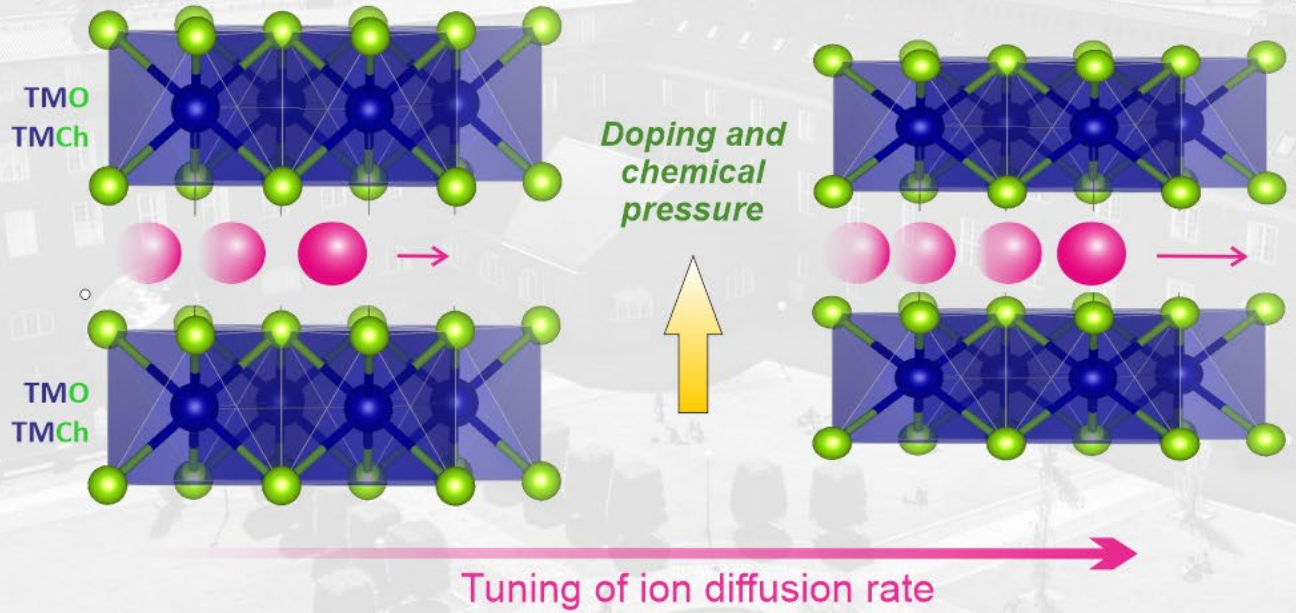
Na-ion Dynamics in the Solid Solution $Ca_{1-x}Na_xCr_2O_4$ Studied by Neutron Diffraction and μ^+SR



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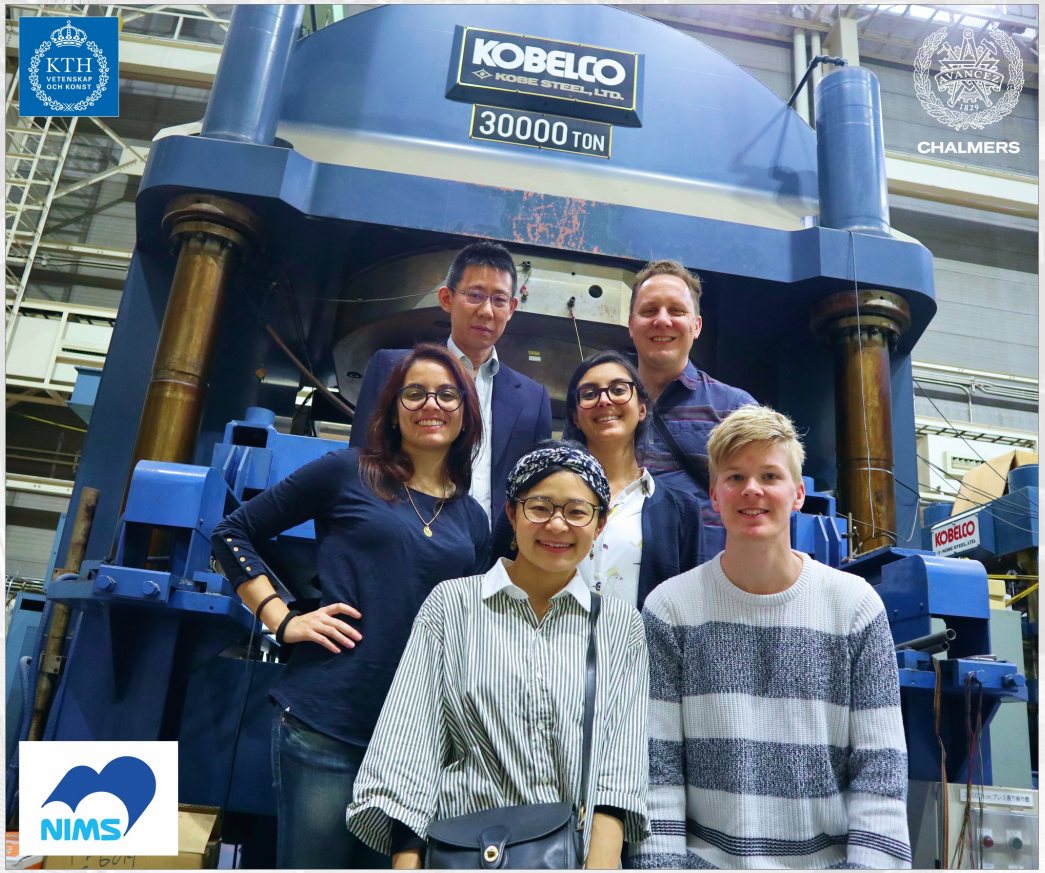
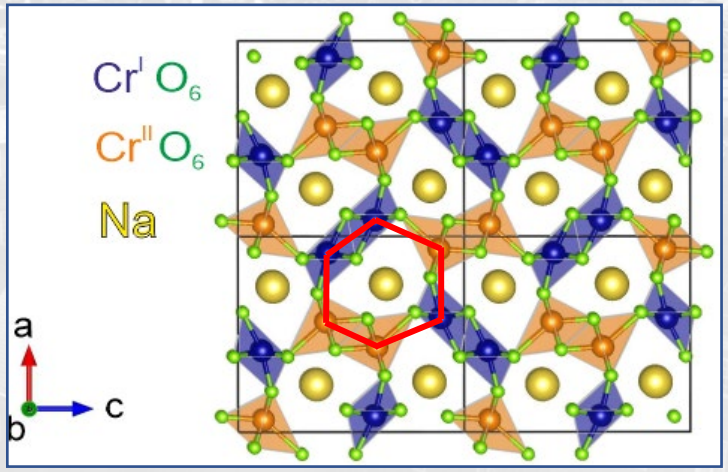
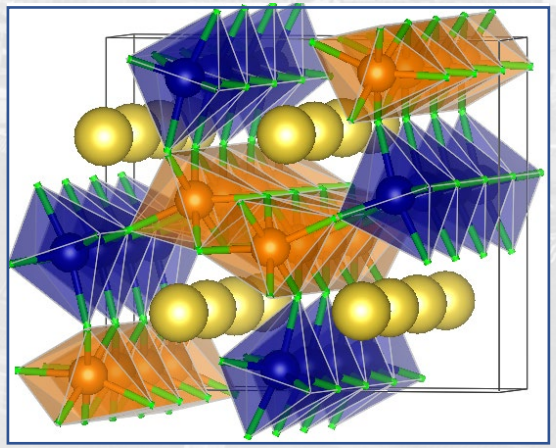
Q1D Zig-zag ladder Transition Metal Oxide $NaCr_2O_4$ and the solid solution $Ca_{1-x}Na_xCr_2O_4$

