What is the most stable oxygen vacancy in βGa_2O_3?

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November 29, 2017

Abstract

Spørsmål:
- Hvordan finne formation energy?

$$E^f = E_d - E_h - \sum_i \Delta n \mu_i = E_d - E_h - \mu_O$$

- Hva betyr isosurfacene mine? Er det bindinger der?
- Skal konvergensresultatene være i results?
- Eller skal bare DOS, band structure og energier være i result? konvergens i metode?
- Hva sier dos? Utslag på samme verdi → binding. Noe mer?
- Mindre utsalg - hva betyr det?
- Kortere avstander - mindre formation energy?
- Mine konvergenskriterer er?

0.1 To do

4. DOS?
Hvordan er dos ulik for atomer nær vakansen og langt ifra?
Sjekk for den som er mest stabil?
5. Undersøke vakansen
Se på vakansen i VESTA
Isosurface

0.2 Info

Primitive unit cell base-centered monoclinic.
Space group: C2/m
Structural info:

Ga	O
Space Group:	P 1 (# 1-1)
a = 12.23000 Å	α = 90.0000°
b = 3.04000 Å	β =103.7000 °
c = 5.80000 Å	γ = 90.0000 °
V = 209.5042 Å^3	

Contents

1 Introduction

In my master thesis I will look at n-type dopant diffusion in the semiconductor β-Ga_2O_3. This diffusion is believed to be oxygen vacancy aided and dependent. In this project the three different oxygen vacancies in β-Ga_2O_3 was studied with density functional theory.

We started with convergence tests of the primitive unit β-Ga_2O_3, both with respect to cut-off energy and k-point density. We also looked at the density of states and plotted the band structure of β-Ga_2O_3.

After that, we increased the unit cell size to a super cell. This, to be able to insert an oxygen vacancy. We relaxed the structure and calculated the energy of the bulk β-Ga_2O_3.

After that we made three different supercells each with an oxygen vacancy at different oxygen sites. We relaxed the structure and then calculated the total energy. To find the formation energy of the different oxygen vacancies, the energy of an oxygen molecule in vacuum was calculated as well.

At last local density of state was used to investigate the oxygen vacancy further.

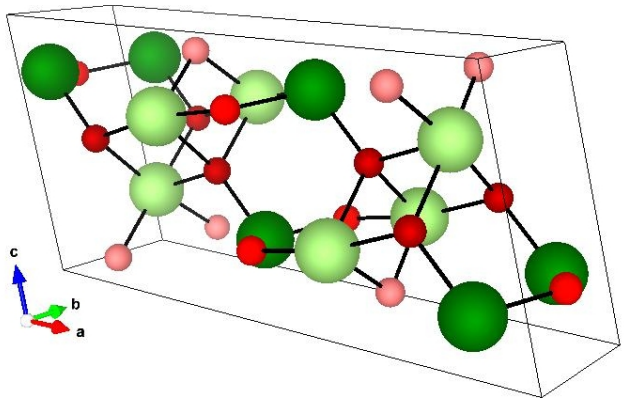


Figure 2.1: This figure shows the primitive unit cell of β-Ga_2O_3.

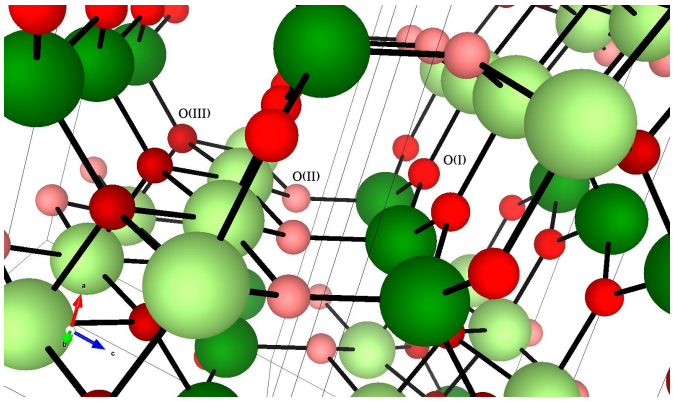


Figure 2.2: This figure shows the inequivalent oxygens in the unit cell. There are three different oxygen sites, they are color coded and named.

