Construction of Wannier orbitals and calculation of crystal field parameters of Ce-doped $Y_3Al_5O_{12}$

Jakub Ježek[1,2] and David Sedmidubský[2]

[1]*Institute of Physics of the Czech Academy of Sciences, Na Slovance 1999/2, 182 00 Prague 8, Czechia*

[2]*Department of Inorganic Chemistry, University of Chemistry and Technology, Technická 5, 166 28 Prague 6, Czechia*

When studying the electronic structure of inorganic crystals using Density Functional Theory (DFT) in Periodic Boundary Conditions (PBC), Bloch orbitals $\psi_{n,\mathbf{k}}(\mathbf{r})$ are typically employed to better describe electron delocalization in solids compared to Gaussian orbitals. Bloch orbitals are characterized by two quantum numbers: n (band index) and **k** (wave vector within the first Brillouin zone). However, for materials containing lanthanides, the 4f and 5d bands tend to be highly localized, making it challenging to accurately estimate intra-band energies of the ground state. This limitation can be addressed by using Wannier orbitals w_n(**r**-**R**), which are localized on atoms at position vector **R**. Transformation to Wannier orbitals enables the extraction of crystal field parameters (CFP) and facilitates calculations of crystal field splitting effects within the local atomic Hamiltonian ansatz.

In this work, the previously developed methodology of CFP extraction through Wannierization of APW-based Bloch functions (calculated by Wien2k code) is combined with the atomic Hamiltonian constructed using Stevens operator equivalents applied on M_J basis set of a given multiplet. This approach is demonstrated on the well known system of Ce-doped $Y_3Al_5O_{12}$ garnet (YAG:Ce) as a test case. Moreover, an atempt is made to assess the effective electron correlation parameter U for Ce-4f states using a similar technique as in CFP analysis, namely bringing the 4f states from valence shell to core. The 4f-4f electronic transitions estimated from crystal field splitting, spin-orbit interaction and possibly electron correlations will be compared with standard DFT+U band structure calculations to highlight the enhanced information content and chemical interpretability achievable through this localization approach. While YAG:Ce is well-characterized experimentally, it might serve as an ideal benchmark system to validate the applicability of Wannier-based crystal field analysis combined with operator equivalent approach, potentially opening new computational pathways for studying less well-known lanthanide-doped materials with improved chemical insight.

This work was funded by Horizon Europe EIC Pathfinder program through project 101098649 – UNICORN.

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