

Modelling Point Defects In Lithium Garnets

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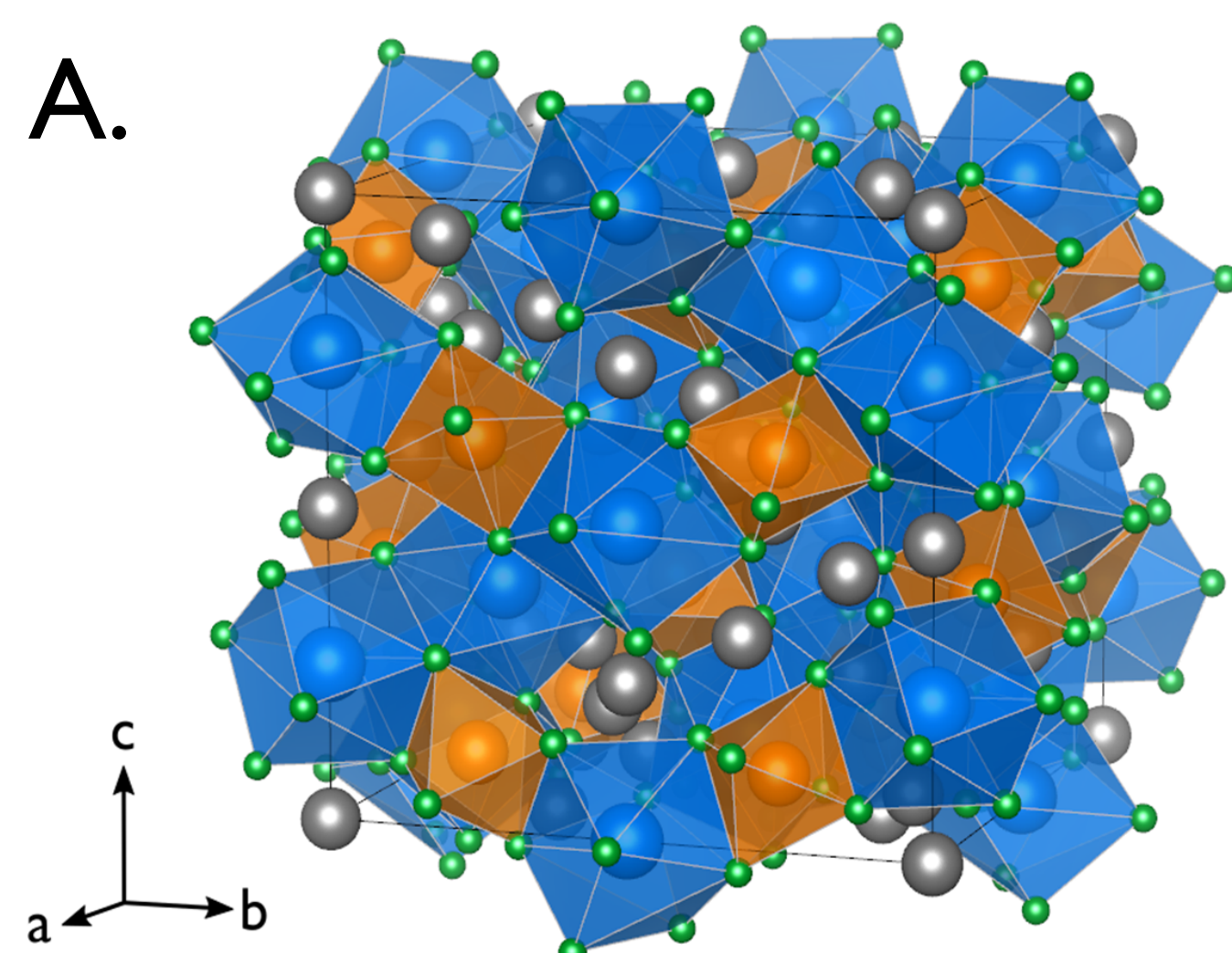
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