^{6}Li MAS NMR study of lithium layered oxides containing Ni^{2+} ions: experiments and DFT calculations

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^{6,7}Li MAS NMR spectra are sensitive to the presence of paramagnetic cations in the local environment of the lithium ions. The paramagnetic ions can result in spin density on the lithium nucleus, leading to large hyperfine shifts. The $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$ materials have recently been shown to be promising cathode materials for use in lithium-ion batteries [1-2]. Yoon et al. studied the $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$ materials by ^{6}Li MAS NMR and in situ X-ray diffraction and absorption [3-4], and showed that these materials are more disordered than implied by their nominal composition. A number of resonances were observed by NMR and their assignments to different local environments was nontrivial.

We recently showed that first principles calculations can be used to aid in the understanding of the mechanism that results in the transfer of spin density from the transition metal ion to Li and to assign the paramagnetic shifts observed by NMR [5]. In order to get the theoretical spin density on Li, we performed Density Functional Theory calculations using the pseudopotential method (VASP code).

In this work, we present a comparison of the ^{6}Li MAS NMR spectra of the $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$ and $LiTi_{0.5}Ni_{0.5}O_2$ materials. The $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$ phases were synthesized by a solid state reaction using lithium hydroxide and nickel manganese hydroxide, whereas the $LiTi_{0.5}Ni_{0.5}O_2$ phase was prepared by ion-exchange from $NaTi_{0.5}Ni_{0.5}O_2$.

In the $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$ phases, both Ni^{2+} and Mn^{4+} ions are paramagnetic and therefore interact with Li, leading to several NMR signals depending on the Li environment. In contrast, in $LiTi_{0.5}Ni_{0.5}O_2$, the Ti and Ni ions oxidation states are thought to be also 4+ and 2+ respectively, hence only the nickel ions are paramagnetic. The experimental data will be compared with results from our DFT calculations.

We will discuss the Ni^{2+}/M^{4+} ordering in these materials together with possible defects. The spectra of $LiTi_{0.5}Ni_{0.5}O_2$ will be compared to those of $LiCo_{0.5}Ni_{0.5}O_2$, which contains Co^{3+} (diamagnetic) and Ni^{3+} (paramagnetic) ions [6].

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References:

[1] T. Ohzuku and Y. Makimura, *Chem. Lett.*, 744 (2001)
[2] Z. Lu, D. MacNeil, J.R. Dahn, *Electrochem. Solid State Lett.*, 4, A191 (2001)
[3] W. S. Yoon, Y. Paik, X.-Q. Yang, M. Balasubramanian, J. McBreen, and C. P. Grey, *Electrochem. Solid State Lett.*, 5, A263 (2002)
[4] W. S. Yoon, C. P. Grey, X.Yang and J. McBreen, abstract of the 202nd ECS meeting, Salt Lake City (UT), Oct. 20-24 2002.
[5] D. Carlier, M. Ménétrier, C. P. Grey, C. Delmas, G.Ceder, *Phys. Rev. B*, submitted (2002).
[6] C. Marichal, J. Hirschinger, P. Granger, M. Ménétrier, A. Rougier and C. Delmas, *Inorg. Chem.*, 34 (7), 1773 (1995).