968) Multiphonon Orbit-Lattice Relaxation of Excited States of Rare-Earth Ions in Crystals. *Phys. Rev.*, **174** (2), 429-438.



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	D3.1 (D15) – First Version (V1)	Date	22/08/2019

- Moos, H.W. (1970) Spectroscopic Relaxation Processes of Rare Earth Ions in Crystals. *J. Lumin.*, 1,2, 106–121.
- 15 van Dijk, J.M.F. and Schuurmans, M.F.H. (1983) On the nonradiative and radiative decay rates and a modified exponential energy gap law for 4 f –4 f transitions in rare-earth ions. *J. Chem. Phys.*, **78** (9), 5317–5323.
- Pukhov, K.K. and Sakun, V.P. (1979) Theory of Nonradiative Multiphonon Transitions in Impurity Centers with Extremely Weak Electron-Phonon Coupling. *phys. stat. sol. (b)*, **95** (2), 391–402.
- 17 Orlovskii, Y.V., Reeves, R.J., Powell, R.C., Basiev, T.T., Pukhov, K.K. (1994) Multiple-phonon nonradiative relaxation: Experimental rates in fluoride crystals doped with Er³⁺ and Nd³⁺ ions and a theoretical model. *Phys. Rev. B*, **49** (6), 3821–3830.
- 18 Pukhov, K.K. (2008) Nonlinear theory of multiphonon relaxation of excited rare-earth ions in laser crystals. *Phys. Solid State*, **50** (9), 1597–1604.
- 19 Egorov, S.A. and Skinner, J.L. (1995) On the theory of multiphonon relaxation rates in solids. *J. Chem. Phys.*, **103** (4), 1533–1543.
- 20 Egorov, S.A. and Skinner, J.L. (1996) An improved theory of multiphonon relaxation in solids. *J. Chem. Phys.*, **105** (22), 10153–10155.
- 21 Ermolaev, V.L. and Sveshnikova, E.B. (1979) Non-radiative transitions as Förster's Energy Transfer to Solvent Vibrations. *J. Lumin.*, **20** (4), 387-395.
- 22 Sveshnikova, E.B. and Ermolaev, V.L. (2011) Inductive-Resonant Theory of Nonradiative Transitions in Lanthanide and Transition Metal Ions (review). *Opt. Spectrosc.*, **111** (1), 34–50.
- Aharoni, A., Oron, D., Banin, U., Rabani, E., Jortner, J. (2008) Long-range electronic-to-vibrational energy transfer from nanocrystals to their surrounding matrix environment. *Phys. Rev. Lett.*, **100** (5), 57404.
- Rabouw, F.T., Prins, P.T., Villanueva-Delgado, P., Castelijns, M., Geitenbeek, R.G., Meijerink, A.
 (2018) Quenching Pathways in NaYF₄:Er³⁺,Yb³⁺ Upconversion Nanocrystals. *ACS Nano*, **12** (5), 4812–4823.
- 25 Latt, S.A., Cheung, H.T., Blout, E.R. (1965) Energy Transfer. A System with Relatively Fixed Donor-Acceptor Separation. *J. Am. Chem. Soc.*, **87** (5), 995–1003.
- 26 Arppe, R., Hyppänen, I., Perälä, N., Peltomaa, R., Kaiser, M., Würth, C., Christ, S., Resch-Genger, U., Schäferling, M., Soukka, T. (2015) Quenching of the upconversion luminescence of NaYF₄:Yb³⁺,Er³⁺ and NaYF₄:Yb³⁺,Tm³⁺ nanophosphors by water: the role of the sensitizer Yb³⁺ in non-radiative relaxation. *Nanoscale*, **7** (27), 11746–11757.



