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**Electron-correlation induced phase separation in $Li_xFePO_4$** GERBRAND CEDER, Department of Materials Science and Engineering, Massachusetts Institute of Technology, FEI ZHOU, Department of Physics, Massachusetts Institute of Technology — $Li_xFePO_4$ is a promising rechargeable Li-ion battery cathode material. The $Li_xFePO_4$ system is known experimentally to phase separate into $FePO_4$ end $LiFePO_4$ up to $\sim$ 400 K, and form solid solutions above $\sim$ 600 K. Phase separation in this system is surprising as one would expect $Li^+$ ions to repel each other and form ordered compounds at compositions between those of the end members $FePO_4$ and $LiFePO_4$. This is exactly what is found in the local density or generalized gradient approximations to DFT, though it is in stark disagreement with experiments. The fact that the LDA+U method corrects this qualitative error points at the role of electron correlation in inducing phase separation in this material. We have thoroughly studied the LixFeO4 phase diagram with LDA+U. We found that the charge ordering of $Fe^{2+}/Fe^{3+}$ on the iron sub-lattice, induced by $d$ electron localization, couples delicately with Li/vacancy ordering on the lithium sublattice. Although the repulsion within each sub-lattice favors compound formation, the Li-$e^-$ attraction favors phase separation. It is the balance of interactions within and between the two sub-lattices that gives rise to the unexpected phase behavior of $Li_xFePO_4$. Possible relevance of this novel phase transition mechanism to other alkali metal-intercalated materials will be discussed.

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