



Utrecht University

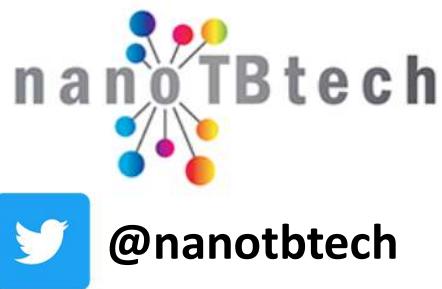
CONDENSED MATTER AND INTERFACES, DEBYE INSTITUTE FOR NANOMATERIALS SCIENCE
PROF. DR. ANDRIES MEIJERINK

11.12.2020

The theoretical guidelines for optimized thermometry

An interplay between thermodynamics and kinetics for targeted design

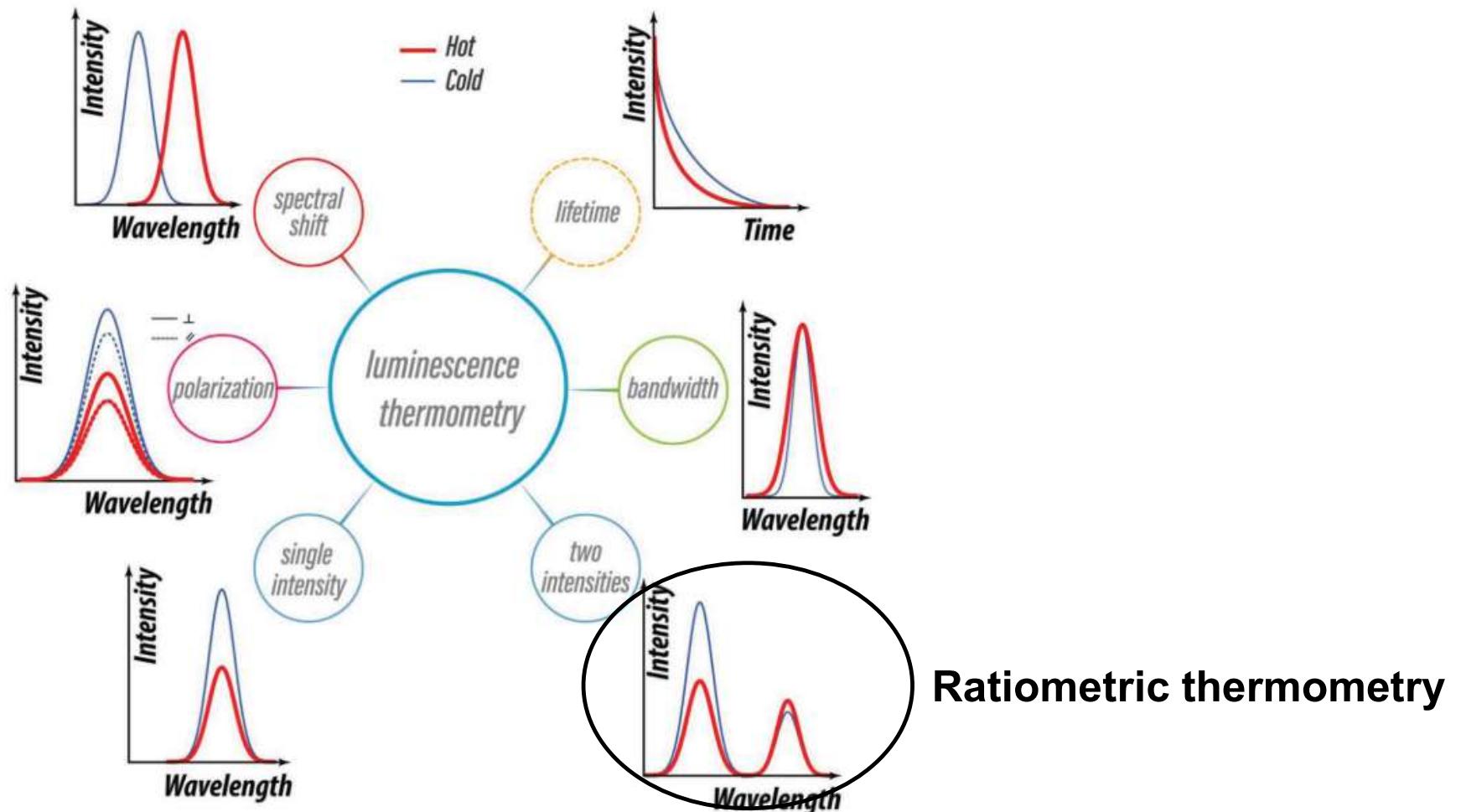
Markus Suta, Andries Meijerink



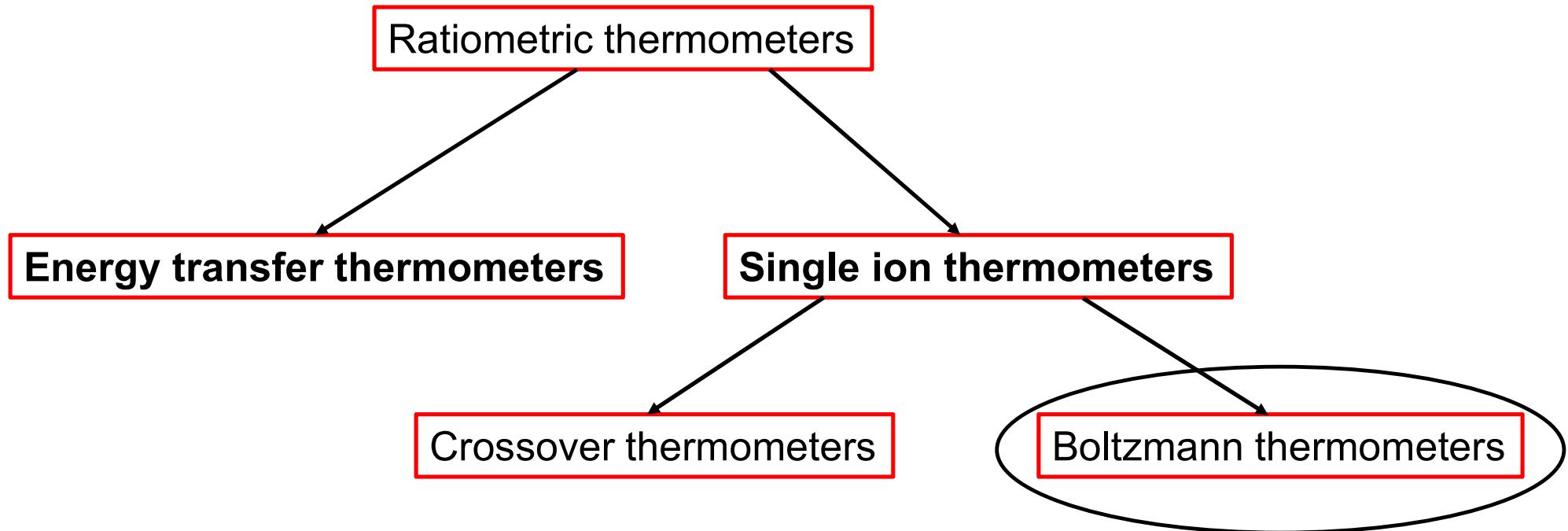
NanoTBTech webinar series
11.12.2020



The various possibilities of luminescence thermometry

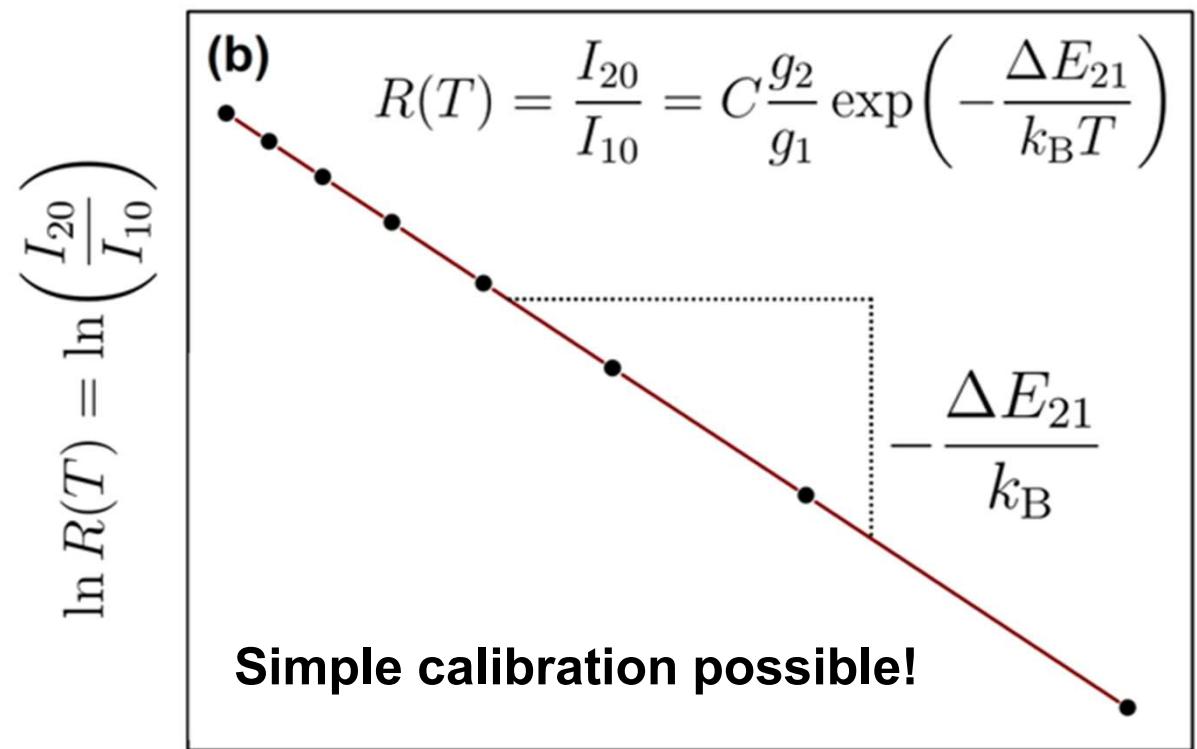
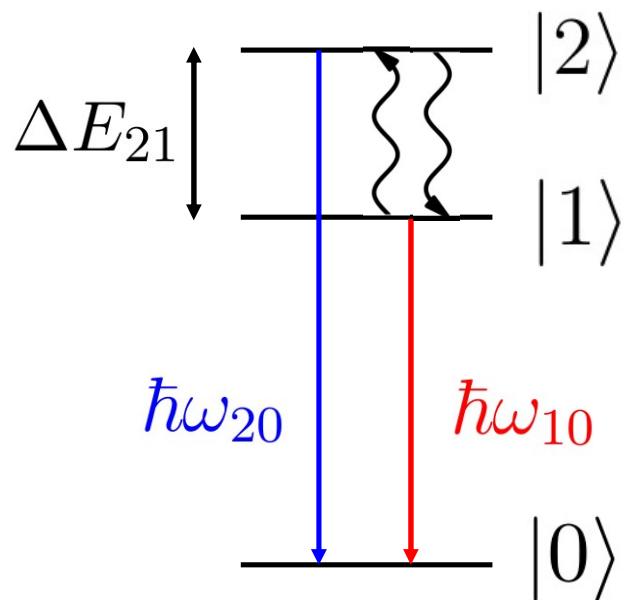


Systematics of ratiometric luminescence thermometers



Single ion (Boltzmann) luminescence thermometry

Concept of **Boltzmann thermometry**: Use thermal equilibrium between two emissive states in a non-interacting ensemble of ions



Trivalent lanthanides ideal for this concept!

A remark on the definition of the electronic constant C

Very often, one finds the following definition in literature:

$$C \frac{g_2}{g_1} = \frac{g_2}{g_1} \frac{A_{20}\omega_{20}}{A_{10}\omega_{10}}$$

Careful: This is only valid if intensities are measured as *power densities* (in W m^{-2})! If you do *single photon counting detection* (as is usual today), it is:

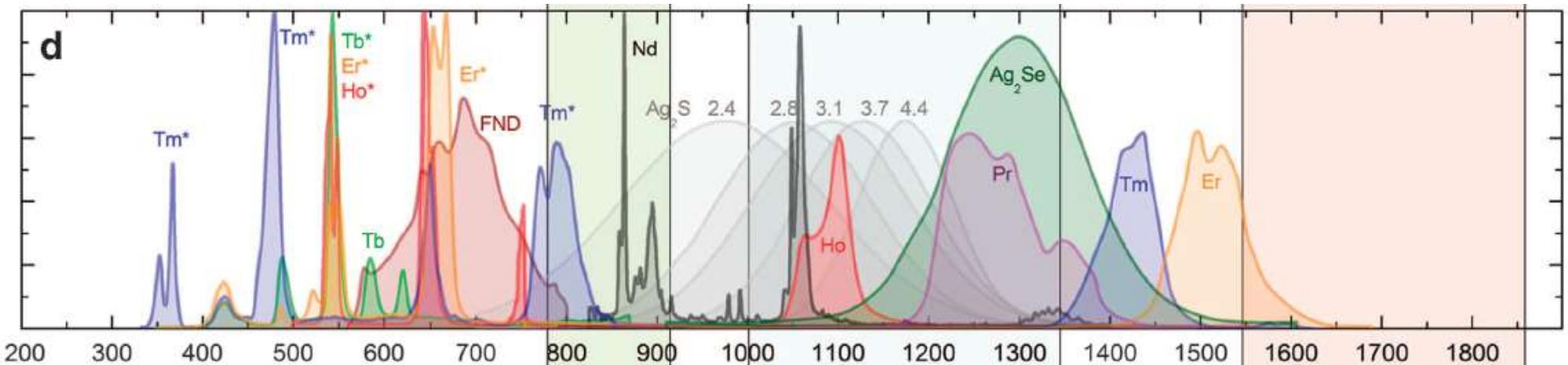
$$C \frac{g_2}{g_1} = \frac{g_2}{g_1} \frac{A_{20}\cancel{\omega_{20}}}{\cancel{A_{10}\omega_{10}}}$$



$$C \frac{g_2}{g_1} = \frac{g_2}{g_1} \frac{A_{20}}{A_{10}}$$

But: Usually, the error in accidentally leaving the emission energies is very small as they are mostly very similar ($\omega_{10} \approx \omega_{20}$). However, be aware of this issue!!

Seemingly endless choices for luminescence thermometry?



Reviews on thermometry:

E. Hemmer, A. Benayas, F. Légaré, F. Vetrone, *Nanoscale Horiz.* **2016**, *1*, 168 – 184.
T.-M. Liu, J. Conde, T. Lipiński, A. Bednarkiewicz, C.-C. Huang, *NPG Asia Mater.* **2016**, *8*, e295.

