

Tackling Oxygen Defects in Lithium Titanium Oxide (LTO) using First Principle Simulation Methods

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Motivation

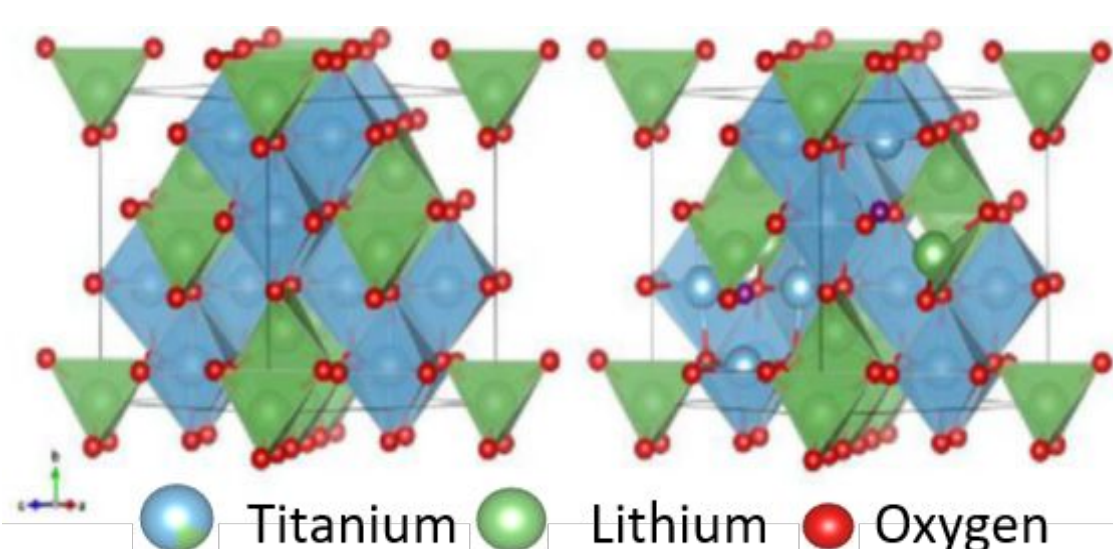
Lithium titanium oxide(LTO) is an intriguing anode material promising particularly **long lived batteries**, due to its remarkable phase stability during (dis)charging of the cell. However, its usage is limited by its low intrinsic electronic conductivity. Introducing oxygen vacancies can be one method to overcome this drawback, possibly by altering the charge carrier transport mechanism. Getting detailed insight in its **defect chemistry** is a non trivial task which needs to be tackled by theory and experiment. Here, we present extensive theoretical **two component density functional theory (TCDFT)** calculations in order to interpret **positron annihilation** measurements used to reveal defect influences on Li mobility. In addition we used **Hubbard corrected DFT (DFT+U)** calculations to gauge electron mobility to shed a light on the experimentally observed increase in electronic conductivity. By explicitly calculating hopping barrier heights our simulations indeed show that a **polaron hopping** mechanism can be the source for the increased electronic conductivity.

Experimental and Theoretical background: Application to LTO

How to produce defects in LTO?



