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# Investigation of the crystal field in rare earth titanate pyrochlores by resonant inelastic x-ray scattering

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## Context

- Rare earth titanate pyrochlores $R_2Ti_2O_7$ (R = Sm, Tb, Dy, Er, Yb) possess **fascinating magnetic states** [1-2] depending on the rare earth element R.
- The **structural argument** (e.g. different lattice parameters) **cannot solely explain** the variety of observed states: quantum spin liquids, spin ices or spin glasses.
- Characterization of the **crystal electric field** (CEF) acting on the R sites is a key ingredient for the understanding of those states.
- The **large variety** of CEF **parametrizations** that came over time led to many misconceptions in the litterature, thus needing a **clear definition** for further work.

## 1. CEF potential expansion

- CEF potential $H_{\mathrm{CEF}}$ pertubates the spherical symmetry of the free ion Hamiltonian $H_{\mathrm{F}}$:

$$H = H_{\mathrm{F}} + H_{\mathrm{CEF}}$$

- One can express $H_{\mathrm{CEF}}$ as the sum of the potential $V$ felt by every single electron $i$ at a position $r_i$ of the R metal:

$$H_{\mathrm{CEF}} = -e\sum_{i=1}^{n} V(\boldsymbol{r}_i)$$

with $V$ expressed with a time dependent charge distribution $\rho(\boldsymbol{R})$

$$V(\boldsymbol{r}_i) = \int \frac{\rho(\boldsymbol{R})}{|\boldsymbol{R}-\boldsymbol{r}_i|}\mathrm{d}\tau$$

$$H_{\mathrm{CEF}} = -e\sum_{i=1}^{n}\int \rho(\boldsymbol{R})\sum_{k=0}^{\infty}\frac{r_i^k}{R^{k+1}}P_k(\cos\omega)\mathrm{d}\tau$$

where $P_k(\cos\omega)$ are the *Legendre polynomials* [3]:

$$P_k(\cos\omega) = \frac{4\pi}{2k+1}\sum_{q=-k}^{k}\underbrace{Y_k^{q*}(\theta,\varphi)}_{\boxed{\substack{\text{expansion coefficients}\\ Y_k^{q*}(\theta,\varphi)=(-1)^q Y_k^{-q}}}}\underbrace{Y_k^q(\theta_i,\varphi_i)}_{\boxed{\substack{\text{operators}\\ Y_k^q(\theta_i,\varphi_i)=Y_k^q(i)}}}$$

## 2. CEF as a sum of parameters

$$P_k(\cos\omega) = \frac{4\pi}{2k+1}\left[Y_k^0 Y_k^0(i) + \sum_{q=-k}^{k}(-1)^q\left(Y_k^{-q}Y_k^q(i) + Y_k^q Y_k^{-q}(i)\right)\right]$$

We introduce the **tesseral harmonics** $Z_{kq}$ to get rid of complex quantities:

$$Z_{k0}^c = Y_k^0,\quad Z_{kq}^c = \frac{1}{\sqrt{2}}\left(Y_k^{-q} + (-1)^q\, Y_k^q\right),\quad Z_{kq}^s = \frac{\mathrm{i}}{\sqrt{2}}\left(Y_k^{-q} - (-1)^q\, Y_k^q\right)$$

as well as **tensor operators** which have the same transformation properties as $Y_k^q$:

$$\mathbf{C}_q^k = \sqrt{\frac{4\pi}{2k+1}}Y_k^q(i)$$

It comes:

$$H_{\mathrm{CEF}} = \sum_{k=0}^{\infty}\sqrt{\frac{4\pi}{2k+1}}\left[Z_{k0}^c\mathbf{C}_0^k + \sum_{q=-k}^{k}\left(Z_{kq}^c\frac{1}{\sqrt{2}}\left(\mathbf{C}_{-q}^k + (-1)^q\mathbf{C}_q^k\right)\right.\right.$$
$$\left.\left. + Z_{kq}^s\frac{\mathrm{i}}{\sqrt{2}}\left(\mathbf{C}_{-q}^k - (-1)^q\mathbf{C}_q^k\right)\right)\right] \times \int \rho(\boldsymbol{R})\frac{r_i^k}{R^{k+1}}\mathrm{d}\tau$$

