Electronic structures of four crystalline phases of $FePO_4$

Ping Tang, N. A. W. Holzwarth, Yaojun Du, and Xiao Xu

Department of Physics, Wake Forest University
Winston-Salem, NC, USA

$FePO_4$ in its "olivine" structure is the delithiated product of $LiFePO_4$, known as a promising cathode material for rechargeable Li ion batteries.[1] In addition to the olivine structure, several other crystalline forms have been identified,[2] including a quartz-like form, a monoclinic form, and a high-pressure form related to the $CrVO_4$ structure. The question of the stability of the olivine phase relative to other less electrochemically active forms is important for the possible adoption of $LiFePO_4$ in commercial batteries. Recent calorimetry measurements[3] show clear evidence of the stability of the olivine structure relative to the quartz-like phase.

In the study of the 4 crystalline phases of $FePO_4$ within the framework of density functional theory, we have used 3 different computer codes including the linearized augmented plane wave (LAPW) code (WIEN2k available at http://www.wien2k.at) used in earlier work on related materials,[4] our projector augmented wave (PAW) code (*pwpaw* – http://pwpaw.wfu.edu), and the plane-wave pseudopotential code (*PWscf* – http://www.pwscf.org). With careful attention to the calculational parameters and to accuracy and convergence issues, we are able to achieve very similar results for the 3 independent computational methods. We report our results for the relative stability of the four crystal structures as well as present partial densities of states and other qualitative information about the crystal field splittings and bond hybridizations which can help rationalize our understanding of the electrochemical and stability properties of these materials. Our results indicate that a complete understanding of these materials will require additional work analyzing the electron self-interaction and correlation corrections.

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