Order/Disorder Effects on $LiNiO_2$ as a Battery Material

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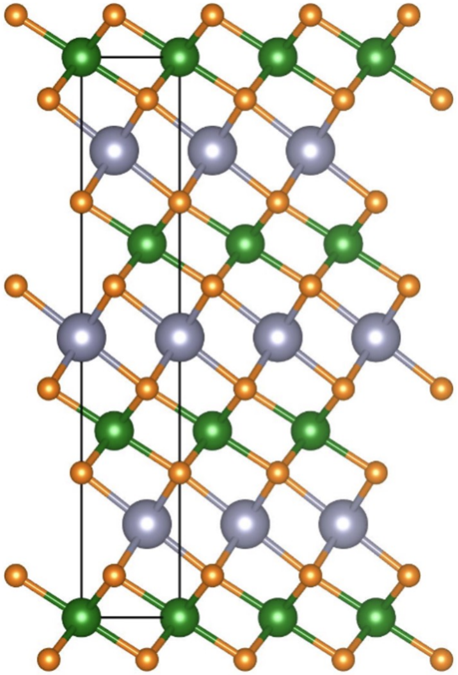
Basic Structure and Applications of $LiNiO_2$

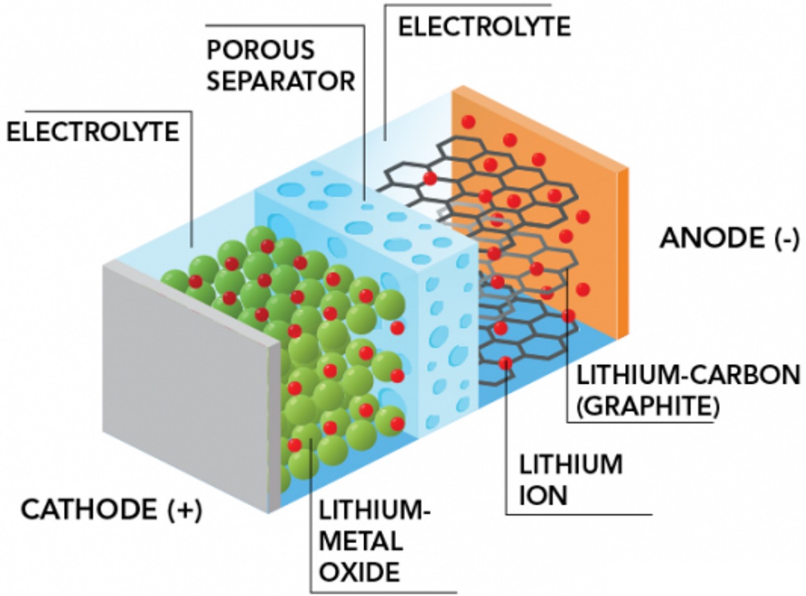
- Battery grade $LiNiO_2$ belongs to the R-3m space group (#166)
- $LiNiO_2$ can also take on the less ordered rocksalt space group Fm-3m (#225)
- $LiNiO_2$ is a major component of commercial battery cathodes
  - Increasing Ni content as Co decreases
- 5% of the world's annual 2.5 million ton of Ni production goes to batteries



