

Operando Raman spectroscopy to understand the reaction mechanisms of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in Li-ion batteries

L. Boulet-Roblin¹, D. Streich¹, P. Borel², C. Tessier², M. Ben Yahia³, C. Villevieille¹

¹Paul Scherrer Institut, Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland

²SAFT, 111 Boulevard Alfred Daney, F-33074 Bordeaux, France

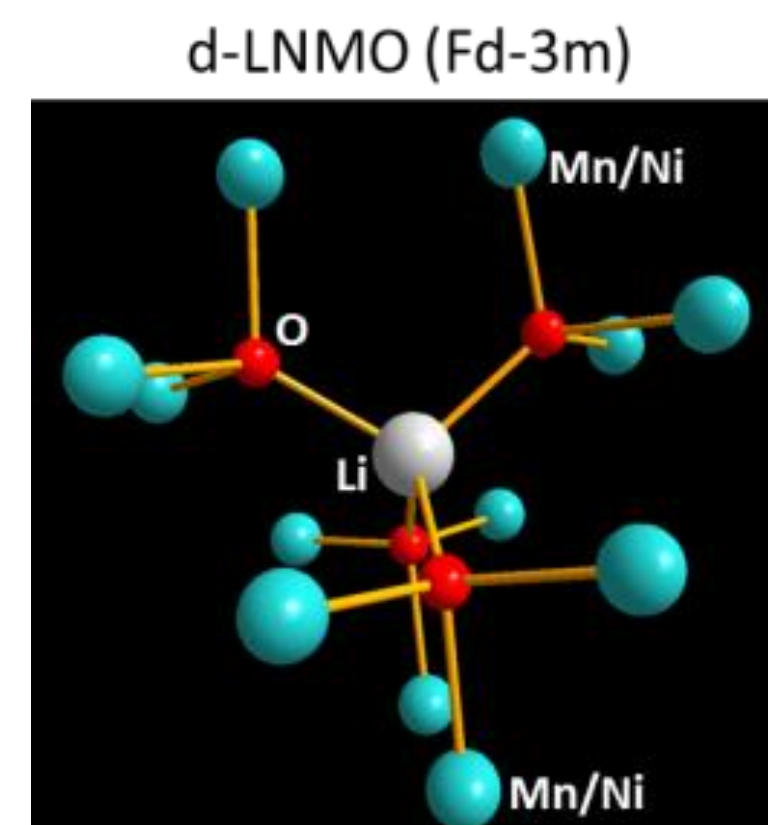
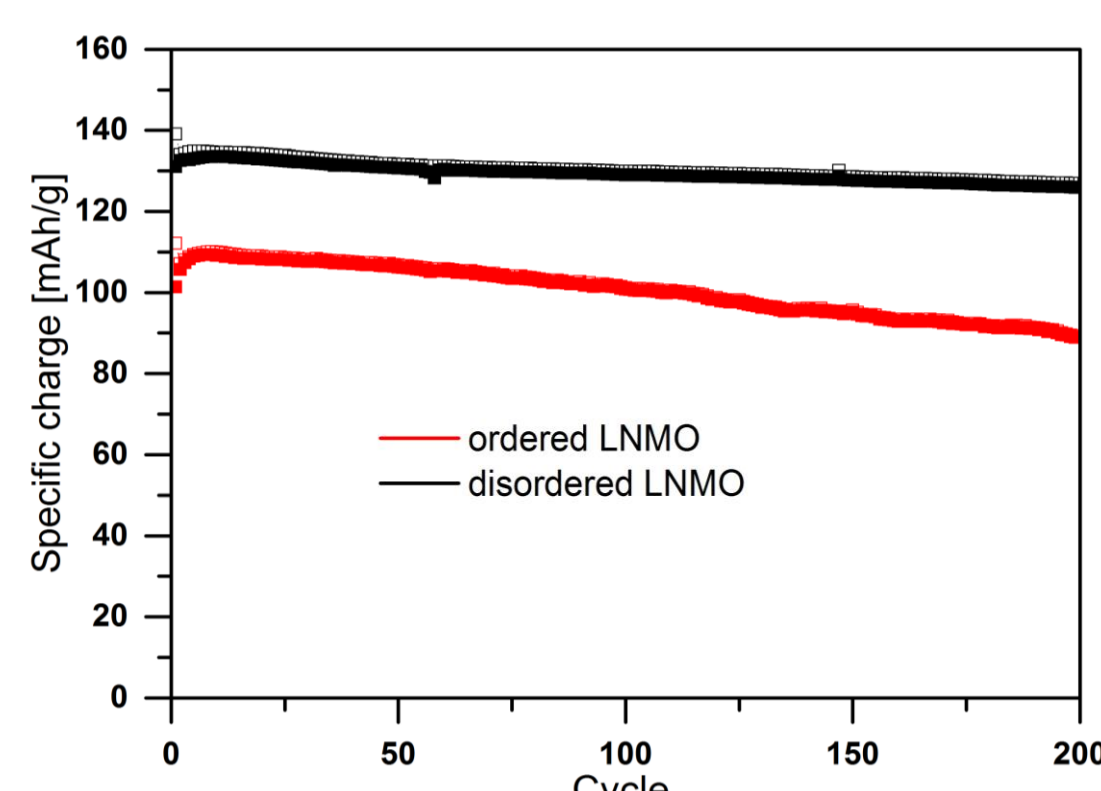
³Institut Charles Gerhardt, CTMM, CNRS 5253, Université Montpellier, Place Eugène Bataillon, 34095 Montpellier, Cedex 5, France
lucien.boulet@psi.ch