High pressure synthesis technique



Sakurai, H.. "High-Pressure Synthesis and Electronic Properties of Cr(IV) Oxides." Journal of The Japan Society of Powder and Powder Metallurgy 64 (2017): 163-172.





- Orthorhombic *Pnma* structure with Cr double chains along *b*
- Unconventional CMR, complex magnetic ground state
- In β-$CaCr_2O_4$-$NaCr_2O_4$ the Na^+ substitution for Ca^{2+} (hole doping) leads to the partial oxidation of Cr^{3+} to Cr^{4+} (mixed valence), induces a change from IC-AF to C-AF, charge frustration and geometrical frustration in $NaCr_2O_4$
- 1D hexagonal diffusion channels for Na ions

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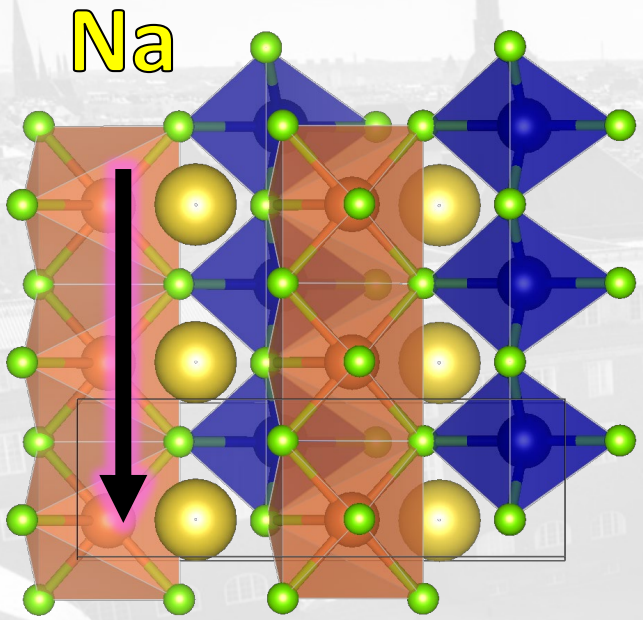
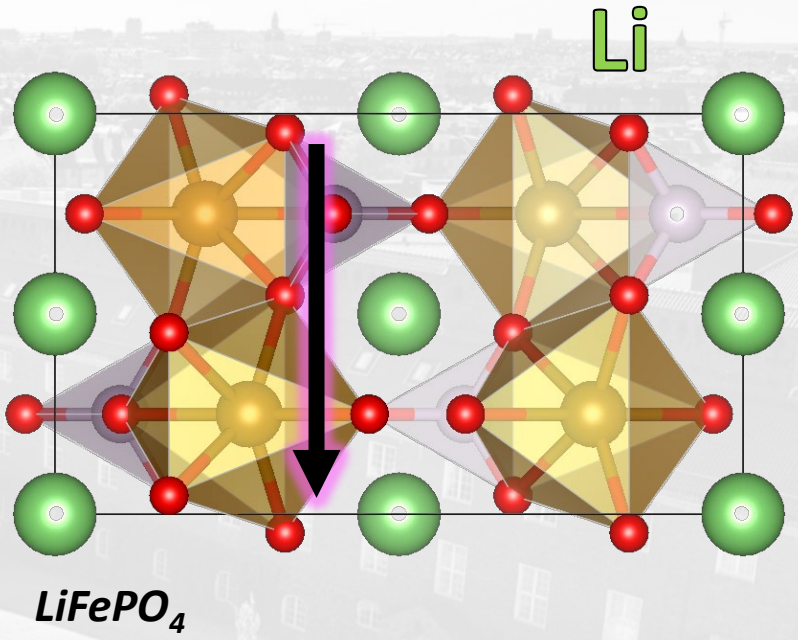
Motivation



$NaCr_2O_4$



$LiFePO_4$

Systematic doping-dependent study on $Ca_{1-x}Na_xCr_2O_4$ with [x = 0.3, 0.5, 0.7, 0.85, 0.90, 0.95, 1] to investigate how the size and the ionic content of the 1D CrO_6 diffusion channels affects the kinetics of Na ions. If the Ca ions are regarded as ”defects”, this study provides a description of phenomena occurring in low dimensional battery materials affected by defects.