D. Jaque, F. Vetrone, *Nanoscale* **2012**, *4*, 4301-4326.

C. S. Brites, A. Millán, F. Palacio, L. D. Carlos et al., *Nanoscale* **2012**, *4*, 4799-4829.

L. Marciniak, A. Bednarkiewicz, D. Kowalska, W. Strek, *J. Mater. Chem. C* **2016**, *4*, 5559-5563.

M. D. Dramićanin, *Meth. Appl. Fluoresc.* **2016**, *4*, 042001.

B. del Rosal, E. Ximenes, U. Rocha, D. Jaque, *Adv. Opt. Mater.* **2017**, *5*, 1600508.

C. S. D. Brites, S. Balabhadra, L. D. Carlos, *Adv. Opt. Mater.* **2019**, *7*, 1801239.

M. D. Dramićanin, *J. Appl. Phys.* **2020**, *128*, 040902.

A. Bednarkiewicz, L. Marciniak, L. D. Carlos, D. Jaque, *Nanoscale* **2020**, *12*, 14405-14421.

A. Bednarkiewicz, J. Drabik, K. Trejgis, D. Jaque, E. Ximenes, L. Marciniak, *Appl. Phys. Rev.* **2020**, almost accepted.

Figures of merit for luminescent thermometers

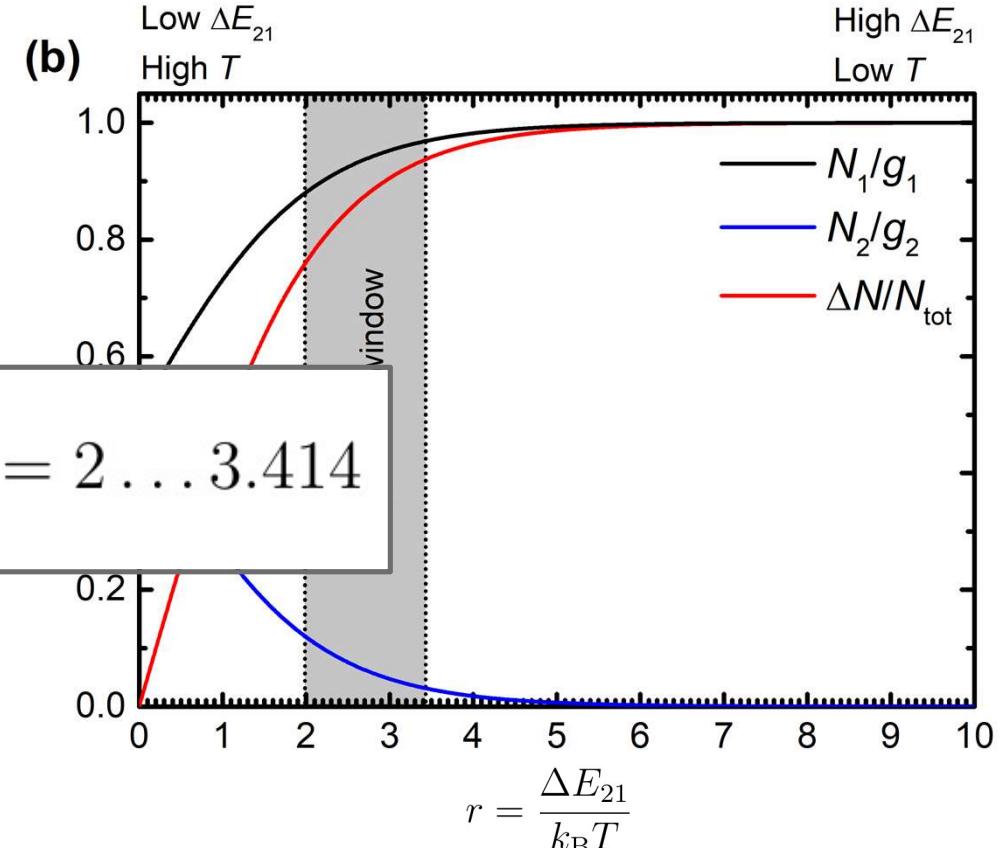
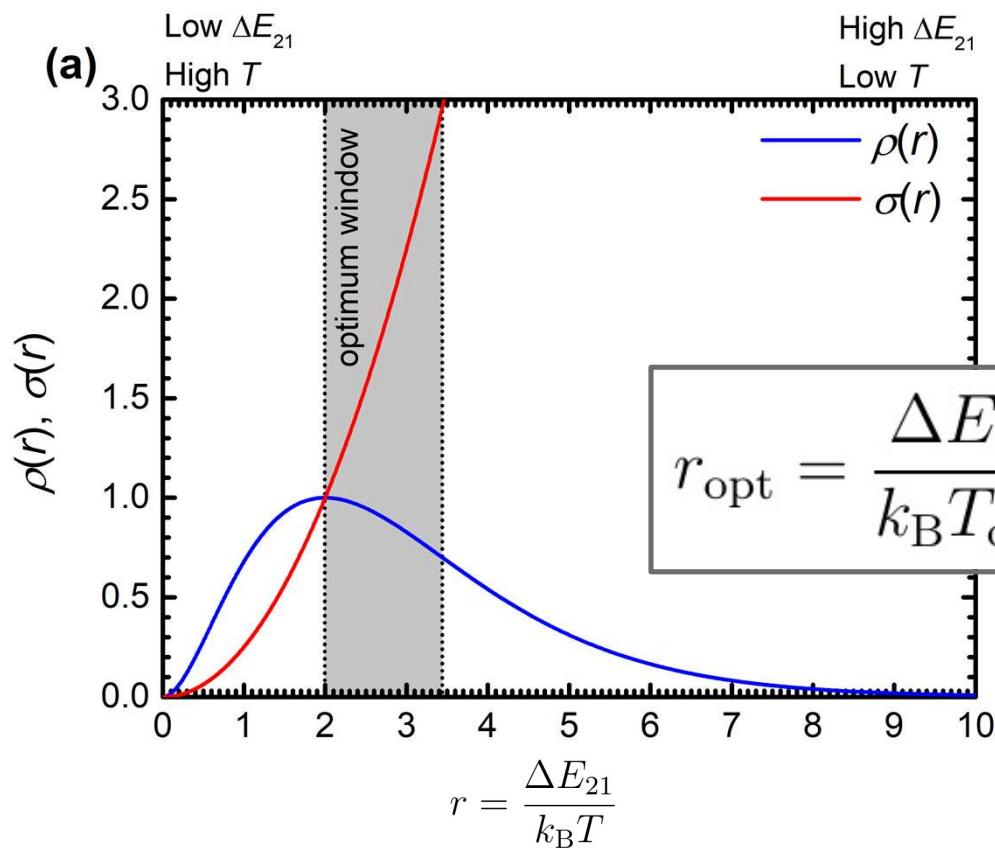
- A measure for the **thermal response** $S_a(T)$ is the temperature-dependent change in intensity ratio $R(T)$

$$S_a(T) = \left| \frac{dR}{dT} \right|$$

- If this response is related to the temperature-dependent quantity ($R(T)$), the **relative sensitivity** S_r results:

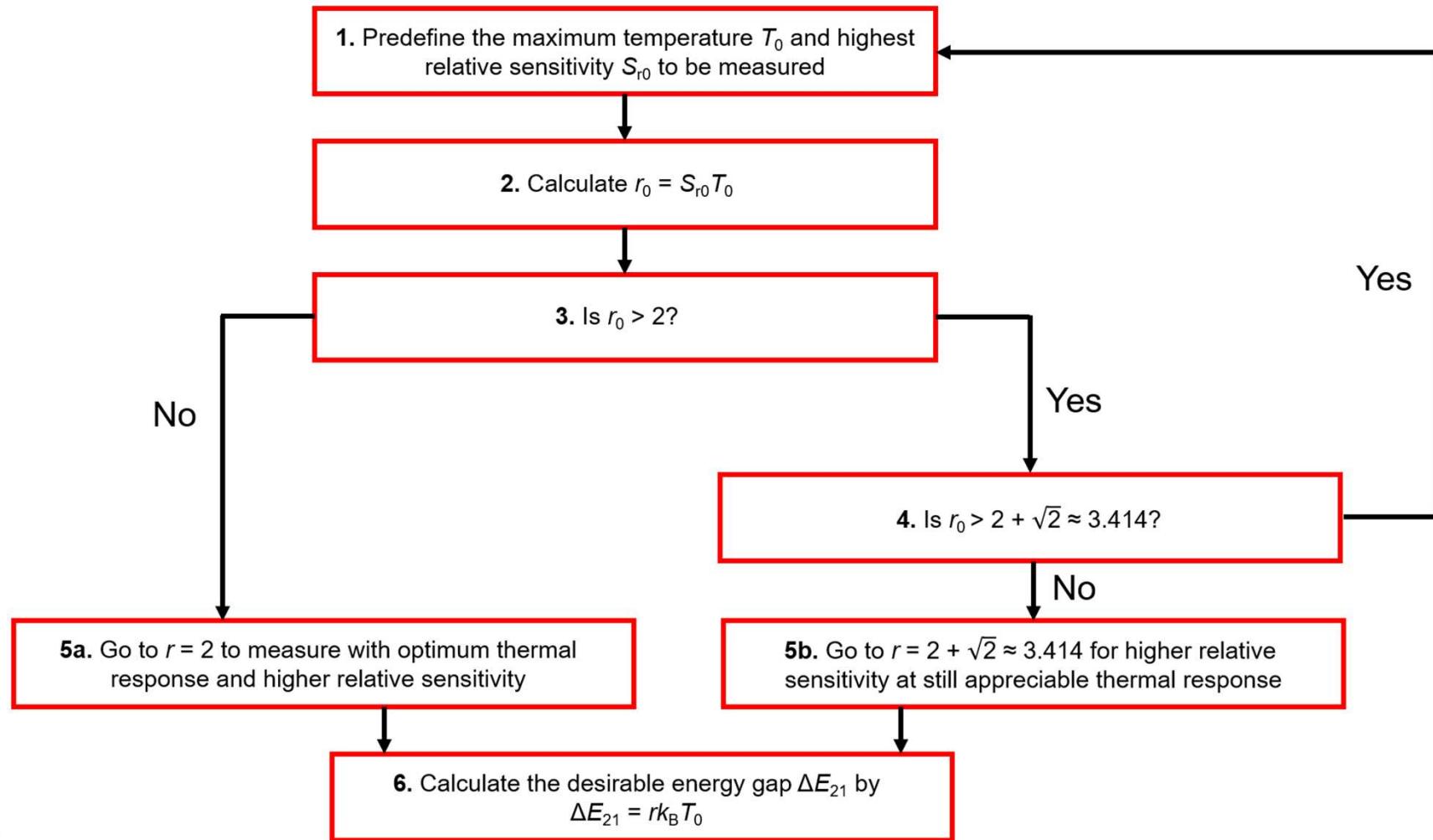
$$S_r(T) = \left| \frac{1}{R(T)} \frac{dR}{dT} \right| = \frac{\Delta E_{21}}{k_B T^2}$$

Every Boltzmann thermometer is thermodynamically limited!



As a user, one is always interested in highest temperature precision. This means:
Find a good compromise between response and sensitivity!

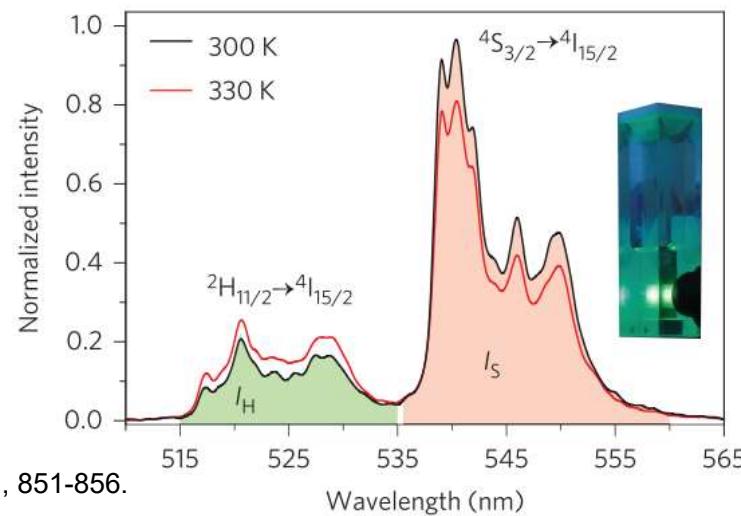
Practical example – Boltzmann thermometry at room temperature?



Practical example – Boltzmann thermometry at room temperature?

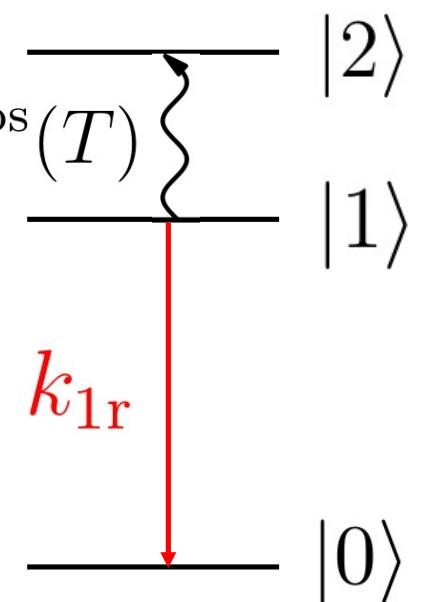
- Example: Suppose you want to measure $T_0 \sim 300$ K with a relative sensitivity of at least $S_{r0} \geq 1\% \text{ K}^{-1}$
 - $r_0 = S_{r0} T_0 = 3.0 > 2 \rightarrow$ Flowchart tells you to go for an energy gap
- $$\Delta E_{21} = 3.41 k_B T_0 \sim 710 \text{ cm}^{-1} \text{ (e.g. Er}^{3+} : {}^2\text{H}_{11/2} - {}^4\text{S}_{3/2} \text{ gap)}$$
- The relative sensitivity will have increased to $S_r(300 \text{ K}) = 1.13\% \text{ K}^{-1} > 1\% \text{ K}^{-1}$

Thermodynamics intuitively explains the big success of Er^{3+} for room temperature Boltzmann thermometry!

