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LLNL-TR-678696

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October 27, 2015

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Complex Electronic Structure of Rare Earth Activators in Scintillators

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Abstract

To aid and further the understanding of the microscopic mechanisms behind the scintillator nonproportionality that leads to degradation of the attainable energy resolution, we have developed theoretical and experimental algorithms and procedures to determine the position of the 4f energy levels of rare-earth dopants relative to the host band edge states.

Background and Research Objectives

Understanding of the scintillation mechanism of rare-earth (RE) doped scintillators requires a detailed understanding of the electronic structure of the dopant-host complex. In particular, to ensure that excitons or separate electron or hole carriers can be trapped on the RE, and thus ultimately produce photon emission, its 4f and 5d levels need to reside within the forbidden band gap region. Furthermore, the so-obtained electronic structure also serves as a starting point to compute e.g. carrier capture/emission rates. Standard density functional theory (DFT) is unfortunately not capable of treating the RE open-shell structure and results in partially unoccupied RE 4f levels that always reside inside the gap. More elaborate cluster calculations using modern quantum mechanical approaches lack proper band alignment between the periodic host and model cluster. In this light, this project was aimed and succeeded both in developing computational tools to address this issue, and to design and perform experiments using x-ray techniques to validate the modeling.

Scientific Approach and Accomplishments

Modeling of the 4f states were performed using two different approaches, which will be outlined in the following. Following an idea of Miyake and Aryasetiawan [Miyake, T. 2008] for the localized states in correlated 3d transition metals, the first approach consisted of constructing an effective

4f Hamiltonian by extracting screened Coulomb matrix elements in the constrained random phase approximation (cRPA) for a RE doped into a large supercell. To that end, we started implementation into the popular software package VASP [Kresse, G. (1993)] based on the projector augmented-wave method (PAW) [Blöchl, P.E. (1994)]. The PAW method has proven very successful both in terms of efficiency and accuracy for DFT calculations of point defects and dopants in large supercells, but its accuracy for this application was at the time unknown. While we were able to exactly reproduce Hartree-Fock results for the *unscreened* matrix elements, we found that the current state-of-the-art PAW representation of the dielectric response function needed to calculate the RPA matrix elements lacks the needed accuracy. In fact, the matrix elements turned out to severely underestimated. This was later verified in another context by the VASP group [Klimeš, J. (2014)].

To address this shortcoming we instead chose represent the response function using the so-called mixed basis set [Aryasetiawan, F. (1994)]. This type of basis set is specifically designed to accurately handle products of wave functions within the linear muffin-tin orbital (LMTO) or augmented projected wave (APW) formalisms, and is therefore suitable for both calculations of the response functions as well as the screened Coulomb matrix elements. We here chose to modify the existing, very well documented, GW code of Jiang et al, called FHI-gap [Jiang, H. (2013)], with input DFT wave function and energies from the WIEN2k code [Blaha, P. (2001)].

FHI-gap is, like most GW codes, specifically optimized to efficiently compute energy corrections for smaller unit cells. In particular, the parallelization is not optimal in terms of memory as every node needs to store the full response function and Coulomb matrices. This quickly leads to exceeding the available memory and cannot be alleviated by increasing the number of nodes. We therefore re-parallelized the entire code using scaLAPACK, which is a subset of the popular netlib LAPACK routines that are redesigned for distributed memory parallel computers [Blackford, L. S. (1997)]. In this fashion, we are now able to calculate screened matrix elements for large cells, see Fig. 1 for an example of Pr in a 12 Å cell. However, going beyond this will prove significantly harder in terms of

memory requirements and we therefore developed another alternative.