2 Theory

2.1 The material, β-Ga_2O_3

The primitive unit cell of β-Ga_2O_3 is base-centered monoclinic. The structure has three inequivalent oxygen sites and two inequivalent gallium sites. The unit cell is shown in Figure 2.1. The oxygen sites are named O(I), (OII) and O(III). O(I) and O(II) are threefold coordinated, while O(III) is fourfold coordinated (Figure 2.2). The gallium sites are called Ga(I) and Ga(II). Ga(I) and Ga(II) are tetrahedrally and octahedrally coordinated, respectively [1]. Figure 2.3 shows the different sites in the super cell.

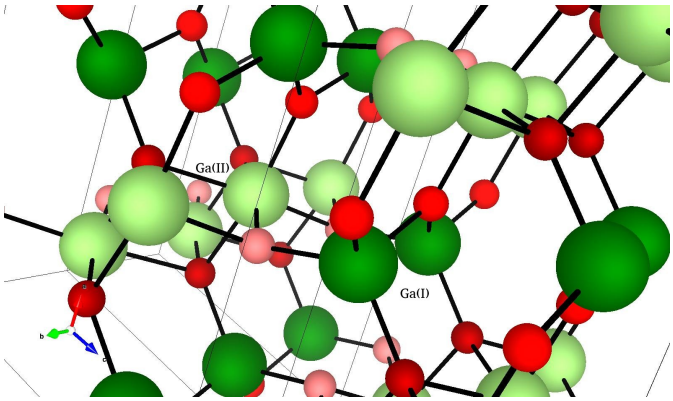


Figure 2.3: This figure shows the inequivalent gallium sites in the unit cell.

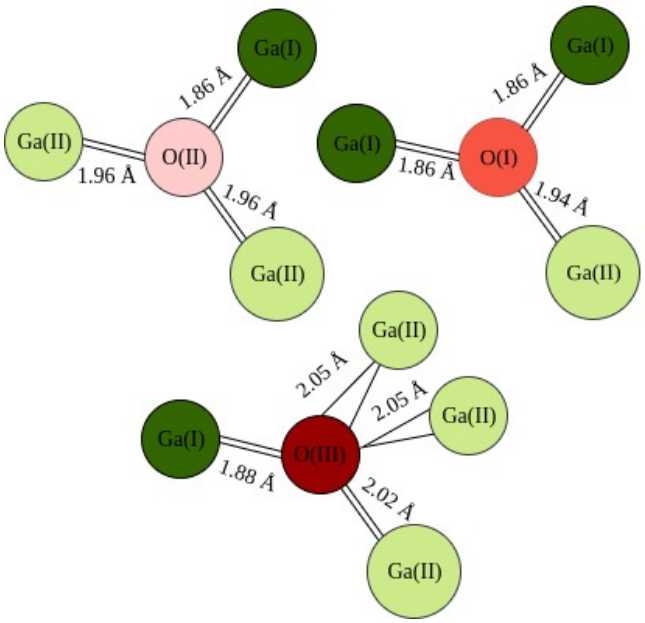


Figure 2.4: This figure shows the distances at the diffrent oxygen sites of in the relaxed super cell. We assume that the distances are similar for all equivalent sites in the supercell.

2.2 DFT Convergence

Should I write some on the 'theory' of DFT convergence?

What do energy cut off represent and what does the k-point density represent?

Balance between CPU time and accuracy in results.

2.3 DFT Formation Energy

Should I write something on how to compare energies?

Write about oxygen molecule (difference in INCAR). Assumptions about o-rich conditions.

$$E_f = E_b - E_v - \mu_O$$

3 Method

3.1 Set up

Type of GGA.