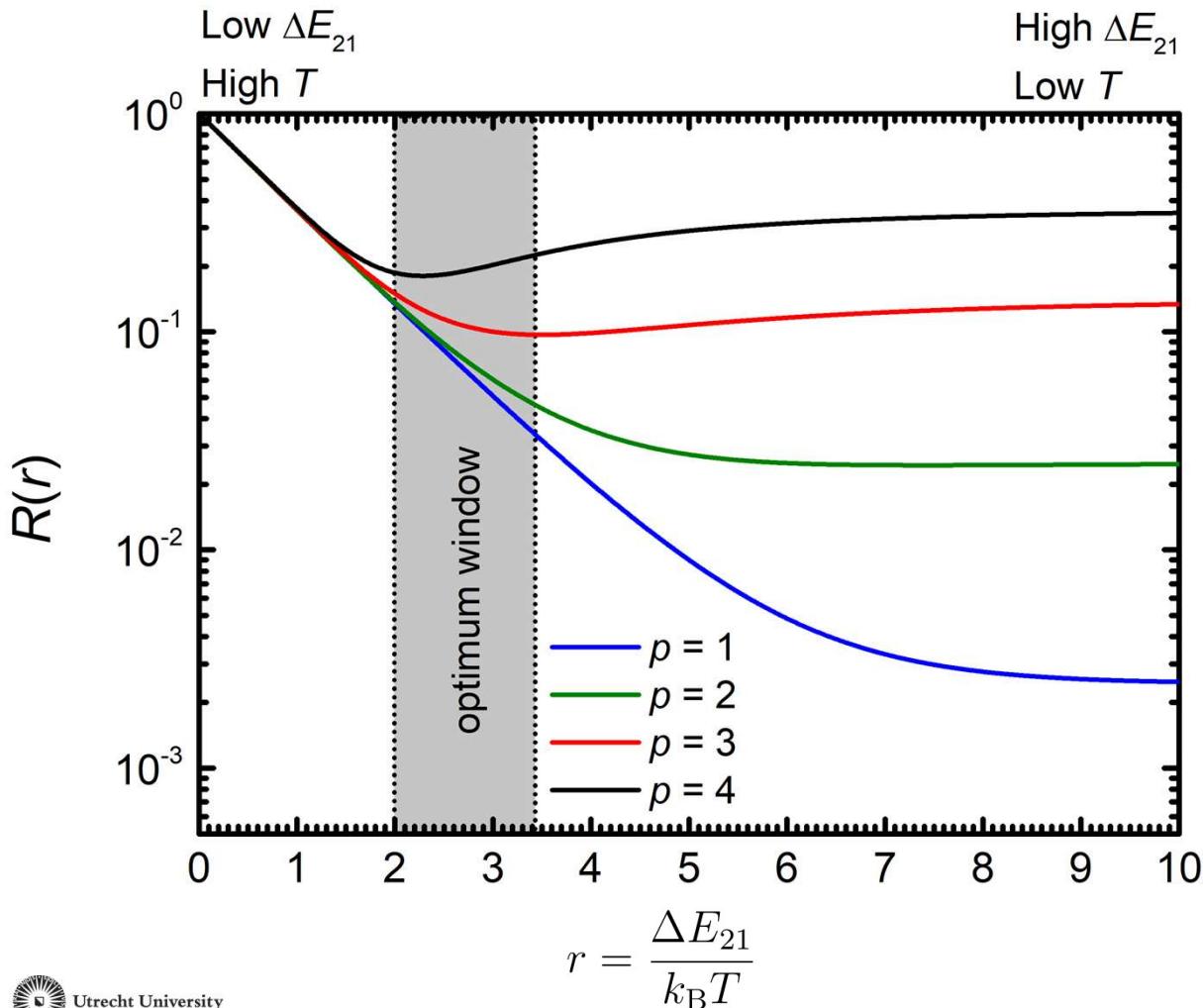


Kinetic limitations of luminescent thermometers

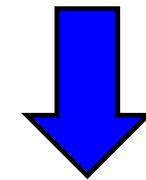
- Boltzmann distribution is only given if excited states have sufficient time for thermalization!
- Rate determining step: Non-radiative absorption from $|1\rangle$ to $|2\rangle$
$$k_{\text{nr}}^{\text{abs}}(T) > k_{1r} (+ \langle k \rangle_{\text{quench}})$$
- This can be endangered at **low temperatures!**



Controlling Boltzmann behavior with the host material



Vibrational energy of host has
to be adjusted to energy gap



Performance of a luminescent
thermometer also controlled by
the **host!**

An estimate for expected onset of Boltzmann behavior?

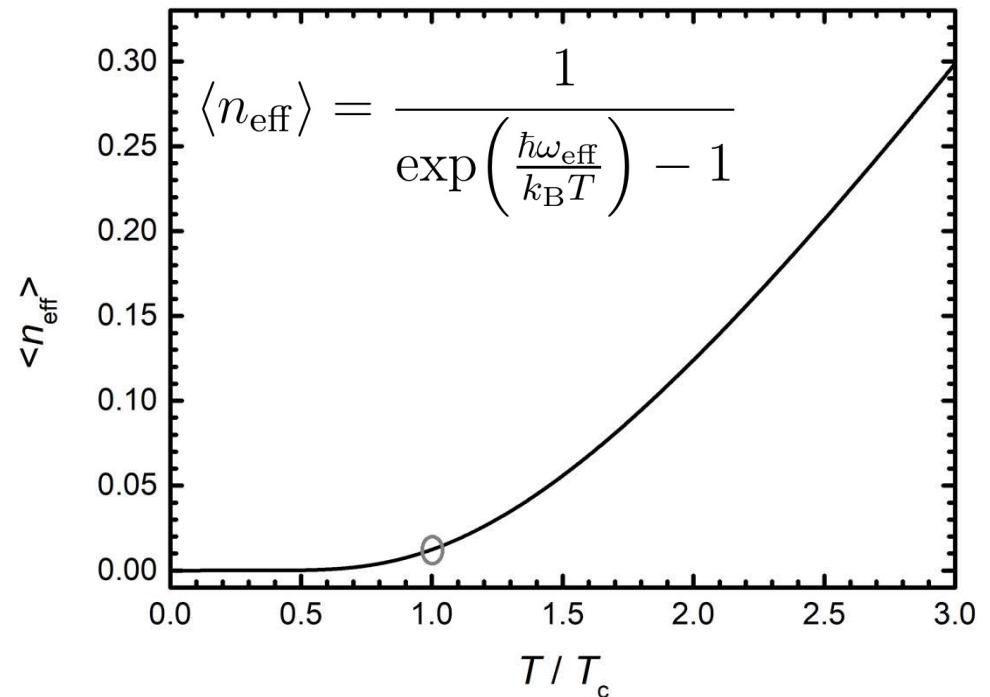
Idea: **Thermal activation of phonons rate-determining** → at what critical temperature T_c does the thermal average phonon number start to increase strongly?

Calculation affords:

$$T_c = 0.2227 \frac{\hbar\omega_{\text{eff}}}{k_B}$$

And for a general p -phonon process:

$$T_{\text{on}} \approx p T_c = 0.2227 \frac{\Delta E_{21}}{k_B}$$



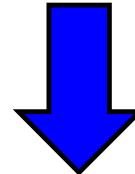
Consequence: Go for maximum two-phonon processes!

Thermodynamics

$$r_{\text{opt}} = \frac{\Delta E_{21}}{k_{\text{B}} T_{\text{opt}}} = 2 \dots 3.414$$

Kinetics

$$T_{\text{on}} \approx p T_c = 0.2227 \frac{\Delta E_{21}}{k_{\text{B}}}$$



$$T_{\text{on}} < T_{\text{opt}}$$

$$p_{\text{opt}} = 1 - 2$$

Try to match the phonon energy to the energy gap you want to use. At maximum go for a two-phonon process, otherwise Boltzmann thermometry does not work properly!

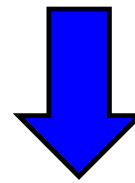
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Thermodynamics

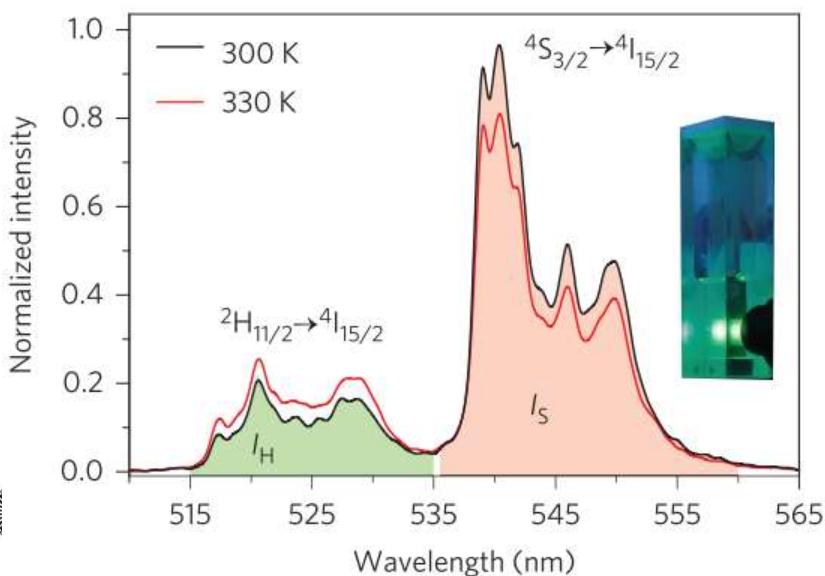
$$r_{\text{opt}} = \frac{\Delta E_{21}}{k_B T_{\text{opt}}} = 2 \dots 3.414$$

Kinetics

$$T_{\text{on}} \approx pT_c = 0.2227 \frac{\Delta E_{21}}{k_B}$$



$$T_{\text{on}} < T_{\text{opt}}$$

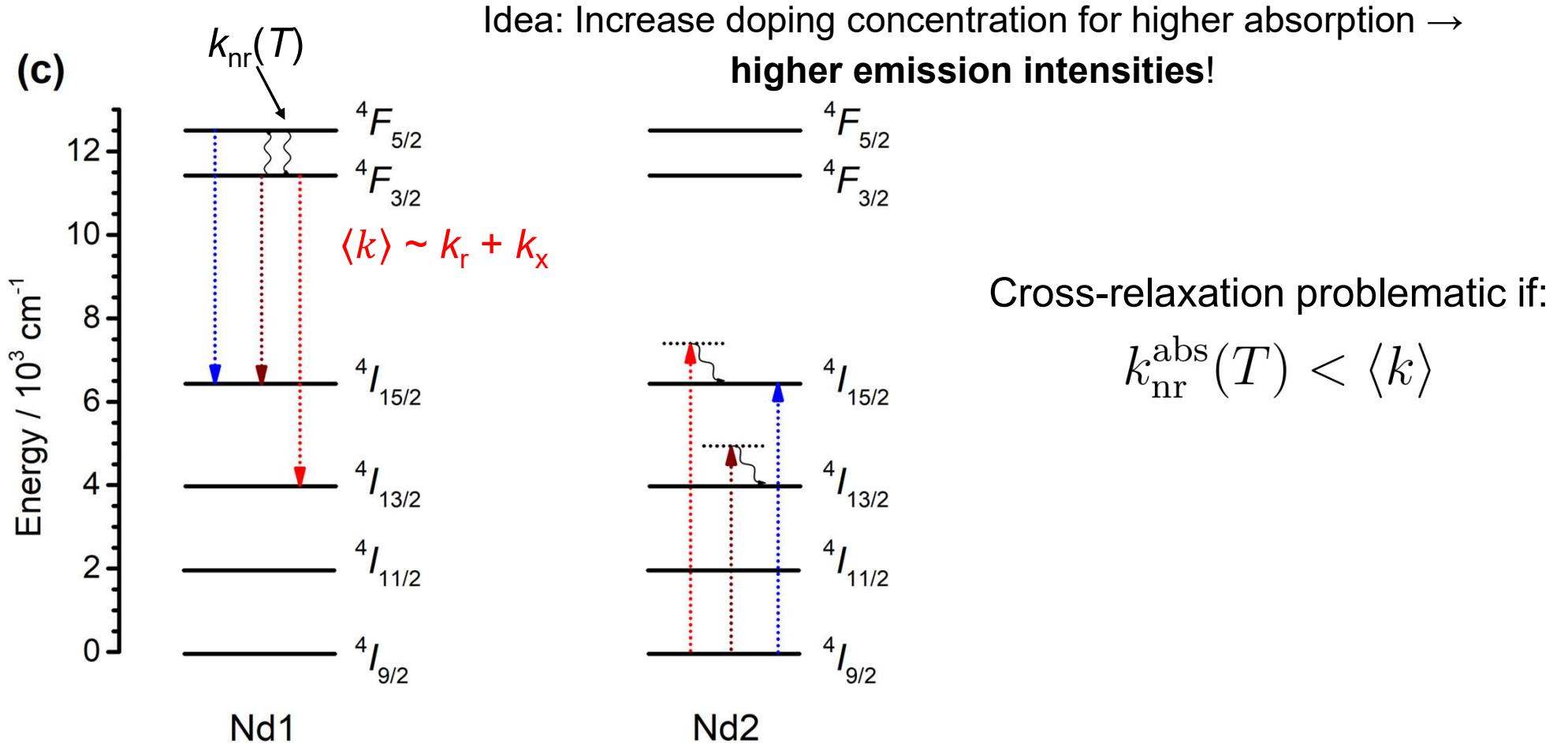


$\beta\text{-NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$:

- Phonon energy of $\sim 400 - 450 \text{ cm}^{-1}$
- ΔE_{21} of around $700 - 800 \text{ cm}^{-1} \approx 2$ phonons

Explains again the success of this compound!

Example: Cross-relaxation of Nd³⁺ - Can get a problem!



M. Suta, Ž. Antić, V. Đorđević, S. Kuzman, M. D. Dramićanin, A. Meijerink, *Nanomaterials* **2020**, *10*, 543.
M. Suta, A. Meijerink, *Adv. Theory Simul.* **2020**, *3*, 2000176.

Example: Cross-relaxation of Nd³⁺ - Can get a problem!

NANO LETTERS

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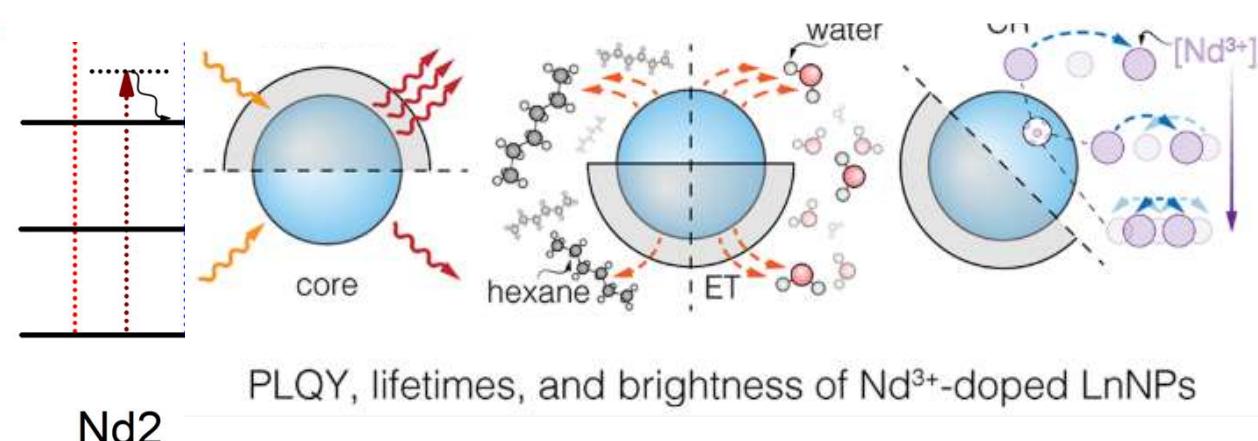
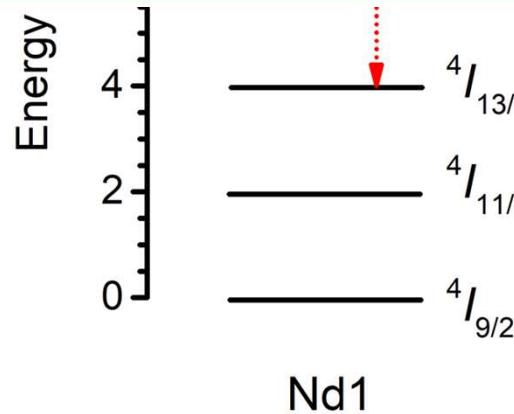
ration for higher absorption →
on intensities!

