Utilizing Density Functional Theory to Investigate Polaron Formation in Compositionally Complex Oxides

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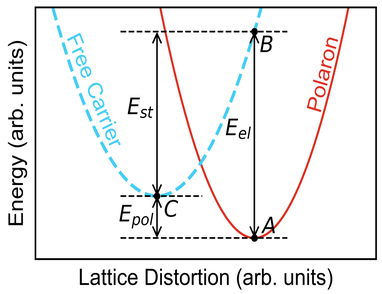
Background

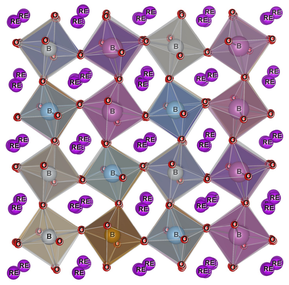
- Polarons: self-trapped or localized charge carrier coupled with a lattice distortion. [1]
- Utilized to explain properties of photovoltaics and piezoelectrics. [2, 3]
- Significance of polarons in new materials such as multifunctional compositionally complex oxides (CCO) is not well understood.



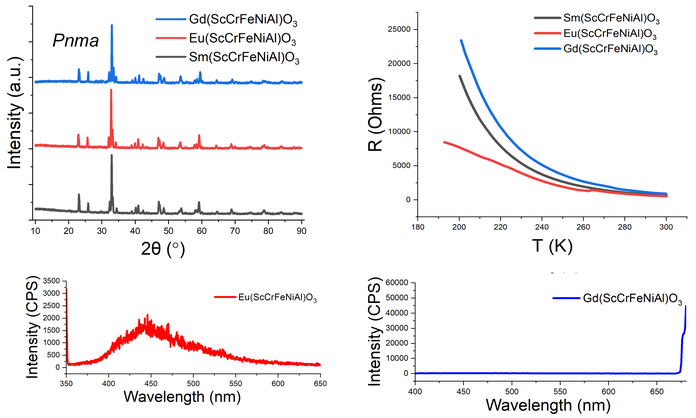
- Figure 1: Under certain conditions, the formation of a polaron is thermodynamically favorable ($E_{pol} = E_{el} - E_{st} < 0$) [1]

Experiment

- The multifunctional CCO $Eu(Sc_{0.2}Al_{0.2}Cr_{0.2}Fe_{0.2}Ni_{0.2})O_3$ was formulated to combine properties of ferroelectricity and ferromagnetism.



- Figure 2: $Eu(Sc_{0.2}Al_{0.2}Cr_{0.2}Fe_{0.2}Ni_{0.2})O_3$ is a variation of $A^{2/3+}B^{3/4+}O_3^{2-}$ structure with rare earth metals (RE) at the A site.



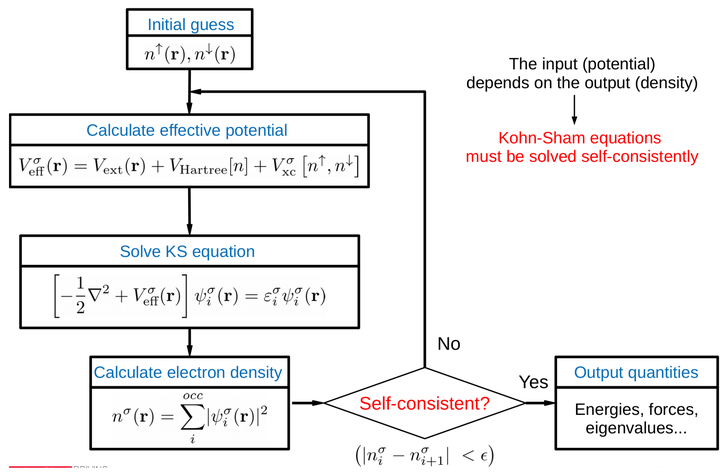
- Figure 3: From top left to bottom right: XRD illustrating the same crystal structure, resistance data highlighting different trends, and photoluminescence spectroscopy data of Eu with extra peaks compared to data collected for Gd.

Research Questions

- Is there polaron formation on Eu in $EuXO_3$?
- How can Density Functional Theory (DFT) be used to efficiently model the formation of polarons in compositionally complex oxides?

Density Functional Theory

Simplifies many body Schrodinger equation to a single variable functional of the total electron density.