3.2 Execution

- Found structure for $\beta - Ga_2O_3$
- Checked convergence for energy cut off and k-point density for primitive unit cell
- Convergence criteria result:

  ENCUT = 600

  makekpoints -d 5 $\rightarrow$ (3x11x6)
- Relaxed the unit cell
- Plotted DOS and band structure for primitive unit cell
- Made super cell (1x 3y 2z)
- Changed convergence criteria:

  EDIFFG = -0.01

  ENCUT = 500

  ISIF = 3

  makekpoints -d 3 $\rightarrow$ (2x3x2)
- Relaxed super cell (both electronic and pressure)
- Calculated energy for relaxed unit cell
- Made three different structures for three different oxygen vacancies
- Relaxed all three structures
- Calculated energy for the relaxed structures
- Calculated energy of oxygen molecule in vacuum

  EDIFFG = -0.01

  ENCUT = 500

  ISIF = 3

  makekpoints -d 3 $\rightarrow$ (2x3x2)
- Found formation energy
- Plotted local DOS near vacancy and far away from it

4 Result and discussion

The units and uncertainties of the properties in this section are set here. The energy unit is eV

with uncertainty ± 0.003 eV, pressure is in units kbar with uncertainty ± 1 kbar and force in units eV/Å with uncertainty ± 0.01 eV/Å.

4.1 Convergence

We started by checking the convergence. The figures have some normal convergence criteria plotted with the results.

4.1.1 Energy cut-off

$$|\Delta E^i_{rel}| = \left|\left(E^{i+1}_a - E^i_a\right) - \left(E^{i+1}_b - E^i_b\right)\right| \quad (1)$$

We started with the energy convergence. Figure 4.1 shows the plot of the change in relative energy (Equation 1) between the total energy of the unit cell, E_a, and the total energy of the unit cell with one less oxygen, E_b, against the cut-off energy. The plot shows that a cut-off energy of 600 eV would give a good convergence well below 1 meV for the energy.

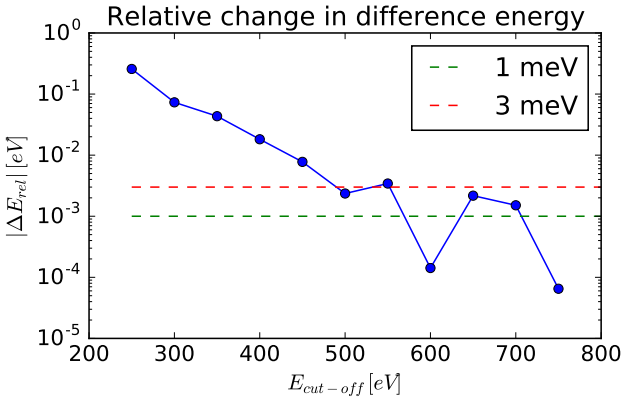


Figure 4.1: This is a plot of the difference between change in energy for Ga_2O_3 with and without a oxygen vacancy. We can see from the plot that a cut-off energy of 600 eV is sufficient.

We also looked at the force and the pressure with respect to the cut-off energy. Figure 4.2 shows the result. A cut-off energy of 600 eV gives a good convergence for force and pressure also.

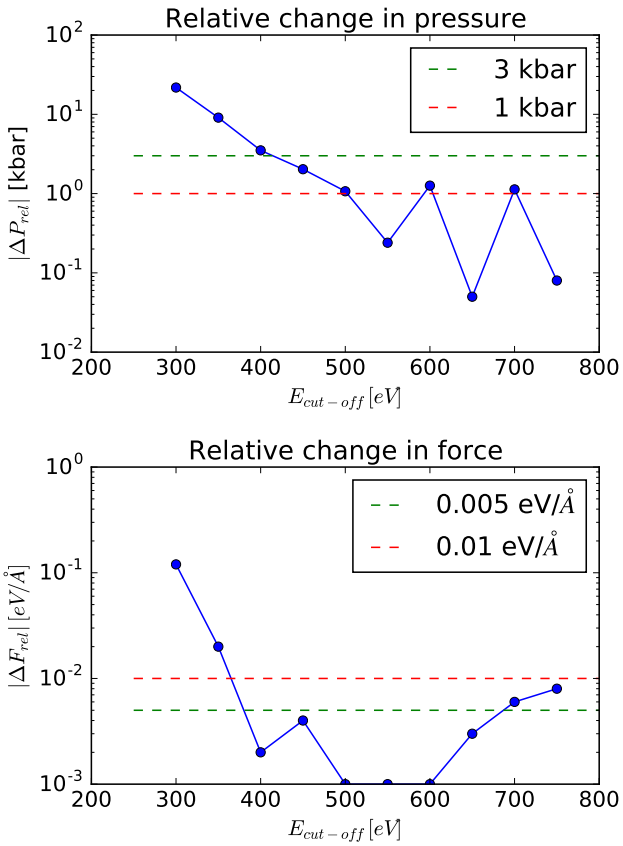


Figure 4.2: This is a plot of the difference between change in both force and pressure for Ga_2O_3 with and without a oxygen vacancy. We can see from the plot that with respect to pressure and force 600 eV is more than sufficient. The change in force increases, but it is still small.