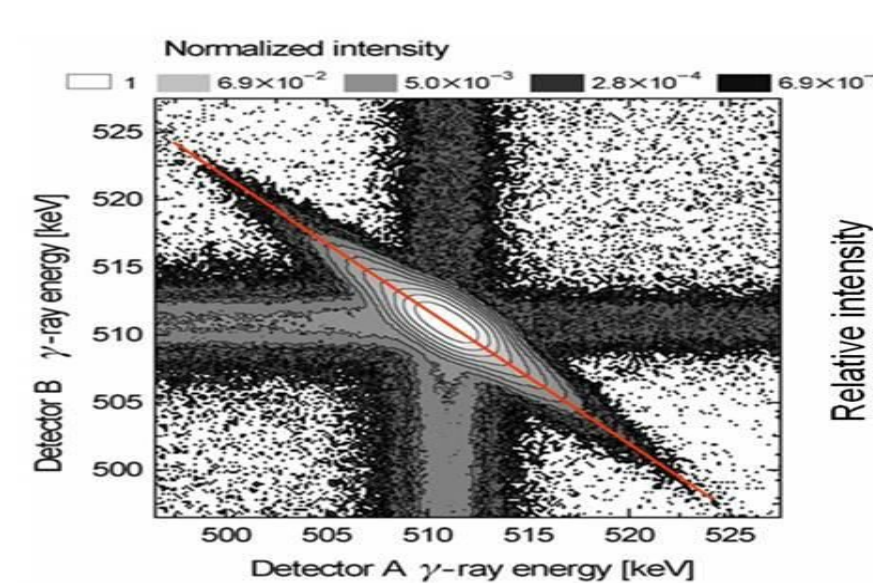
Ar/5%H₂, 700°C, hold t



Sintering of pristine, white LTO (left) under reducing conditions yields a blue defect rich material (right) with improved conductivity.

Positron annihilation spectroscopy

CDBS

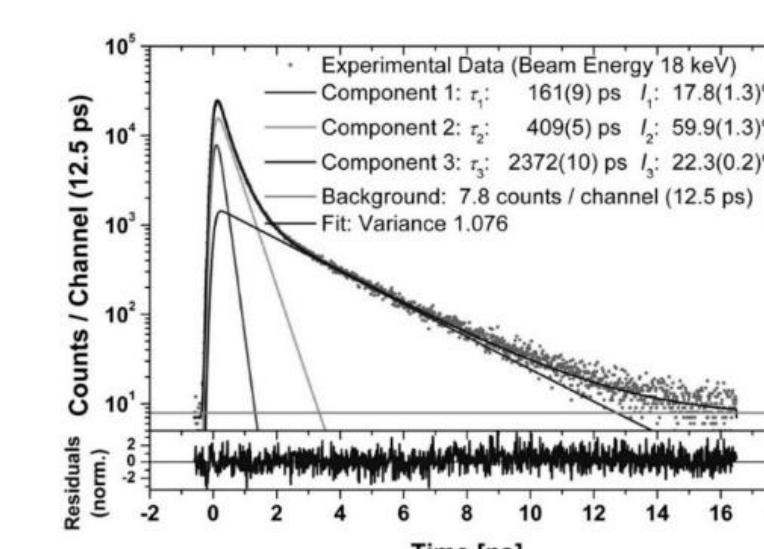


$$E_1 + E_2 = 2m_0c^2 = 1022 \text{ keV}$$

$$\Delta E = \frac{p_x c}{2}$$

□ Defect surrounding

PLEPS



$$\kappa_d = \mu C_d = \frac{I_2}{I_1} \left(\frac{1}{\tau_b} - \frac{1}{\tau_d} \right)$$