- Figure 4: Self consistent field calculations scale based on N^3 where N is the number of electron wavefunctions; many other factors impact computational time such as functional type, density of k-space sampling, and convergence criteria. [4]

Type of Energy Functional	Parameters Used	Computational Cost	Accuracy
Local Density Approximation	ρ	Low	Low
Generalized Gradient Approximation	$\rho, \nabla\rho$	Varies	Varies
Hybrid-Functionals	$\rho, \nabla\rho, \nabla^2\rho, \tau$	High	High

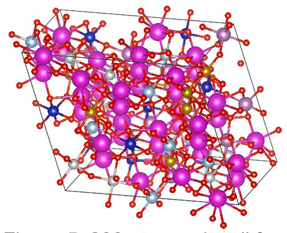
- Table 1: The generalized gradient approximation (PBE) was used to reduce computational cost while maximizing accuracy.

Citations:

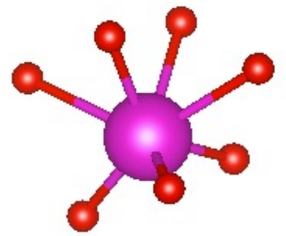
[1] Franchini, C., et al. Nature Reviews Materials, 2021. 6(7): p. 560-586.
[2] Zhang, H., et al. Journal of Physics: Energy, 2023. 5(2): p.6-7
[3] Wang, F, et al. Proceedings of the National Academy of Science, 2022. 119(30): p. 2-3
[4] "The Self-Consistent-Field Cycle¶." *Siesta Documentation*, docs.siesta-project.org/projects/siesta/en/latest/tutorials/basic/scf-convergence/index.html. Accessed 15 July 2024.
[5] Pham, T., et al. American Chemical Society, 2020. p. 1

Procedure

- Generate quasirandom unit cell and compare with Monte Carlo simulation.



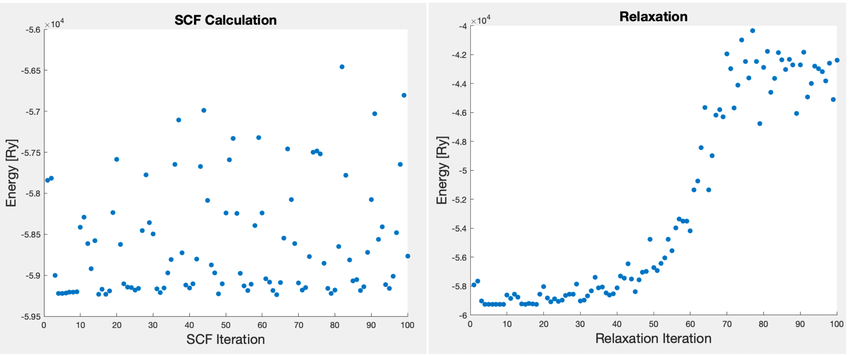
- Figure 5: 200 atom unit cell for $Eu(Sc_{0.2}Al_{0.2}Cr_{0.2}Fe_{0.2}Ni_{0.2})O_3$



- Figure 6: Eu atom bonding with adjacent oxygen atoms

- Bond distortion method[5]: increase the distance between oxygen atoms and an Europium atom.
- Increase the Hubbard correction, DFT+U, around the selected Europium atom.
- Add an extra electron.
- Perform self-consistent field calculations to determine electron wavefunctions.

Results



- Energy vs algorithm iterations illustrate the difficulty of converging CCOs in quantum ESPRESSO.

Conclusions

- Due to the experimental indication of both Eu^{2+} and Eu^{3+}, it is very likely that polarons form in this material. However, DFT calculations are currently inconclusive.

Future Work

- Randomize wavefunctions, compare polaron formation energies for different types of polarons, various magnitudes of bond distortion, and models of $Eu(Sc_{0.2}Al_{0.2}Cr_{0.2}Fe_{0.2}Ni_{0.2})O_3$
- Demonstrate that the procedure does not form polarons in $Gd(Sc_{0.2}Al_{0.2}Cr_{0.2}Fe_{0.2}Ni_{0.2})O_3$ and $Sm(Sc_{0.2}Al_{0.2}Cr_{0.2}Fe_{0.2}Ni_{0.2})O_3$

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