After increasing the primitive unit cell to a super cell, the CPU time of the relaxation increased a lot. To make the calculations more workable, the convergence criteria was made a little less strict and the new cut-off energy was sat to 500 eV. When we look at Figure 4.1 and 4.2 we see that a cut-off energy at 500 eV gives a good convergence as well, it is still around 1-10 meV for the energy and around 1 kbar for the pressure and 0.005 eV/Å for the force.

4.1.2 k-point density

Thereafter, we evaluated the necessary k-point density. Figure 4.3 shows the result for the relative change in energy and Figure 4.4 force and pressure.

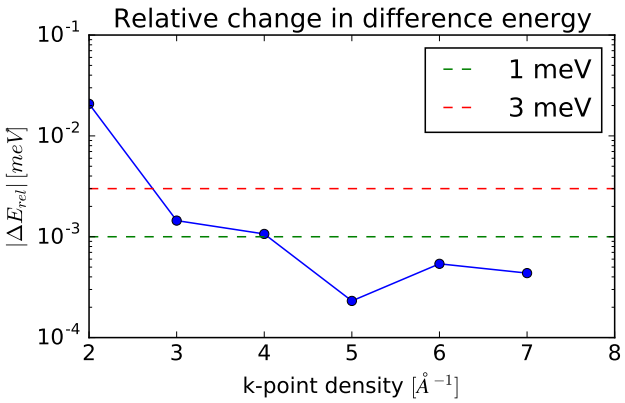


Figure 4.3: This is a plot of the difference between change in energy for Ga_2O_3 with and without a oxygen vacancy. We can see from the plot that a k-point density of 5 $Å^{-1}$ is sufficient.

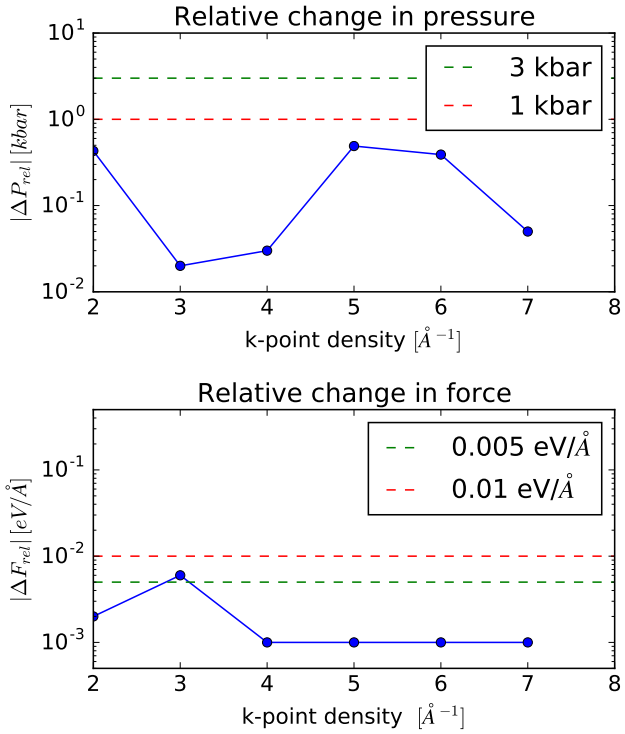


Figure 4.4: This is a plot of the difference between change in both force and pressure for Ga_2O_3 with and without a oxygen vacancy. All the k-point densities gives good convergence.

The k-point density was changed to 3 k-points per Å, when the cell size as increased to a super cell.

Should I put this in another subsection with the super cell?

4.2 Primitive unit cell

With the decided convergence criteria and the resulting energy cut-off and k-point density, we relaxed the primitive unit cell. Table 4.1 shows both the maximum force and the pressure decreasing.

