

First-principles study on magnetism and electronic structures of Li_xFePO_4

Dorj Odkhuu¹, Tumurbaatar Tsevelmaa¹, Namsrai Tsogbadrakh² and Soon Cheol Hong^{1*}

¹Department of Physics, University of Ulsan, Ulsan 680-749, Republic of Korea

²Department of Theoretical Physics, School of Physics and Electronics,
National University of Mongolia, University Street-1, Ulaanbaatar-210646, Mongolia

* Corresponding author : schong@mail.ulsan.ac.kr

A first-principles calculation implemented the general gradient approximation (GGA) excluding and including Hubbard U (GGA+U) is performed for the electronic and magnetic properties of the olivine phases Li_xFePO_4 ($0 \leq x \leq 1$). The calculated structural properties of the present study are in good agreement with experimental and other theoretical results. Total energy calculations show that an antiferromagnetic (AFM) state is more stable by the energy difference of 0.12 ($x=0$) and 0.03 eV/f.u. ($x=1$) than a ferromagnetic (FM) state. The present results are in consistent with experiments, in which AFM orderings of FePO_4 and LiFePO_4 were found below $T_N=125$ K and at $T_N=50$ K, respectively. The insertion/extraction of lithium affects slightly the spin moments of Fe, 3.96 (4.29) μ_B for FePO_4 and 3.56 (3.77) μ_B for LiFePO_4 from the GGA (GGA+U) approach. Consistent with observations, a different easy magnetization axes between $x=0$ (along a -axis) and 1 (along b -axis) reflects also the differences between their electronic structures, where the e_g state is found to be a crucial. Both GGA and GGA+U approaches are valid to describe the valence electronic structure, but only the utilization of GGA+U is able for the conduction bands, in resulting appropriate solution for the band gaps. We also predict that partially intercalated single crystals ($x=0.25, 0.5, \text{ and } 0.75$), which were synthesized at high temperature recently as solid solutions, are compensated half-metallic regardless of the exchange-correlation approaches.