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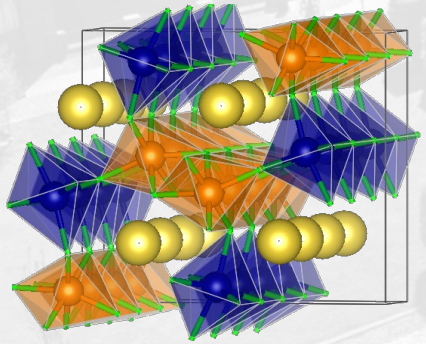
Experimental Techniques

Neutron Diffraction

Time of flight diffractometers iMATERIA + SPICA.
T range [2, 300] K
Powder samples ~ 0.7 g
V sample holder

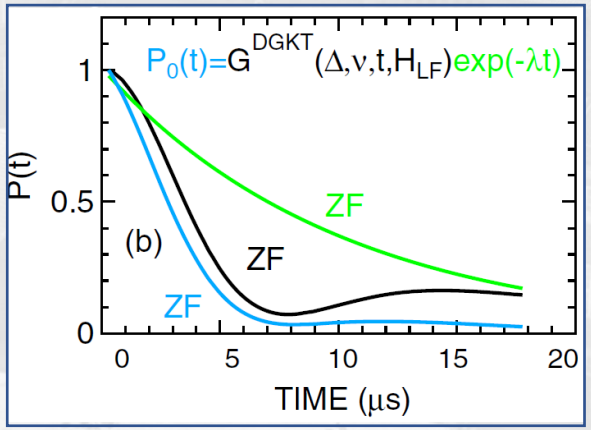
RT structural evolution of the solid solution



LF μ^+SR

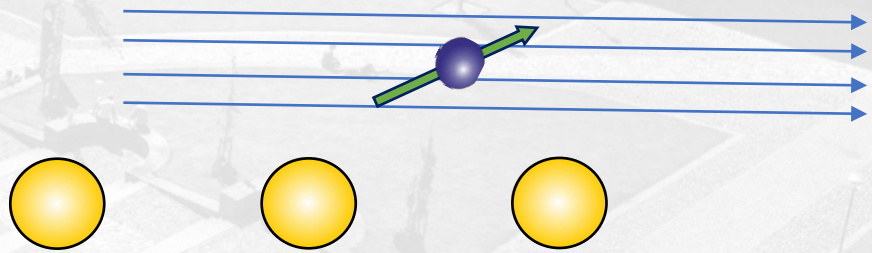
Science & Technology Facilities Council ISIS

Muon spectrometers EMU + RIKEN-Ral
T range [100, 600] K
Powder samples ~1.4 g
Ti sample holder



M. Månsson and J. Sugiyama, Phys. Scr. 88 (2013)

Muons sense fluctuating electronic moments + changes in nuclear dipole field due to ion diffusion.
A longitudinal field (LF) is used to decouple the magnetic and nuclear dipole interactions



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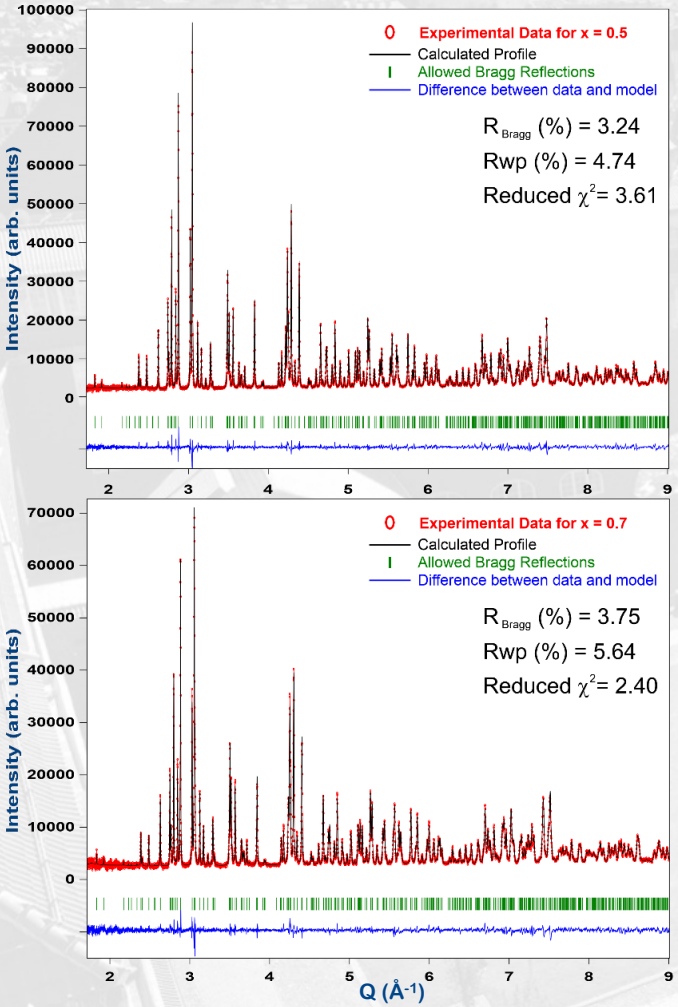
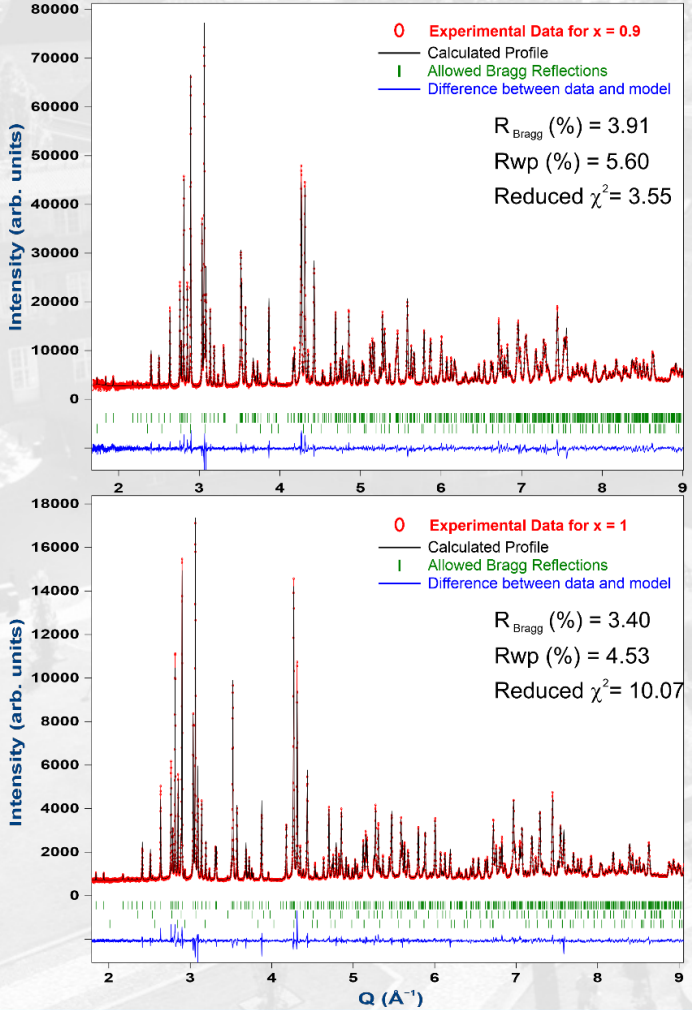
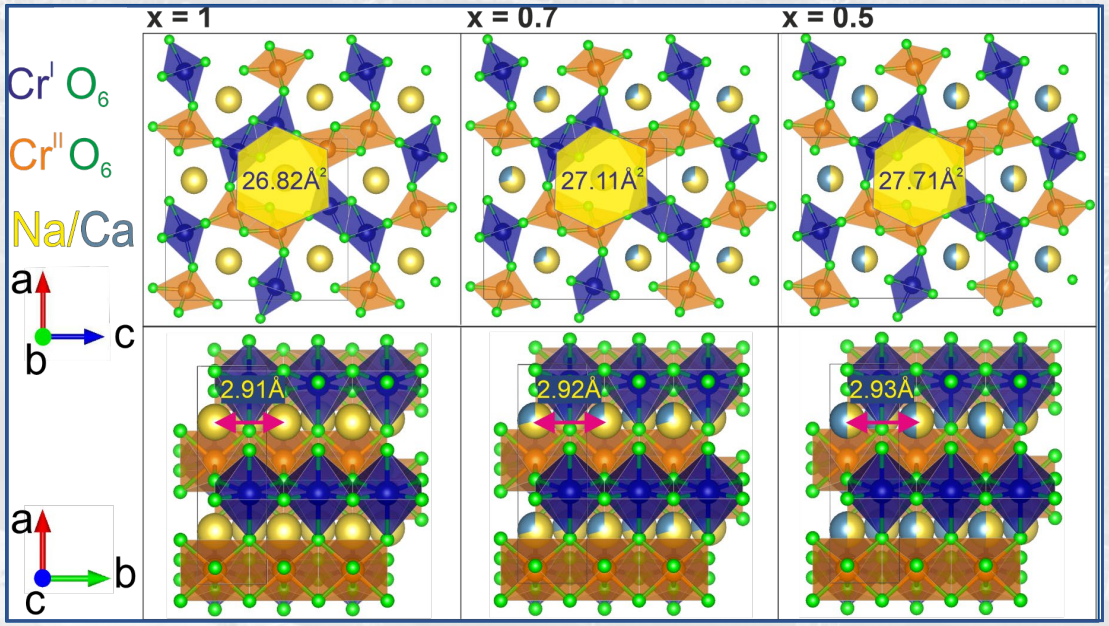
Neutron Diffraction results