$LiNiO_2$ R-3m Unit Cell

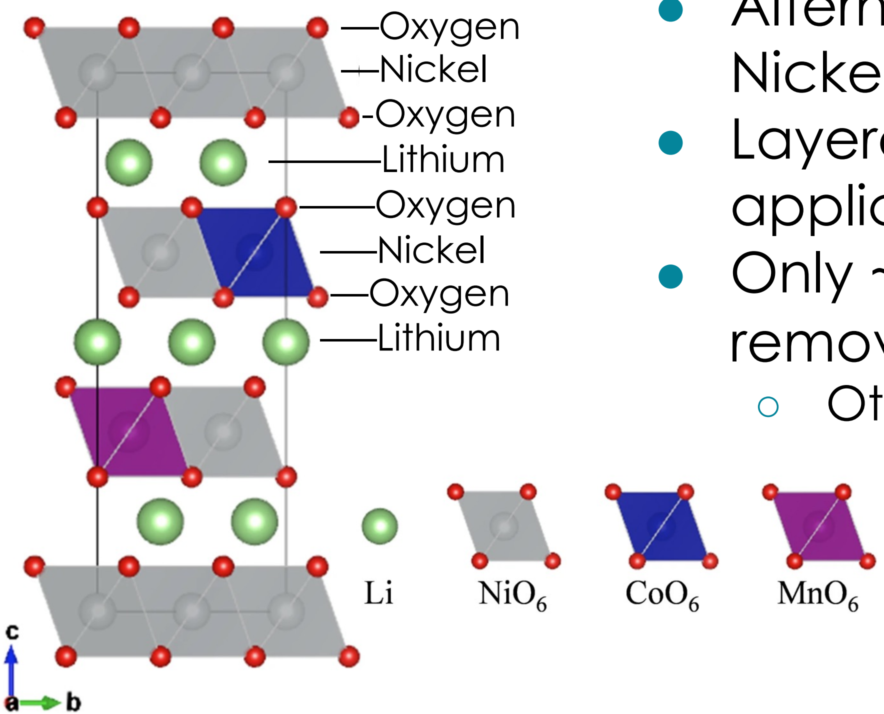
Battery Fundamentals

- Lithium ion batteries work by shuttling Li^+ ions and electrons between the anode and the cathode
- Good battery materials can accept Li^+ ions into their structure
  - Quickly
  - Predictably
  - Repeatably



https://letstalkscience.ca/educational-resources/stem-in-context/how-does-a-lithium-ion-battery-work

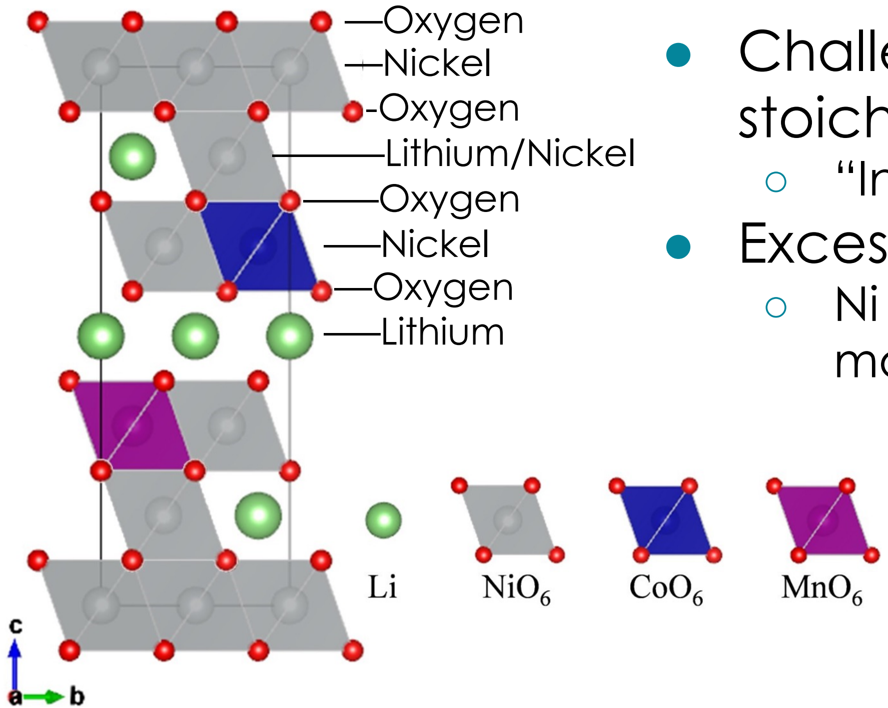
$LiNiO_2$ in Lithium Ion Batteries



- Alternating layers of Oxygen and Nickel or Lithium
- Layered structure is critical for battery applications
- Only ~50% of Lithium ions can be removed from structure
  - Otherwise crystal structure collapses

Lim, JM., Hwang, T., Kim, D. *et al.* Intrinsic Origins of Crack Generation in Ni-rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ Layered Oxide Cathode Material. *Sci Rep* **7**, 39669 (2017). https://doi.org/10.1038/srep39669

