Comparison of the electronic structures of four crystalline phases of FePO$_4$

PING TANG, N. A. W. HOLZWARTh, Wake Forest University — LiFePO$_4$ in the olivine structure is a promising cathode material for Li-ion batteries. During normal battery operation, an olivine form of FePO$_4$ is formed. Experimental evidence suggests that the olivine phase is meta-stable relative to a quartz-like trigonal phase. In addition, several other meta-stable phases have been reported including a monoclinic and a high pressure CrVO$_4$ structure. We have carried first-principles electronic structure calculations on all of these phases in order to investigate their relative stability and other properties using both LAPW and PWPAW methods. We find that the LSDA approximation systematically underestimates the lattice constants and the calculated stability ordering of the phases is inconsistent with experiment. In contrast the GGA approximation models the phase stability in closer agreement with experiment, although the lattice constants are systematically over-estimated.

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$^3$http://www.wien2k.at/; http://pwpaw.wfu.edu/