



Magnetism of NaFePO₄ and related polyanionic compounds

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Abstract

Magnetic properties of maricite (m) and triphlyte (t) polymorphs of NaFePO₄ are investigated by combining *ab initio* density functional theory with a model Hamiltonian approach, where a realistic Hubbard-type model for magnetic Fe 3d states in NaFePO₄ is constructed entirely from first-principles calculations. For these purposes, we perform a comparative study based on the pseudopotential and linear muffin-tin orbital methods while tackling the problem of parasitic non-sphericity of the exchange–correlation potential. Upon calculating the model parameters, magnetic properties are studied by applying the mean-field Hartree–Fock approximation and the theory of superexchange interactions to extract the corresponding interatomic exchange parameters. Despite some differences, the two methods provide a consistent description of the magnetic properties of NaFePO₄. On the one hand, our calculations reproduce the correct magnetic ordering for t-NaFePO₄ allowing for magnetoelectric effect, and the theoretical values of Néel and Curie–Weiss temperatures are in fair agreement with reported experimental data. Furthermore, we investigate the effect of chemical pressure on magnetic properties by substituting Na with Li and, in turn, we explain how a noncollinear magnetic alignment induced by an external magnetic field leads to magnetoelectric effect in NaFePO₄ and other transition-metal phosphates. However, the origin of a magnetic superstructure with $\mathbf{q} = (1/2, 0, 1/2)$ observed experimentally in m-NaFePO₄ remains puzzling. Instead, we predict that competing exchange interactions can lead to the formation of magnetic superstructures along the shortest orthorhombic *c* axis of m-NaFePO₄, similar to multiferroic manganites.