Rietveld refinement of the diffraction data at T = 300K





Structural evolution of the 1D channel



Pnma

a = 9.0154(1) -> 9.0418(1)
b = 2.9128(1) -> 2.9297(1)
c = 10.4138(9) -> 10.5640(2)

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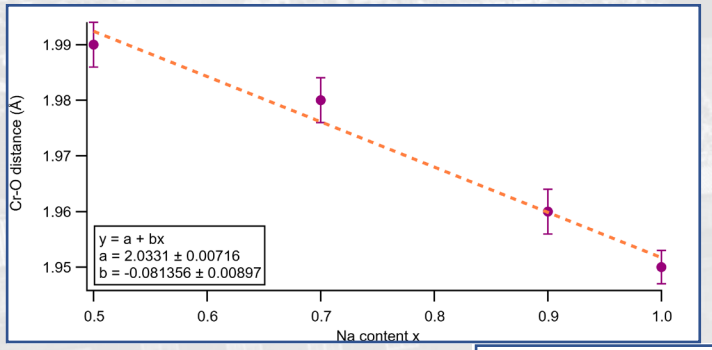
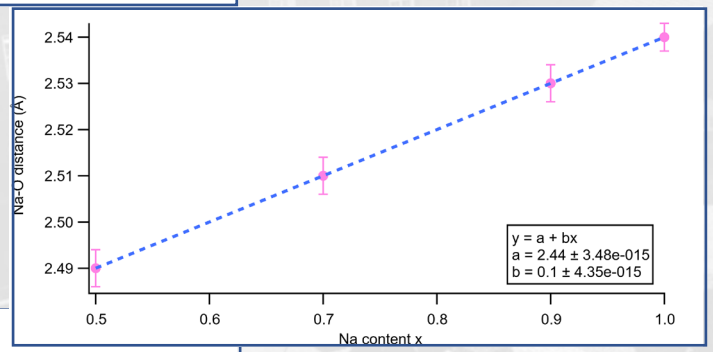
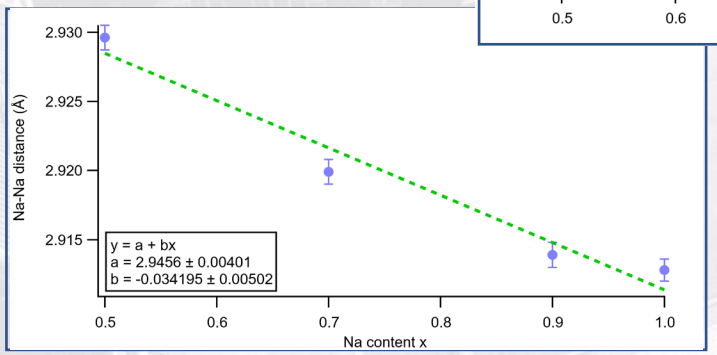
Neutron Diffraction results

Atomic distances







- Cr-O distance decreases due to charge separation from Cr^{3+} (x = 0.5) to $Cr^{3.5+}$ (x = 1)
- Lower occupation of *3d* orbitals → enhanced Cr-O bond stability
- Reduction of Cr atomic radius → TMO octahedra contracts
- Na-O distance increases → weakened Na-O bond
- Unit cell volume decreases
- The 1D channels shrink