Inert Shell Effect on the Quantum Yield of Neodymium-Doped Near-Infrared Nanoparticles: The Necessary Shield in an Aqueous Dispersion

Artiom Skripka,¹ Antonio Benayas,¹ Carlos D. S. Brites, Inocencio R. Martín, Luís D. Carlos,*
and Fiorenzo Vetrone*

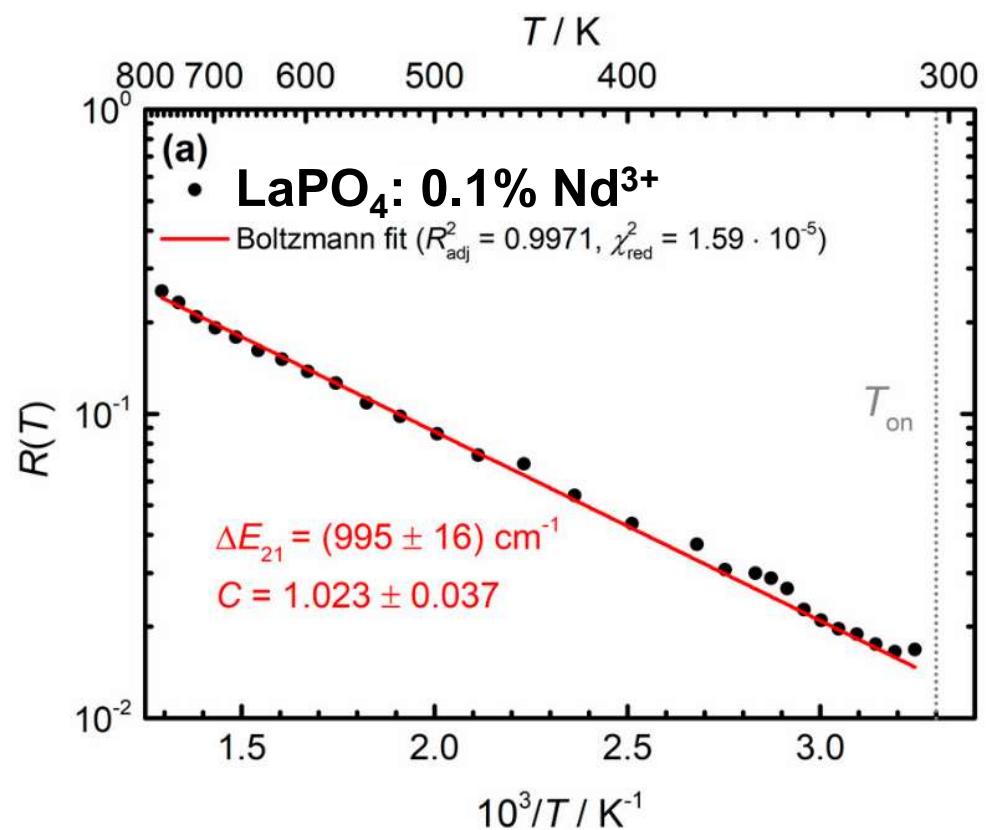
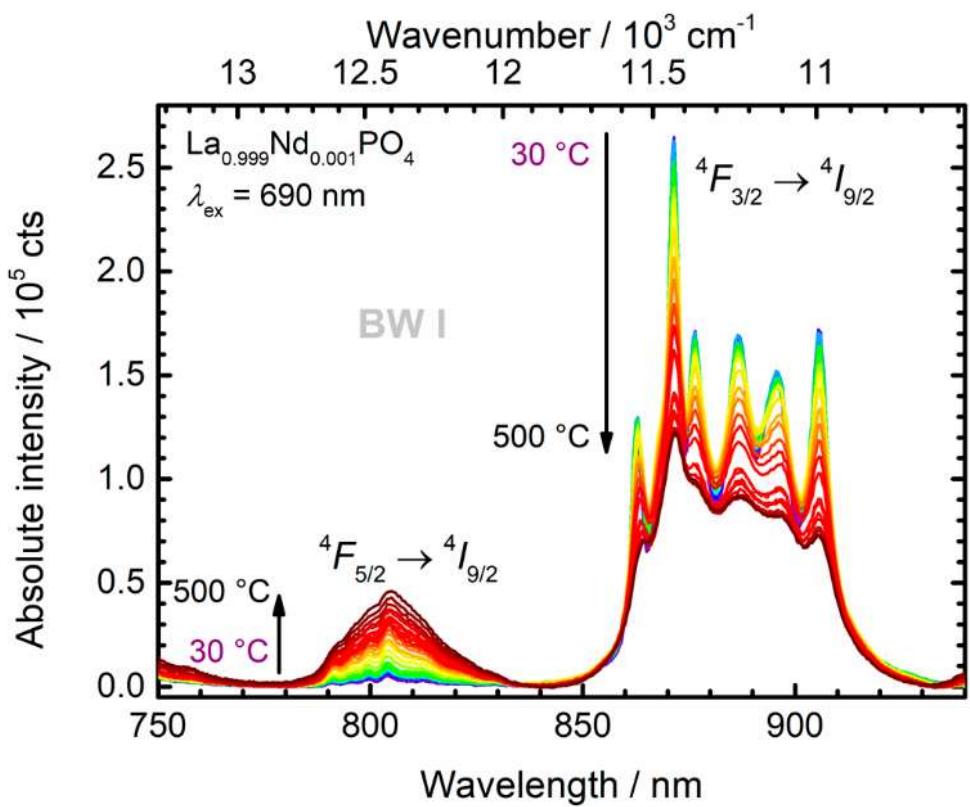
Cite This: *Nano Lett.* 2020, 20, 7648–7654

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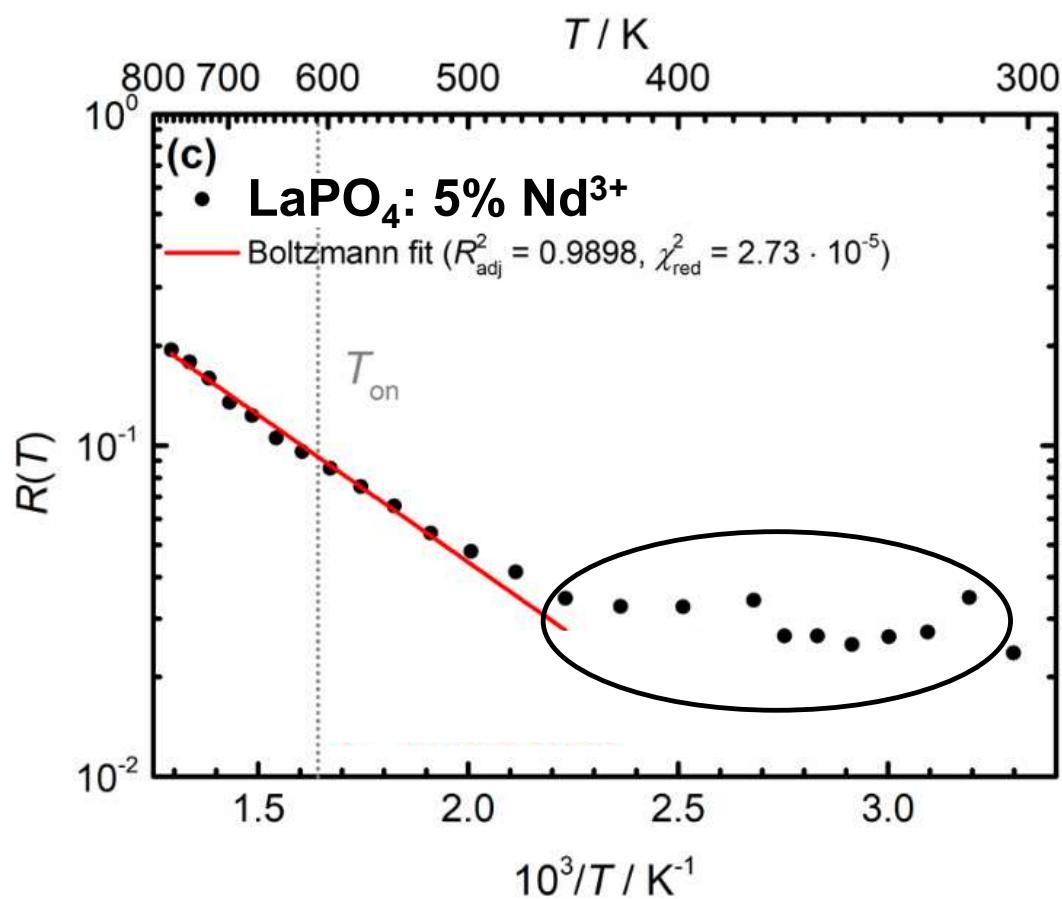
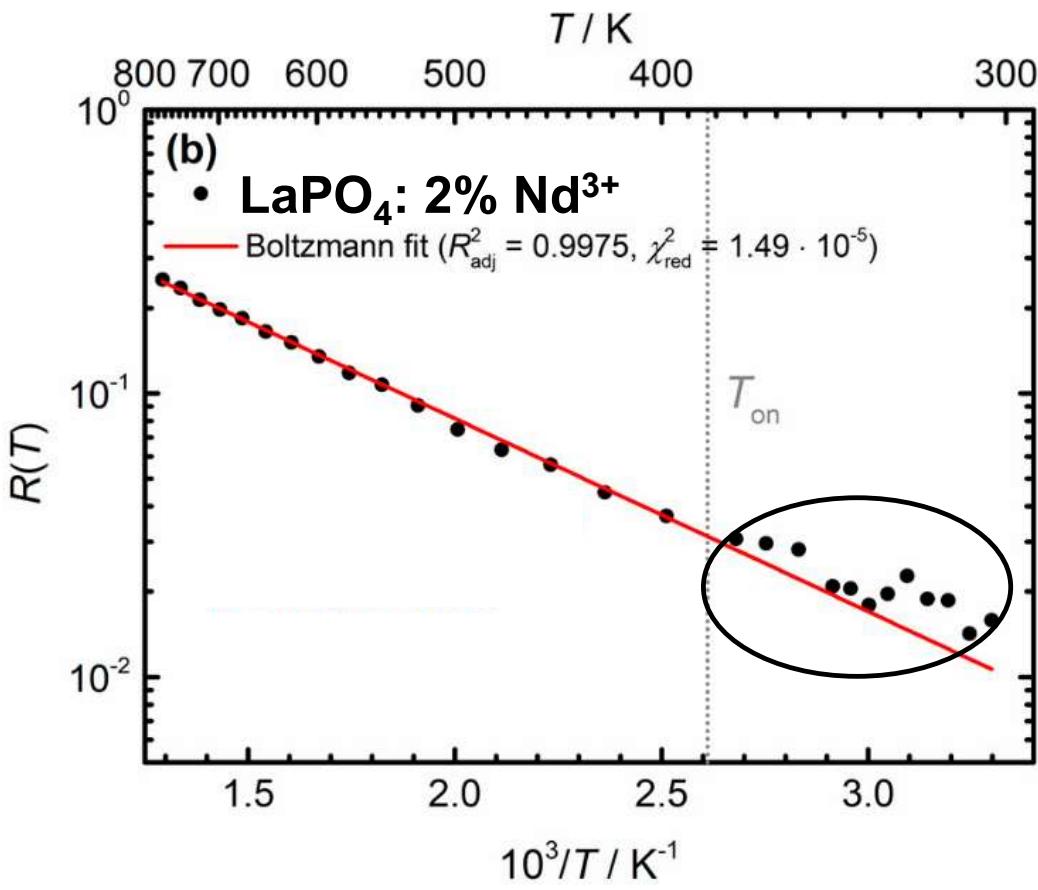


M. Suta, Ž. Antić, V. Đorđević, S. Kuzman, M. D. Dramićanin, A. Meijerink, *Nanomaterials* **2020**, *10*, 543.
M. Suta, A. Meijerink, *Adv. Theory Simul.* **2020**, *3*, 2000176.

Implications for Boltzmann thermometry



Implications for Boltzmann thermometry



Caught your interest? Check out even more rules in the paper!

PROGRESS REPORT

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A Theoretical Framework for Ratiometric Single Ion Luminescent Thermometers—Thermodynamic and Kinetic Guidelines for Optimized Performance

Markus Suta and Andries Meijerink*



Utrecht University

Summary

- Luminescence thermometry is an interplay of thermodynamics and kinetics!
- Luminescent Boltzmann thermometers only suited for a limited temperature range!
$$\Delta E_{21} = 2k_B T_0 \dots 3.41k_B T_0$$
- Make the phonon energy match the energy gap: no. of required phonons p to bridge the energy gap should not exceed 2
- The **host material** can decide quite a lot here by:
 - *Mutual lanthanide distances*
 - *Vibrational energies*
 - *Lanthanide-ligand distances*
- **A beautiful example of a bridge between physics & chemistry!**

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- Dechao Yu
- Robin Geitenbeek
- CMI team



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- Luís Carlos, Eliana Cavaleiro
- Łukasz Marciniak, Artur Bednarkiewicz
- Daniel Jaque, Erving Ximendes
- Bruno Viana



FET Open
Grant agreement no. 801305

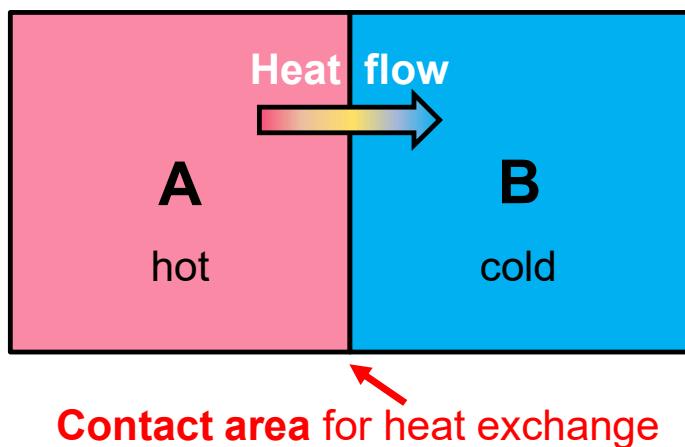
Thank you for your kind attention!

Questions or feedback?

Backup

Primer: How does thermometry fundamentally work?