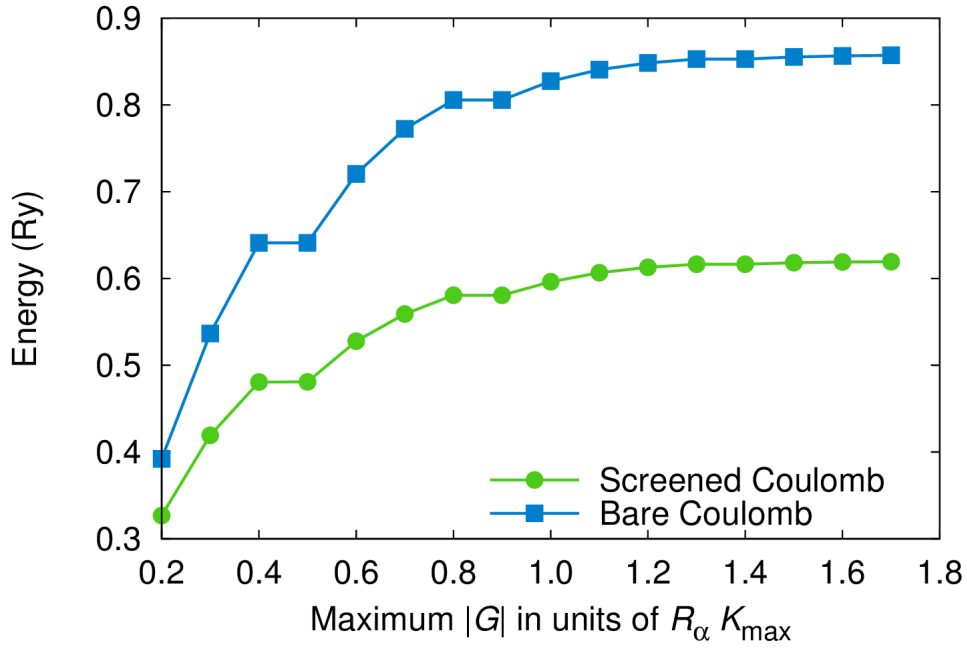


Figure 1: Convergence of screened and unscreened Coulomb matrix elements for Pr³⁺ in a 12 Å cell.

A second, simpler but more effective, approach was born out of the development of a new co-doping scheme for Ce doped LaBr₃ leading to improved detector performance at Delft University in Holland [Alekhin, M.S. (2014)]. At the time, the mechanism behind the improvement was unknown but we were, in an NA22-sponsored project, able to solve this problem [Åberg, D. (2014)]. However, if this model is to be correct, it should also explain the observed Stokes shifts in the absorption/emission spectra of Ce. We did find three different Ce-Sr-(Br-vacancy) triple-complexes, but the challenge was to calculate their absorption/emission lines. To accomplish that, we first define a subspace of the DFT Kohn-Sham states corresponding to the Ce-4*f* states by selecting only states whose projection onto spherical harmonics with $l=3$ exceeds a suitably chosen threshold. This is made possible by the localized nature of the rare-earth 4*f* states (and only works if the 4*f* states are not hybridized with the host bands). In this particular way, a Ce $4f^1 5d^0 \rightarrow 4f^0 5d^1$ excitation can be emulated by introducing a second Fermi level for the 4*f* subspace. Therefore, the resulting total energies are variational and this allows for

excited state structural relaxations. Using this scheme, we were able to calculate the Stokes shift that agreed very favorable with experiment, see [Erhart, P. (2015)] (Published within this LDRD).

The same approach – without modification – could not be applied to the rest of the RE series in the same material because of the unphysical hybridization of the 4f levels with the host ligands. This makes the identification of the 4f subspace ill defined. To overcome this issue we apply a local constant potential to the 4f states within the PAW sphere that shifts the associated states energetically away from the host bands. Then, the unphysical hybridization is removed and we can perform the subdivision of the orbital spaces and apply an equal occupation to all 4f bands. Once converged, the 4f levels are shifted back by the negative of the applied potential and the level positions with respect to the host band edges can be determined. In this way we have studied all the REs doped into LaBr₃ and compared to experimental values determined within this LDRD and existing literature. The results are shown in Fig. 2 and are very agreeable and show that the developed methodology *can* predict the relative positions of the 4f levels, thus successfully completing one of the major goals of this project.