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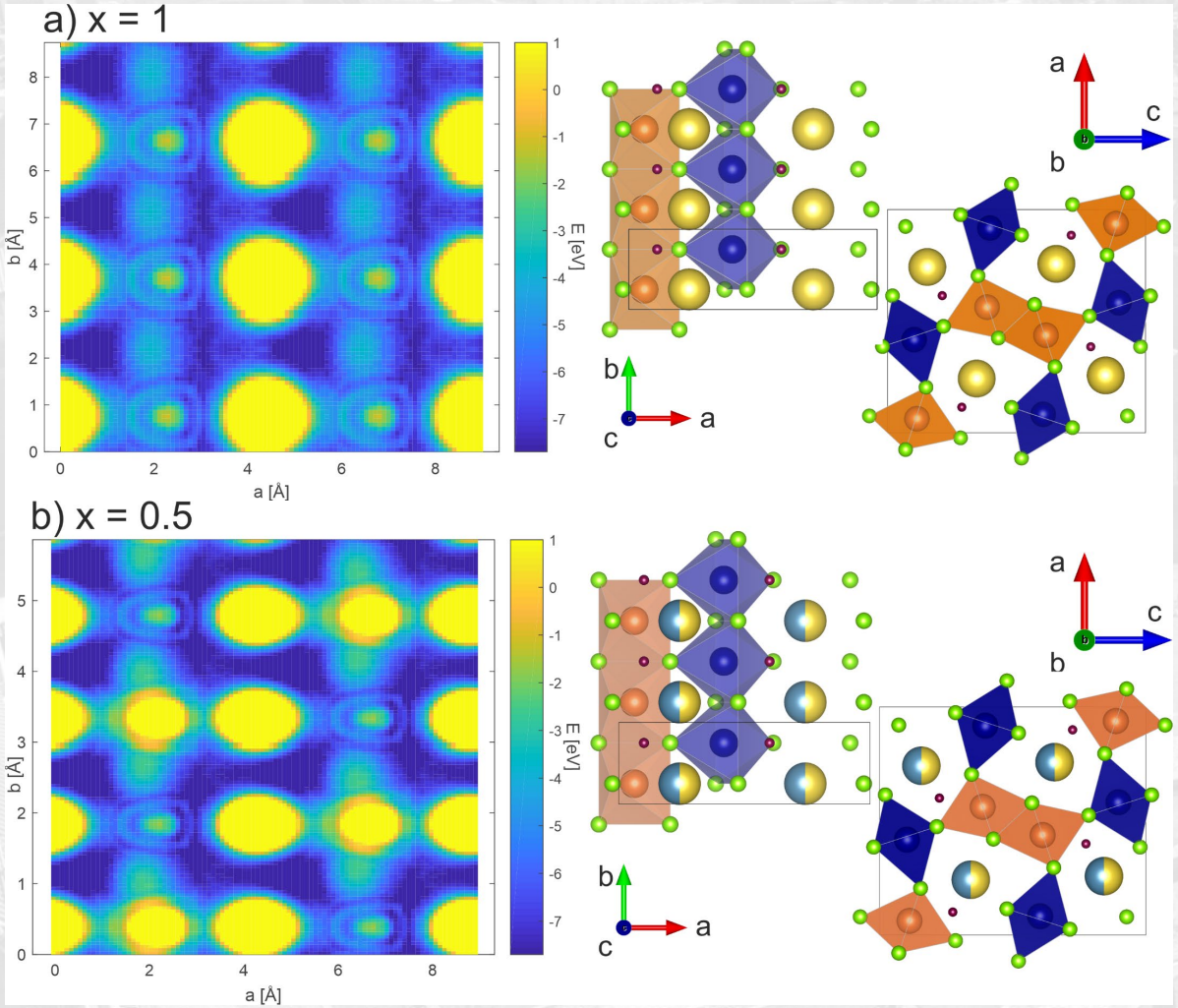
The proposed Na-ion diffusion path

Electrostatic potential energy distribution



We propose Interstitialcy mechanism, since the Na/Ca site is fully occupied
The diffusion path is estimated based on the charge densities in the compound, calculated in the DFT framework with the pseudopotentials method.

$$V_{Hartree} + V_{ionic} + V_{exchange\,corr}$$

Interstitial sites in fractional coordinates:

X = 1 -> [0.114(6), 0.750(0), 0.287(9)]
X = 0.5 -> [0.100(2), 0.750(10), 0.275(1)]

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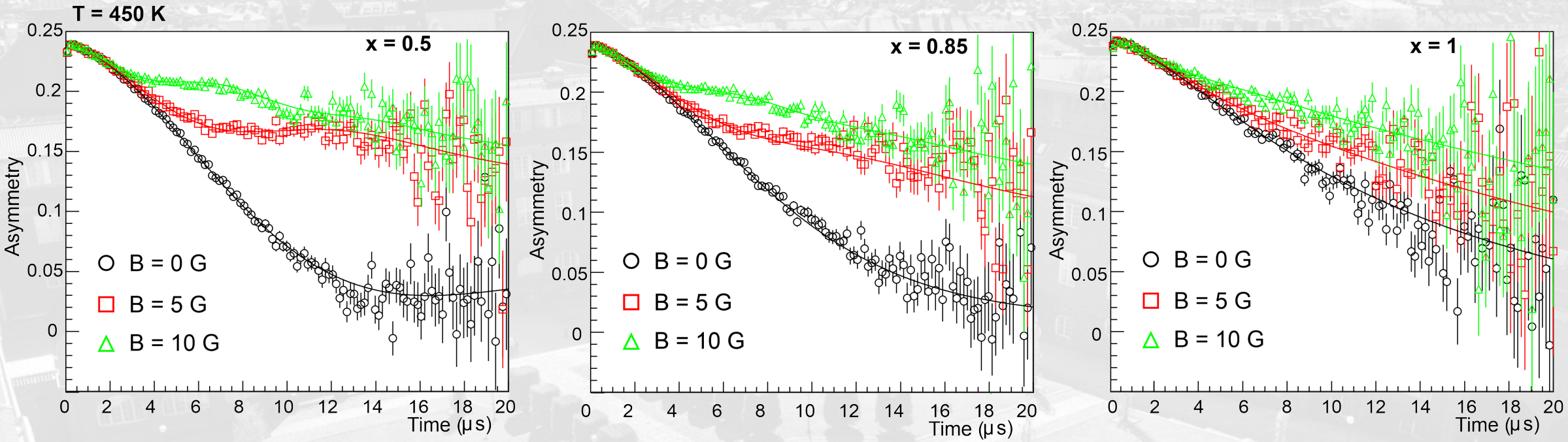
μ^+SR results

$$A_0 P_{LF}(t) = A_{KT} G_{DGKT}(H_{LF}, \Delta, \nu, t) \exp(-\lambda_{KT} t) + A_{BG}$$



