Polaron mobility and disordering of the Na sublattice in Na_xFePO_4

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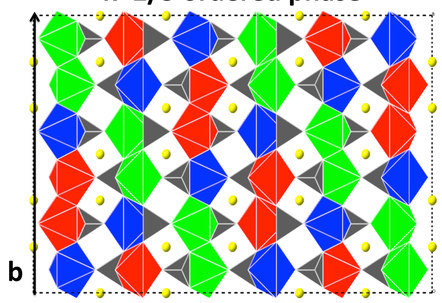
EFree
An Energy Frontier Research Center

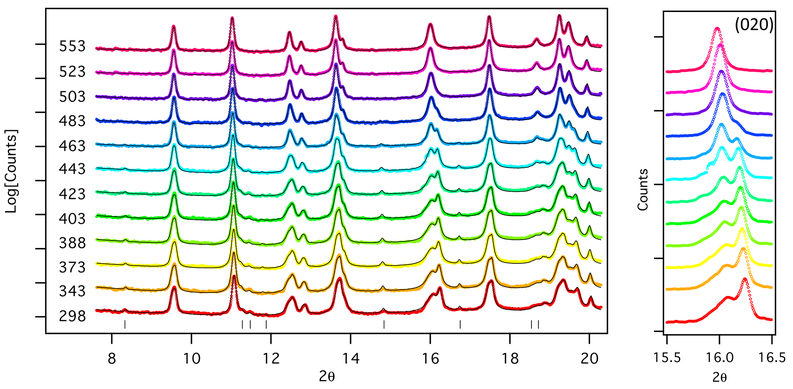
EFree Project: Ion Transport Processes
Goal: *To characterize the structural features that underlie ion transport in battery materials.*

- Low cost and environmental abundance of Na
  → Attractive alternative to Li batteries
- Na analogue to $LiFePO_4$: triphylite-$NaFePO_4$
  → Obtained via ion exchange route
- Ordered structure: 3 distinct Fe sites with a 1/1/1 ratio
  1, 2 & 3 vacancies in their 6-fold Na coordination shell

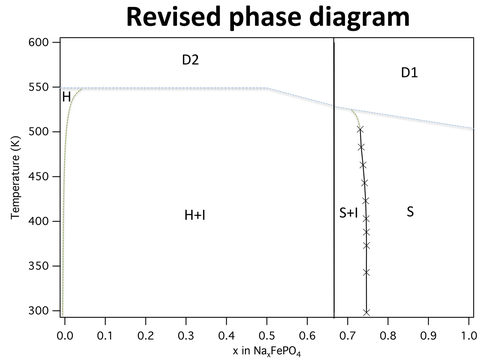
x=2/3 ordered phase



Synchrotron x-ray diffraction $Na_{0.73}FePO_4$



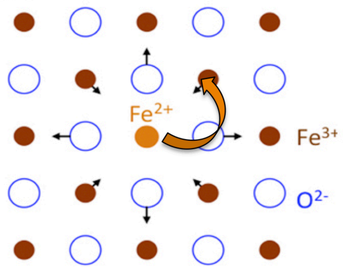
Revised phase diagram



- Superstructure peaks: long range order persists for x>2/3
- Superstructure peaks become increasingly weak & are completely gone by 483 K
- (020) peak has a low angle shoulder → intensity increase with temperature
- Region above x=2/3 is biphasic at 298 K

Small polaron hopping

- Bound carrier can only move if the local distortion travels with it
- Elevated temperature → diffusive Arrhenius-type mobility

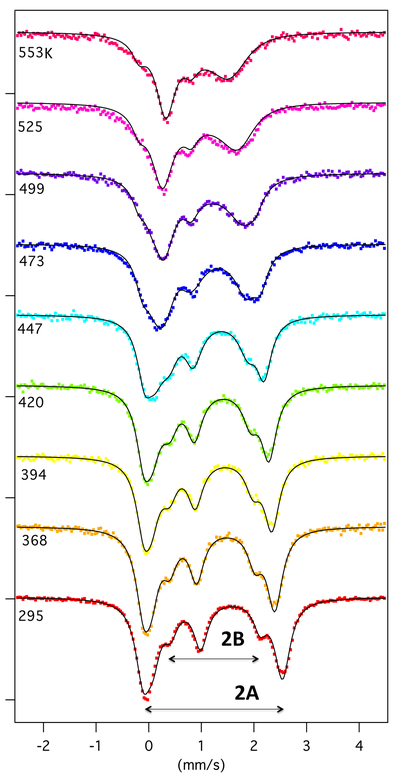


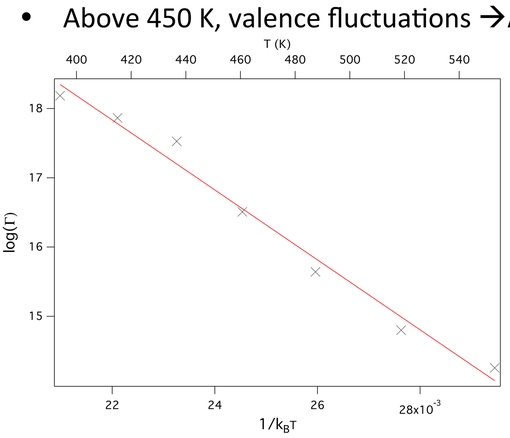
Nuclear resonant scattering: probe for dynamical valence states

- Valence fluctuations at iron ions due to charge hopping
- Spectra are altered when dynamical changes occur on the same time scale of the ^{57}Fe nuclear decay

Secondary ferrous doublet in Mössbauer spectrum

- 2 distinct Fe^{2+} components (A & B)
- Abnormally low QS of the B-site
  → local environment different from parent structure
- x=2/3: area ratio B/A ~35/65
  Seems to contradict the proposed superstructure (50/50)
- B-component no longer present when cooled to 77 K
- Above 450 K, valence fluctuations →Asymmetric line broadening



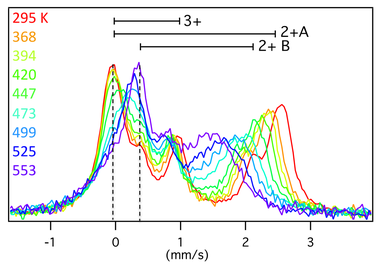


Analyzed with Blume-Tjon model determine polaron hopping frequencies, Γ (T).

