N[2]: Non-Collinear Spin with Nonadiabatic Dynamics for Lanthanide Spectroscopy: from Photoinduced Dynamics to Photoluminescence

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Hexagonal-phase $NaYF_4$, designated as β-$NaYF_4$, is one of the most efficient host materials for down-conversion and up-conversion luminescence of lanthanide ions.[1] Lanthanide ions with partially filled $4f$ orbitals result in open-shell configurations with high value of spin multiplicity. High values of spin-orbit-coupling (SOC) prompt necessity to apply non-collinear spin DFT which enables SOC for modeling lanthanide doped $NaYF_4$.[2] To clarify the role of spin-flip transitions in these doped materials, it is necessary to compare multiple electronic relaxation processes of (i) unrestricted spin-polarized DFT and (ii) non-collinear spin DFT with SOC. In this work, calculations are performed in VASP taking into account unpaired spin configurations using the PBE functional in a plane wave basis set.[3] On-the-fly nonadiabatic coupling calculations provide transition probabilities facilitated by nuclear motion. Electronic structures for β-$NaYF_4$ host lattices doped by Ce^{3+}, Nd^{3+}, Pr^{3+} systems are characterized by electronic density of states, optical spectra, electron localization, and computed photoluminescence spectra. Rates of radiative and non-radiative relaxation are calculated using Redfield theory in the reduced density matrix formalism cast in the basis of spin polarized DFT[4,5] and in the basis of non-collinear spin DFT with SOC, with recently developed suite of codes for nonadiabatic dynamics for 2-component spinor orbitals. Photoluminescence in the SOC approach has more adequate ability to reproduce bright intra-band optical transitions of trivalent lanthanides.

References

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