Basically all thermometers work with the *0th law of thermodynamics*:



Suppose, Bob is interested in the temperature of Alice's object A

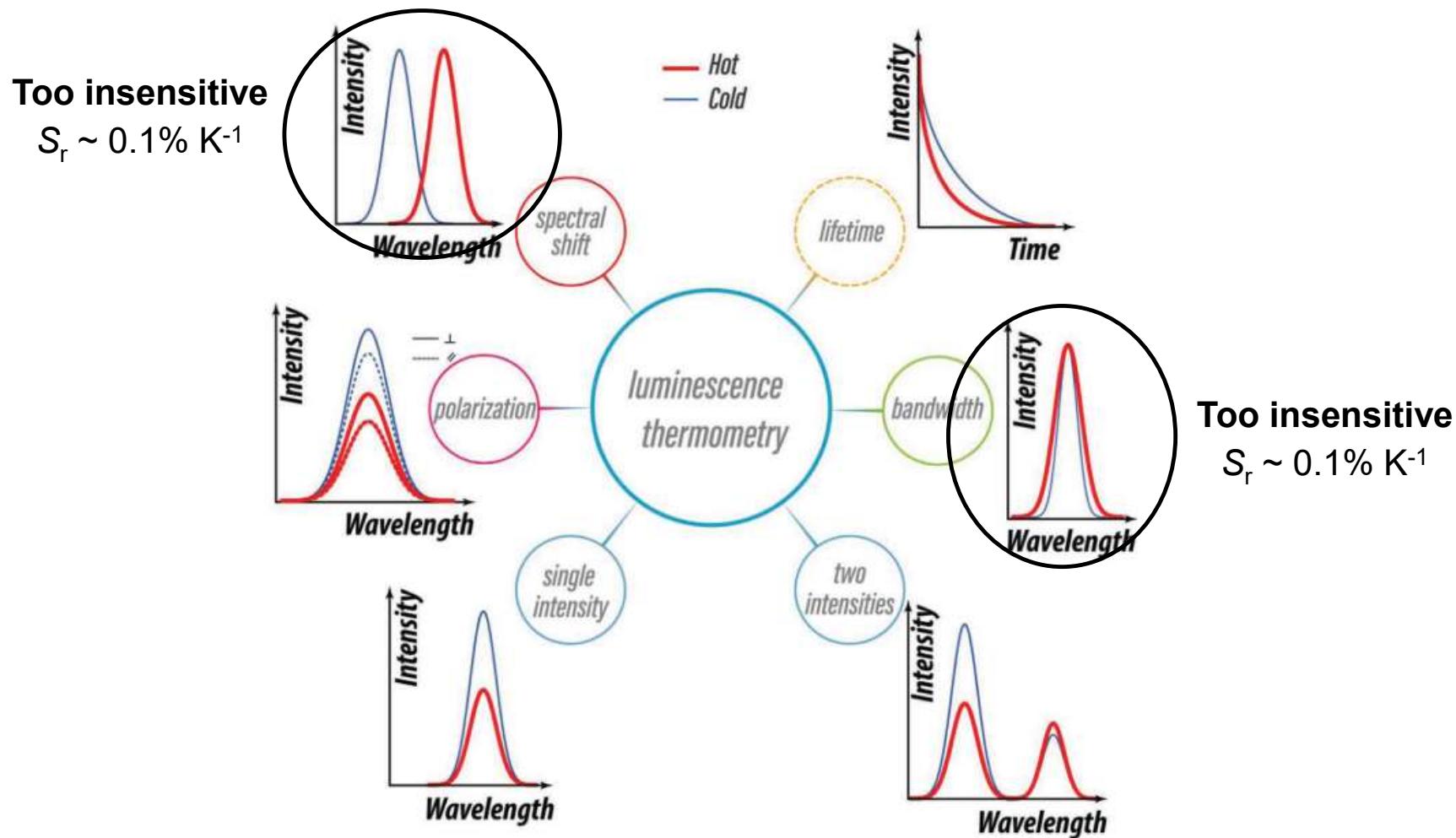
Bob brings object B into contact with A. B shows a certain response to temperature (expansion of a liquid, emitted light intensity etc.)

Once the response does not change anymore upon contact, the two objects are in **thermal equilibrium**: The temperatures of A and B are equal!

Word of warning here: In literature of luminescence thermometry, you often find the term *contactless*. Do not misinterpret that:

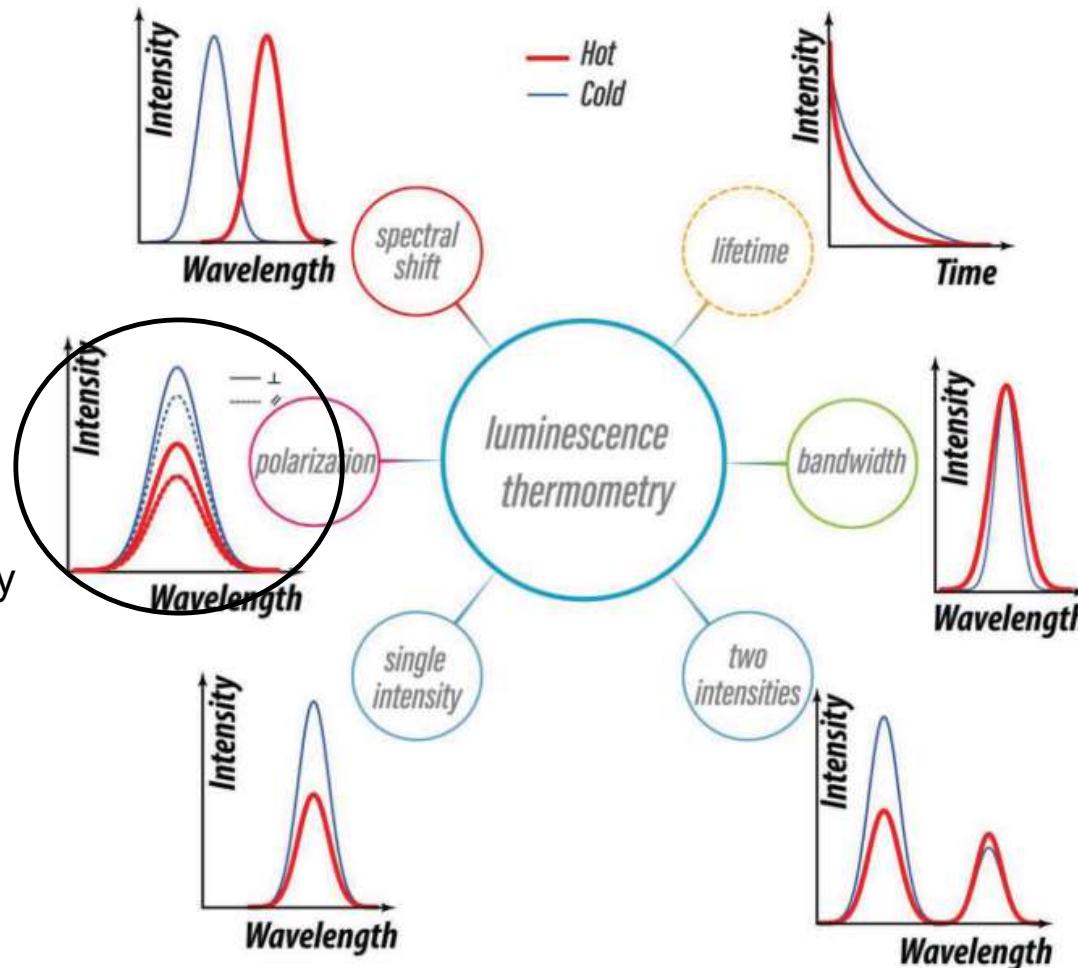
That only applies to the detection principle, the thermometer IS in contact with the object of interest!

The various possibilities of luminescence thermometry

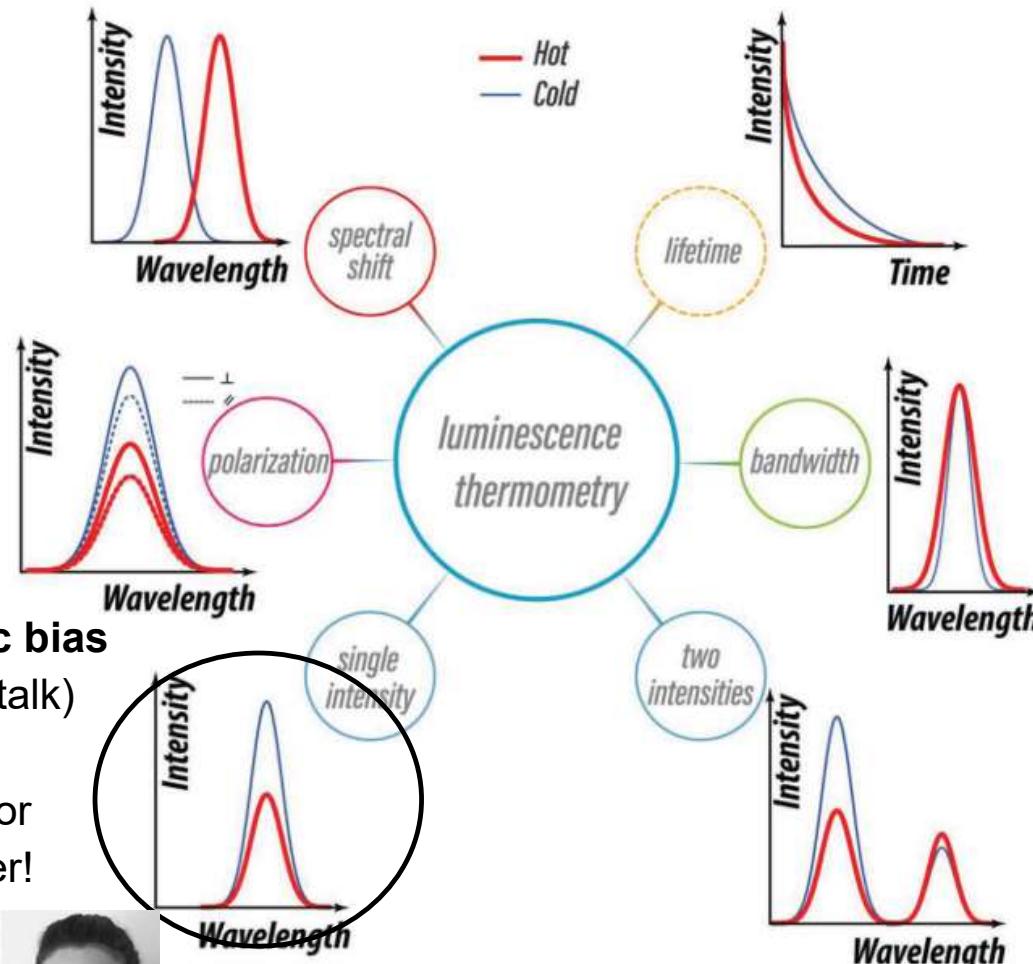


The various possibilities of luminescence thermometry

Only feasible for
(single) crystalline
compounds with
pronounced anisotropy



The various possibilities of luminescence thermometry



Too prone to systematic bias
(see *Erving Ximenes'* talk)

Or not? Stay tuned for
Lise Abiven's talk later!



Systematics of ratiometric luminescence thermometers

Ratiometric thermometers

Energy transfer thermometers

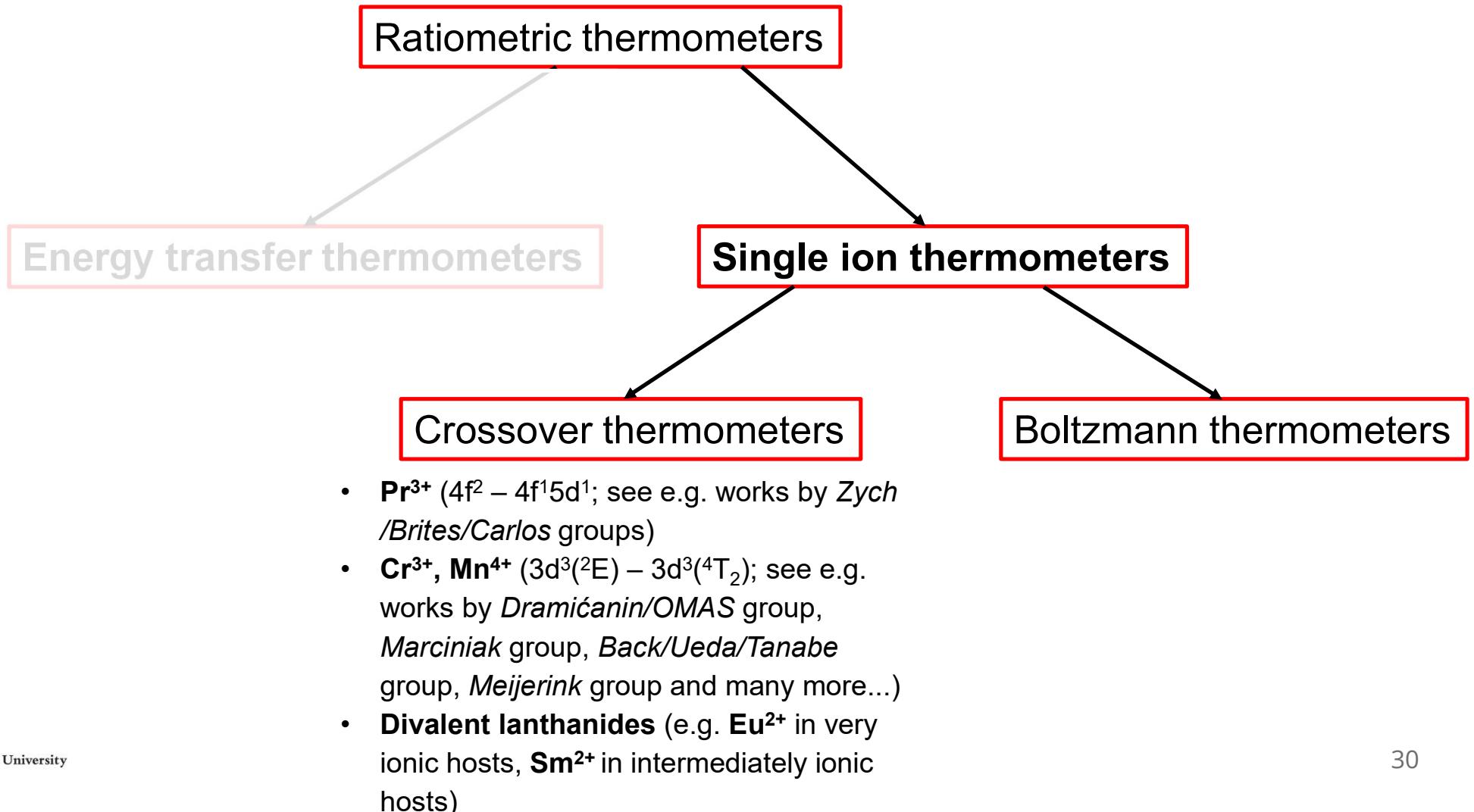
Single ion thermometers

- MOFs/COFs with different lanthanide ions (*Carlos group/Kaczmarek group/Sérier-Brault group...*)
- Competition between cross relaxation and multiphonon relaxation (*Jaque group with Tm³⁺, Meijerink/Rabouw groups with Ho³⁺*)
- Thermally assisted energy transfer, e.g. Yb³⁺/Nd³⁺ (*Jacinto/Jaque groups, Zhou/Jin groups, Bednarkiewicz/Marciniak/Hreniak groups*)
- Different thermal energy transfer rates (*Brites/Carlos/Millán groups*)

