Excited states and Racah parameters of Ni^{2+} in $KMgF_3$ via hybrid density functional theory

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Developing affordable materials capable of serving as host matrices for transition-metal (TM) activator ions—particularly those with unfilled 3d electron shells—has been a major scientific and engineering challenge in recent decades. These materials are essential for creating phosphors that efficiently convert excitation energy into light emission. Optical properties of the TM-dopant in the host lattice depend on charges, bond lengths, covalency, coordination and others. While the absorption energies of d-d transitions can be estimated from these parameters from ground state calculations, here we obtain these energies and electronic structures of excited state by Δ-SCF (self-consistent field) approach in solid-state physics. This approach has been used previously to predict the d-d excitation energies in bulk and surface NiO [1] in good agreement with the experimental values.

In continuation of our work on d-ions in $KMgF_3$[2,3], here we demonstrate results of *ab initio* calculations of 45 microstates of Ni^{2+} in a periodic $KMgF_3$ supercell. These include single-, double-electron and spin-flip transitions ($z^2\uparrow \rightarrow z^2\downarrow$), all within a single computational framework. We analyze the effect of exact exchange and correlation functionals on excitation energies, calculate Racah parameters and pressure-energy curves for every unique electron configuration. Inclusion of high amount of Hartree-Fock exact exchange is important to properly describe the ionic system and improve predicted energies of d-d transitions, CRYSTAL23 code allows to do it at very low computational cost.

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