□ Defect type/size

DFT computation of positron lifetimes

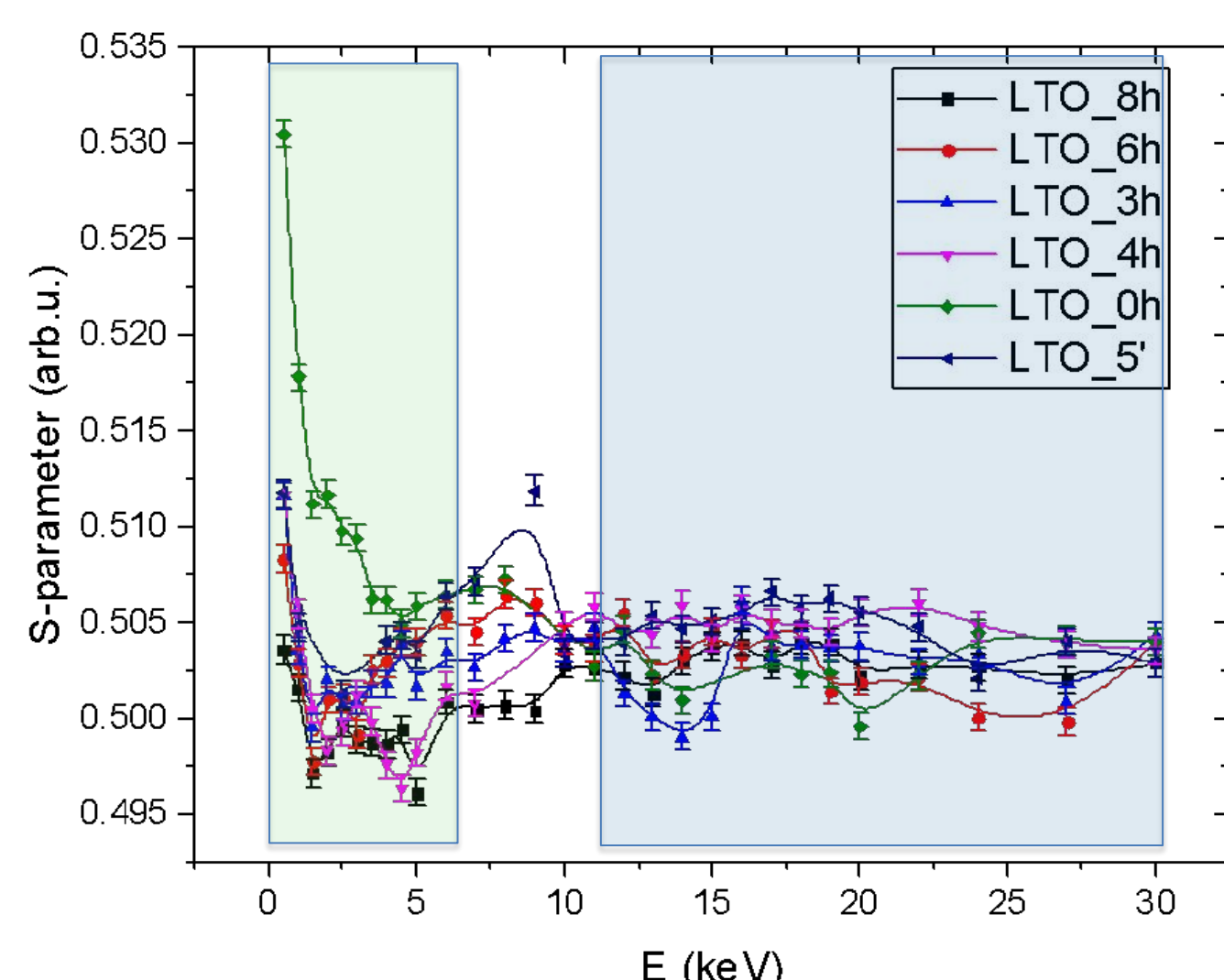
$$\frac{1}{\tau} = \lambda = \pi r_0^2 c \int dr n_+(r)n_-(r)g(n_+(r)n_-(r))$$

from self consistent solutions of two-component DFT (TCDFT) [1,2]

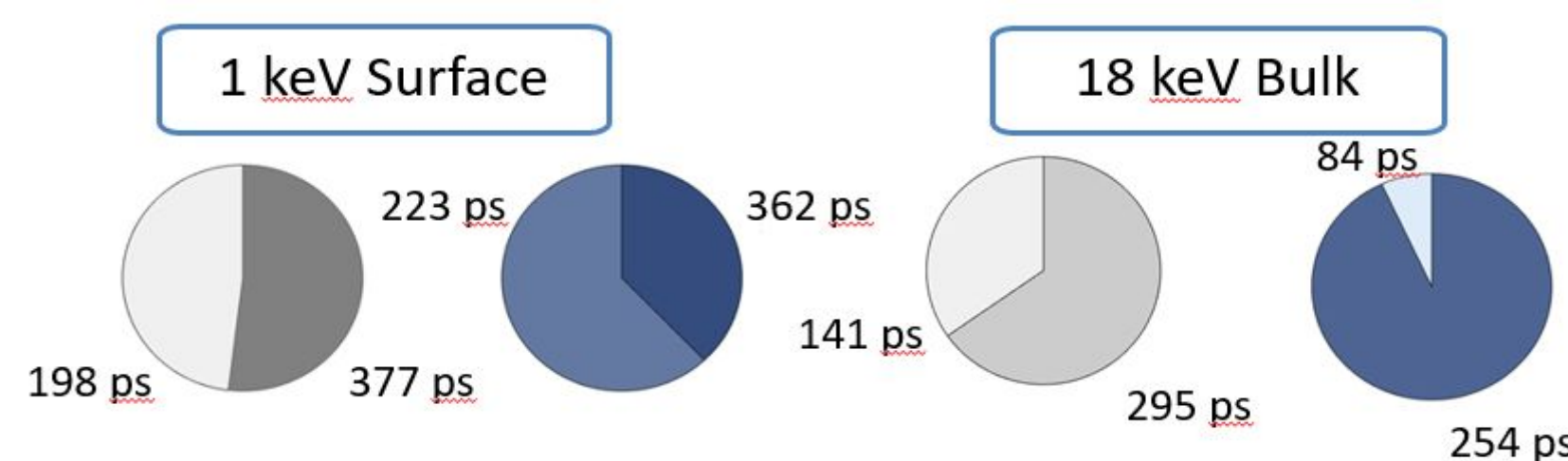
with $n_-(r) = \sum_i |\psi_i(r)|^2$ and $n_+(r) = \sum_i |\psi_+(r)|^2$