Off Stoichiometry in $Li_{1-x}Ni_{1+x}O_2$



- Challenging to synthesize stoichiometric $LiNiO_2$
  - "Intrinsic off stoichiometry"
- Excess Ni will reside in the Li layer
  - Ni residing in the Li layer decreases Li mobility and hinders diffusion

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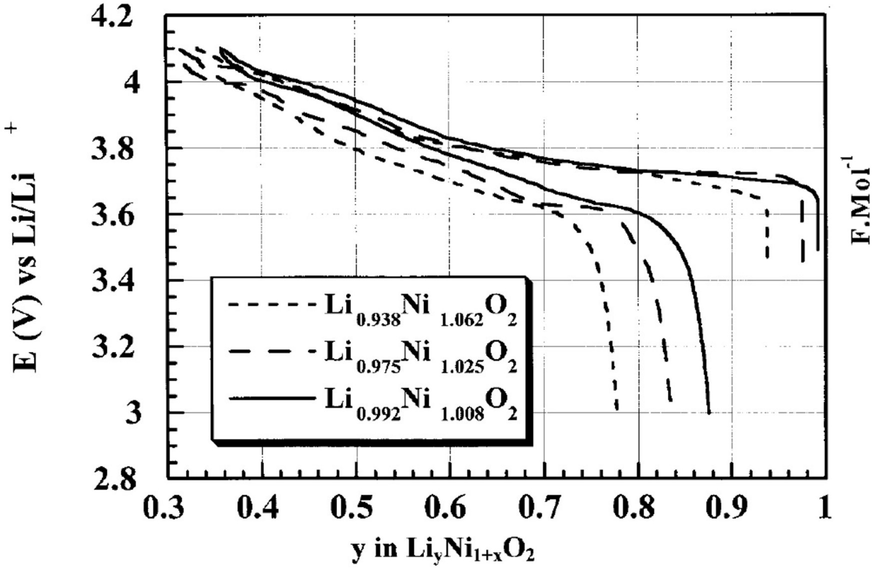
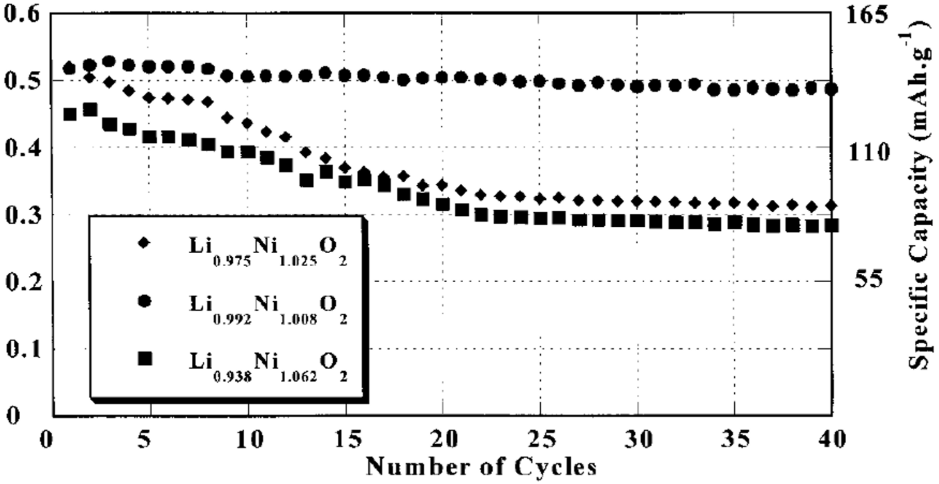
Effect of Off Stoichiometry on Performance

- In $Li_{1-x}Ni_{1+x}O_2$, as x increases, the cell capacity decreases





V Bianchi, S Bach, *et al*. Electrochemical investigation of the Li insertion–extraction reaction as a function of lithium deficiency in Li1−xNi1+xO2, Electrochimica Acta, Volume 46, Issue 7, 2001, Pages 999-1011, ISSN 0013-4686, https://doi.org/10.1016/S0013-4686(00)00681-2.

