

PHASE STABILITY OF LITHIATED TRANSITION METAL OXIDES

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There has been significant interest in the area of lithiated transition metal oxides due to their use in lithium-ion batteries. At present LiCoO_2 is widely used as cathode materials for rechargeable lithium-ion batteries. However the high cost and potential toxicity of cobalt make it imperative to search for alternative cathode materials. It is essential that these replacement materials exhibit the same or higher electrochemical capacity without exhibiting any undesired irreversible phase transformation or decomposition during electrochemical cycling. LiMnO_2 has drawn much attention because of the lower cost and more environmentally friendly nature of manganese as opposed to cobalt. However LiMnO_2 is unstable and some experimental results on Co-doped LiMnO_2 to this effect have been reported. Prediction of the structural stability and the phase transitions in the LiMnO_2 - LiCoO_2 system would therefore be very useful. In this presentation we report the results of the full charge density exact muffin-tin orbital (FCD-EMTO) studies conducted on the orthorhombic (Pmmn), monoclinic (C2/m) and rhombohedral ($R\bar{3}m$) phases of the $\text{LiMn}_{100-x}\text{Co}_x\text{O}_2$ system in ferromagnetic (FM), antiferromagnetic (AF) and the disordered local moment (DLM) states. The latter is known to be a useful approximation describing the paramagnetic (PM) state well above the magnetic transition temperature. The effect of disorder was included within the coherent potential approximation (CPA). The relative stability of the different structures of the $\text{LiMn}_{100-x}\text{Co}_x\text{O}_2$ system is shown in Figure 1. The energies of all states are defined with respect to the energy of the hexagonal FM structure which is taken to be zero. For ordered LiMnO_2 compound we reproduced the correct ground state, the AF orthorhombic structure. If long-range magnetic order is absent, which is really true at elevated temperatures, the DLM orthorhombic structure of LiMnO_2 is still the stable phase. However, the energy difference between the DLM orthorhombic and monoclinic structures of LiMnO_2 is substantially reduced as compared to the energy difference between these structures with the AF order. Thus, it must be easier to stabilize the PM monoclinic phase at elevated temperatures. Substitution of ~ 13 at. % manganese by cobalt destabilized the AF order, making the DLM orthorhombic structure more energetically stable with respect to the AF phase. As more cobalt is introduced into the system (~ 30 at. %) the FM orthorhombic structure becomes the phase with lowest energy. Finally, substitution of ~ 60 at. % of manganese by cobalt helps to stabilize the DLM rhombohedral layered structure over the FM orthorhombic phase. Layered $\text{LiMn}_{100-x}\text{Co}_x\text{O}_2$ oxides ($x \geq 60$ at. %) should therefore provide easy migration of lithium during intercalation, suggesting its possible use as a cathode material.

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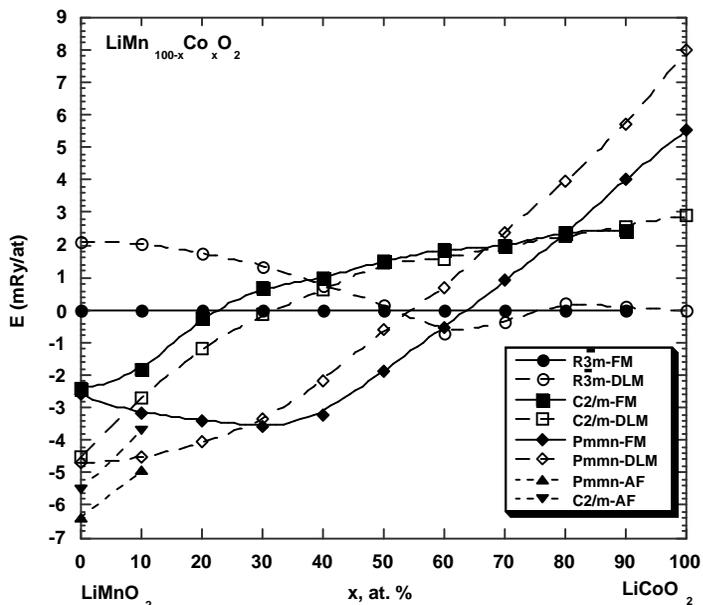


Figure 1. The relative stability of various structures of the $\text{LiMn}_{100-x}\text{Co}_x\text{O}_2$ system as a function of Co (x) calculated within the LAG approximation for the exchange-correlation functional. Note that the energies of all states are defined with respect to the energy of the hexagonal FM structure which was taken to be zero.