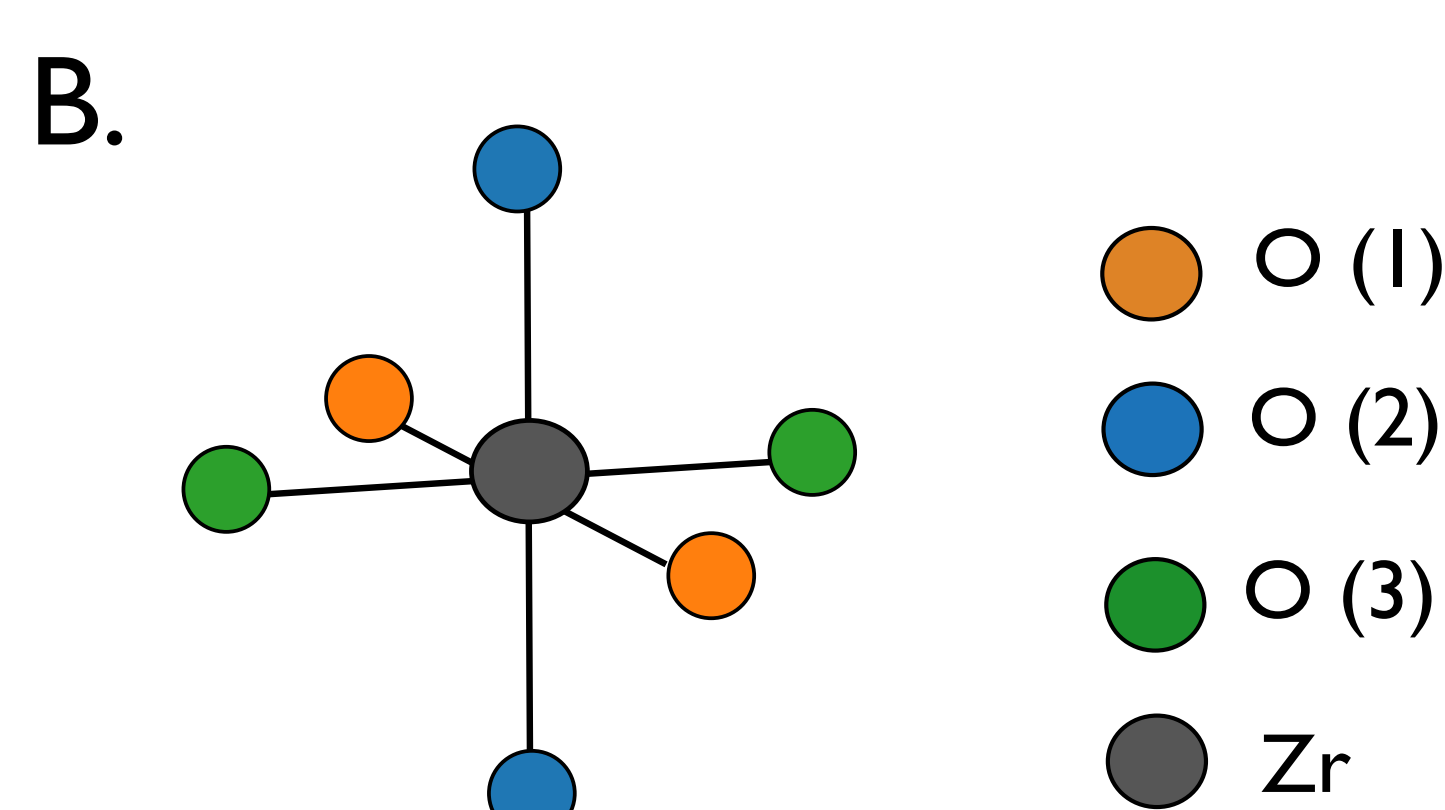
$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is a ceramic electrolyte candidate for all-solid state Li-ion batteries:

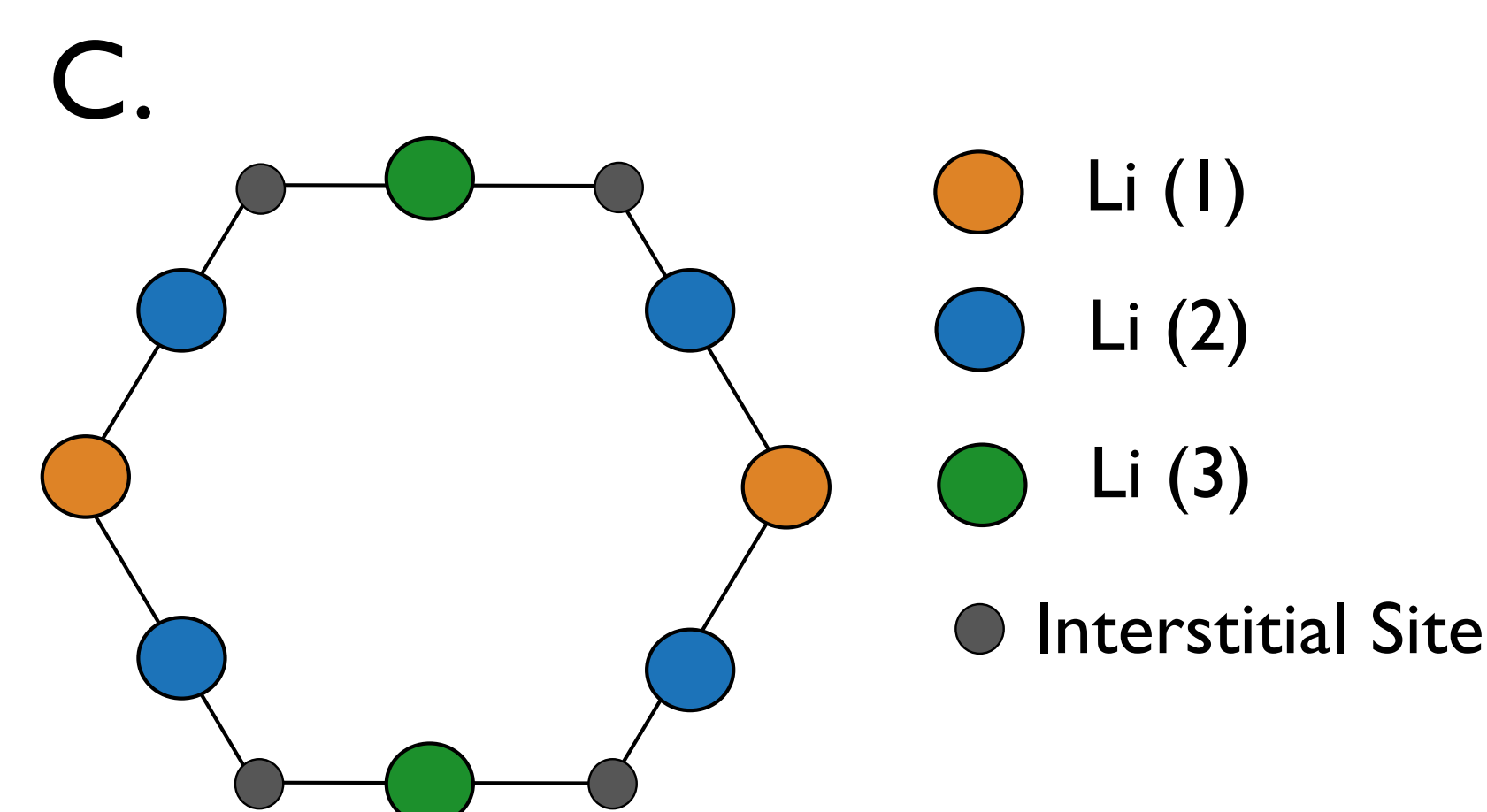
- Experiment suggests that LLZO could contain a large number of O vacancies under typical synthesis conditions.¹
- We have performed DFT calculations to model intrinsic defects in LLZO:
 - GGA in an attempt to identify defect states of interest;
 - GGA+*U* to clarify hole localisation on O 2*p* states;
 - Hybrid DFT in order to obtain a more accurate band gap in order to establish defect concentrations with respect to a self-consistent Fermi level.
- We have established a basis for O vacancy formation and charge compensation: Li vacancies and O vacancies form in a 2:1 ratio maintaining charge neutrality
- We are now investigating the chemical potential stability limits of LLZO in order to relate defect concentration to synthesis conditions.