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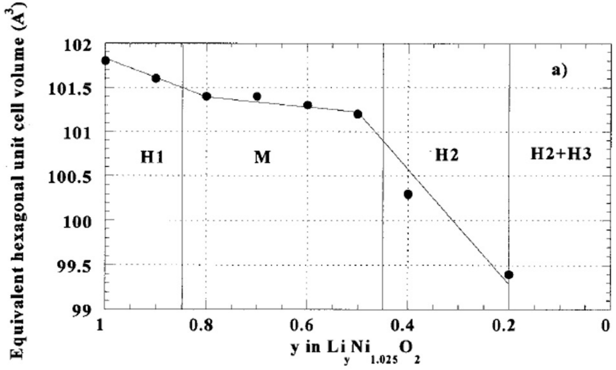

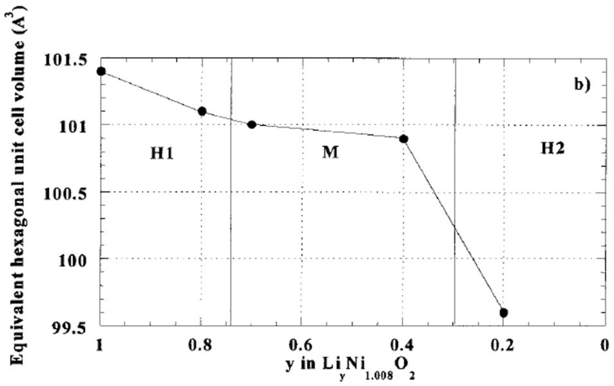

- As Ni content increases, there are larger volume changes associated with charging and discharging the cell
  - Stoichiometric samples see 3 phases
  - Off stoichiometric mixtures see 4 phases
- Changes in the physical structure of the cell lead to cell degradation

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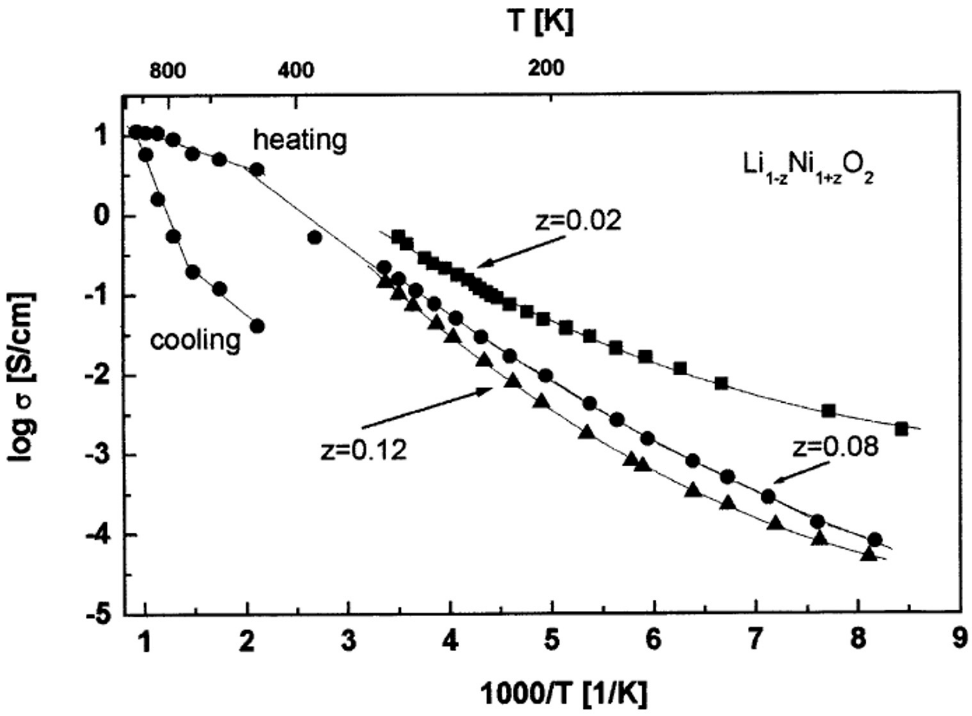
Effect of Off Stoichiometry on Performance