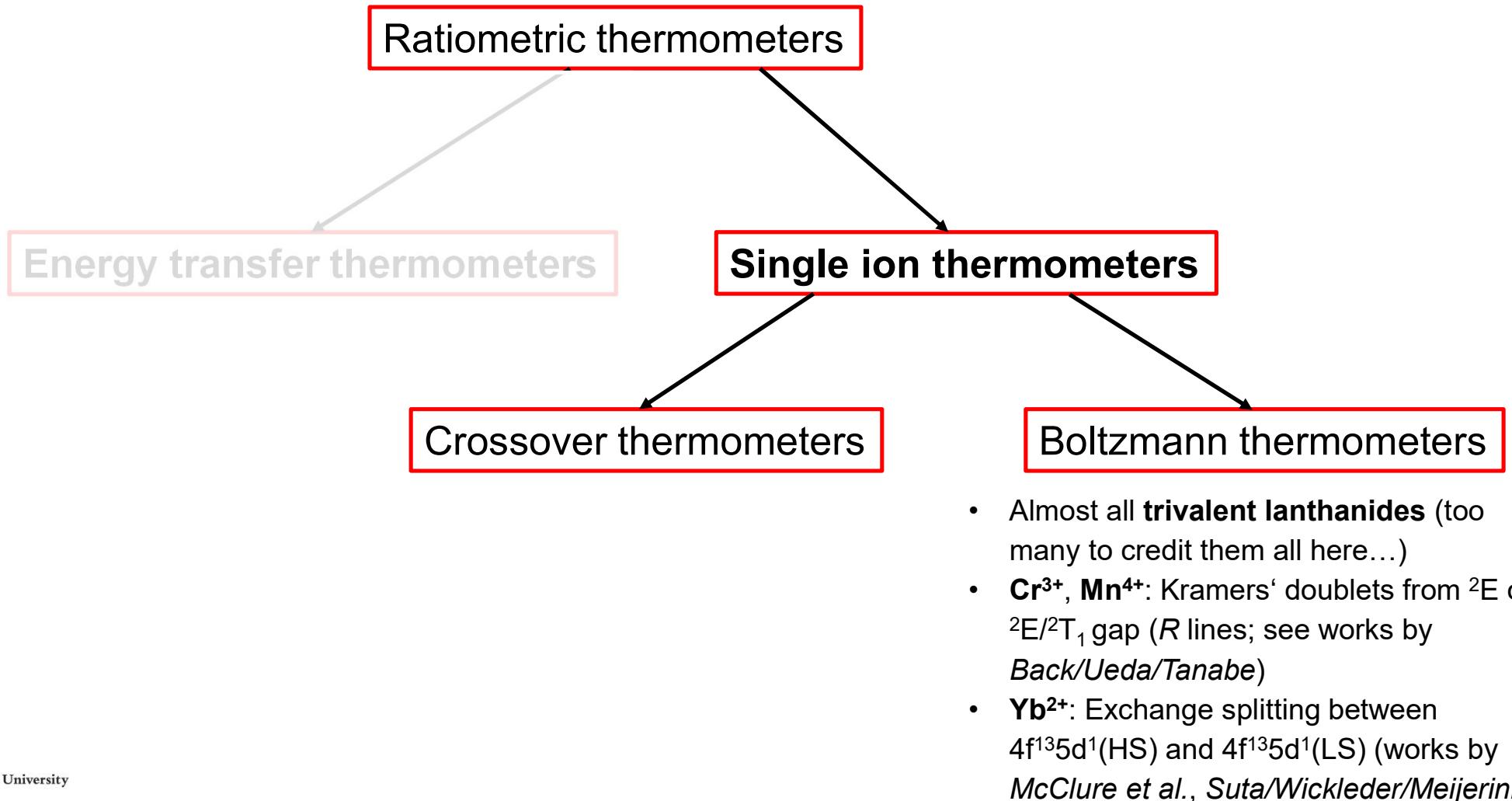


Stay tuned for Rafael Piñol's talk on this issue!

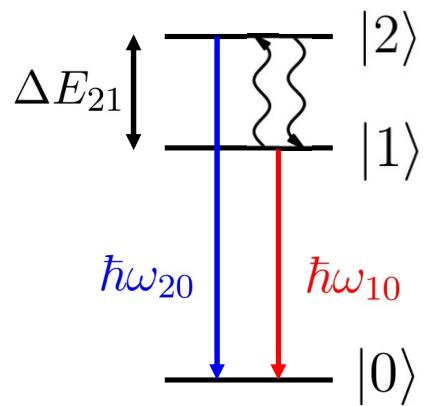
Systematics of ratiometric luminescence thermometers



Systematics of ratiometric luminescence thermometers

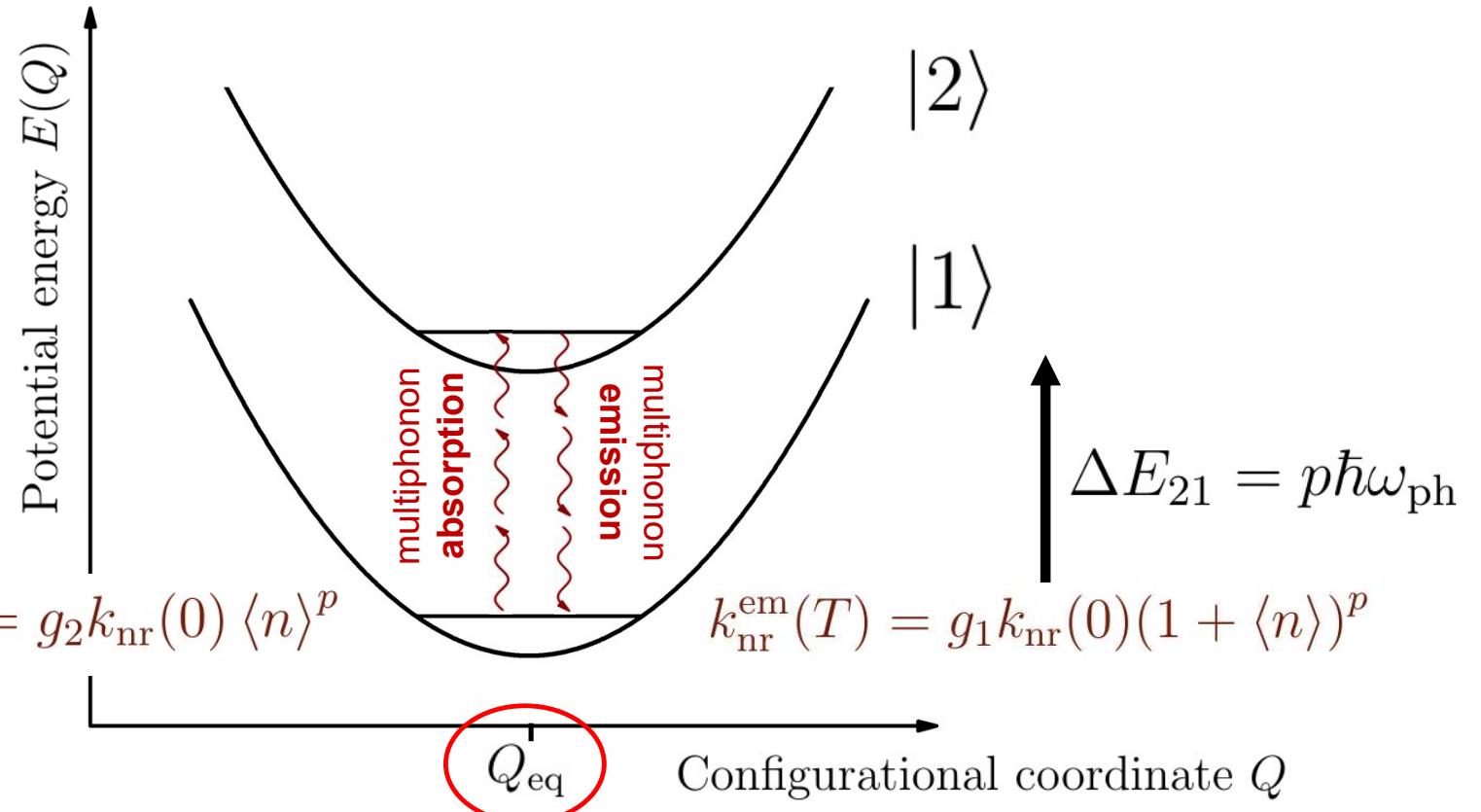


When is a single ion thermometer a true Boltzmann thermometer?



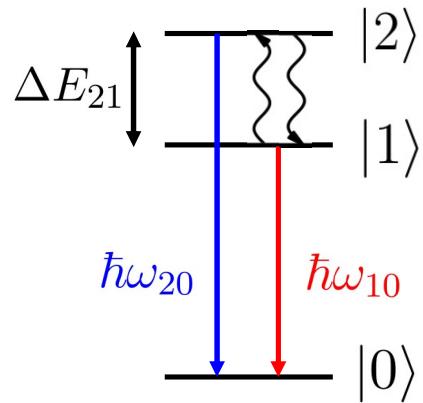
$$\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar\omega_{\text{ph}}}{k_B T}\right) - 1}$$

$$k_{\text{nr}}^{\text{abs}}(T) = g_2 k_{\text{nr}}(0) \langle n \rangle^p$$



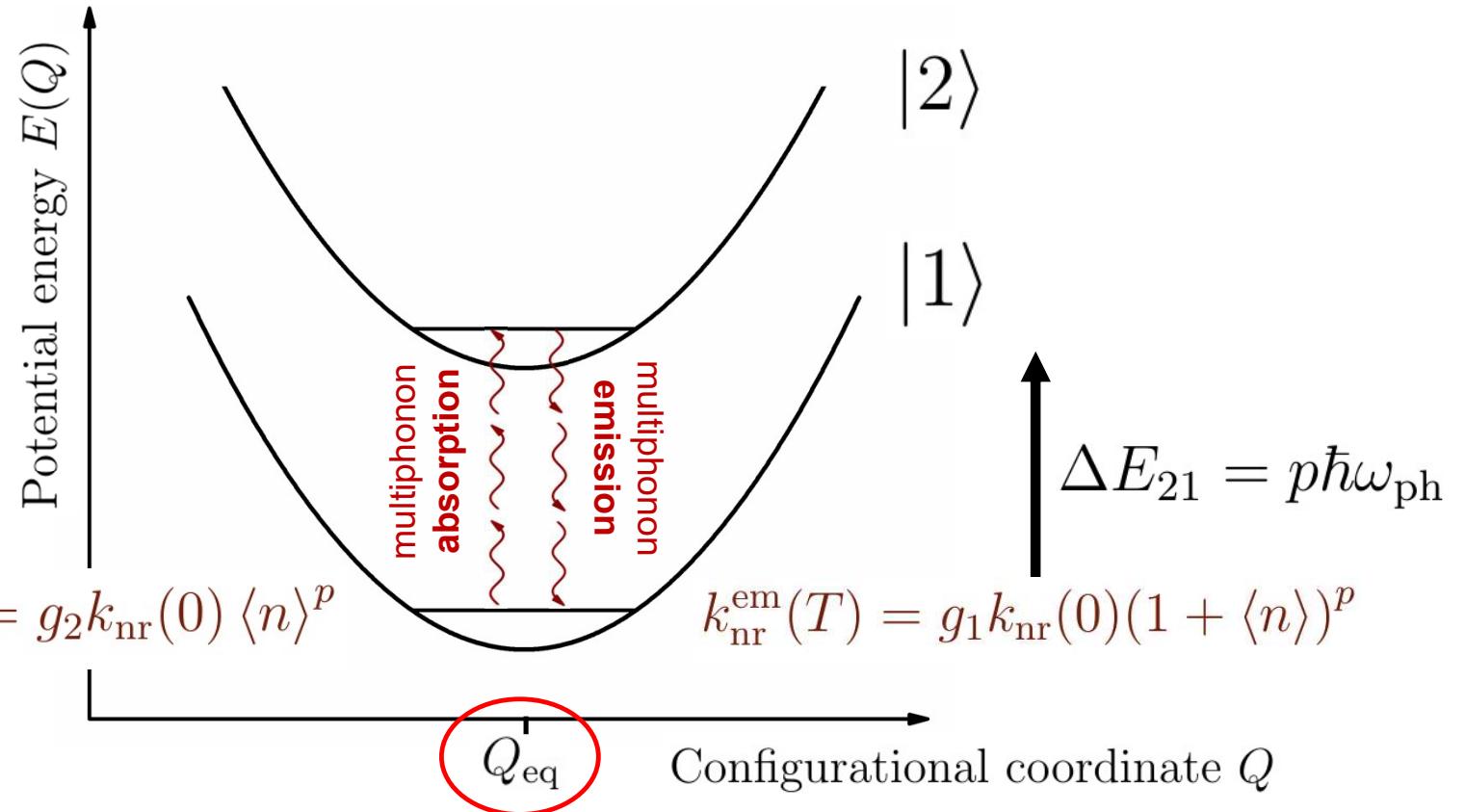
$$\frac{k_{\text{nr}}^{\text{abs}}(T)}{k_{\text{nr}}^{\text{em}}(T)} = \frac{g_2}{g_1} \left(\frac{\langle n \rangle}{1 + \langle n \rangle} \right)^p \stackrel{!}{=} \frac{g_2}{g_1} \exp\left(-\frac{p\hbar\omega_{\text{ph}}}{k_B T}\right) = \frac{g_2}{g_1} \exp\left(-\frac{\Delta E_{21}}{k_B T}\right)$$

When is a single ion thermometer a true Boltzmann thermometer?



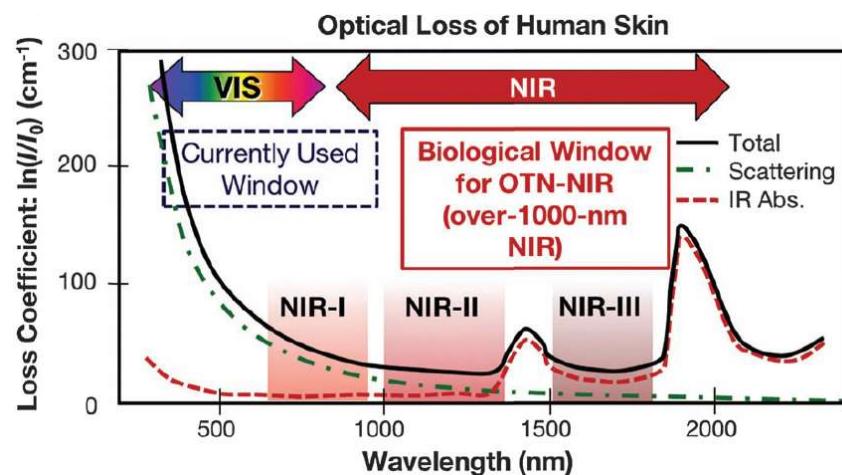
$$\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar\omega_{\text{ph}}}{k_B T}\right) - 1}$$

$$k_{\text{nr}}^{\text{abs}}(T) = g_2 k_{\text{nr}}(0) \langle n \rangle^p$$

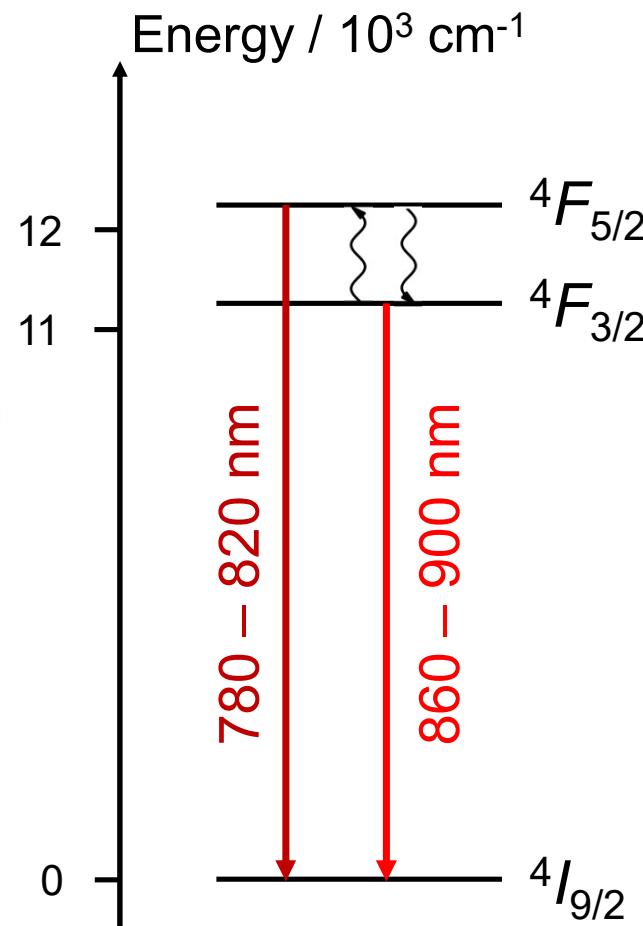


Boltzmann behavior for thermalization between two excited states **only if non-radiative transitions are multiphonon transitions!!**

Nd^{3+} as a physiological luminescent thermometer?