Conventional unit cell of tetragonal LLZO, with Li shown in grey, La in blue, Zr in orange, and O in green.



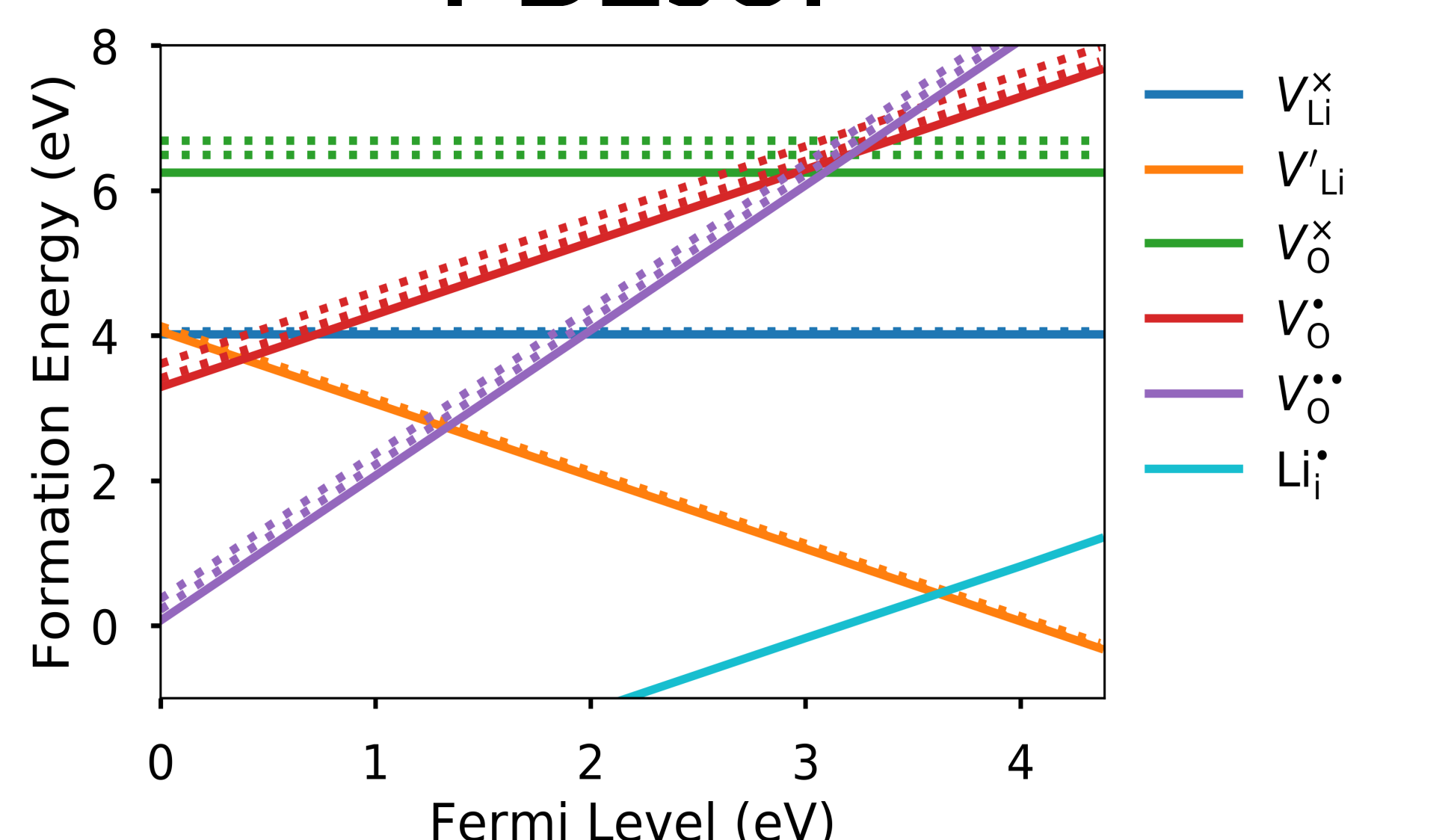
Distortion of the ZrO_6 octahedra imposed by the tetragonal phase, resulting in three symmetrically distinct O sites.