- Stoichiometric $LiNiO_2$ has greater electric conductivity than Ni rich alloys

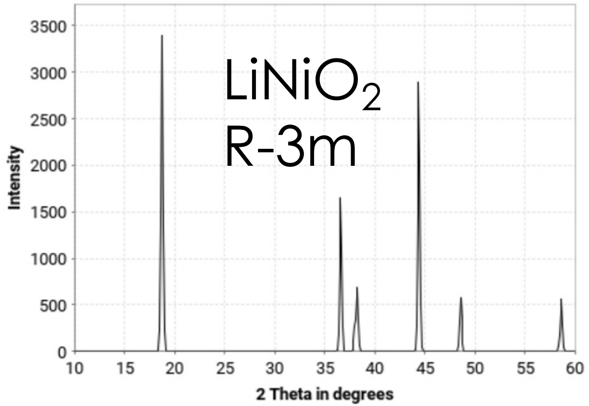
- Increased conductivity contributes to faster charge/discharge rates

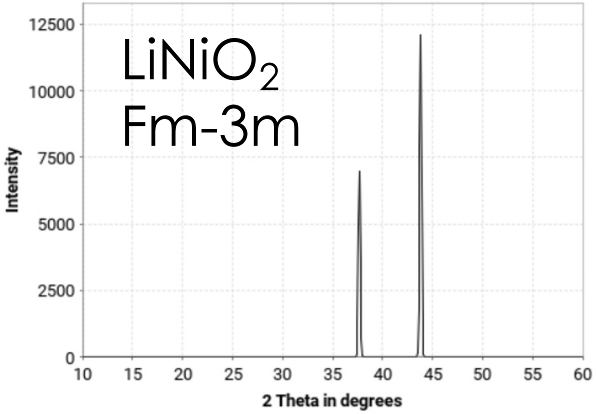


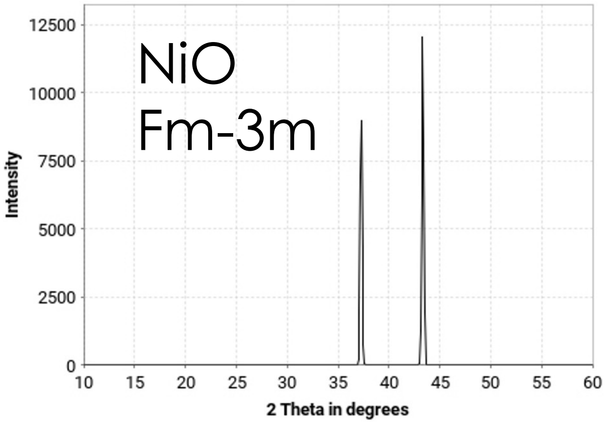
Molenda, J & Wilk, P & Marzec, Jacek. (2002). Structural, Electrical and Electrochemical Properties of LiNiO2. Solid State Ionics. 146. 73-79. 10.1016/S0167-2738(01)00992-4.

How to Determine Order vs Disorder

- Powder XRD gives similar diffraction patterns for space groups R-3m and Fm-3m
  - 37.7° and 43.8° peaks overlap
- Small impurities are very difficult to detect
- Magnetism can highlight structural differences