Goal: Understanding the structure evolution in the near-surface range

Increase specific energy of Li-ion battery
→ 5V cathode
→ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO)

Two LNMO polymorphs:

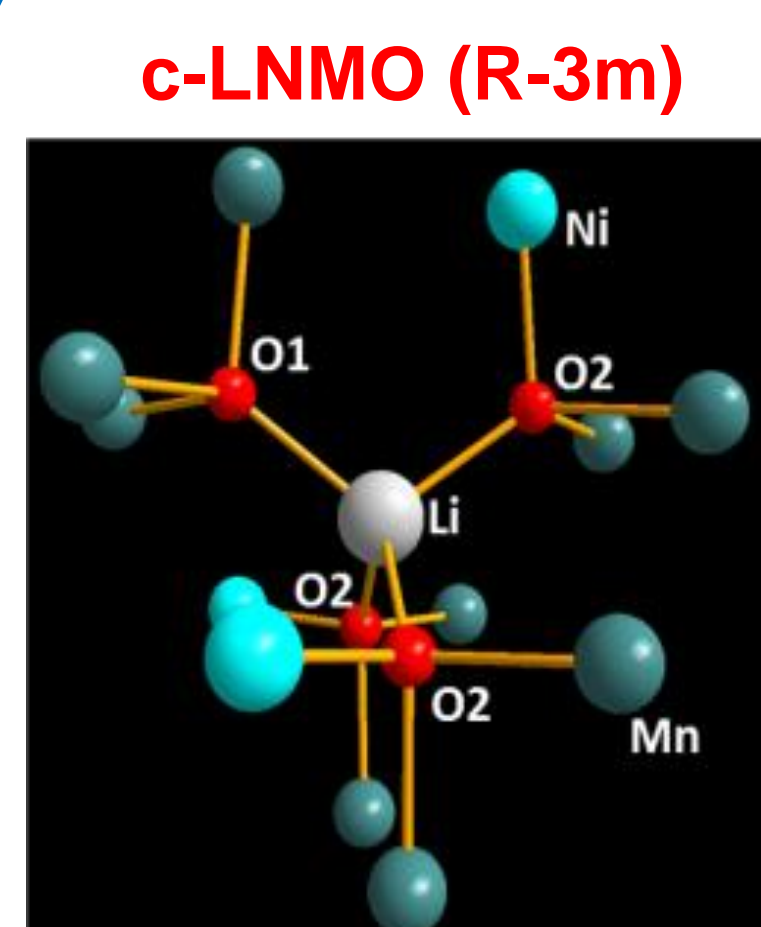
- ordered (o-LNMO, P4₃32)
- disordered (d-LNMO, Fd-3m)