G_{DGKT} -> Muon spin depolarization in an isotropic nuclear dipolar field with a gaussian distribution at the muon site

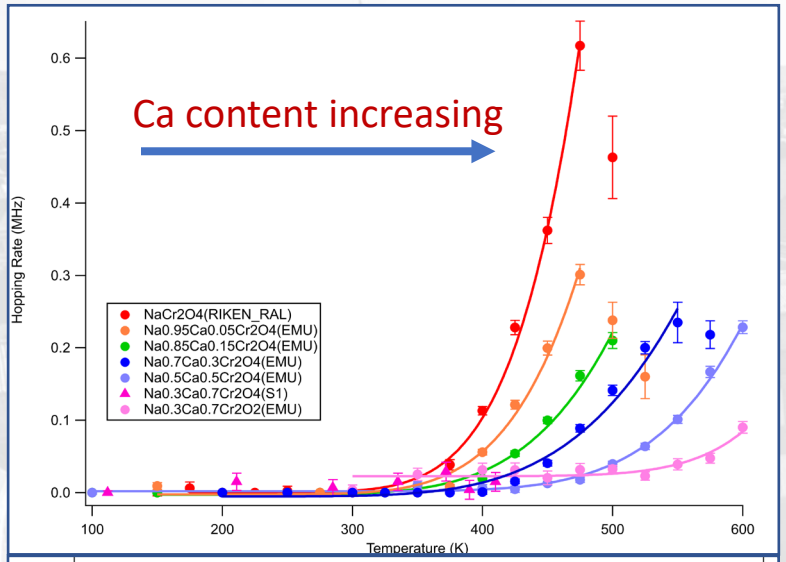
$exp(-\lambda_{KT}t)$ -> exponential decay of the muon spin depolarization with rate λ_{KT} due to the rapidly fluctuating Cr electronic moments

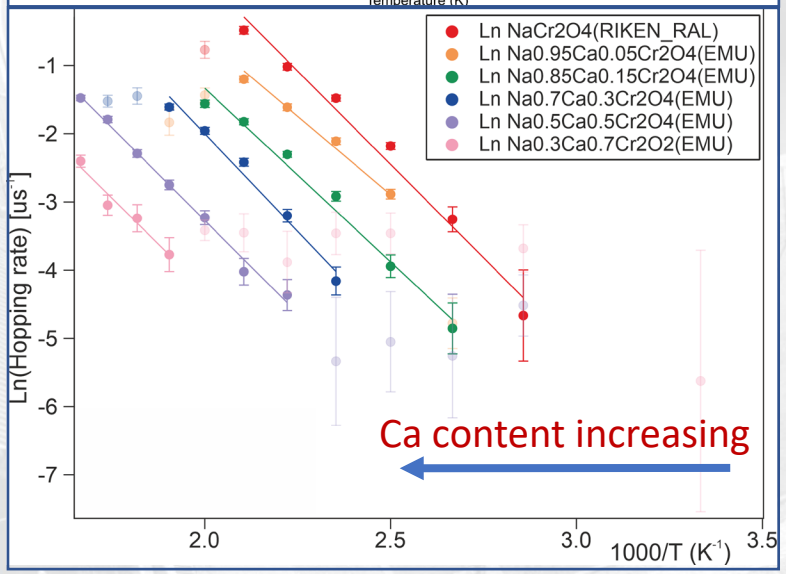
$H_{LF} \equiv$ Applied field

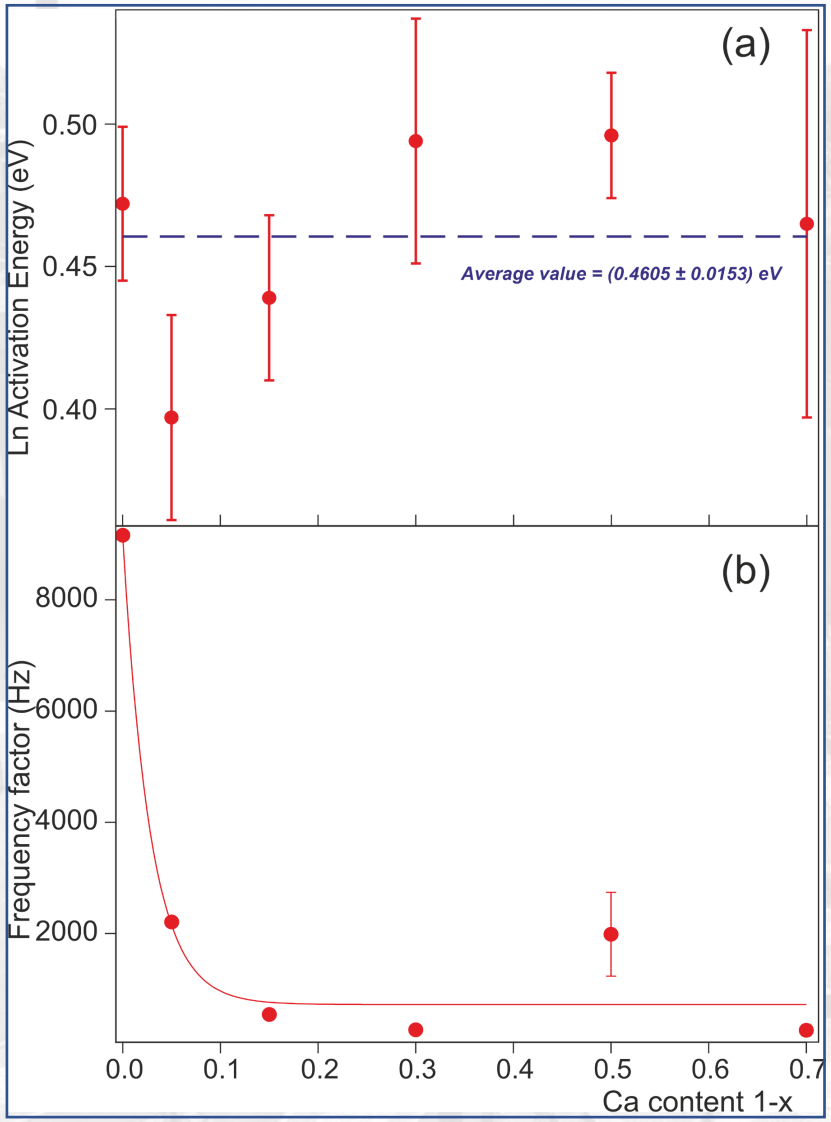
$\Delta \equiv$ static width of the local-field distribution at the muon sites