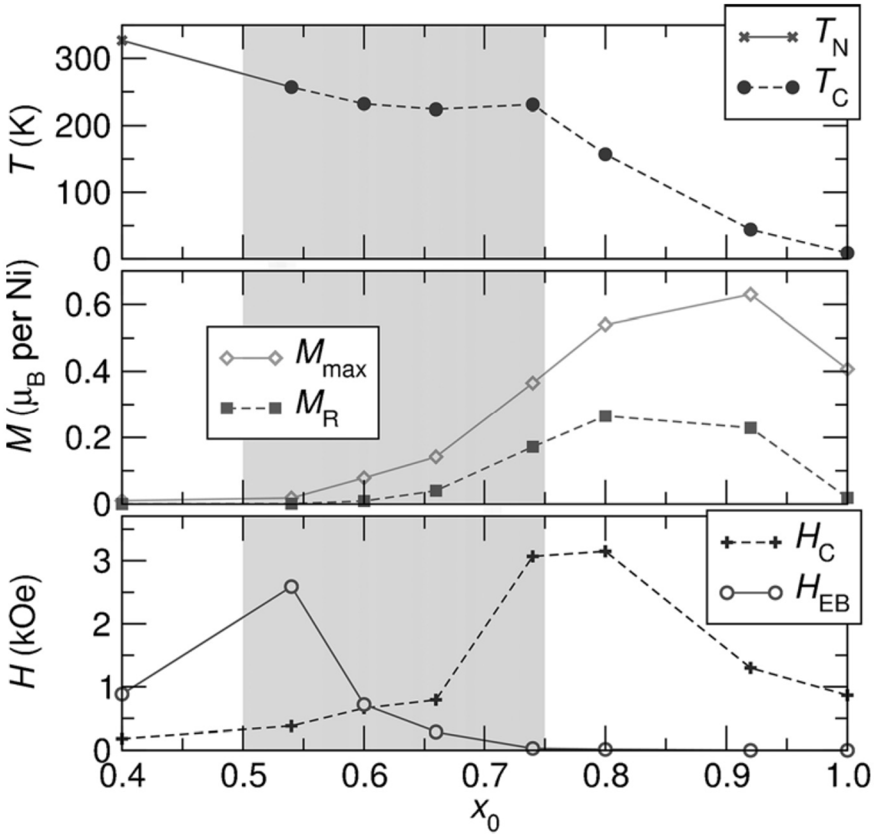




Bianchini, Matteo *et al.* (2020). An in situ structural study on the synthesis and decomposition of LiNiO2. Journal of Materials Chemistry A. 8. 10.1039/C9TA12073D.
Satoshi SASAKI, Kiyoshi FUJINO, Yoshio TAKÉUCHI, X-Ray Determination of Electron-Density Distributions in Oxides, MgO, MnO, CoO, and NiO, and Atomic Scattering Factors of their Constituent Atoms, Proceedings of the Japan Academy, Series B, 1979, Volume 55, Issue 2, Pages 43-48, https://doi.org/10.2183/pjab.55.43

Magnetism of $LiNiO_2$

- $LiNiO_2$ displays complex magnetic behavior with 3 distinct regions
  - Low moment for $Li_{0.5}Ni_{1.5}O_2$
  - Uncompensated magnetism for intermediate $Li_{0.8}Ni_{1.2}O_2$
  - Low moment in pure $LiNiO_2$
- Magnetism caused by structural changes as Li content increases



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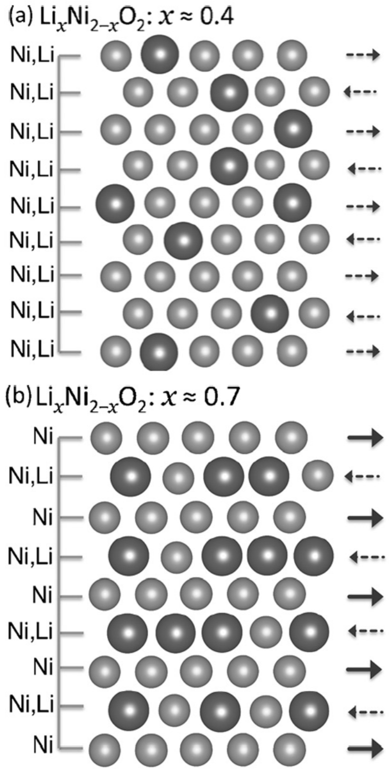
Source of Ferrimagnetism in $Li_{1-x}Ni_{1+x}O_2$



- Rocksalt structure dominated by antiferromagnetic interactions among Ni^{2+} atoms
  - Magnetic moment is compensated
- Ferrimagnetism arises from bridging interactions between Ni^{3+} layers
  - Ni^{2+} atoms bridge Ni^{3+} layers, creating ferromagnetic clusters
  - Uncompensated magnetism