Mn and Ni randomly distributed on same atomic site

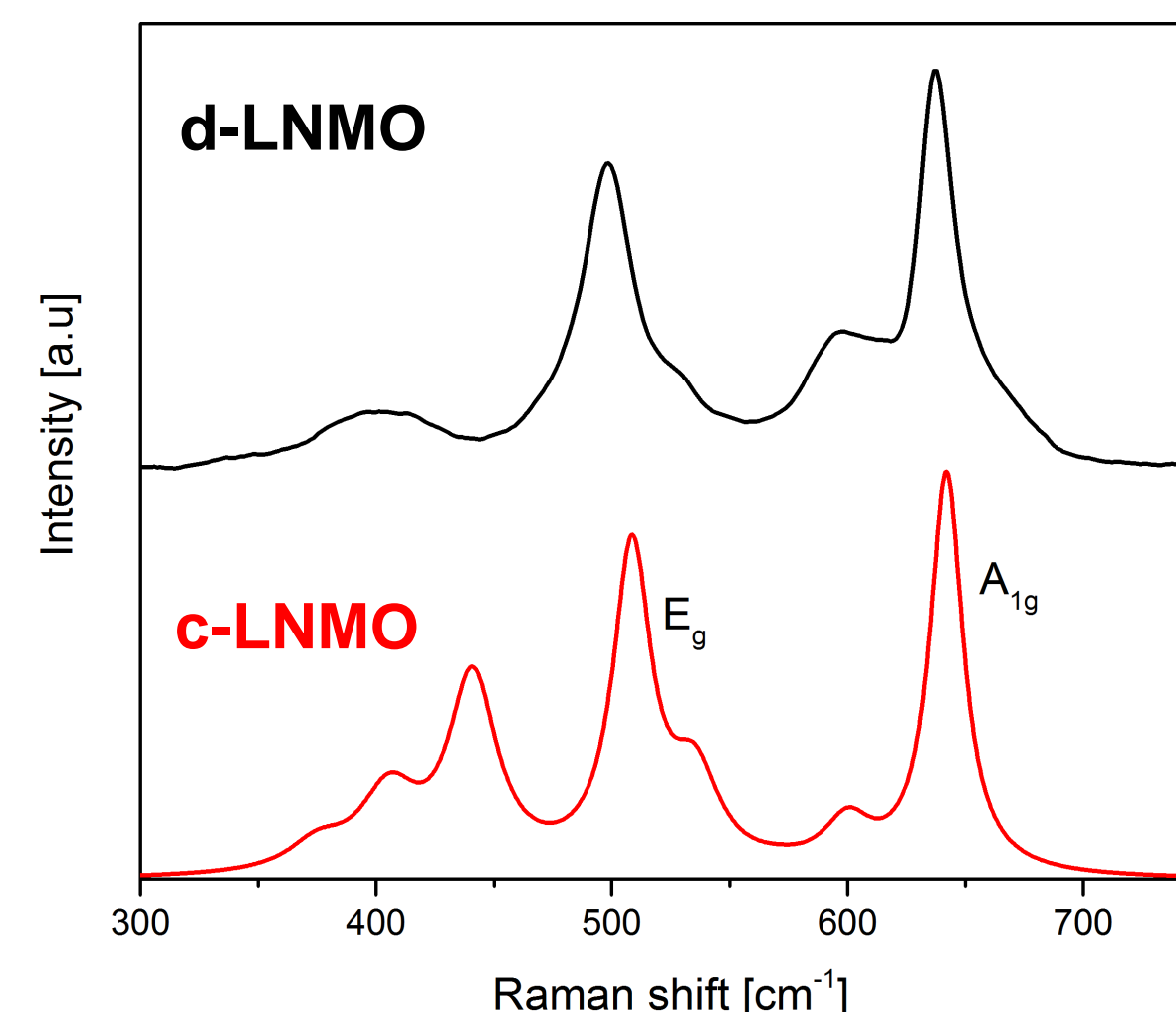
- What are the correct assignments of the Raman vibration modes?
- Are Ni and Mn contributions distinguishable?
- How the structure evolve during cycling in the near-surface range (~100-200 nm)?