$\nu \equiv$ field fluctuation rate (hopping)

Composition dependence of the parameters







Thermally activated process described by an Arrhenius type function:

$$\text{hop} = Ae^{-\frac{E_a}{k_B t}}$$

A ≡ pre-exponential factor, accounts for the probability of the Na to make a diffusive jump

E_a ≡ activation energy determined as the slope of the ln hopping rate.

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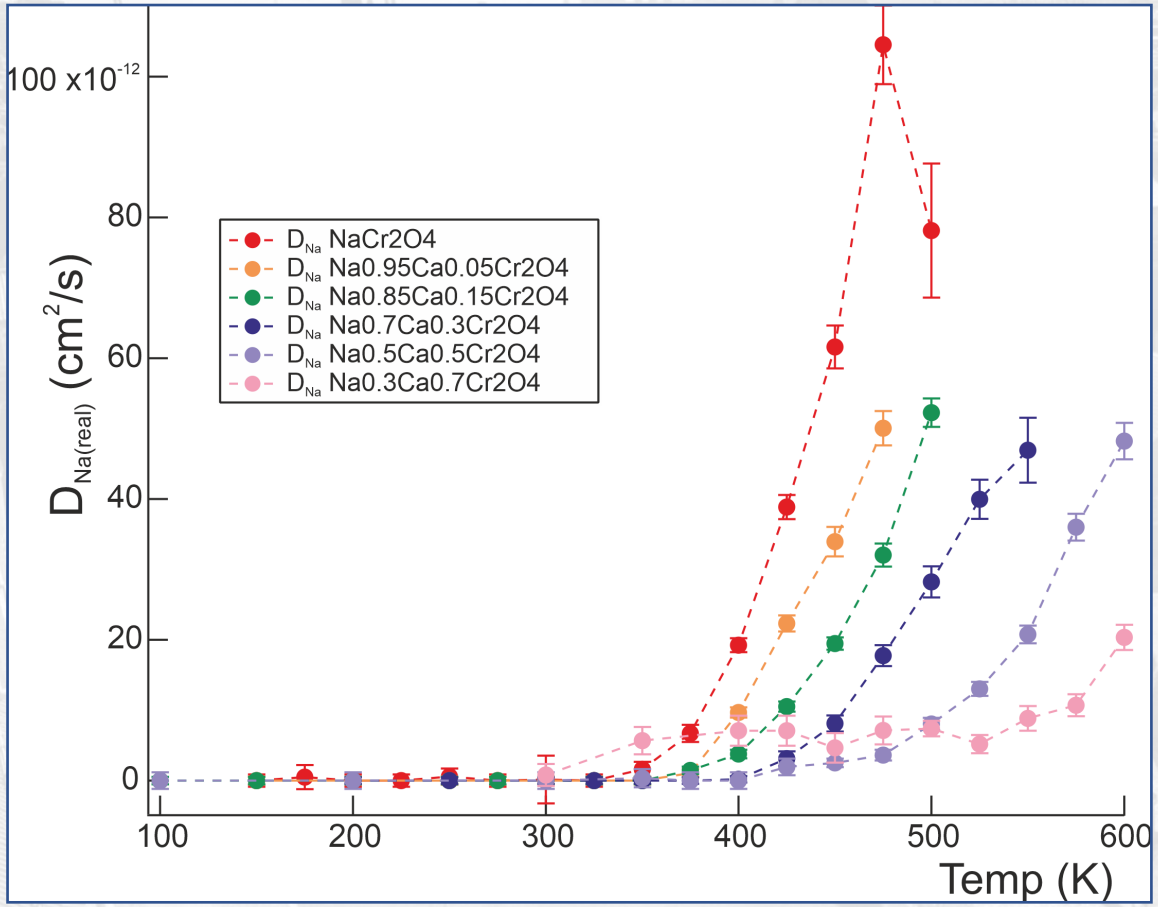
Estimate of the diffusion coefficient



The coefficient is a macroscopic parameter which describes the flow of particles (travel distance in the unit of time).

$$D_{corr} = \underbrace{[1 + \frac{1}{n}\sum_{i=1}^{n-1} < \cos(\theta_{i,i+1}) >]}_{f} \underbrace{[\frac{1}{N} Z_v s^2 \nu]}_{D_{un}}$$

