Interpreting Diffuse Scattering From a Disordered Sodium Lanthanum Fluoride Crystal Showing Upconversion of Light

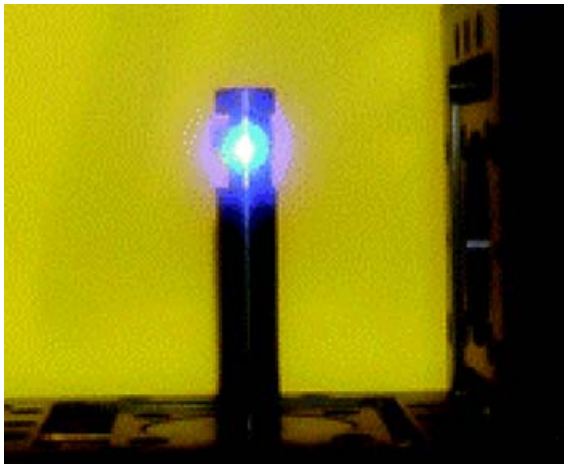
J. Hauser, M. Hostettler,
Th. Weber, H.B. Bürgi
Lab of Crystallography

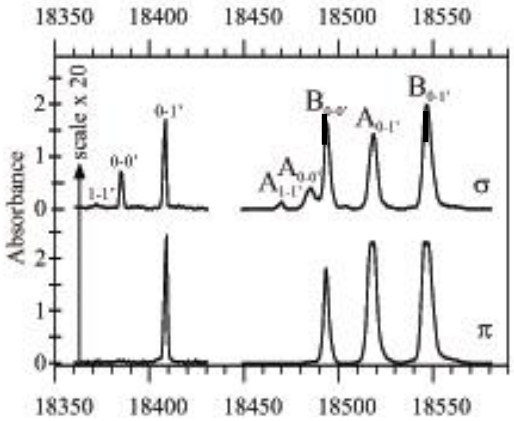
Total scattering PDF analysis using X-rays and neutrons: powder diffraction and complementary techniques
ESRF, October 22-23, 2007

Doped hexagonal $NaLnF_4$ are very efficient up-conversion materials a case study

- What is an upconversion phosphor?
- Occupational disorder and positional disorder above and below the resolution limit
- Combined interpretation of Bragg and of distinct diffuse scattering
- A test case for PDF analysis?

Upconversion phosphors





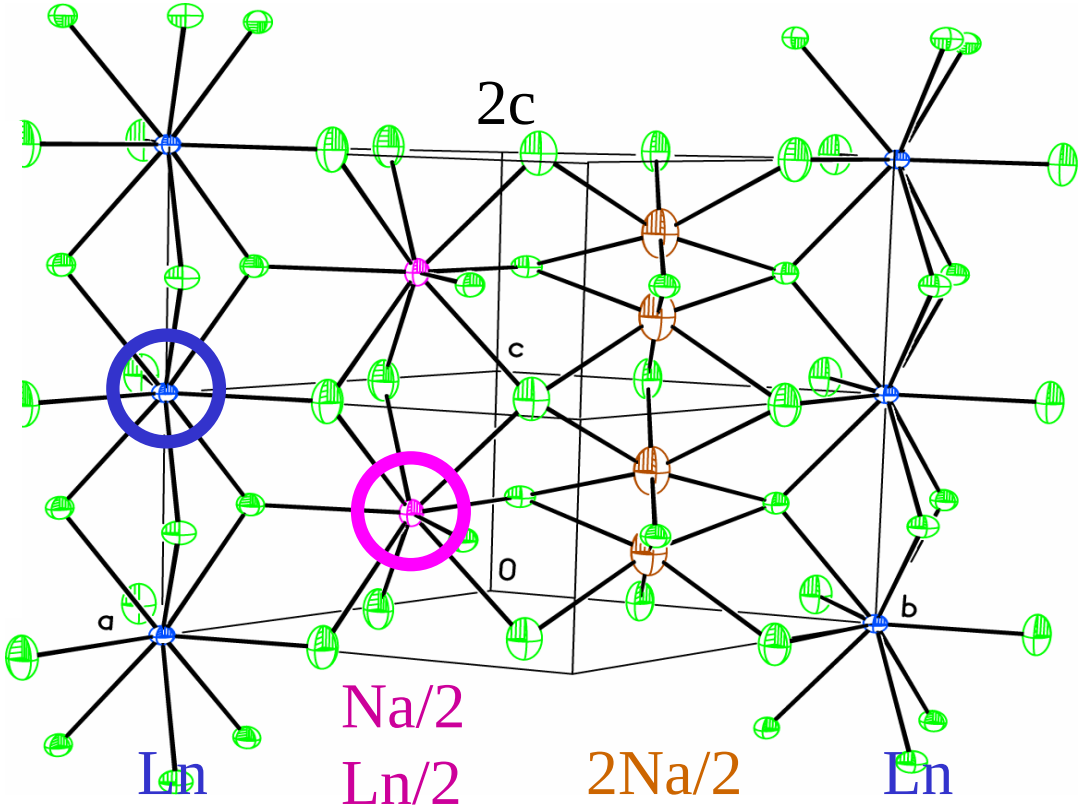
$LaCl_3$:0.1% Er^{3+} $NaGdF_4$:10% Er^{3+}