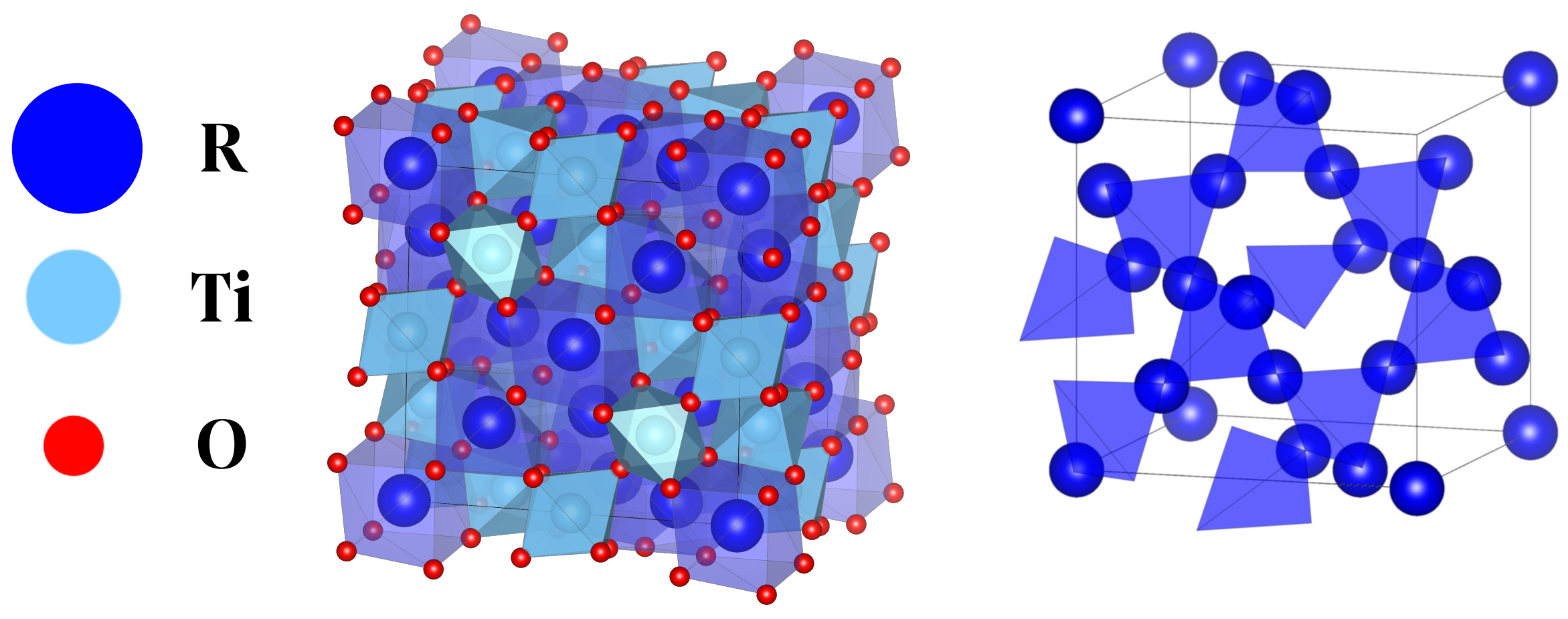
We eventually introduce **CEF parameters** $B_q^k$ to simplify the former expression:

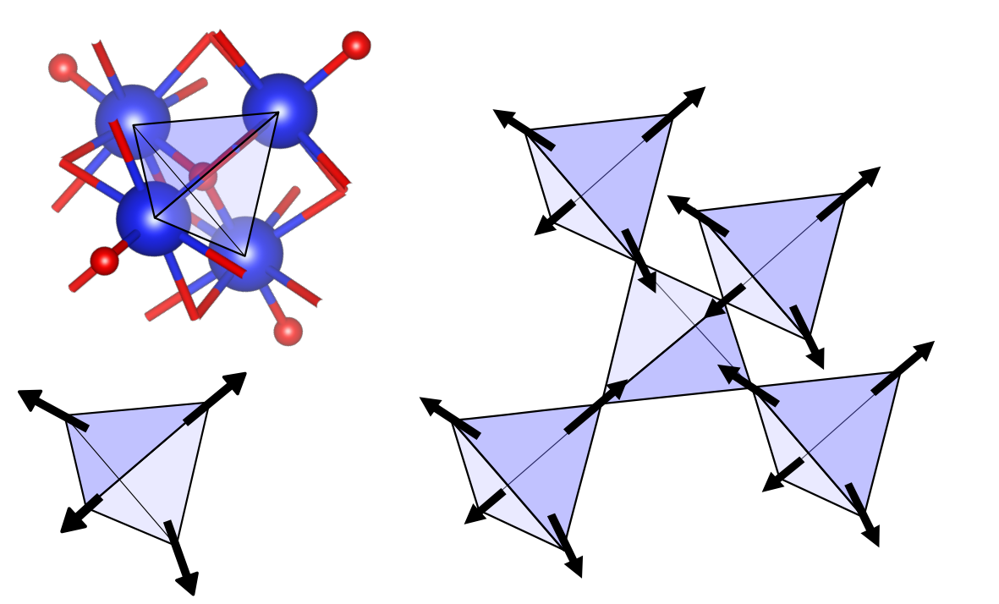
$$B_0^k = \sqrt{\frac{4\pi}{2k+1}}Z_{k0}^c\int \rho(\boldsymbol{R})\frac{r_i^k}{R^{k+1}}\mathrm{d}\tau$$

$$B_q^k = \sqrt{\frac{4\pi}{2k+1}}\frac{Z_{kq}^c}{\sqrt{2}}\int \rho(\boldsymbol{R})\frac{r^k}{R^{k+1}}\mathrm{d}\tau \qquad B_q'^k = \sqrt{\frac{4\pi}{2k+1}}\frac{Z_{kq}^s}{\sqrt{2}}\int \rho(\boldsymbol{R})\frac{r^k}{R^{k+1}}\mathrm{d}\tau$$

$$H_{\mathrm{CEF}} = \sum_{k=0}^{\infty}\left[B_0^k\mathbf{C}_0^k + \sum_{q=-k}^{k}\left(B_q^k\left(\mathbf{C}_{-q}^k + (-1)^q\mathbf{C}_q^k\right) + B_q'^k\left(\mathbf{C}_{-q}^k - (-1)^q\mathbf{C}_q^k\right)\right)\right]$$

