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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 literature, thus needing a **clear definition** for further work.

1. CEF potential expansion

- CEF potential H_{CEF} perturbs the spherical symmetry of the free ion Hamiltonian H_F :

$$H = H_F + H_{\text{CEF}}$$

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

$$H_{\text{CEF}} = -e \sum_{i=1}^n V(r_i)$$

with V expressed with a time dependent charge $V(r_i) = \int \frac{\rho(\mathbf{R})}{|\mathbf{R} - \mathbf{r}_i|} d\tau$ distribution $\rho(\mathbf{R})$

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

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

$$P_k(\cos \omega) = \frac{4\pi}{2k+1} \sum_{q=-k}^k Y_k^{q*}(\theta, \varphi) Y_k^q(\theta_i, \varphi_i)$$

expansion coefficients

$$Y_k^{q*}(\theta, \varphi) = (-1)^q Y_k^{-q}$$

operators

$$Y_k^q(\theta_i, \varphi_i) = Y_k^q(i)$$

2. CEF as a sum of parameters

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

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

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

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

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

It comes:

$$H_{\text{CEF}} = \sum_{k=0}^{\infty} \sqrt{\frac{4\pi}{2k+1}} \left[Z_{k0}^c C_0^k + \sum_{q=-k}^k \left(Z_{kq}^c \frac{1}{\sqrt{2}} (C_{-q}^k + (-1)^q C_q^k) + Z_{kq}^s \frac{i}{\sqrt{2}} (C_{-q}^k - (-1)^q C_q^k) \right) \right] \times \int \rho(\mathbf{R}) \frac{r_i^k}{R^{k+1}} d\tau$$

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

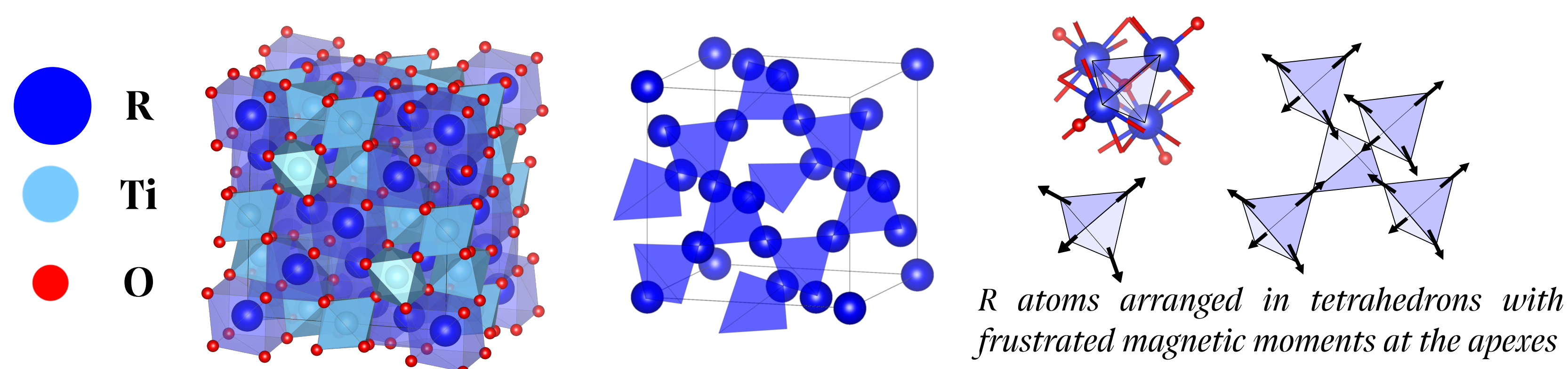
$$B_0^k = \sqrt{\frac{4\pi}{2k+1}} Z_{k0}^c \int \rho(\mathbf{R}) \frac{r_i^k}{R^{k+1}} d\tau$$

$$B_q^k = \sqrt{\frac{4\pi}{2k+1}} \frac{Z_{kq}^c}{\sqrt{2}} \int \rho(\mathbf{R}) \frac{r_i^k}{R^{k+1}} d\tau$$

$$B_q'^k = \sqrt{\frac{4\pi}{2k+1}} \frac{Z_{kq}^s}{\sqrt{2}} \int \rho(\mathbf{R}) \frac{r_i^k}{R^{k+1}} d\tau$$

$$H_{\text{CEF}} = \sum_{k=0}^{\infty} \left[B_0^k C_0^k + \sum_{q=-k}^k \left(B_q^k (C_{-q}^k + (-1)^q C_q^k) + B_q'^k (C_{-q}^k - (-1)^q C_q^k) \right) \right]$$