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- 27 Carnall, W.T., Goodman, G.L., Rajnak, K., Rana, R.S. (1989) A systematic analysis of the spectra of the lanthanides doped into single crystal LaF₃. *J. Chem. Phys.*, **90** (7), 3443–3457.
- 28 Hehlen, M.P., Brik, M.G., Krämer, K.W. (2013) 50th anniversary of the Judd–Ofelt theory: An experimentalist's view of the formalism and its application. *J. Lumin.*, **136**, 221–239.
- 29 Tsuboi, T., McClure, D.S., Wong, W.C. (1993) Luminescence kinetics of Yb²⁺ in NaCl. *Phys. Rev. B*, 48 (1), 62–67.
- 30 Bartelmann, M., Feuerbacher, B., Krüger, T., Lüst, D., Rebhan, A., Wipf, A. (2018) *Theoretische Physik 2: Elektrodynamik*, 2nd edn, Springer Spektrum, Berlin.
- 31 Chua, M., Tanner, P.A., Reid, M.F. (1994) Energy Transfer by Electric Dipole-Magnetic Dipole Interaction in Cubic Crystals. *Solid State Commun.*, **90** (9), 581–583.
- 32 Dexter, D.L. (1953) A Theory of Sensitized Luminescence in Solids. *J. Chem. Phys.*, **21** (5), 836–850.
- 33 Geitenbeek, R.G., Wijn, H.W. de, Meijerink, A. (2018) Non-Boltzmann Luminescence in NaYF₄:Eu³⁺: Implications for Luminescence Thermometry. *Phys. Rev. Applied*, **10** (6), 64006.
- 34 Krämer, K.W., Biner, D., Frei, G., Güdel, H.U., Hehlen, M.P., Lüthi, S.R. (2004) Hexagonal Sodium Yttrium Fluoride Based Green and Blue Emitting Upconversion Phosphors. *Chem. Mater.*, **16** (7), 1244–1251.
- Geitenbeek, R.G., Prins, P.T., Albrecht, W., van Blaaderen, A., Weckhuysen, B.M., Meijerink, A. (2017) NaYF₄:Er³⁺,Yb³⁺/SiO₂ Core/Shell Upconverting Nanocrystals for Luminescence Thermometry up to 900 K. *J. Phys. Chem. C*, **121** (6), 3503–3510.
- 36 Wang, J., Deng, R., MacDonald, M.A., Chen, B., Yuan, J., Wang, F., Chi, D., Hor, T.S.A., Zhang, P., Liu, G., Han, Y., Liu, X. (2014) Enhancing multiphoton upconversion through energy clustering at sublattice level. *Nat. Mater.*, **13**, 157–162.
- Walsh, B.M., Barnes, N.P., Di Bartolo, B. (1998) Branching ratios, cross sections, and radiative lifetimes of rare earth ions in solids: Application to Tm³⁺ and Ho³⁺ ions in LiYF₄. *J. Appl. Phys.*, 83 (5), 2772–2787.
- 38 Zhou, S., Jiang, G., Wei, X., Duan, C., Chen, Y., Yin, M. (2014) Pr³⁺-doped β-NaYF₄ for temperature sensing with fluorescence intensity ratio technique. *J. Nanosci. Nanotechnol.*, **14** (5), 3739–3742.
- 39 Geitenbeek, R.G., Nieuwelink, A.-E., Jacobs, T.S., Salzmann, B.B.V., Goetze, J., Meijerink, A., Weckhuysen, B.M. (2018) In Situ Luminescence Thermometry To Locally Measure Temperature Gradients during Catalytic Reactions. *ACS Catal.*, 8 (3), 2397–2401.
- 40 Geitenbeek, R.G., Salzmann, B.B.V., Nieuwelink, A.-E., Meijerink, A., Weckhuysen, B.M. (2019) Chemically and thermally stable lanthanide-doped Y₂O₃ nanoparticles for remote temperature sensing in catalytic environments. *Chem. Eng. Sci.*, **198**, 235–240.



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- 41 Haro-González, P., Martín, I.R., Martín, L.L., León-Luis, S.F., Pérez-Rodríguez, C., Lavín, V. (2011) Characterization of Er³⁺ and Nd³⁺ doped Strontium Barium Niobate glass ceramic as temperature sensors. *Opt. Mater.*, **33** (5), 742–745.
- 42 Villanueva-Delgado, P. W., Biner, D., Krämer, K. W. (2017) Judd-Ofelt analysis of β-NaGdF₄: Yb³⁺, Tm³⁺ and β-NaGdF₄: Er³⁺ single crystals *J. Lumin.* **189**, 84-90.
- 43 Struck, C.W. and Fonger, W.H. (1975) Unified model of the temperature quenching of narrowline and broad-band emissions. *J. Lumin.*, **10** (1), 1–30.