Results

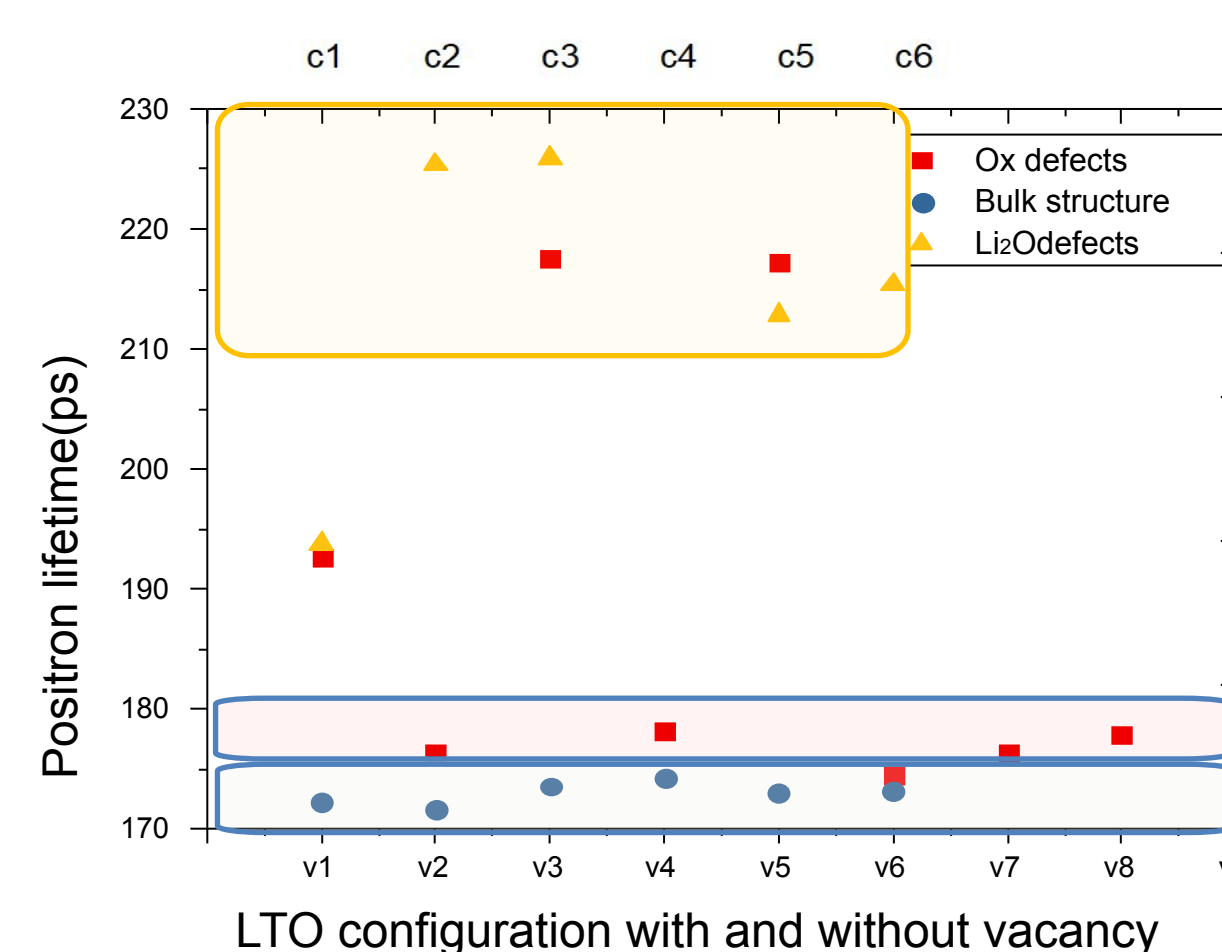


Experimental CDBS S-parameter scans as function of incident positron energy. Energies in the range of 1-5 keV correspond to **surface** and 18-20 keV to **bulk defects**. LTO samples with varying reductive treatment (annealing time) differ most in the surface defect distribution.