Arrhenius fit → E_a~500 meV

- Ratio of B to A-type Fe^{2+} sites varied as fit parameter
- Charge hopping was limited to the B-type Fe^{2+} sites

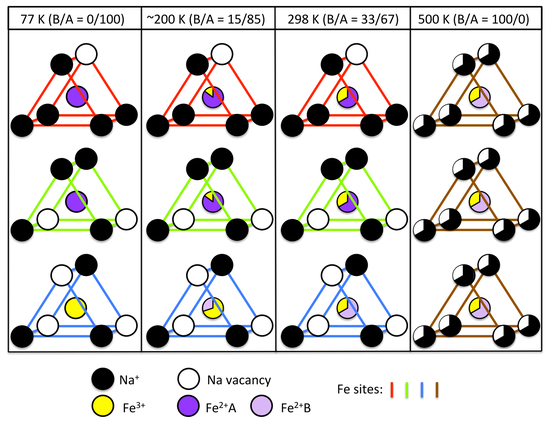
Temperature evolution of Fe and Na site occupancies



- Rapid conversion of A-type to B-type ferrous Fe sites above 450 K
- At low temperature (red) the Fe^{2+} absorption lines at ~0 mm/s are distinct. By 473 K, B-type environment becomes the majority divalent component
- For absorptions at ~2 mm/s, effect is obscured by the spectral collapse of the Fe^{2+} and Fe^{3+} lines from the concurrent onset of fast charge hopping

While diffraction rules out a significant rearrangement of Na ions between 77-298 K, a charge localization transition is possible

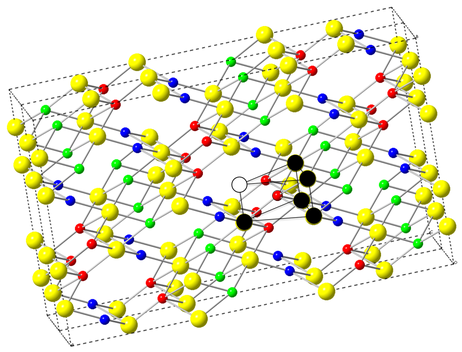
3 Fe sites with their Na coordination shell for 4 temperatures 77-500 K



Low temperature: charge order
Fe^{3+} prefer the blue sites
Fe^{2+} prefer the red or green sites

Increasing temperature: electronic disorder
Partial ferrous occupancy of blue site
Fe^{2+} site with unusually low QS (B-site)

298 K: total electronic disorder
Fe^{3+} evenly distributed over all 3 sites
→ 33/66 B/A ratio



Loss of local order on the Na sub-lattice
→ 3 Fe sites start to look the same (brown)
→ overall reduction of Na coordination of the Fe sites

Relationship between the onset of fast electron dynamics & the redistribution of sodium

Clarifies details related to the Na and electronic charge ordering in the structure and suggest that electron-ion interactions may play an important role in the dynamics

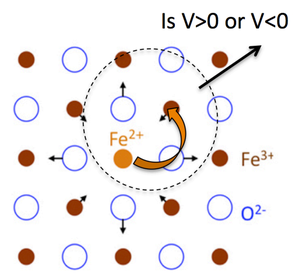
Activation volume (V_A): local distortion in activated state

$$H_a = E_a + PV_a$$

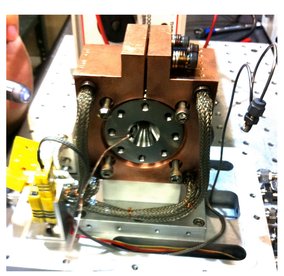
Energy barrier for polaron transfer between adjacent sites

Extra energy cost due to the finite volume change in the activated state

Is V>0 or V<0 ?

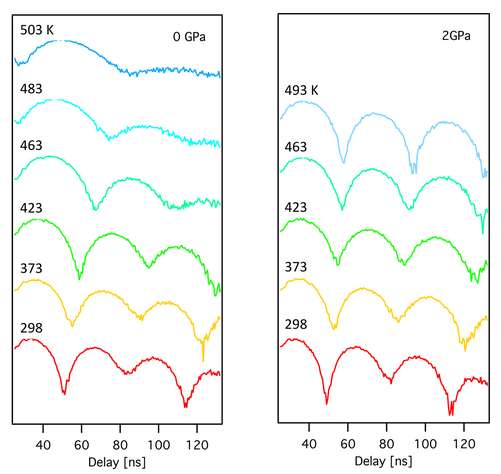


- Synchrotron Mössbauer extends these measurements to elevated pressure
- Due to phase transition above 500 K at 2 GPa we are only able to put a lower bound on V_A
- At 493 K at 2 GPa little indication of spectral effects from polaron hopping
- Large positive V_a is not typical of polaron hopping. Indicates electron ion-interactions may play a role in the dynamics



V_A> +3 A^3

Diamond Anvil cell in Vacuum Block Furnace



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