E. Hemmer, A. Benayas, F. Légaré, F. Vetrone, *Nanoscale Horiz.* 2016, 1, 168 – 184.

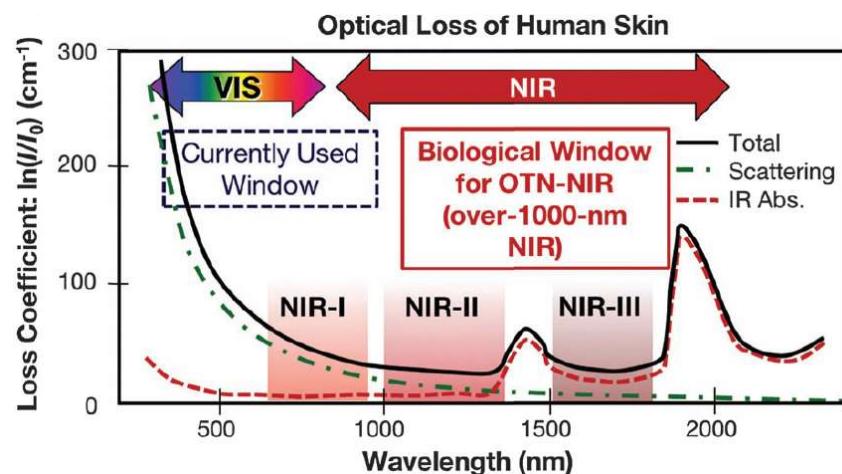


For physiological temperatures:
 $\rightarrow \Delta E_{\text{opt}} = 800 \text{ cm}^{-1} \dots 850 \text{ cm}^{-1}$

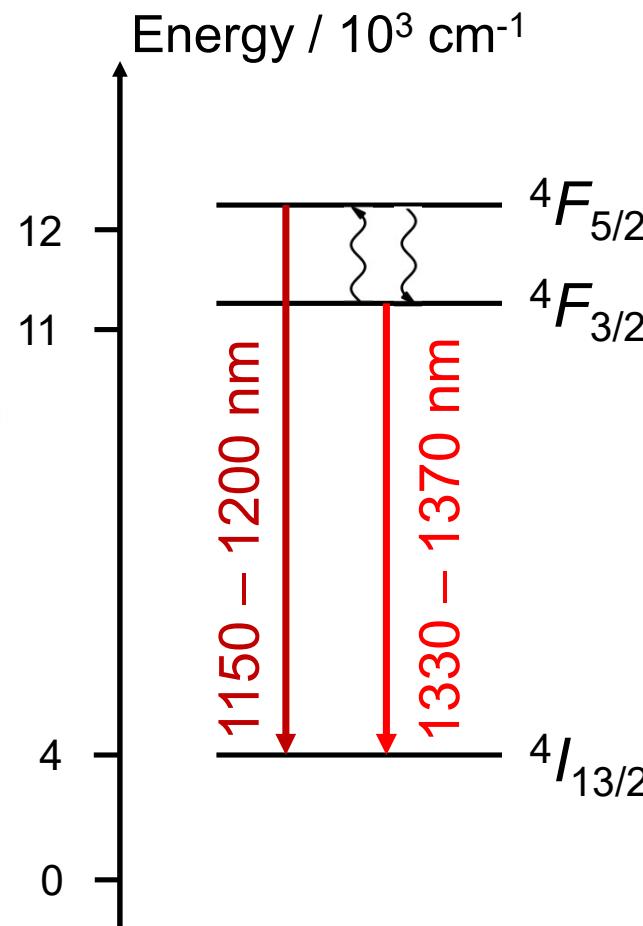
$$\Delta E_{21} \approx 700 - 1000 \text{ cm}^{-1}$$

Biological window I
 $(750 \text{ nm} - 950 \text{ nm})$

Nd^{3+} as a physiological luminescent thermometer?



E. Hemmer, A. Benayas, F. Légaré, F. Vetrone, *Nanoscale Horiz.* 2016, 1, 168 – 184.



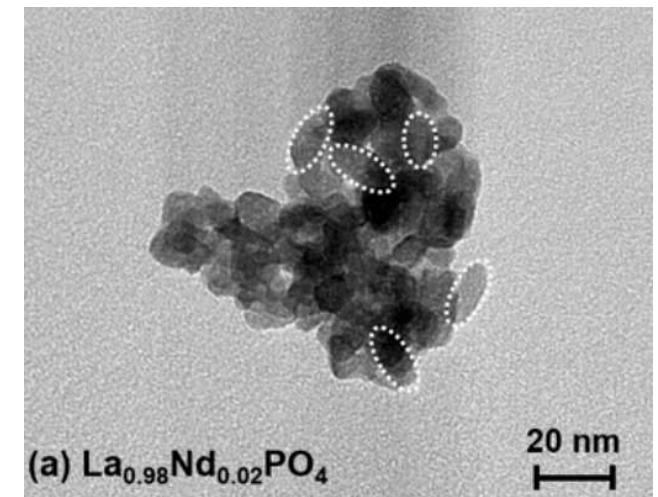
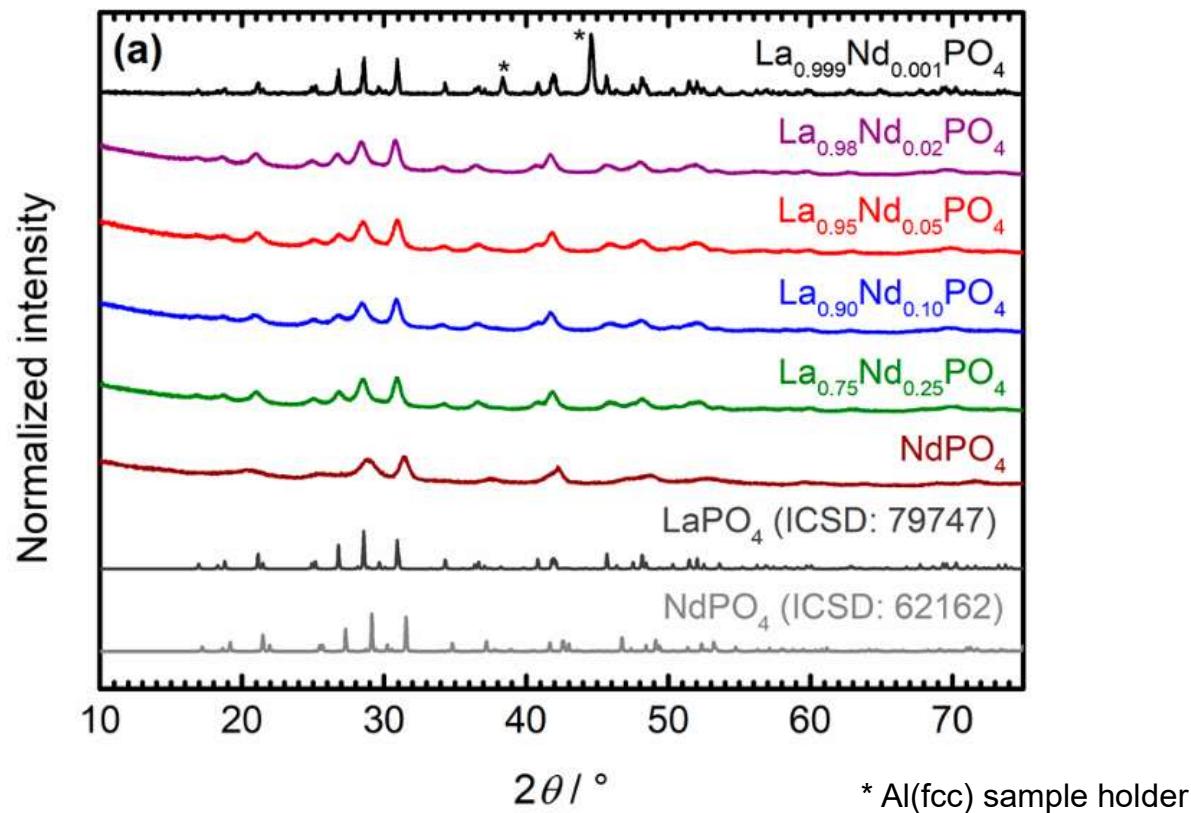
For physiological temperatures:
 $\rightarrow \Delta E_{\text{opt}} = 800 \text{ cm}^{-1} \dots 850 \text{ cm}^{-1}$

$$\Delta E_{21} \approx 700 - 1000 \text{ cm}^{-1}$$

Biological window II
(1000 nm – 1350 nm)

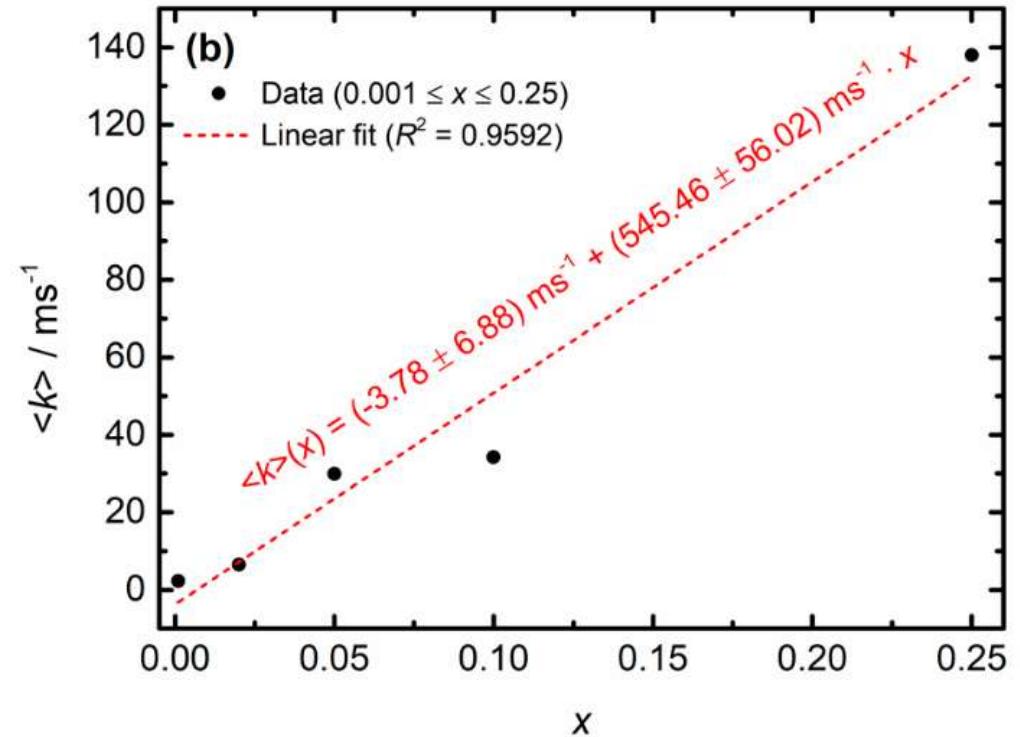
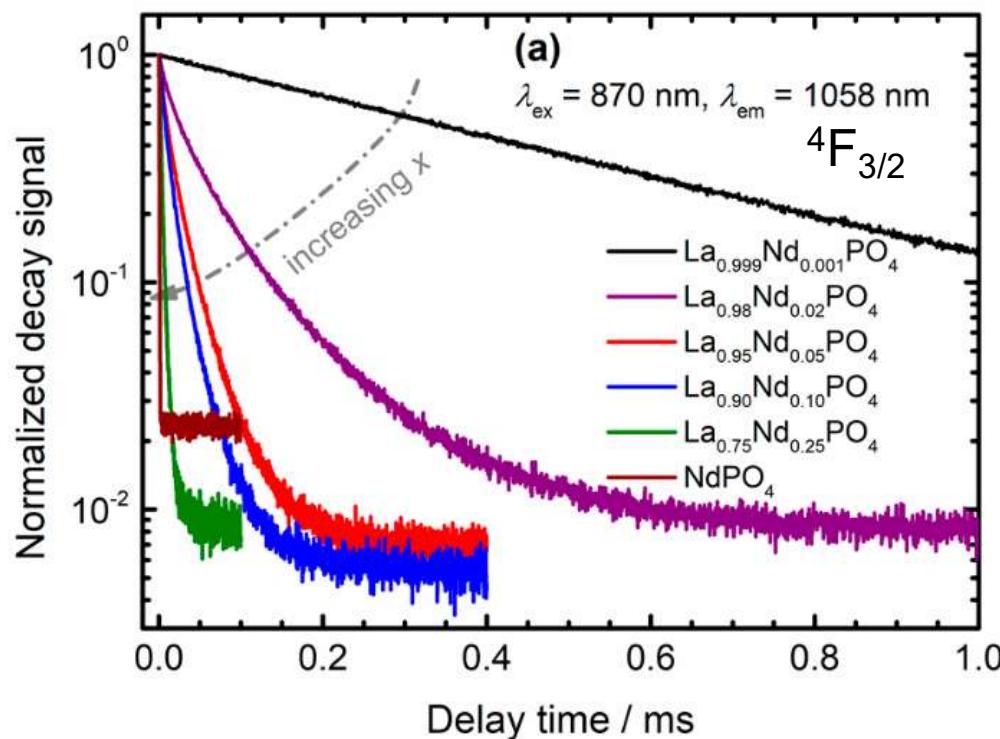
How about doping concentration?

Guinea pig: $\text{La}_{1-x}\text{Nd}_x\text{PO}_4$ ($x = 0.1; 2; 5; 10; 25; 100$)



Higher doping concentrations reveal a kinetic problem!

