Magnetic structure of some battery materials and why it matters

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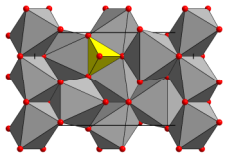
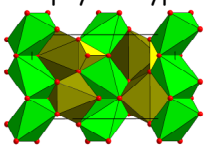
$NaFePO_4$: triphylite vs. maricite two polymorphs – two structures

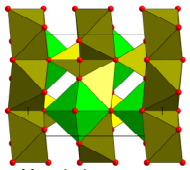
$Fe_2SiO_4 \equiv FeFeSiO_4$ fayalite (end member of olivine)



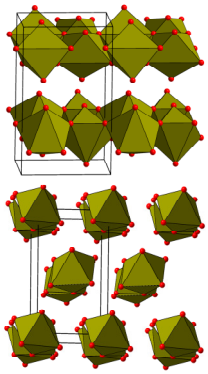
Fe1 substitution → Triphylite-type



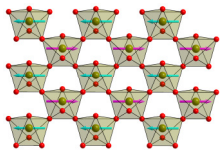
Fe2 substitution → Maricite-type



Fe (magnetic) sublattice

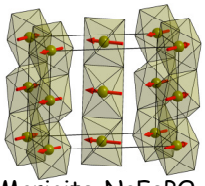


T_N~50K → Triphylite-$NaFePO_4$



collinear AFM layers

T_N~13K → Maricite-$NaFePO_4$

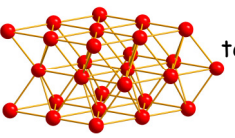


non-collinear FM chains

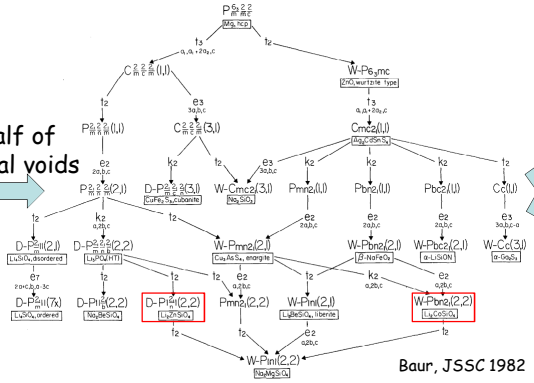
[IC 52 (2013) 8685]

Li_2MnSiO_4 and Li_2CoSiO_4: two structure types – same magnetic structure

hexagonal close-packing of oxygen atoms: N octahedral voids, 2N tetrahedral voids

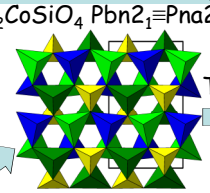


filling half of tetrahedral voids

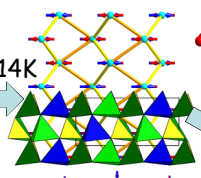


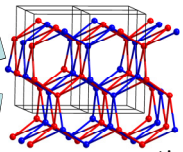
Baur, JSSC 1982

Li_2CoSiO_4 $Pbn2_1 \equiv Pna2_1$

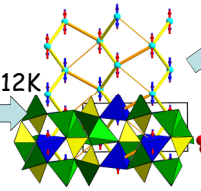


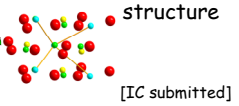
T_N~14K





T_N~12K





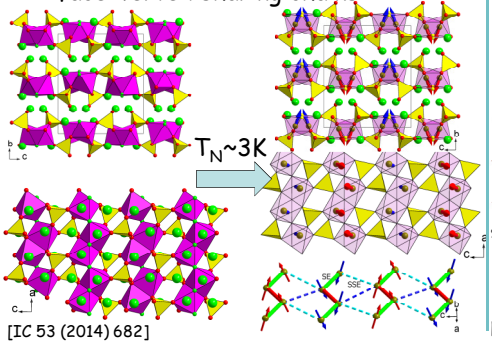
same magnetic structure

Li_2MnSiO_4 $P2_1/n$

[IC submitted]

Na_2FePO_4F, $LiNaMPO_4F$ (M=Fe,Co,Ni) - similar composition, different structure

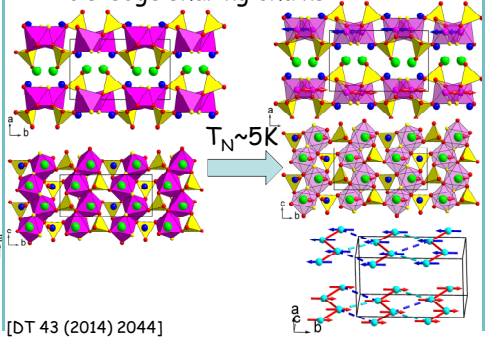
Na_2FePO_4F (Pbcn 5.2x13.8x11.8) face+vertex sharing chains