Table 4.1: This table lists the start and stop of the relaxation of the primitive unit cell. Both the maximum force, F_{max}, and the pressure, P, is decreasing in the relaxation.

F_{max}	$\#_{atom}$	P	Drift	E_{tot}
1.716	9	139.52	0.000	-119.461
⋮	⋮	⋮	⋮	⋮
0.006	9	0.42	0.000	-120.224
CPU	time:			685.881 s

The total energy per atom with a primitive unit cell was $\frac{E_{tot}}{\#\text{of atoms}} = \frac{\text{fill}}{\text{fill}}$ after the relaxation.

4.2.1 Density of States

To examine the different oxygen sites, the local density of state for the inequivalent sites were plotted in Figures 4.5 to 4.9 the total density of state of the primitive unit cell is plotted in Figure 4.10.

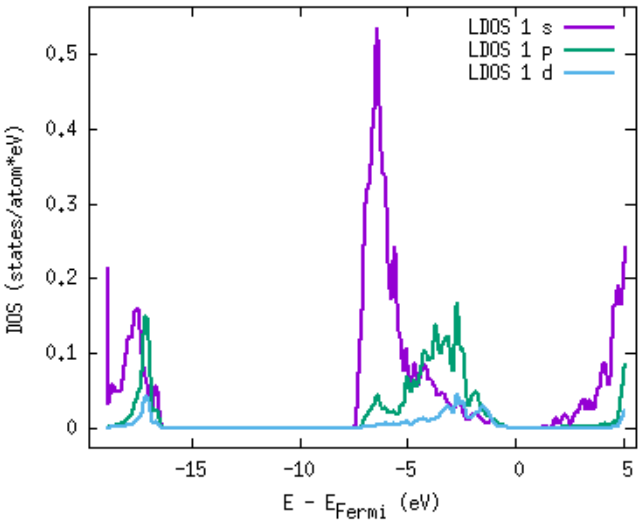


Figure 4.5: This is a plot of local density of state at the Ga(I) site.

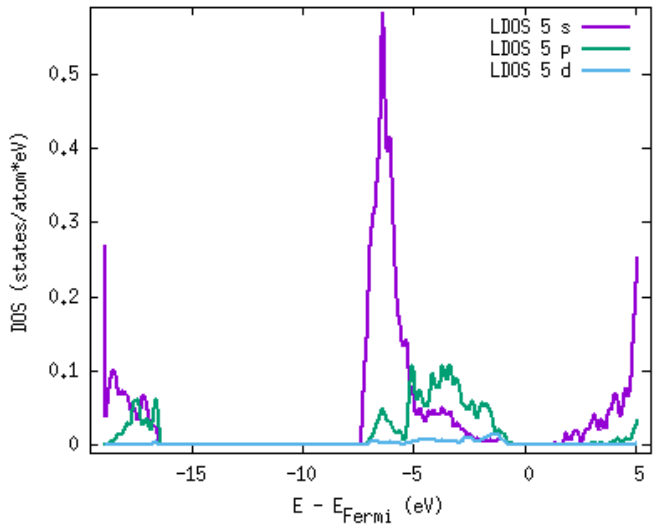


Figure 4.6: This is a plot of local density of state at the Ga(II) site.

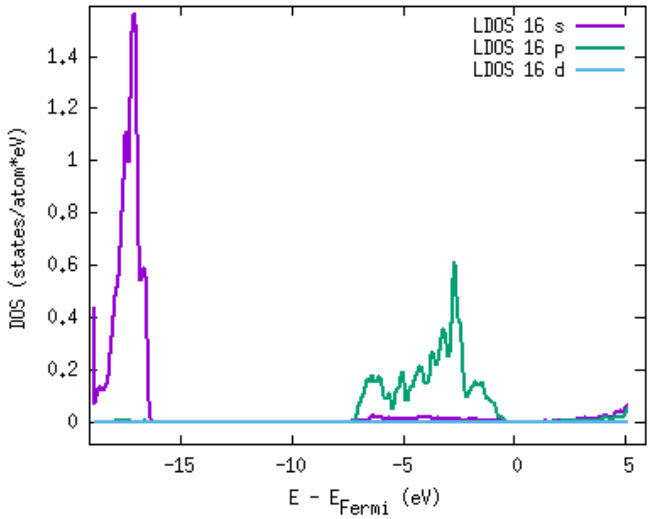


Figure 4.7: This is a plot of local density of state at the O(I) site.