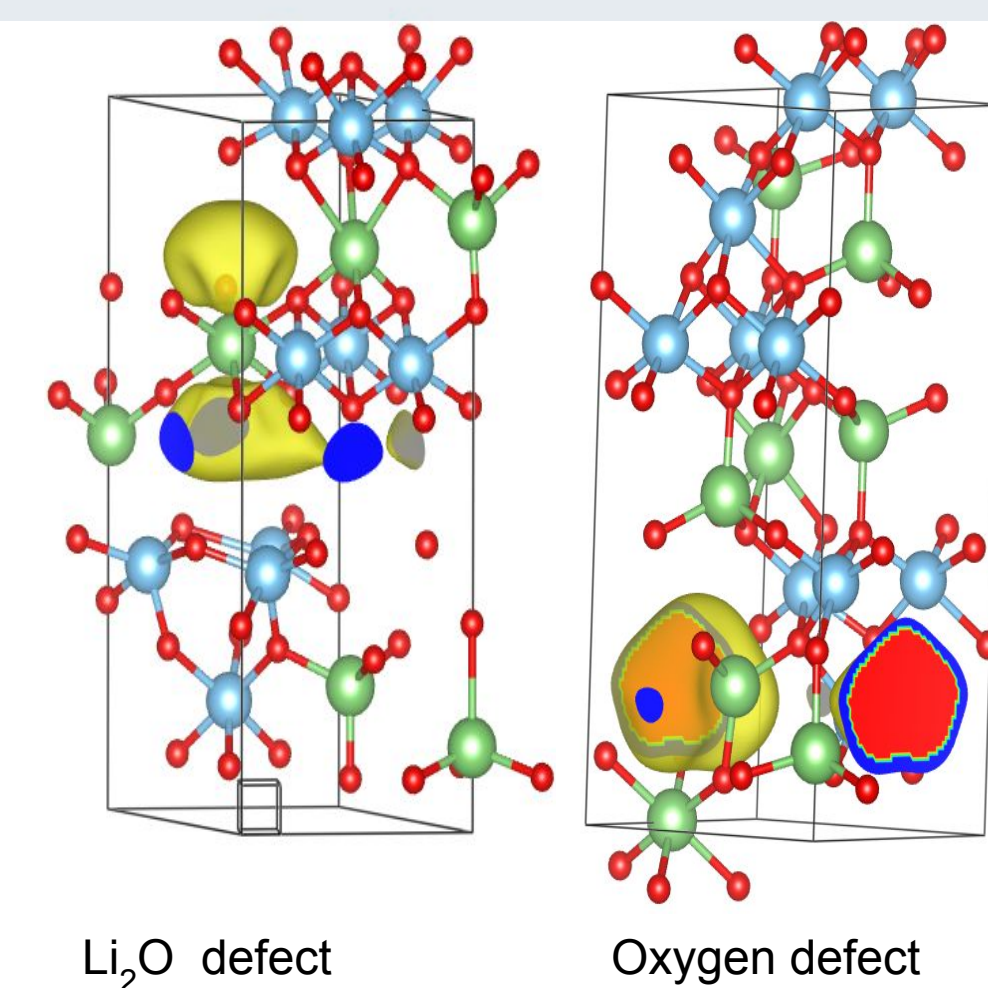


| Samples | LTO-white | | LTO-blue | |
|--------------------|---------------|---------------|---------------|---------------|
| Positron lifetimes | τ_1 [ps] | τ_2 [ps] | τ_1 [ps] | τ_2 [ps] |
| Surface 1 keV | 198 | 377 | 223 | 362 |
| Bulk 18 keV | 141 | 295 | 84 | 254 |