T_N~3K

[IC 53 (2014) 682]

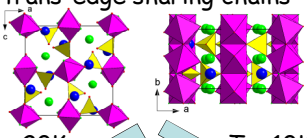
$LiNaNiPO_4F$ ($P2_1/c$ 6.8x11.2x5.0) cis-edge sharing chains



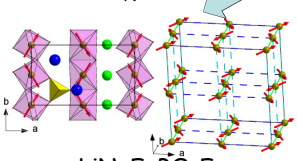
T_N~5K

[DT 43 (2014) 2044]

$LiNaFePO_4F$, $LiNaCoPO_4F$ (Pnma,10.9x6.3x11.3) trans-edge sharing chains

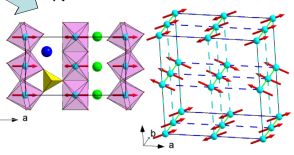


T_N~20K



$LiNaFePO_4F$

T_N~10K



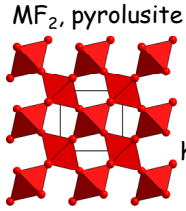
$LiNaCoPO_4F$

[DT 41 (2012) 11692]

[IC 51 (2012) 8729]

"$Li_xMF_{2-x}O_x$" ($M(OH)_xF_{2-x}$), M=Mn,Fe,Co

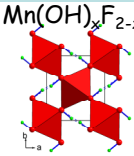
MF_2, pyrolusite



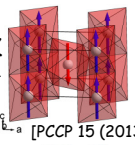
idea: $Li_xMF_{2-x}O_x$ → hydrothermal synthesis

$Li_xMF_{2-x}O_x$ or $M(OH)_xF_{2-x}$? Where are Li^+ or H^+?

$Mn(OH)_xF_{2-x}$

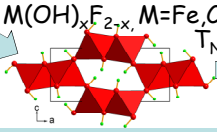


T_N~70K

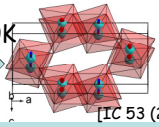


[PCCP 15 (2013) 13061]

$M(OH)_xF_{2-x}$, M=Fe,Co



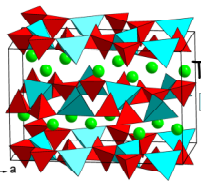
T_N~40K



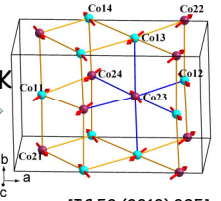
[IC 53 (2014) 365]

$Na_2CoP_2O_7$

layered "blue" form $Pna2_1$, 15.4x10.2x7.7



T_N~6.5K



[IC 52 (2013) 395]

General features

- Magnetic structures in polyanion materials: relatively easy to explain, extremely difficult to predict
- Goodenough-Kanamori rules typically work: chain/face sharing (i.e. M-O-M~90-110°) → FM; vertex sharing → AFM. Overall – typically AFM.
- Fe^{2+}, Co^{2+} - often orbital moment contribution → non-collinear structures

Why it matters: accurate DFT calculations

$LiNaFePO_4F$: *GGA+U*, V:NSP/SP/exp=782/813/772 Å^3, predicted - FM(! see above) [EPL 87 (2009) 18001]
Na_2FePO_4F: *GGA+U*, V:NSP/SP/exp=810/827/845 Å^3, Voltage:NSP/SP/exp=3.6/3.0/3.0 V [JAP 106 (2009) 043510]
Li_2FeSO_4F: *GGA+U*, V:NSP/SP/exp=167/177/183 Å^3, Voltage:NSP/SP/exp=4.3/3.7/3.6 V [PRB 82 (2010) 125101]
$P2_1/n$-Li_2MnSiO_4: *GGA*, Voltage:FM/AFM/exp=1.8/3.2(?)/3.8 [J. Mater. Chem. A, 2013, 1, 2847]
$LiCoPO_4$: *LDA+U*, V:SP/exp=270/280, Voltage:NSP/SP/exp=2.9/4.6/4.8 V [PRB 69 (2004) 245107]

And finally:

- Have you done magnetic property measurements?
- Do you know magnetic structure of your material?
- Have you found all Li^+ or H^+ in your structure?
- Have you done symmetry analysis?

All of that can take only a few days!