DFT calculation (CRYSTAL14, B3LYP): Raman simulation



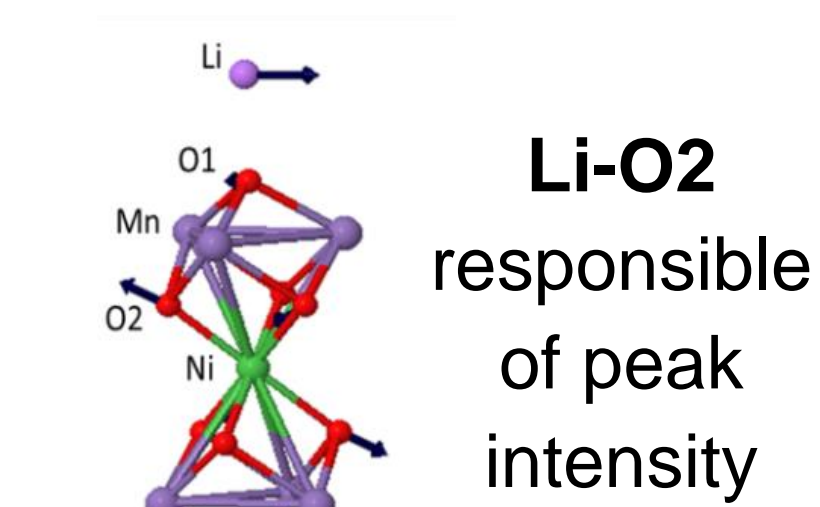
Calculated c-LNMO structure
→ Ni position fixed
two oxygen types:
O1 (Mn, Li) // O2 (Ni, Mn, Li)

Simulation of Raman peak positions **AND** intensities



[Raman peak intensity = variation of polarizability ≡ variation of electronic density]

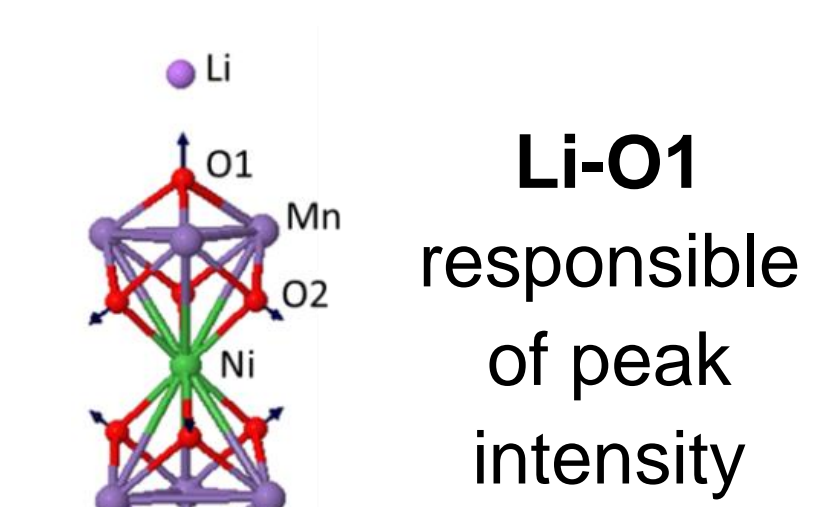
E_g mode
(509 cm⁻¹)



Li-O2 responsible of peak intensity

Ni contribution

A_{1g} mode
(642 cm⁻¹)