f = accounts for the correlation between successive jumps

D_{un} = uncorrelated diffusion coefficient

n = average number of jumps = $(\frac{1}{\rho_{Ca}}$ -1)2 - 1

θ = angle between ith and i+1th jump

N = number of Na sites

Z_v = interstitial sites fraction

s = jump distance between Na lattice site and interstitial site

ν = measured hopping rate

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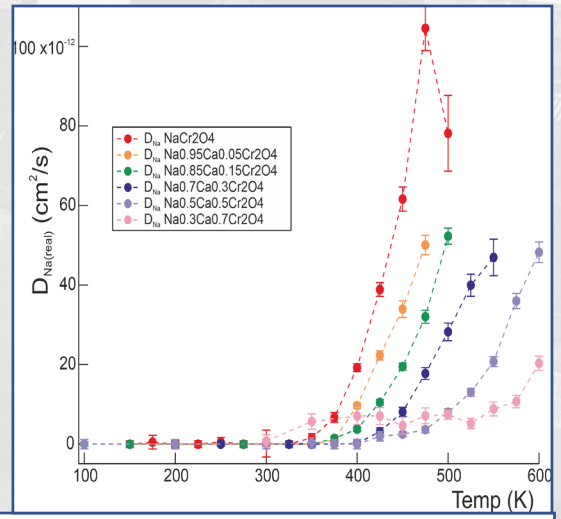
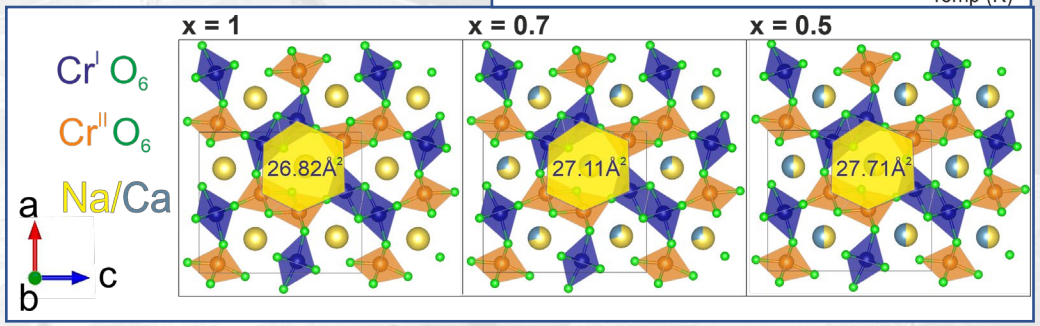
Conclusions

This study shows how the Na ion kinetics is obstructed by the Ca doping in the solid solution $Ca_{1-x}Na_xCr_2O_4$. This behavior is to be ascribed to the concomitant contribution of several factors:

- The presence of Ca ions constitutes a physical impediment for the Na diffusion since it can only occur along the 1D channel.
- The mixed valence state $Cr^{3.5+}$ induces enhanced Cr-O bond stability, a reduction of the atomic radius of Cr atoms. A consequent contraction of the transition metal oxide octahedra occurs, which results in a reduced volume for the 1D diffusion channels on one hand and on a weakened Na-O bonds the other hand.
- The downsized 1D channels provide a more confined and advantageous diffusion path for the Na ions to move in a correlated fashion.





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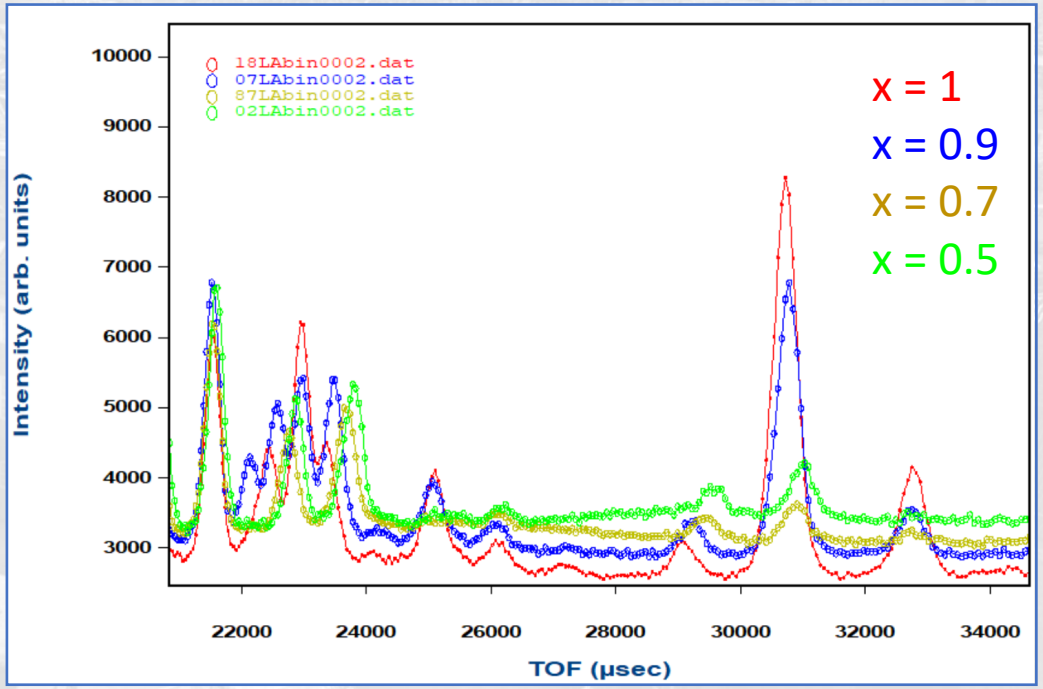
Perspectives

A correction factor to account for the change in the Na concentration is probably necessary

The evolution of the magnetic structure will be determined

Hydrostatic pressure dependent study



Ca substitution in the Na lattice sites affects dramatically the magnetic properties of the material

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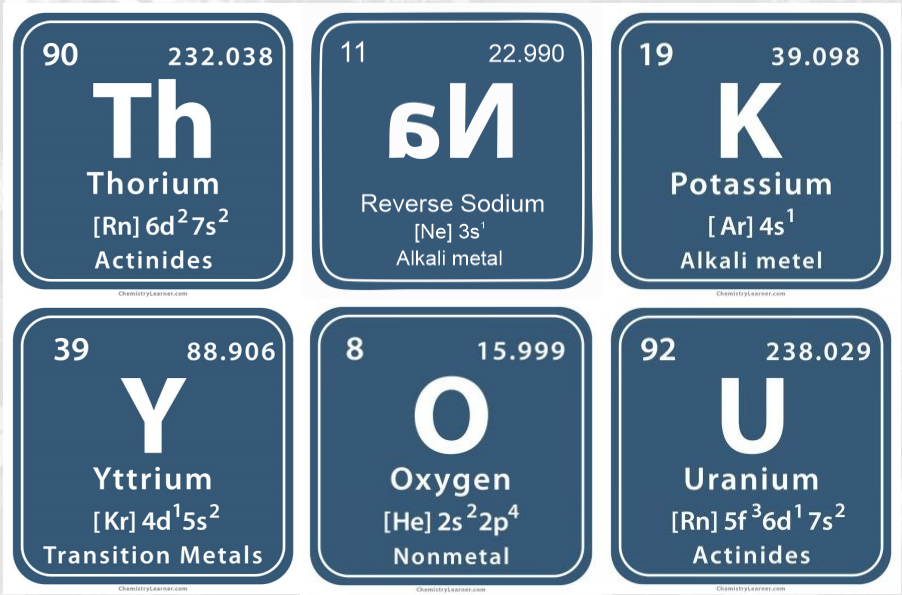
Acknowledgements







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