$NaLaF_4 : Yb^{3+}$, Er^{3+} and $NaGdF_4 : Yb^{3+}$, Er^{3+} are the best materials for converting NIR into visible light

Polarized absorption spectra

- **Right: $NaGdF_4$:10% Er^{3+} two sites: A (C_{3h}), B (C_1)**
- Left: $LaCl_3$:0.1% Er^{3+} one site (C_{3h})

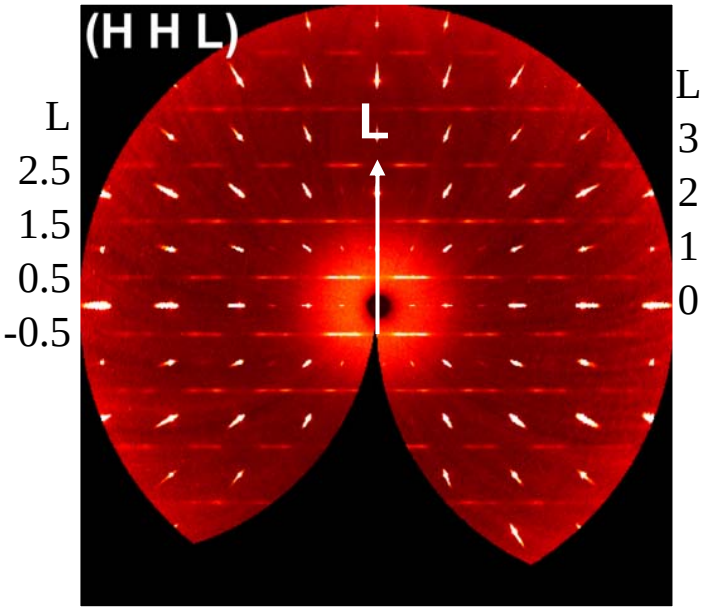
Best structure from Bragg reflections



- $P\bar{6}$, R ~ 0.01

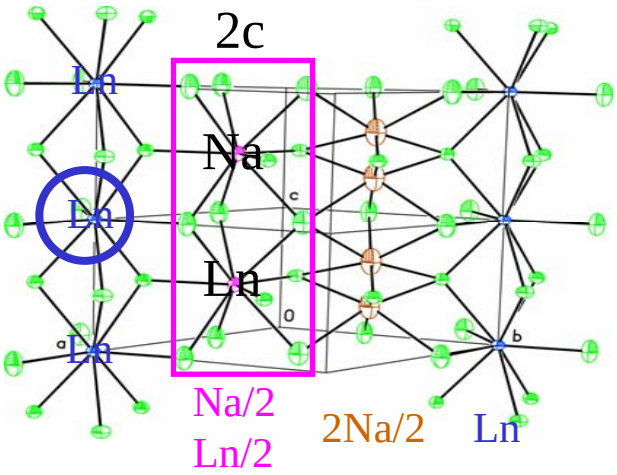
- **two Ln-sites, but both with C_{3h} symmetry!!**

- one disordered (Na/2, Ln/2), one fully ordered (Ln)