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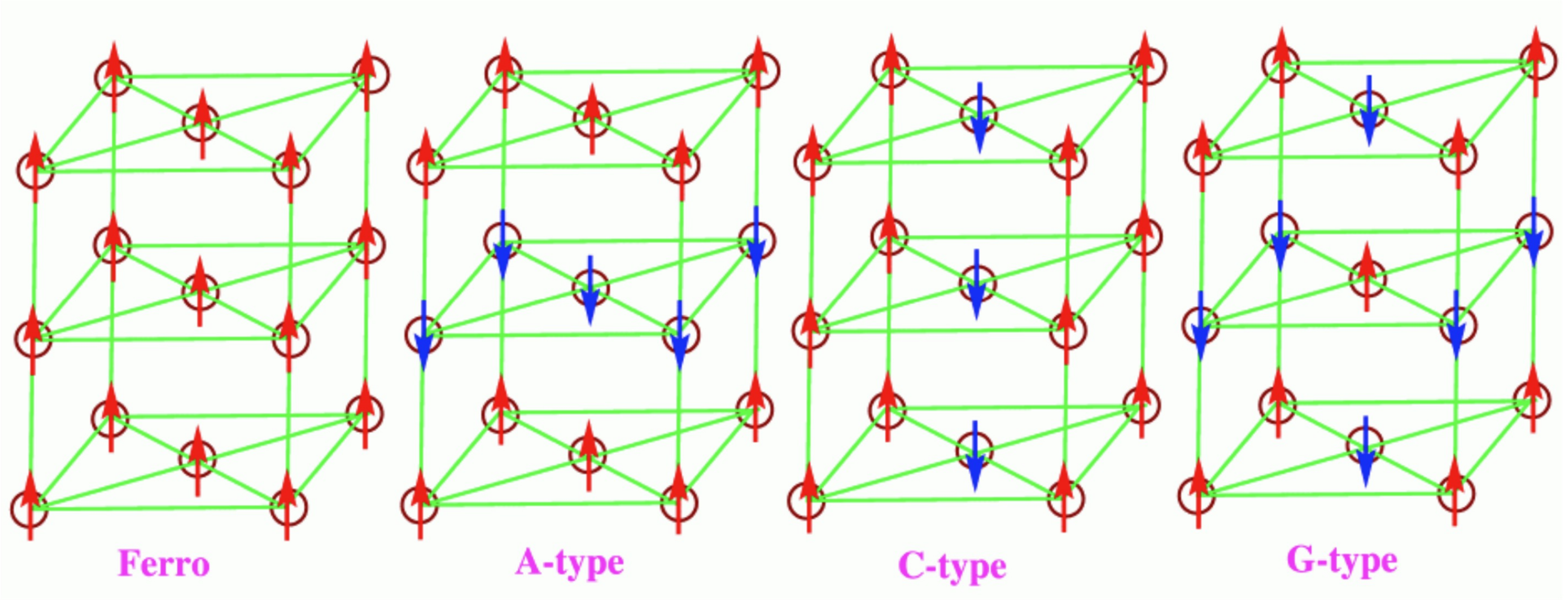
Summary of Magnetism in $NiLiO_2$

$Li_{1-x}Ni_{1+x}O_2$ Composition	$Li_{0.4}Ni_{1.6}O_2$	$Li_{0.7}Ni_{1.3}O_2$	$LiNiO_2$
Magnetism	G-type Antiferromagnet	Ferrimagnet	A-type Antiferromagnet
Structure	Rock Salt	Connected Layers	Repulsive Layers
Ni^{2+}/Ni^{3+} Interactions	Ni^{2+} dominates Ni^{3+}	Ni^{2+} connects Ni^{3+} layers	Only Ni^{3+} present
T_N	327K	240K	9K

