

Abstract Submitted
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Configurational Electronic Entropy and the Phase Diagram of Mixed-Valence Oxides: The Cases of Li_xFePO_4 and Fe_3O_4 ¹ FEI ZHOU, Materials Science and Engineering, MIT, THOMAS MAXISCH, GERBRAND CEDER — We demonstrate that configurational electronic entropy, previously neglected, in *ab initio* thermodynamics of materials can qualitatively modify the finite-temperature phase stability of mixed-valence oxides, in our case Li_xFePO_4 . First-principles LDA+U calculations were performed on 245 Li_xFePO_4 structures with different lithium/vacancy and electron/hole distributions, and Monte Carlo simulations were used to determine the phase diagram based on a coupled cluster-expansion model. While transformations from low-T ordered or immiscible states are almost always driven by configurational disorder (i.e. random occupation of lattice sites by multiple species), in FePO_4 – LiFePO_4 the formation of a solid solution is almost entirely driven by electronic, rather than ionic configurational entropy. We argue that such an electronic entropic mechanism, rather than an ionic one, may be relevant to most other mixed-valence systems. Details in Phys. Rev. Lett. **97**, 155704 (2006). Recently we have studied the Verwey transition in magnetite Fe_3O_4 . The configurational entropy of the t_{2g} electrons on the iron B sub-lattice is found to lead to a first-order phase transition, although the mechanism is substantially more complicated than that Verwey originally proposed.

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