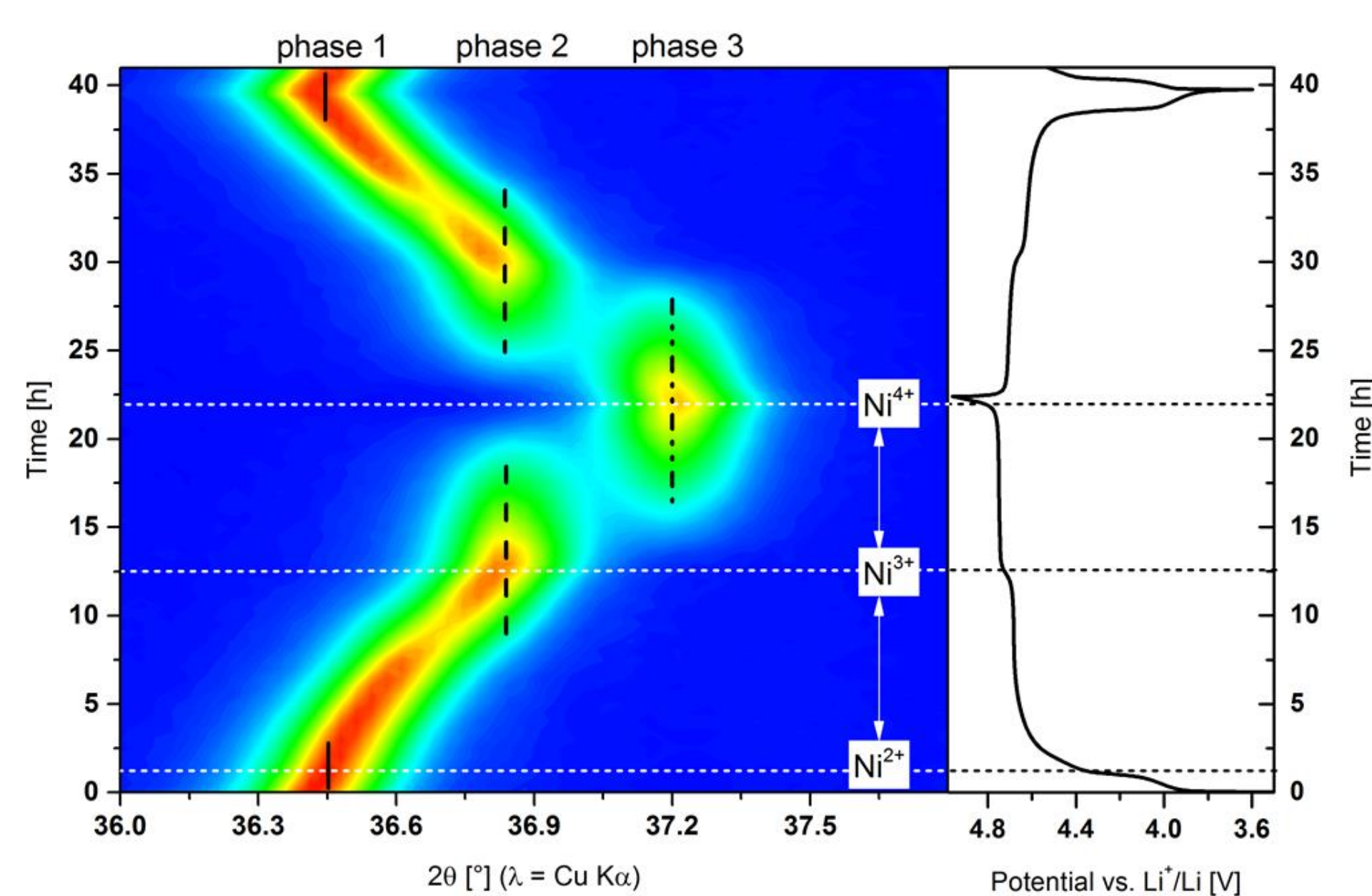


Li-O1 responsible of peak intensity

Mn contribution