$NaLnF_4$, planar diffuse scattering

- Regular array of Bragg peaks
- plus sharp lines at half-integer L

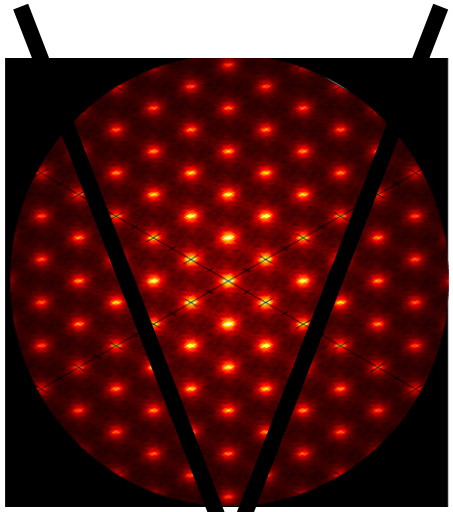


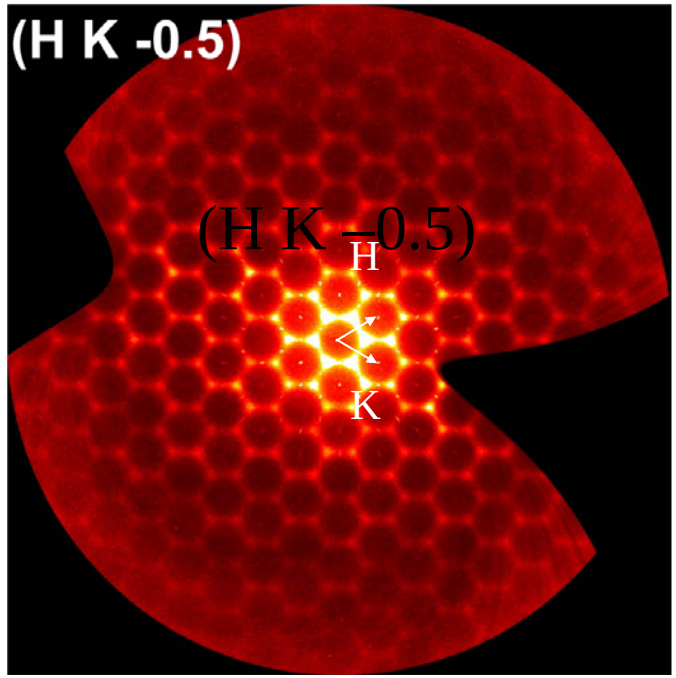
> Translational symmetry along c

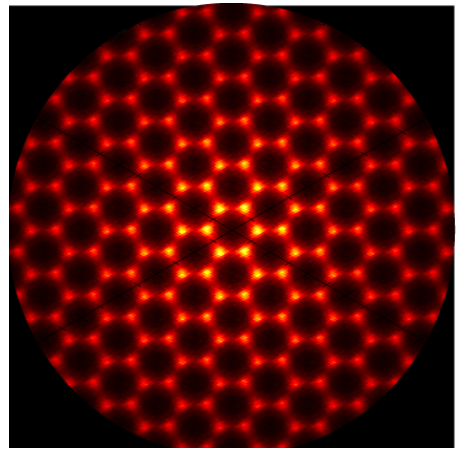
> Columns with Ln…Na…Ln…Na

> strictly alternating along c

$NaLnF_4$, planar diffuse scattering

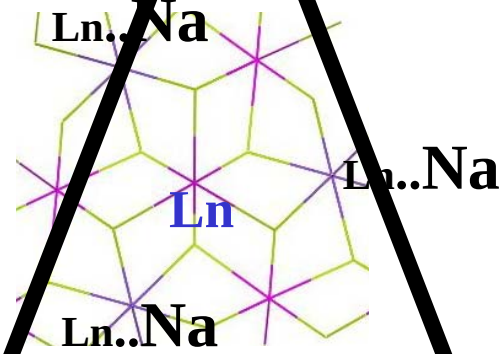




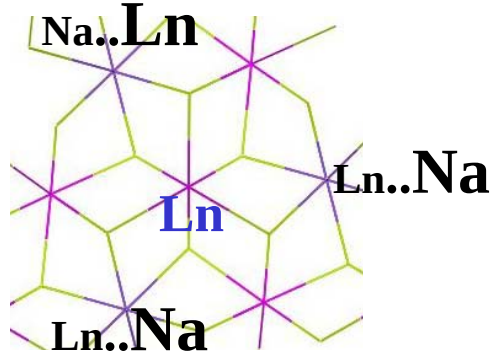


Positive Correlation