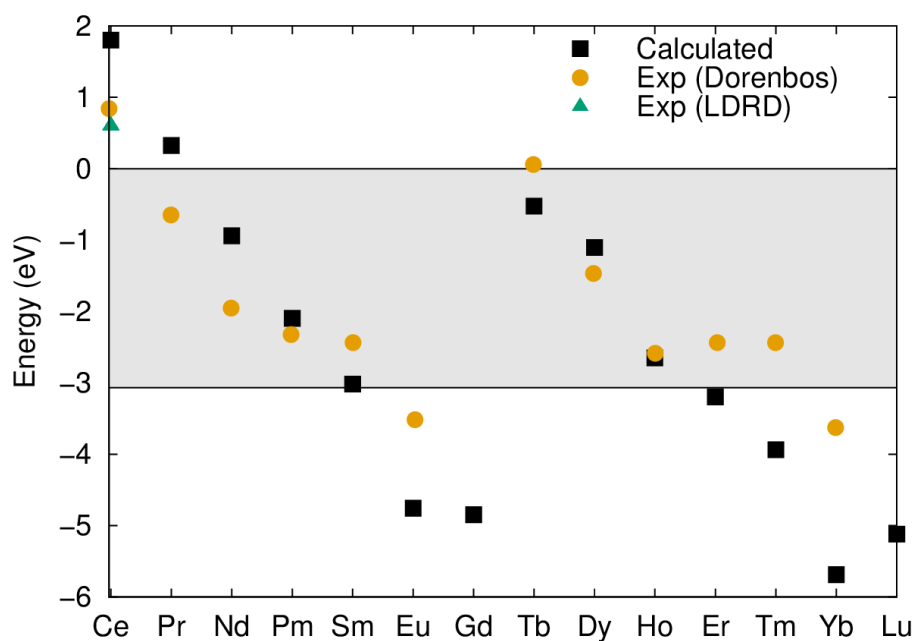


Figure 2: Experimental and calculated position of the 4f levels for all REs in LaBr₃. Experimental data from this LDRD and [Dorenbos, P. (2006)]

For the experimental part, we applied x-ray absorption spectroscopy, x-ray emission spectroscopy and resonant photoemission spectroscopy to determine the Ce $4f$ state of the activator with respect to the top of the valence band. For the YAP(Ce) scintillator, we determined the Ce $4f$ position relative to the top of the valence band to be 1.8 ± 0.5 eV. In case of $\text{LaBr}_3(\text{Ce})$ scintillator, it is determined to be 0.6 ± 0.4 eV. The LaBr_3 value differs by roughly 1 eV compared to the theoretical prediction, but that is to be expected given the choice of exchange correlation functional. Application of a hybrid functional together with the theoretical approach developed here will further improve upon this value and will be the subject of further research.

Publications from this project:

- I. *“Energy levels of the Ce activator relative to the YAP(Ce) scintillator host”*, S.-W. Yu, M. H. Carpenter, F. Ponce, S. Friedrich, J.-S. Lee, P. Olalde-Velasco, W. L. Yang, and D. Åberg, J. Phys. Condens. Matter **27**, 185501 (2015).
- II. *“Atomic origin of $3d^9 4f^1$ configuration in La^{3+} solids”*, S.-W. Yu, M. H. Carpenter, F. Ponce, S. Friedrich, and J.-S. Lee, J. Phys. Condens. Matter **27**, 405501 (2015)
- III. *“First-principles study of codoping in lanthanum bromide”*, P. Erhart, B. Sadigh, A. Schleife, and D. Åberg, Phys. Rev. B, **91**, 165206 (2015)
- IV. *“Ce $4f^1$ energy level in the band gap of $\text{LaBr}_3(\text{Ce})$ scintillator by resonant photoelectron spectroscopy”*, S.-W. Yu, Submitted to J. Phys. Condens. Matter (2015)

Impact on Mission

This project led to the hiring of a new member of the technical staff. As described above, we have already been able to leverage an NA22-sponsored project on scintillator proportionality and we expect this to

continue over an extended period of time. We will also find applications within phosphor research within the context of the Critical Materials Institute led by Ames Laboratory.

Conclusion

To summarize, we have successfully developed theoretical and experimental methodologies to study the position of RE 4f levels in relation to the host band edges. Next steps will be to continue our investigation on thermal non-radiative quenching in Ce-doped YAG and other materials, as well as developing a methodology for carrier capture cross sections within the context of a newly funded NA22 project.

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