Structural evolution of bulk and near-surface regions

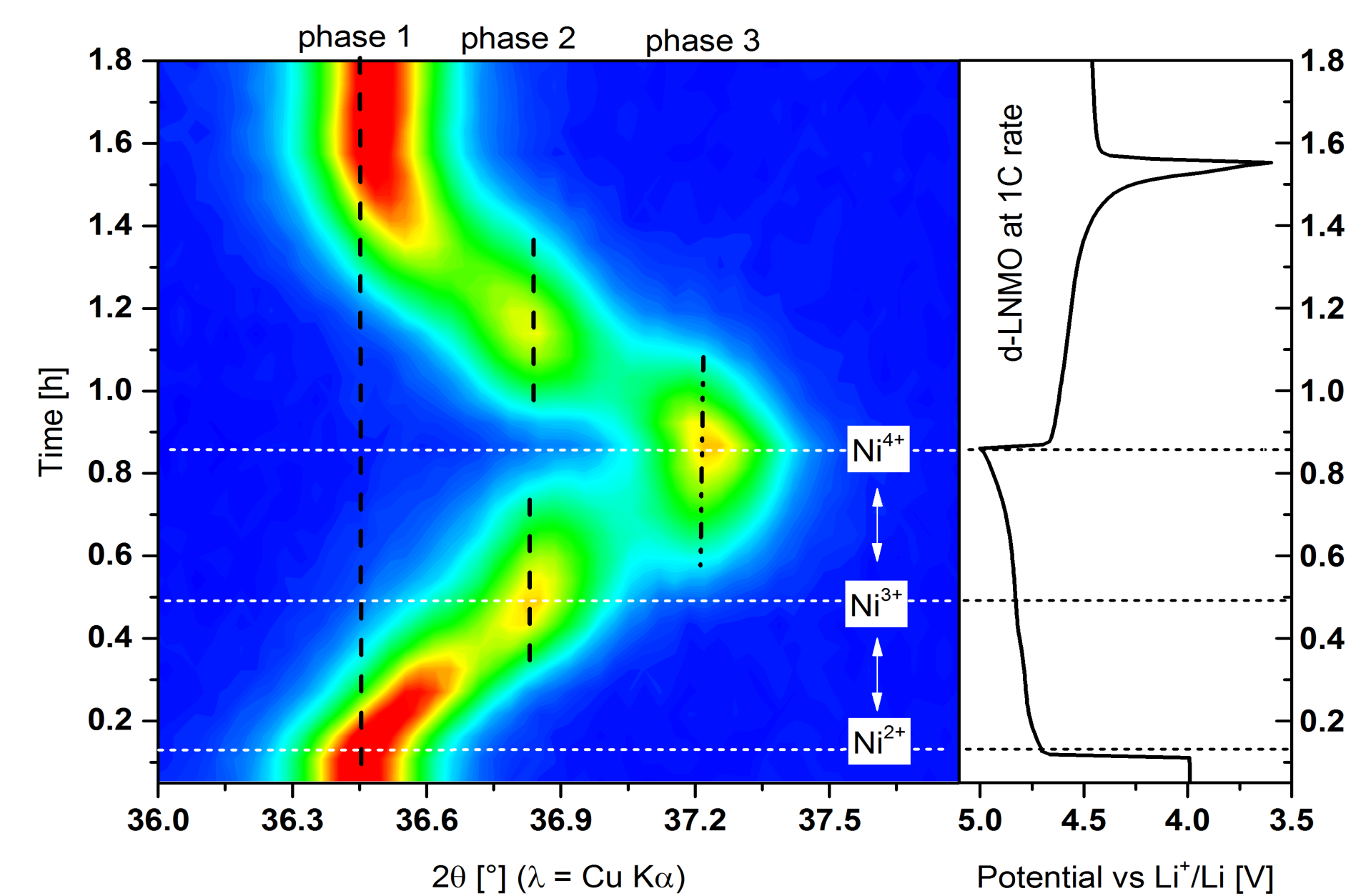
Slow rate (C/20)