Unique positions considered in the Li sub-lattice, including the location of Li interstitials.²

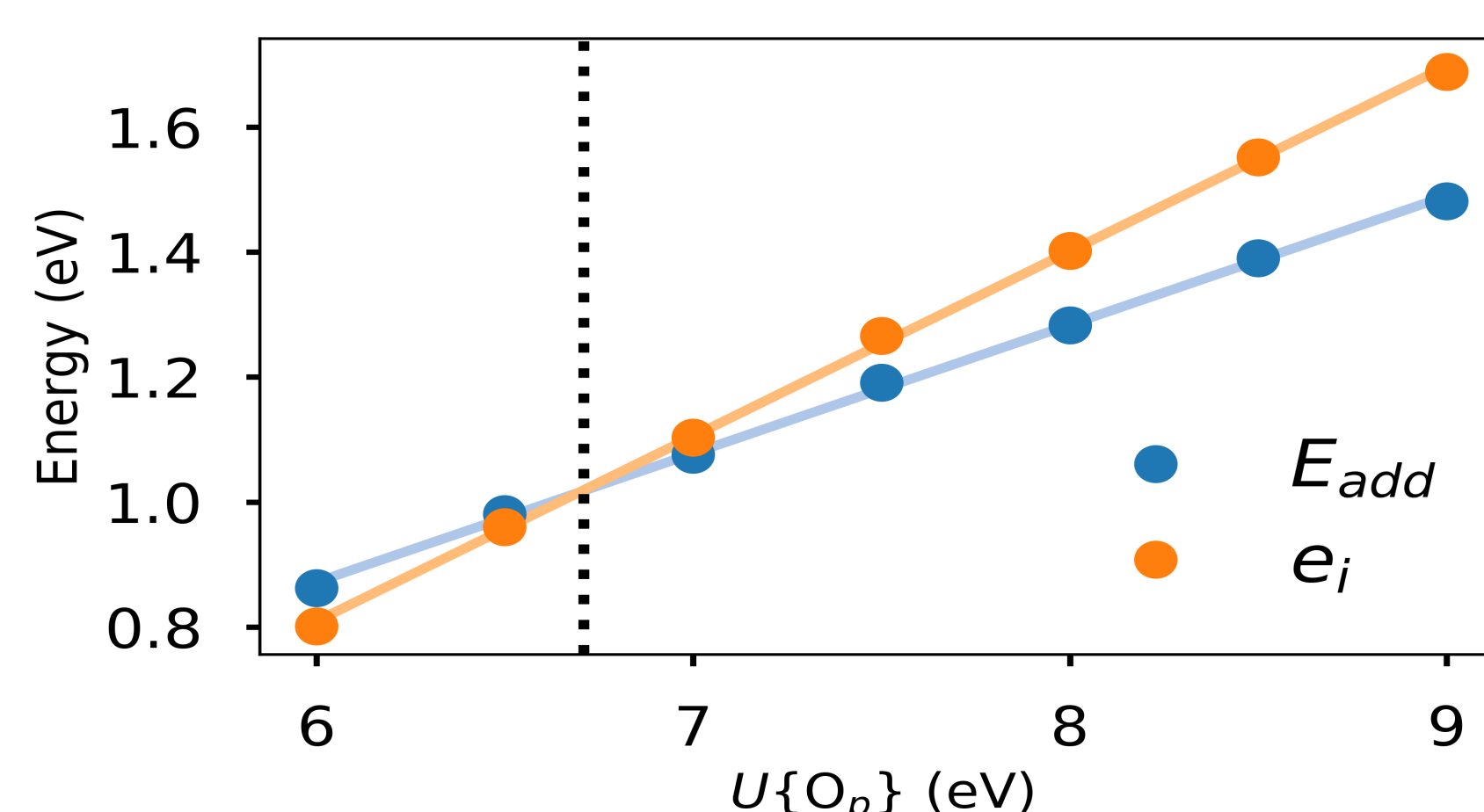
Results

PBEsol

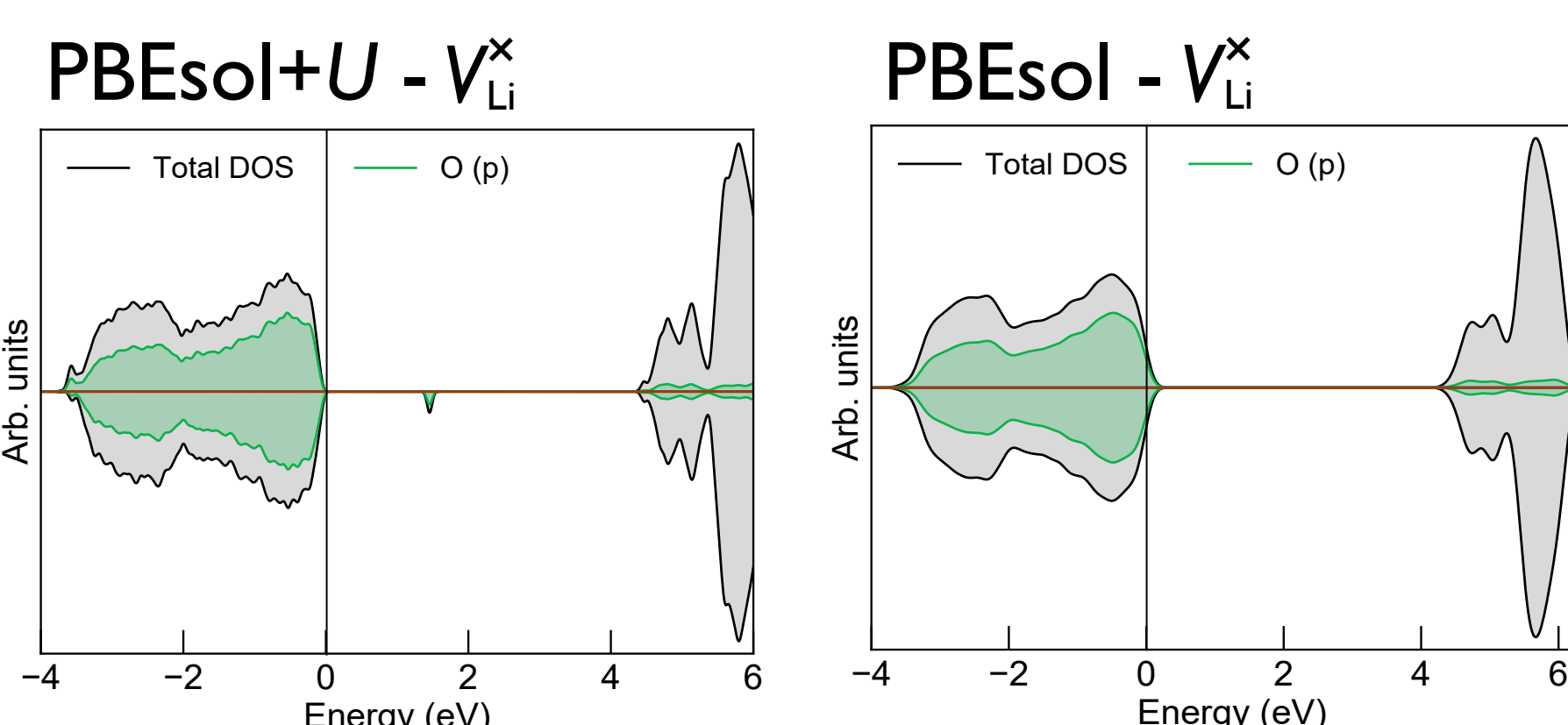


- PBEsol was used to investigate all symmetrically distinct sites in the tetragonal LLZO lattice.
- equivalent defect species occupying distinct lattice sites do not have vastly varied energies.
- The two lowest energy points of charge neutrality are $\text{Li}_i/\text{V}_{\text{Li}}$ compensation, and $\text{V}_{\text{O}}/\text{V}_{\text{Li}}$ compensation.
- This suggests that within the chemical potential stability limits of LLZO, we may see significant V_{O} formation.
- Excess charge associated with a defect will not be localised owing to artificial bias towards electron/hole delocalisation owing to the self interaction error inherent in GGA calculations.