## 3. The $R_2Ti_2O_7$ case



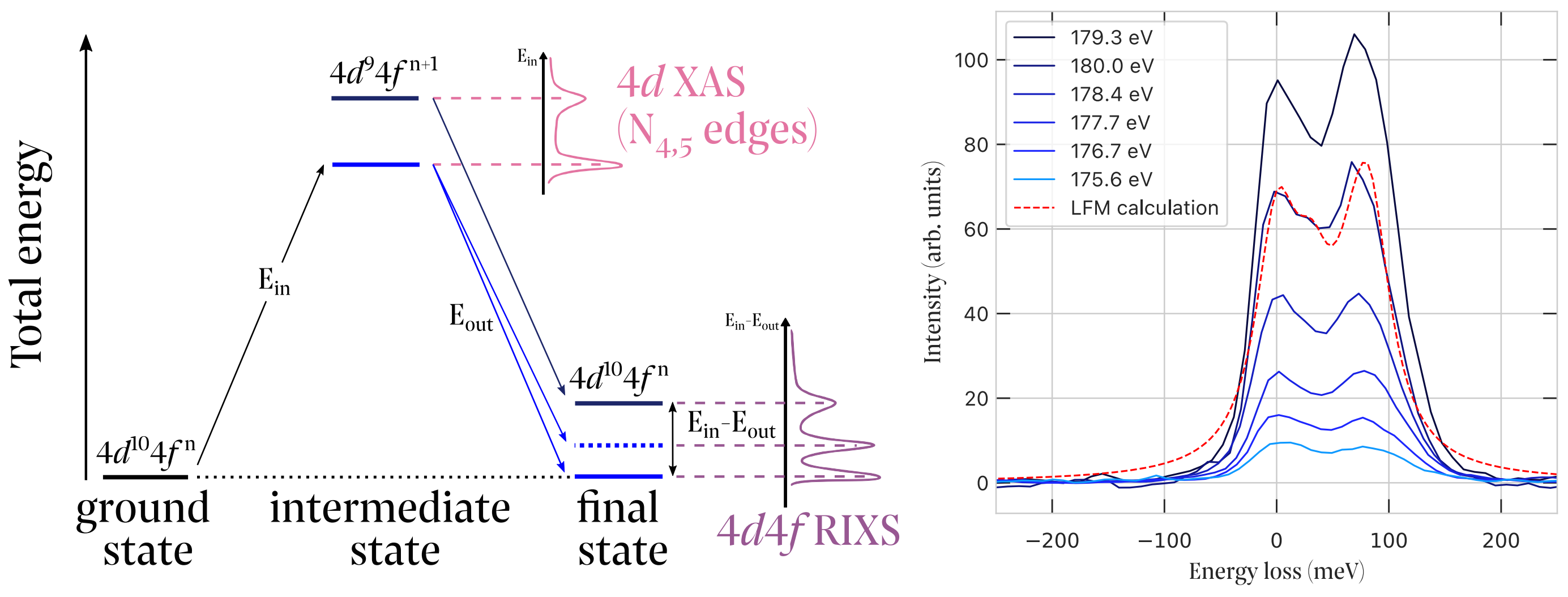


*R atoms arranged in tetrahedrons with frustrated magnetic moments at the apexes*

- **R** atoms and **Ti** atoms are situated in two different **apexes-sharing tetrahedrons sub-lattices** that interpenetrate into one another;
- **Magnetic moments** are geometrically **frustrated** (**3D kagomé lattices**);
- $D_{3d}$ **point symmetry group**, $k$ and $q$ are limited and CEF in $R_2Ti_2O_7$ compounds can be described by:

$$H_{\mathrm{CEF}} = B_0^2\mathbf{C}_0^2 + B_0^4\mathbf{C}_0^4 + B_3^4(\mathbf{C}_{-3}^4 - \mathbf{C}_3^4) + B_0^6\mathbf{C}_0^6 + B_3^6(\mathbf{C}_{-3}^6 - \mathbf{C}_3^6) + B_6^6(\mathbf{C}_{-6}^6 + \mathbf{C}_6^6)$$

## 4. How to characterize the CEF



*RIXS process representation and RIXS spectra of the CEF effect in $Yb_2Ti_2O_7$ measured on SEXTANTS beamline in SOLEIL, at the Yb $N_{4,5}$ edge.*

- **High-resolution RIXS** allows probing the CEF;
- AERHA spectrometer [4] on SEXTANTS is **worldwide** the only instrument offering the required **energy resolution**
- Simulations run through **Quanty** software package [5]: **Ligand Multiplet Theory** calculations with CEF contribution, expanded on **spherical tensors**.

## 5. Conclusion and outlook

- Choice of a clear definition based on spherical tensors, that can directly be used in Quanty code.
- First observation of the CEF effect in pyrochlore crystals at the R $N_{4,5}$ edges with RIXS.
- Precise extraction of CEF parameters in $R_2Ti_2O_7$ ongoing, with new experiments and machine learning.

more:

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