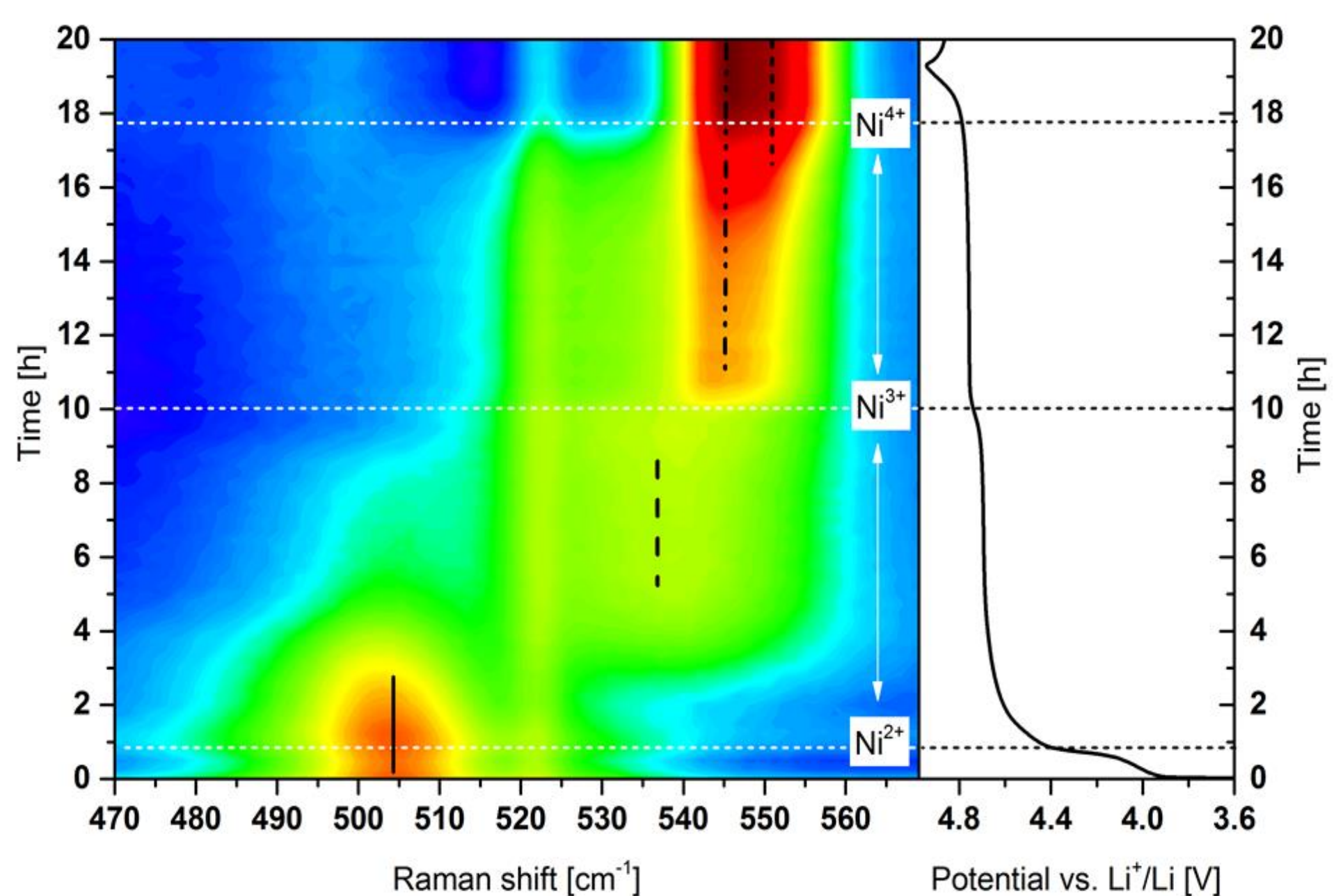
- 3 cubic phases (Fd-3m)
- Solid-solution and two-phase reactions

BULK
→ XRD

Fast rate (1-C)