PBEsol+*U*

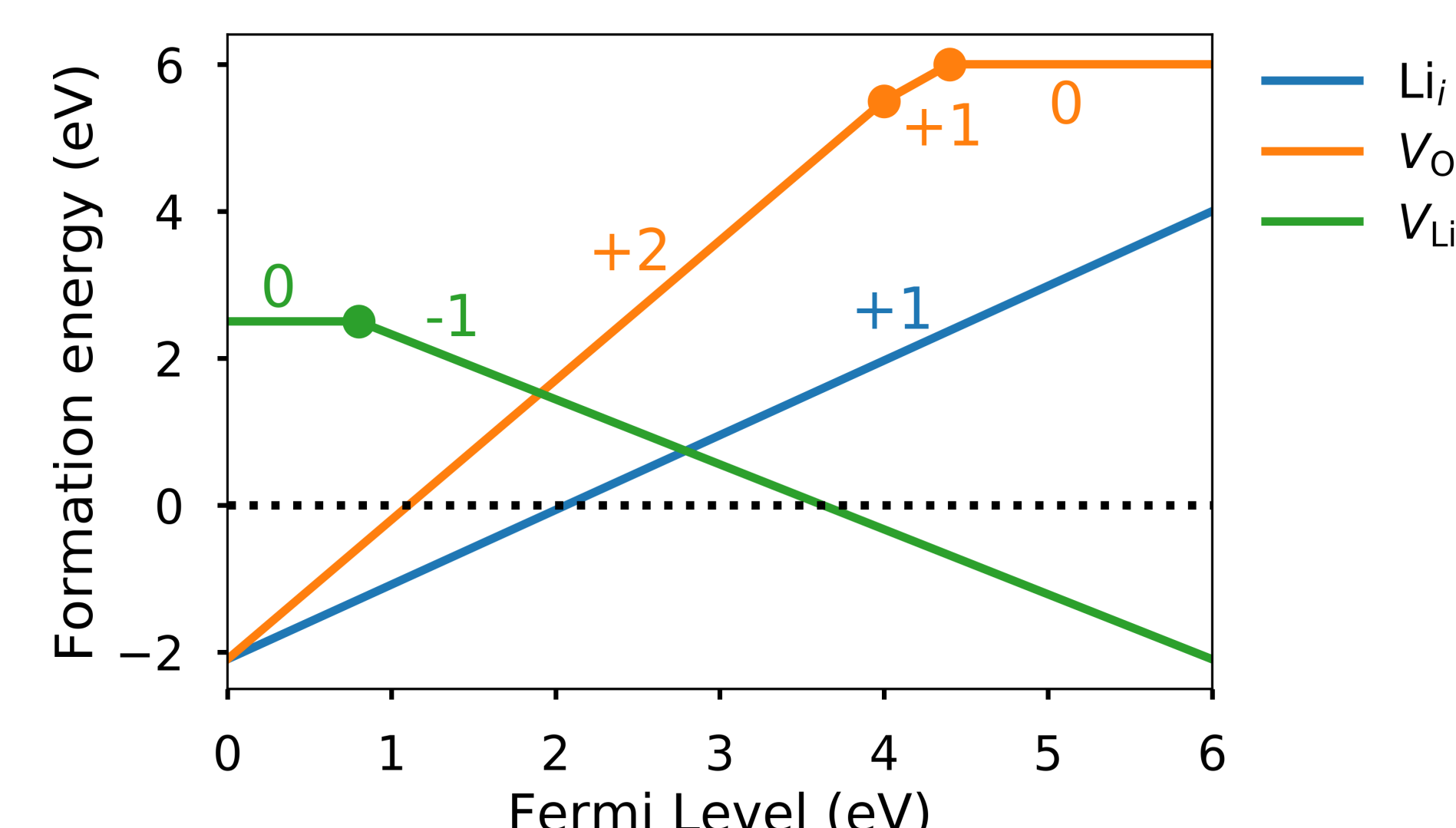


- Experiment shows that on ionisation of wide gap oxides such as LLZO, holes typically form localised O 2*p* states.³
- Such behaviour is not observed in PBEsol calculations for LLZO (See DOS plots below)
- Using the *ab initio* +*U* fitting procedure of Lany and Zunger³ we have demonstrated that this behaviour is observed in LLZO.
- Owing to band gap underestimation (~ 4.5 eV vs. ~ 6.0 eV)⁴, however, DFT+*U* predicts within the chemical potential stability limits of LLZO, the Fermi level could lie in the conduction band (unexpected in wide-gap insulator).