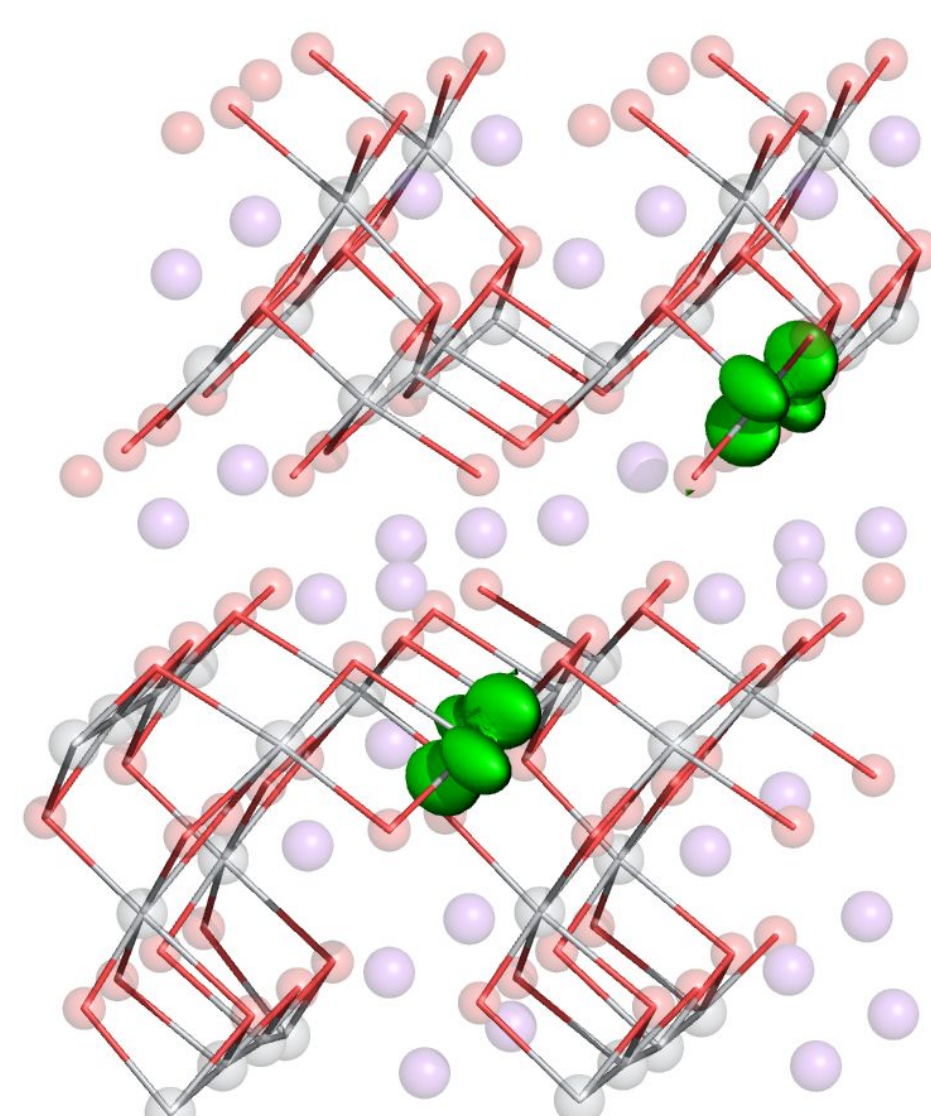
Experimental PLEPS positron lifetimes for white and blue LTO as a function of incident positron energy. Each measurement contains two dominant lifetime contributions with probability represented by the pie charts. The surface lifetimes are consistently longer, indicating generally larger defect volumes. The significance of the short bulk lifetime ($\tau_1 = 84$ ps) in reduced, blue LTO is still unclear.



DFT calculated lifetimes (left) and corresponding self-consistent positron densities in LTO. The bulk structures (c1-c6) correspond to the six possible mixed Li/Ti occupancies in the primitive Li₄Ti₅O₁₂ spinel unit cell. Positron lifetimes in these structures are given by blue circles and vary around 172 ps only within the experimental accuracy (blue box). Into these base structures, oxygen (red squares) and Li₂O (yellow triangles) defects are introduced, resulting in distributions of longer **positron lifetimes** in general **agreement with the experimental surface observations**. Computations covering large surface defects with lifetimes >350 ps have not yet been performed. Further structural sampling of defect structures is underway.