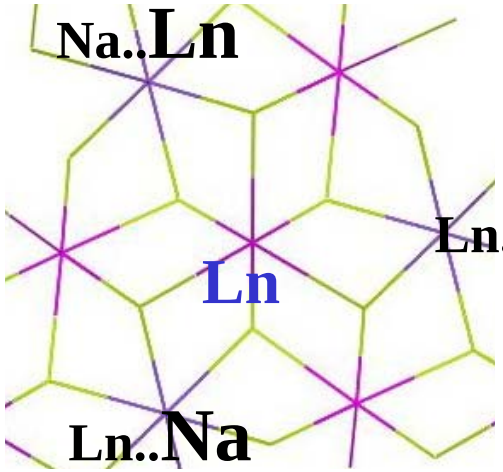
Negative Correlation

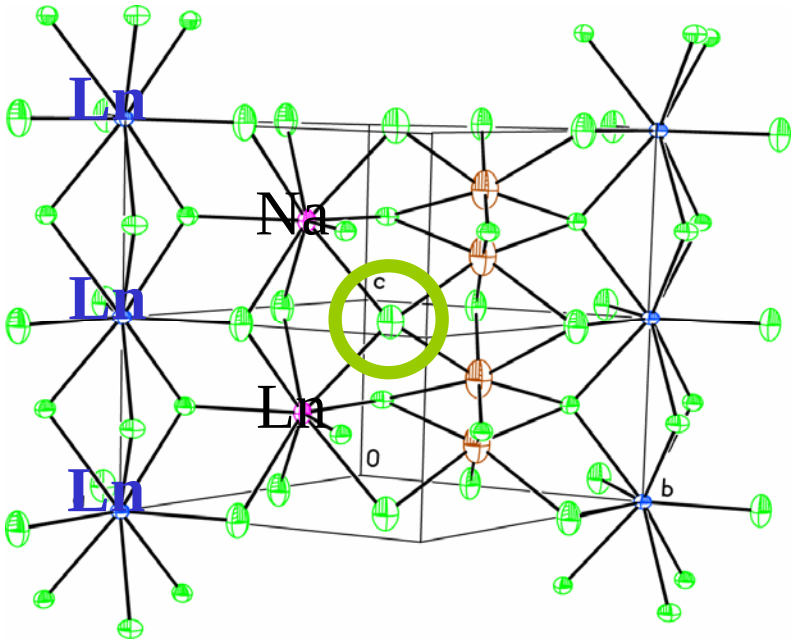


Honeycomb pattern at half integer L,



A. Aebischer, et al., *Angew. Chem. Int. Ed.*, 45 (2006) 2802-2806





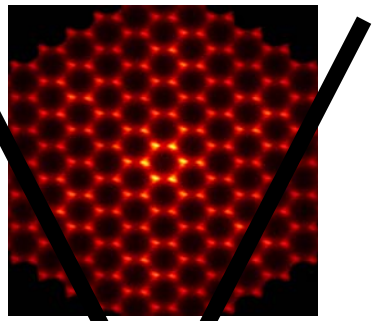
$NaLnF_4$, Fluorine

- Both ligand geometries $(F^-)_9$ still with local C_{3h}-symmetry

- U_{33} of circled F larger than any other U_{ii} component of F's
- No necessity for F^- to be exactly midway between Ln^{3+} and Na^+