3. The $R_2Ti_2O_7$ case



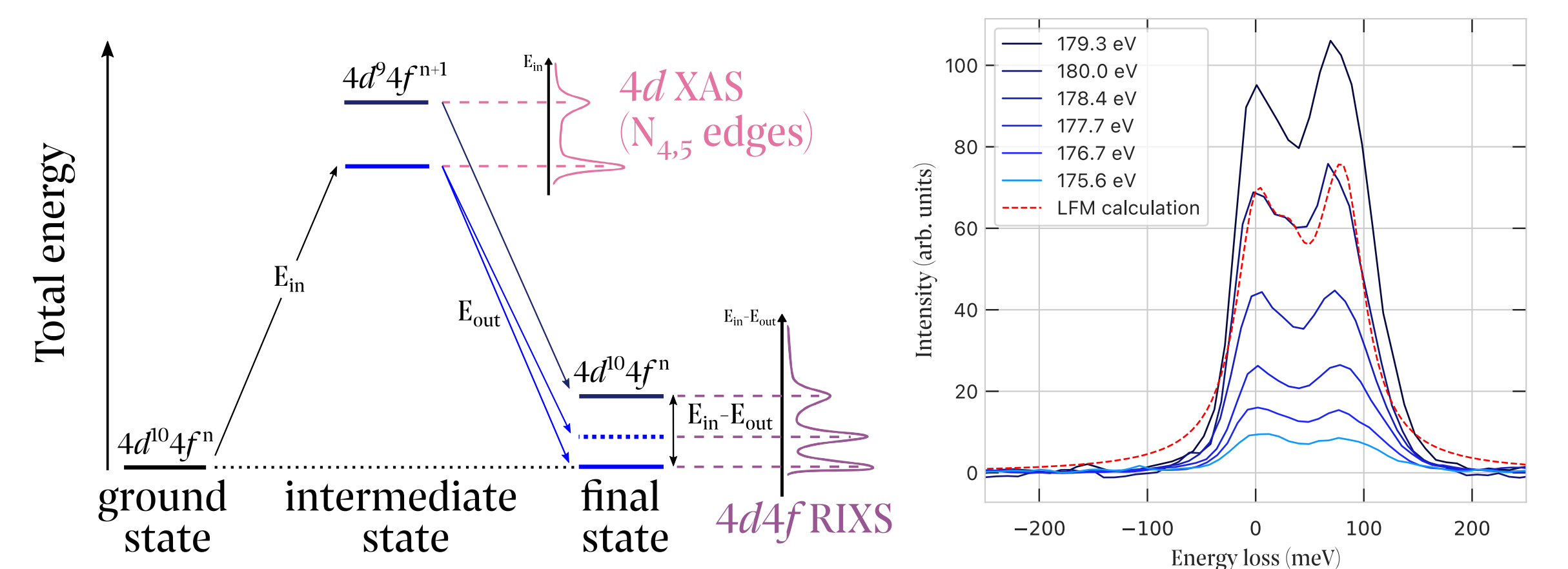
- R atoms and Ti atoms are situated in two different **apexes-sharing tetrahedrons sub-lattices** that interpenetrate into one another;
- **Magnetic moments** are geometrically **frustrated (3D kagomé lattices)**;
- D_{3d} **point symmetry group**, k and q are limited and CEF in $R_2Ti_2O_7$ compounds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

$$H_{\text{CEF}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_3^4 (C_{-3}^4 - C_3^4) + B_0^6 C_0^6 + B_3^6 (C_{-3}^6 - C_3^6) + B_6^6 (C_{-6}^6 + C_6^6)$$

5. Conclusion and outlook

- Choice of a clear definition based on spherical tensors, that can directly be used in Quany 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.

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 **Quany** software package [5]: **Ligand Multiplet Theory** calculations with CEF contribution, expanded on **spherical tensors**.



- more:
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