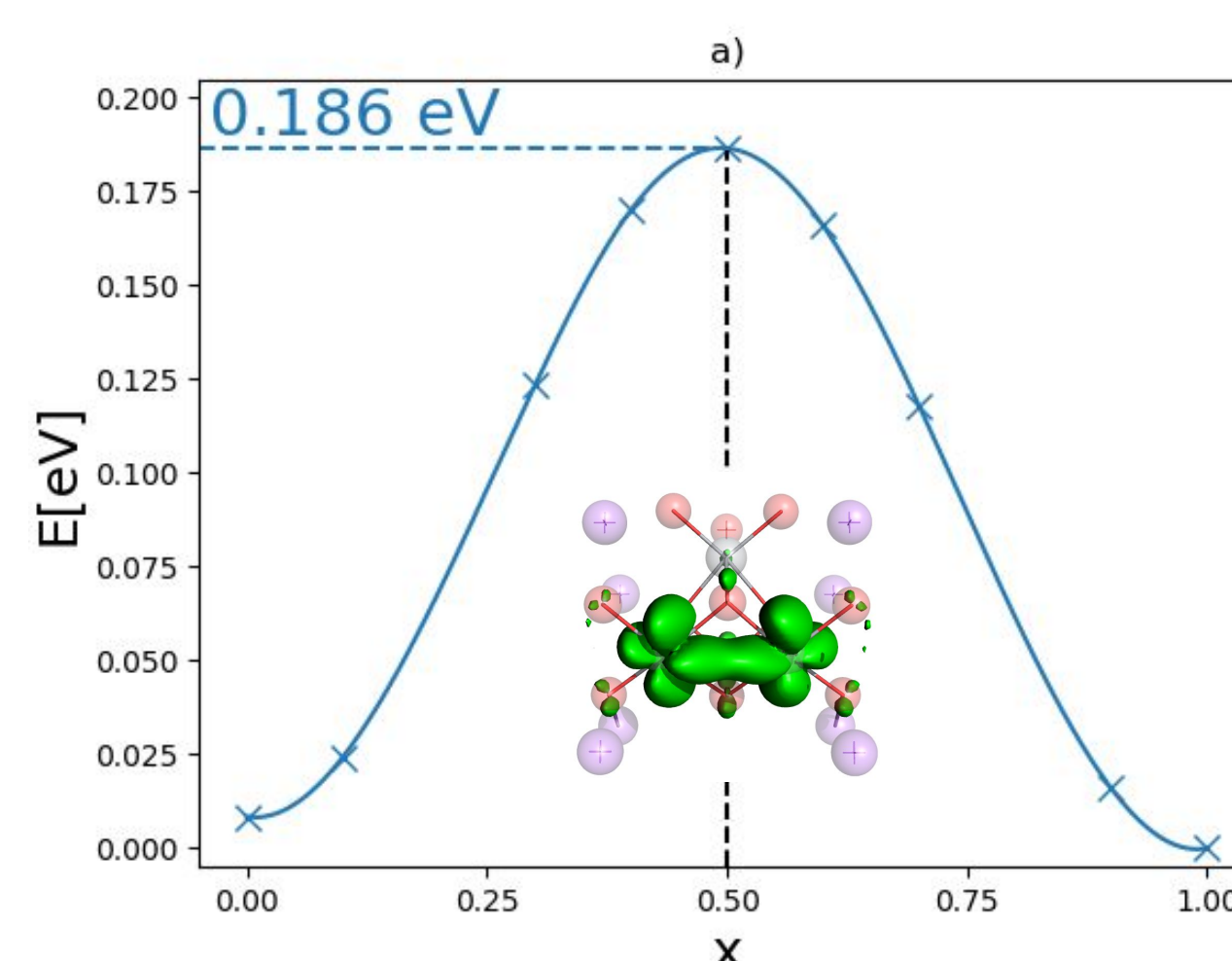
Polaron Hopping in LTO



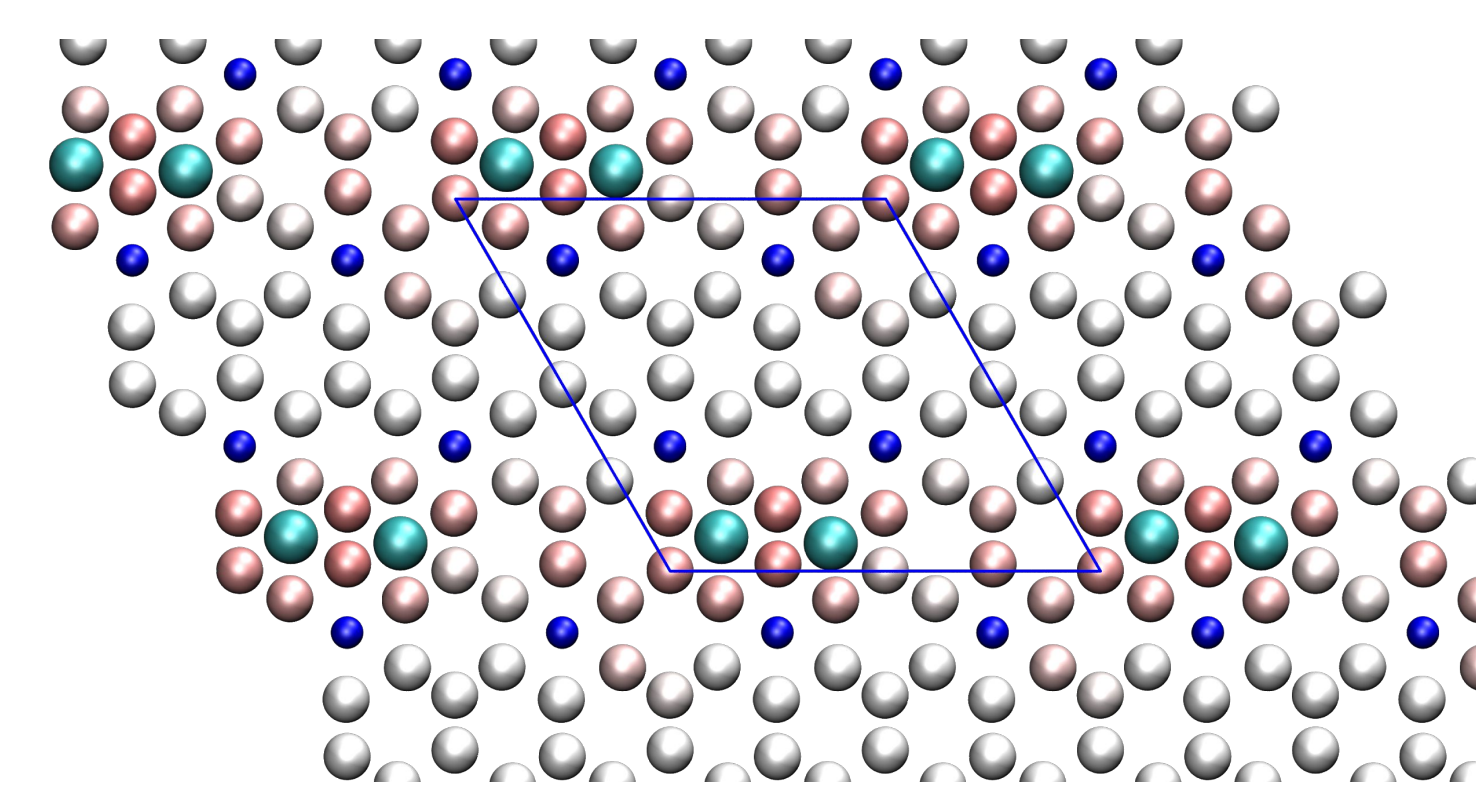
We are using **Hubbard corrected DFT** to simulate possible polaron hopping in order to calculate the theoretical increase in LTO's electronic conductivity.

Standard **semi-local DFT** is not able to capture the physics of localized polarons as the large amount of self-interaction error (SIE) leads to over-delocalization of the electron density.

PBE+U (= 2.65 eV)



Hopping barrier height: 186 meV indicates polaron hopping already at room temperature



Top view: Only nearest neighbour oxygen atoms relax during hopping. Indeed, this indicates a small polaron hopping mechanism.

Acknowledgements:



projectID: Itopolaron

References:

- [1] R. M. Nieminen et al. *Physical Review B* Volume 32, Number 2 15 July 1985 *Rapid Communication*
- [2] <http://www.abinit.org>



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