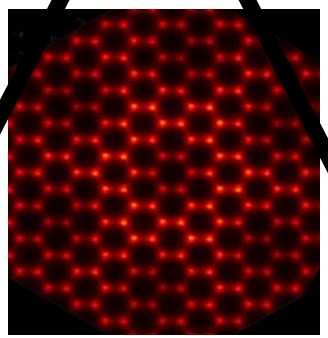
$NaLnF_4$, Displacement of Fluorine

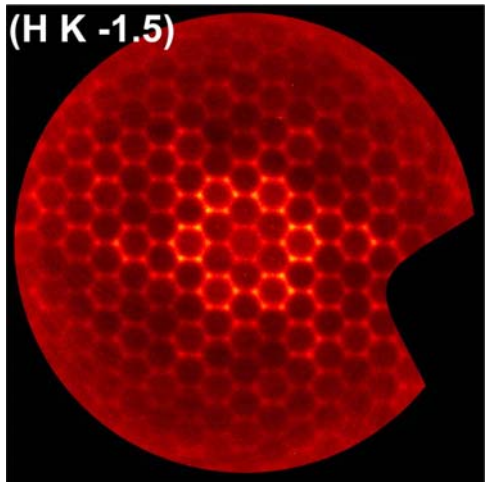
Simulation

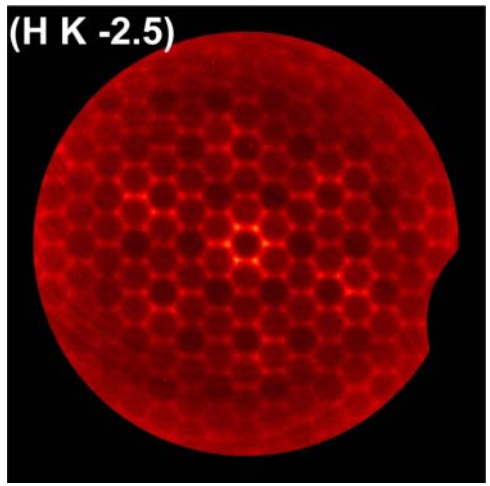


F^- towards Na^+

$d(Ln\text{-}F) > d(Na\text{-}F)$







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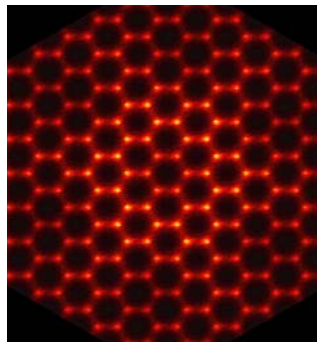
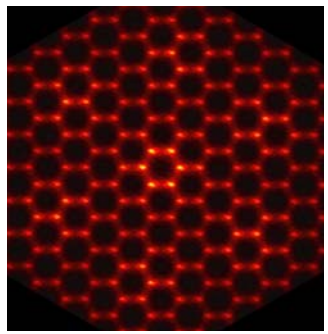


F^- towards Ln^{3+}

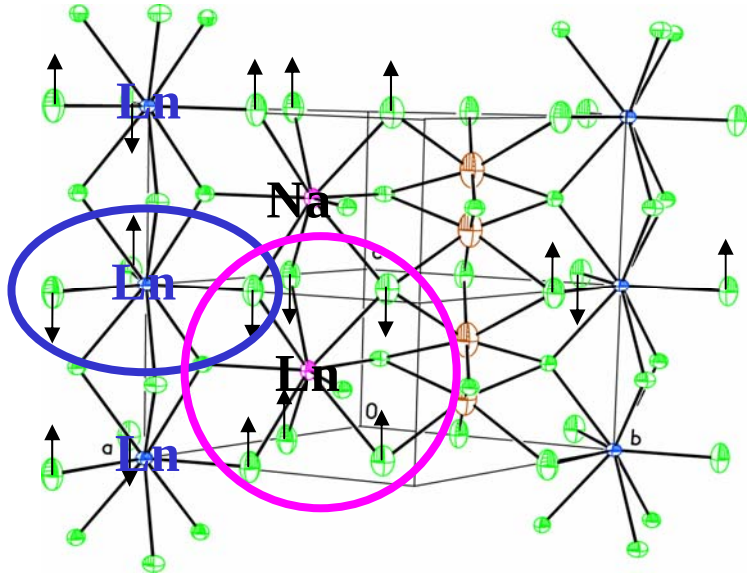
$d(Ln\text{-}F) < d(Na\text{-}F)$

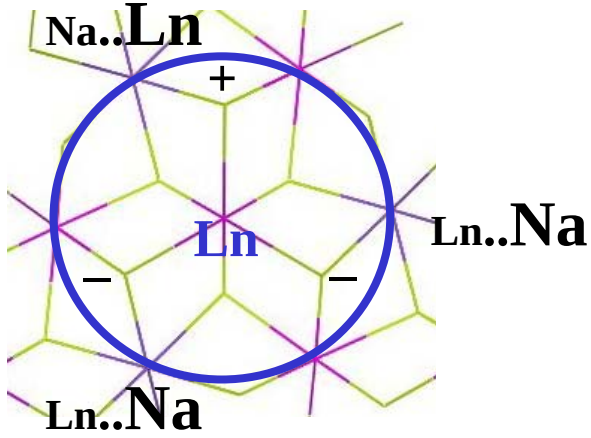


$NaLnF_4$, Results

- Two different Ln-sites in disordered structure
  one with C_{3h} symmetry
  one with C_1 symmetry

- Explains spectroscopic observation, provides a basis for modeling the high efficiency of upconversion





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Loss of Translation – Lost in Translation

- Dopped Na Ln F_4 is an interesting optical material

- Na Ln F_4 shows particularly simple occupational and positional disorder phenomena

- Probabilistic/Monte Carlo modeling of ‘crystal’

- how much information could be retrieved from a PDF analysis?