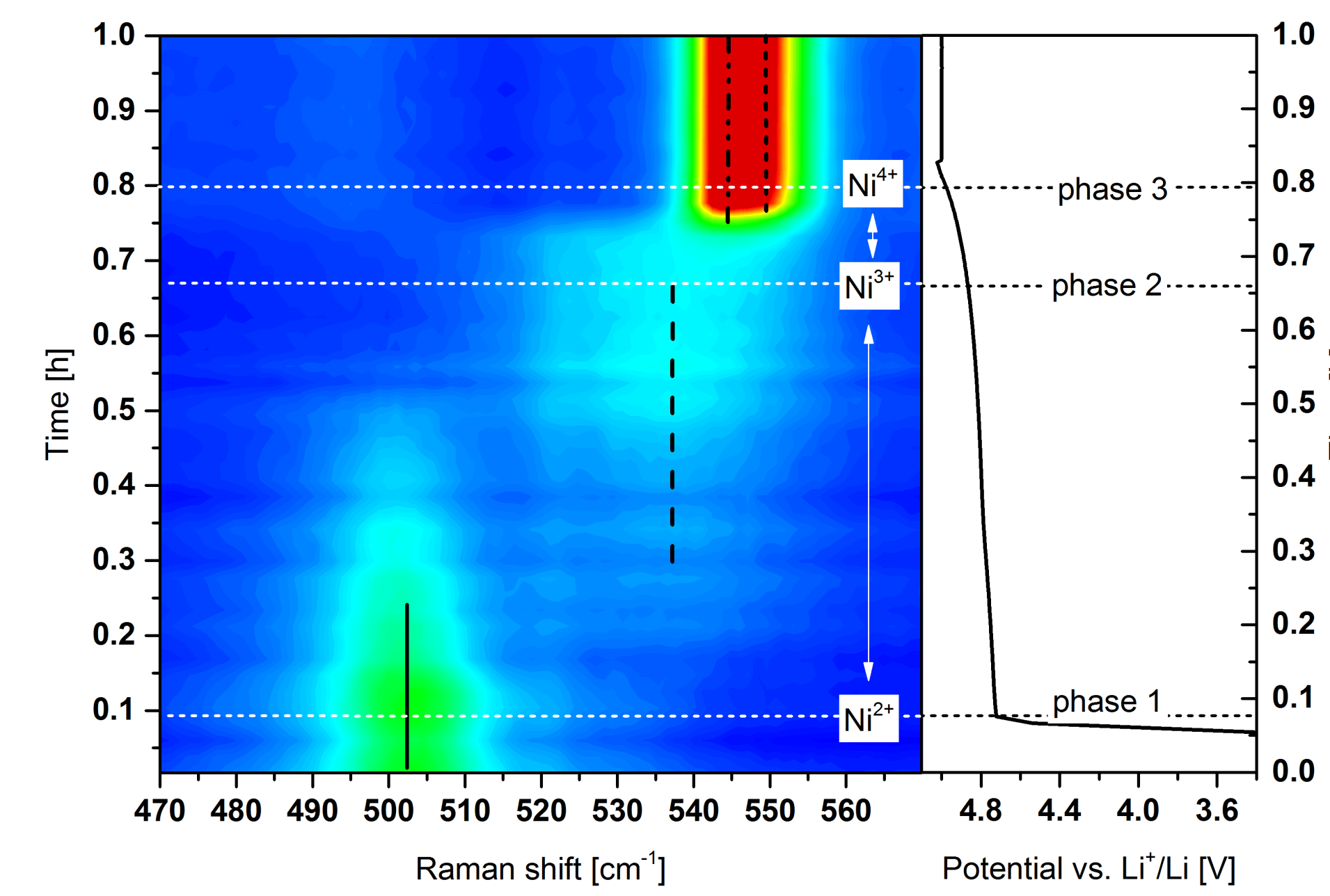


- 3 cubic phases (Fd-3m)
- Solid-solution and two-phase reactions



- Three different Raman spectrum types for the three cubic phases

Near-SURFACE
→ Raman



- Preferable phase 1 to 2 transition (solid-solution reaction)
- Delayed phase 2 to 3 transition (two-phase reaction)

➤ Homogeneous change in near-surface region

➤ Inhomogeneous change in near-surface region

❖ Lithium concentration gradient kinetically dependent and emphasized by the two-phase reaction

Conclusions

- ❖ Raman DFT simulation → correct assignment with better understanding of peak intensity
- ❖ Near-surface structure changes of disordered LNMO are rate dependent → possible lithium gradient

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