Types of Antiferromagnetism

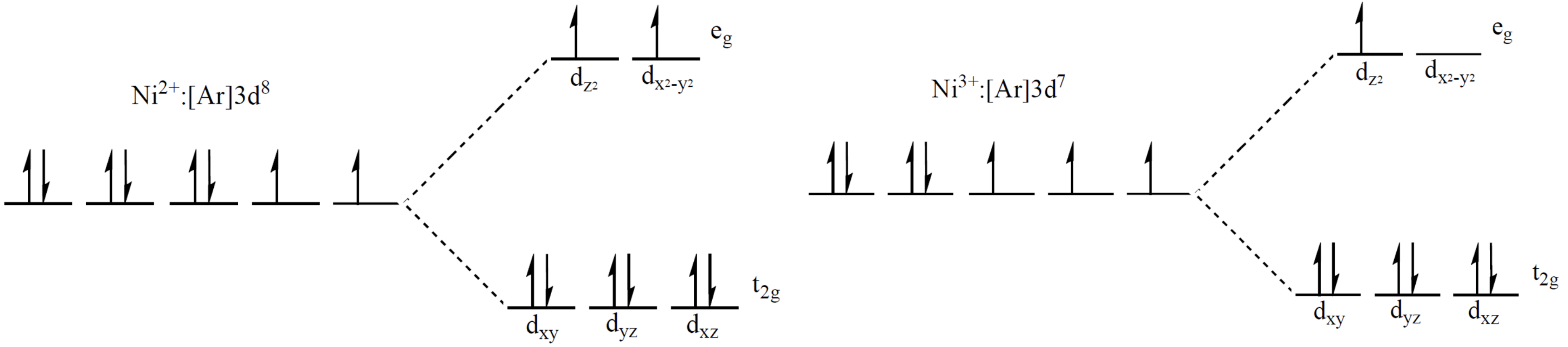
- $LiNiO_2$ displays A-type and $Li_{0.4}Ni_{1.6}O_2$ displays G-type



Helmer Fjellvåg, Arne Kjekshus, https://folk.universitetetioslo.no/ravi/activity/ordering/spinfig.html

Electronic structure of Ni^{2+} vs Ni^{3+}

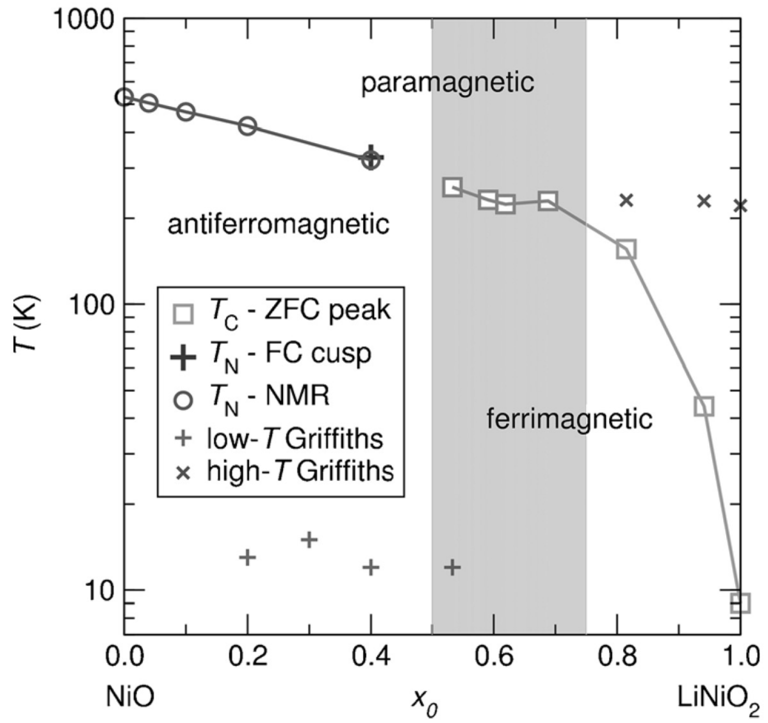
"A larger negative free energy change for a reaction
$xA + MX_n = A_xMX_n$
is expected when *A* is small and electropositive, MX_n contains a metal atom *M* in a high oxidation state, and *X* is small and electronegative."



K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, LixCoO2 (0<x<-1): A new cathode material for batteries of high energy density, Materials Research Bulletin, Volume 15, Issue 6, 1980, Pages 783-789, ISSN 0025-5408, https://doi.org/10.1016/0025-5408(80)90012-4.

Determining $LiNiO_2$ Order With Magnetism

- Lower magnetic ordering temperatures correspond to more stoichiometric samples
- "The complex magnetism of $Li_{1-x}Ni_{1+x}O_2$ evolves as Ni enters the Li plane, the Ni^{3+}/Ni^{2+} ratio changes, and the chemical coherence length shrinks"



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