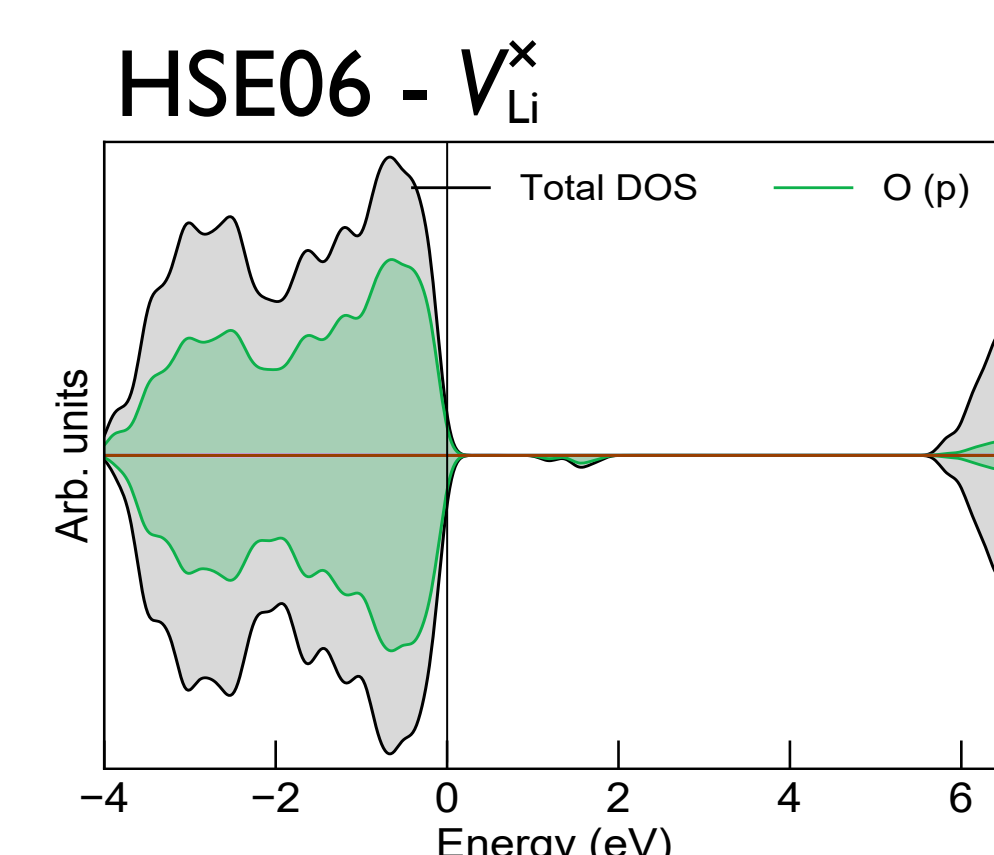


Electronic densities of states for the neutral Li vacancy. The hole state is shown localised on O 2*p* orbitals in the GGA+*U* calculation, no such localisation is observed in the GGA description.

HSE06



- Hybrid DFT widens the band gap, and shows correct defect localisation behaviour.
- Owing to the expense of these calculations, only one formation energy per defect species has been calculated.
- Still see broadly the same defect compensation behaviour as observed in PBEsol calculations.
- We are currently running total energy calculations on competing phases in the Li-La-Zr-O phase diagram to determine chemical potential stability limits so that defect concentrations can be determined.



Electronic density of states for the neutral Li vacancy. The hole state is shown localised on O 2*p* orbitals at ~ 1.8 eV.

Methods

Functionals: PBEsol, HSE06

U Value: 6.7 eV

Plane-wave cut-off: 520 eV

k-point grid: 2 × 2 × 2 (Monkhorst-Pack)

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2. Awaka, J., Takashima, A., Kataoka, K., Kijima, N., Idemoto, Y., & Akimoto, J. (2011), Chemistry Letters, 40(1), 60–62.

3. Lany, S., & Zunger, A. (2009), Physical Review B - Condensed Matter and Materials Physics, 80(8), 1–5.

4. Thompson, T., Yu, S., Williams, L., Schmidt, R. D., Garcia-Mendez, R., Wolfenstine, J., ... Sakamoto, J. (2017), ACS Energy Letters, 2(2), 462–468.