Average decay rate of ${}^4F_{3/2}$ level increases with dopant fraction

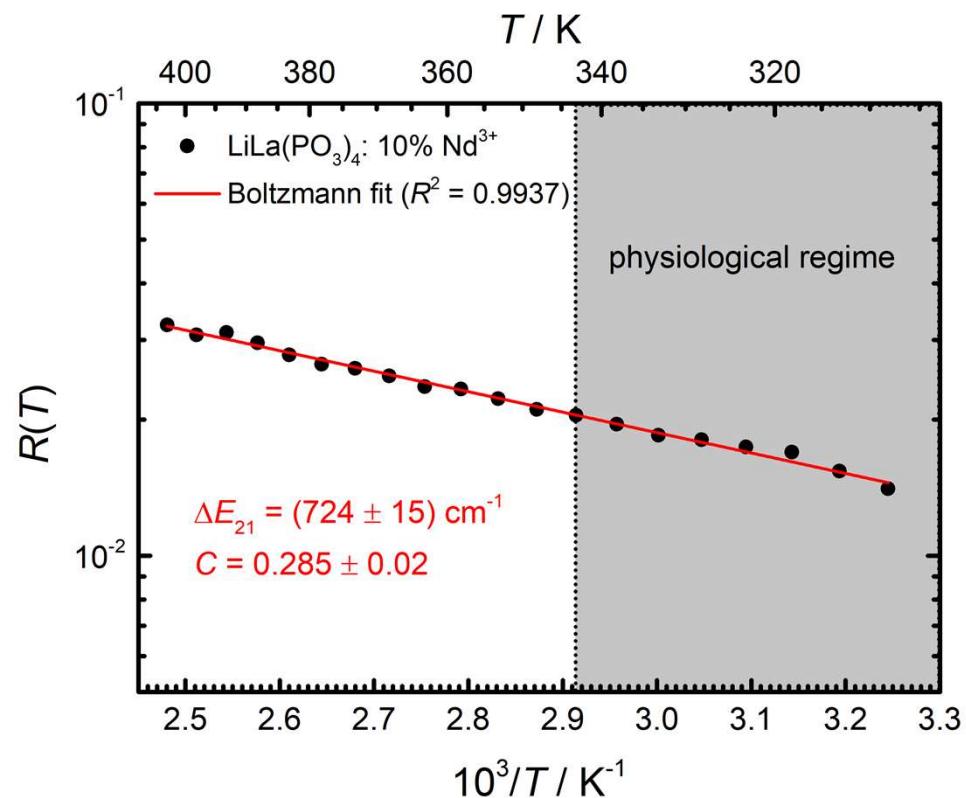
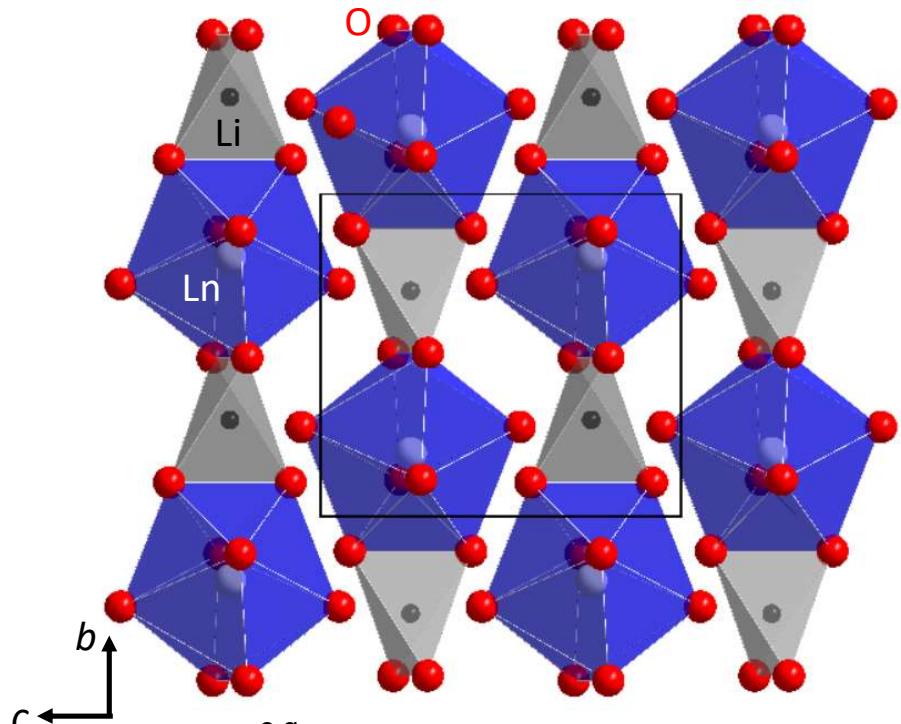


→ signature of cross relaxation/surface quenching!

Ways to overcome this problem

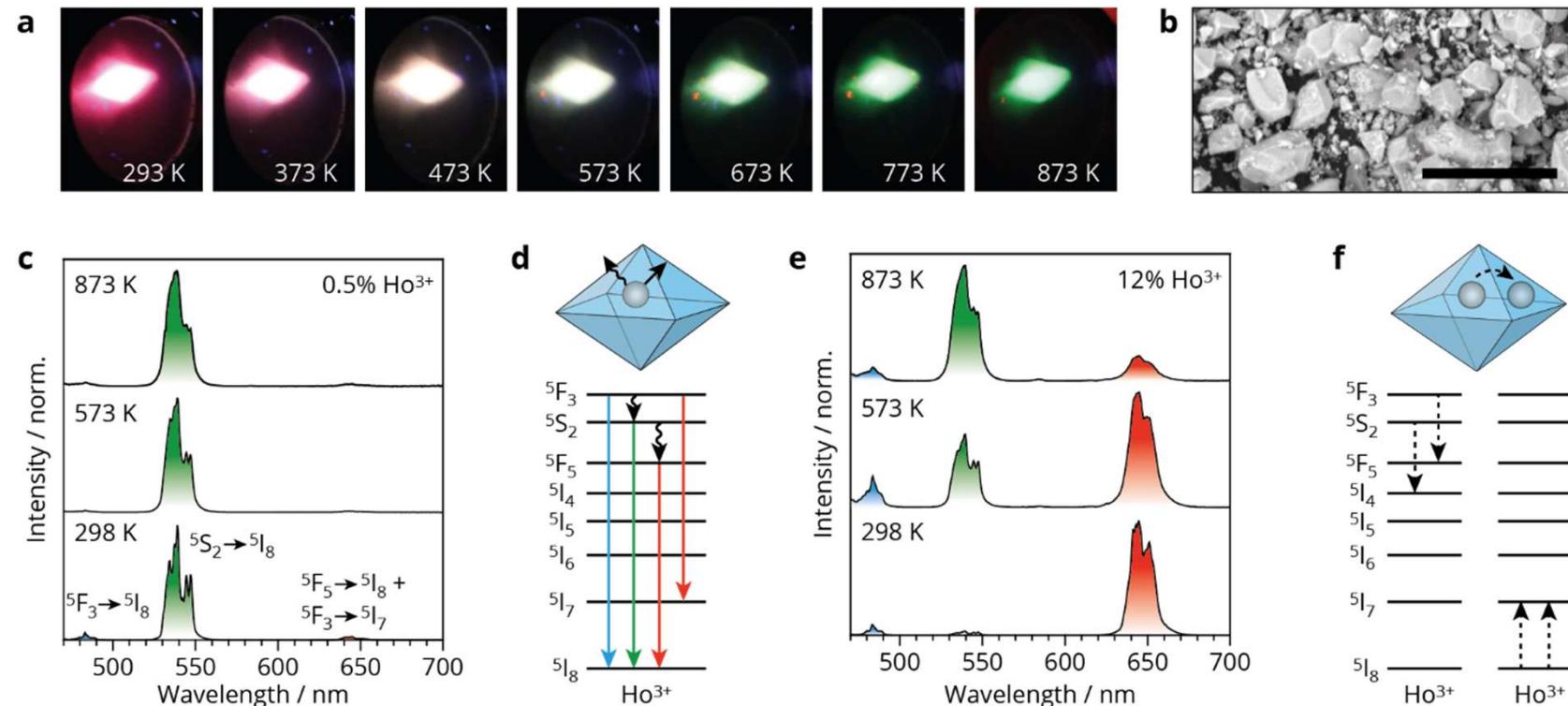
Structurally impose large mutual Nd-Nd distances for slower cross-relaxation!

Example: $\text{LiLa}_{1-x}\text{Nd}_x(\text{PO}_3)_4 \rightarrow$ minimum La-La distance $\sim 5.70 \text{ \AA}$ (vs. 4.10 \AA in LaPO_4)

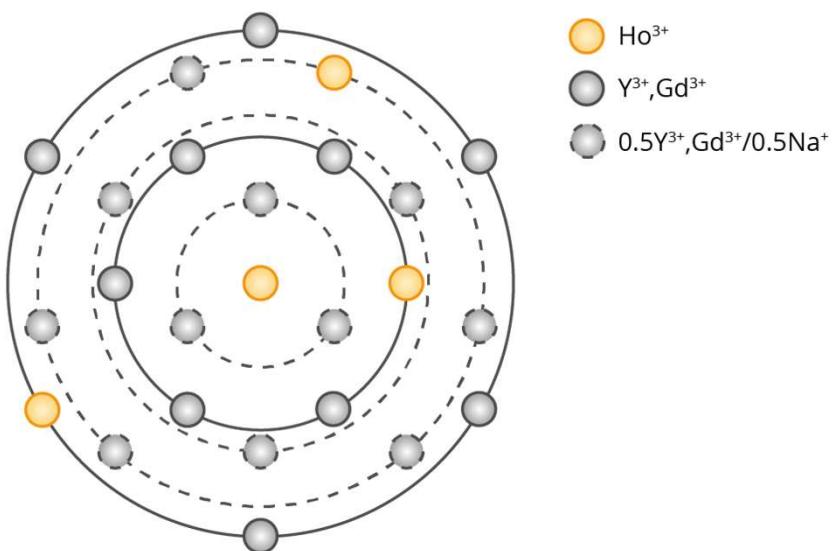


Make use of cross relaxation – Modelling and design of an energy transfer thermometer

$\beta\text{-NaY}_{0.75}\text{Gd}_{0.25}\text{F}_4$: $\phi\%$ Ho^{3+} ($\phi = 0.5; 4; 8; 12; 20; 30$): Synthesis from $\text{NaBF}_4 + (\text{Y, Gd})\text{F}_3 \& \text{HoF}_3$ at 500°C



Make use of cross relaxation – Modelling and design of an energy transfer thermometer



ET introduces an additional, independent decay pathway:

$$I(t) = I_0 \exp(-k_{\text{rad}}t) \cdot X(t)$$

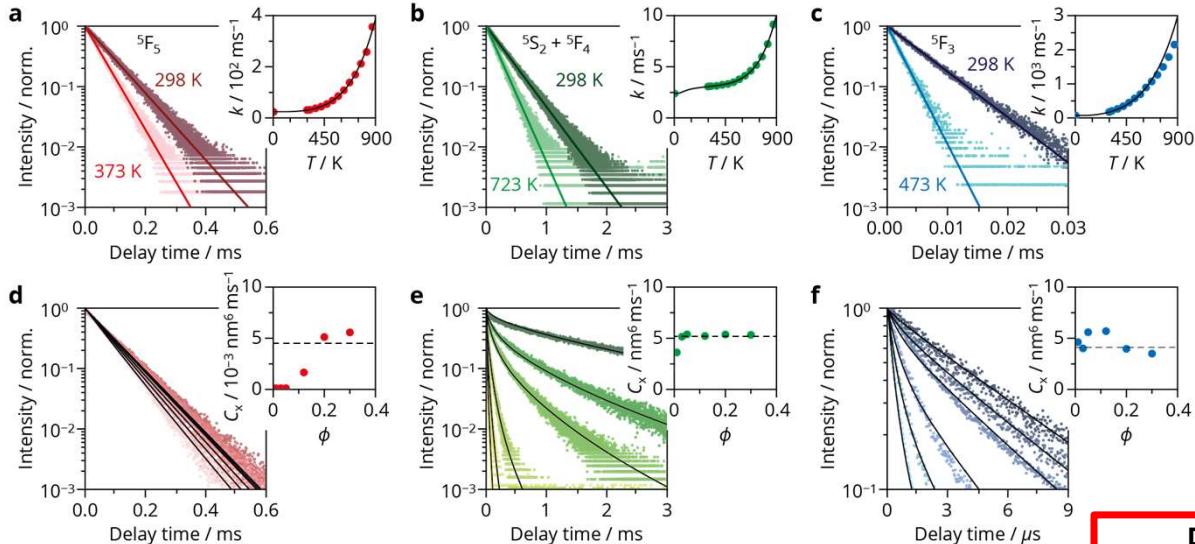
Shell model: Discretize the lattice and consider probabilities that n_j cation sites per shell j may be occupied by acceptors with probability ϕ :

$$X(t) = \prod_{j=1}^{\text{shells}} \left(1 - \phi + \phi \exp\left(-\frac{C_X}{r_j^6}t\right) \right)^{n_j}$$

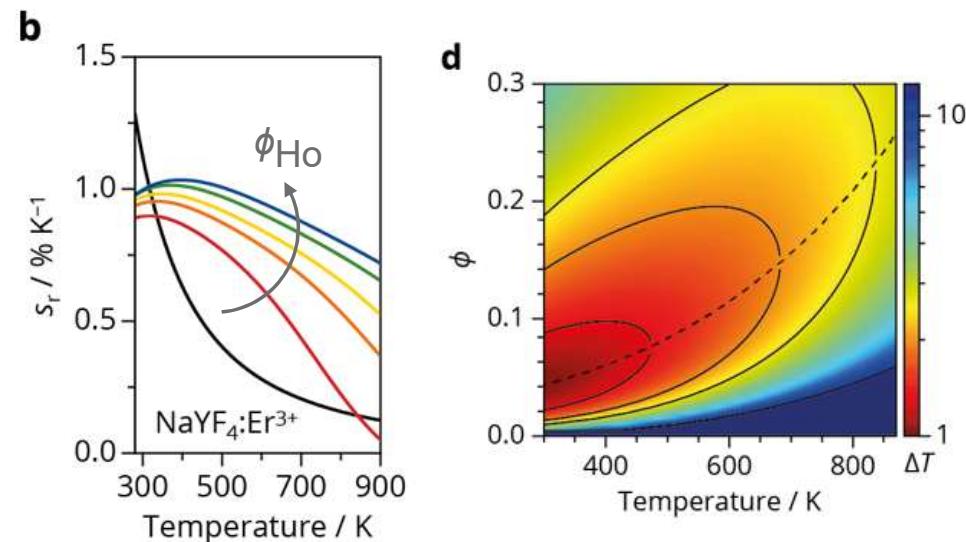
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Make use of cross relaxation – Modelling and design of an energy transfer thermometer



S_r can be retained at high value!



Possible to predict the optimum concentration per temperature for most precise temperature measurements!