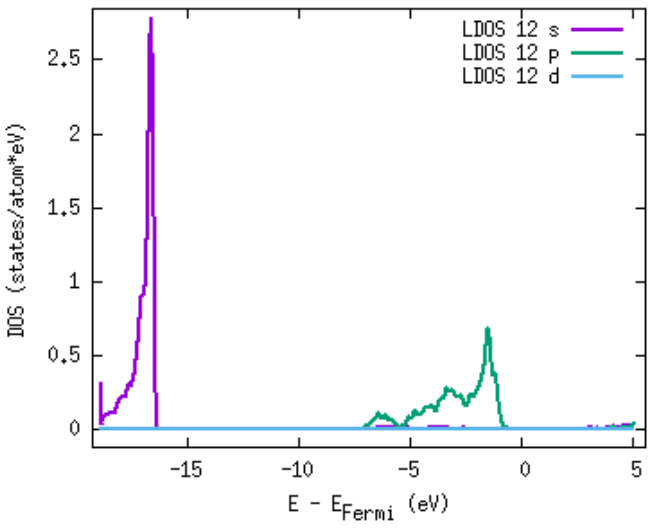


Figure 4.8: This is a plot of local density of state at the O(II) site.

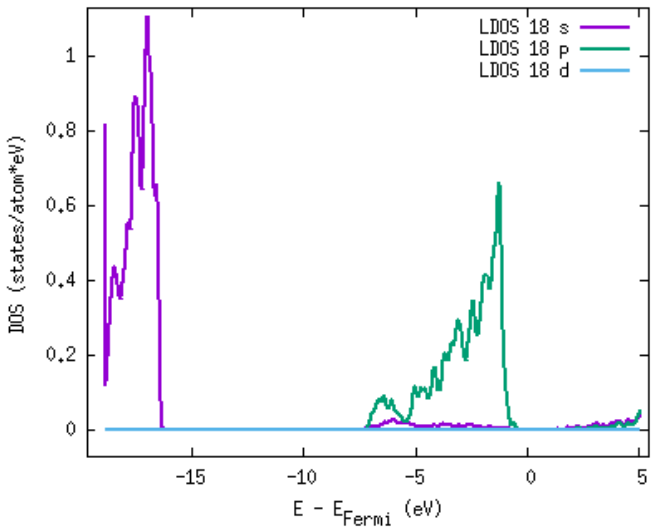


Figure 4.9: This is a plot of local density of state at the O(III) site.

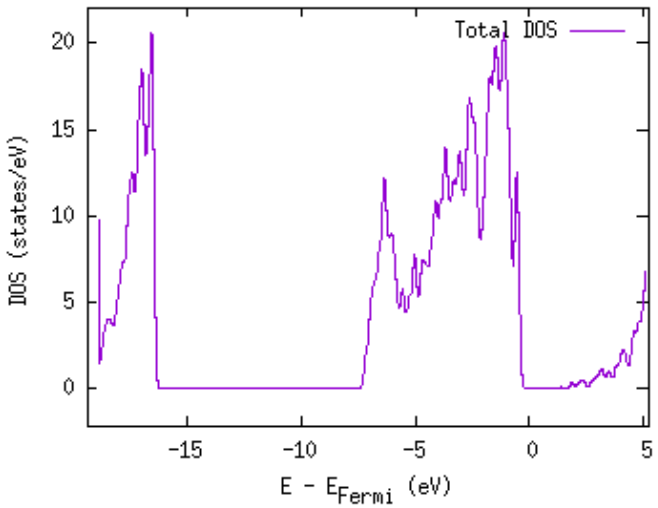


Figure 4.10: This is a plot of density of state of the primitive unit cell.

In the section about the structure we can see that all the oxygen sites are 'bonded' to both gallium sites, but the number of each bonds differ. We can see the p-orbitals with energy, $E - E_{Fermi}$, form -15 eV to 0 eV in all the local density plots indicating bonds between them all. There is also s-orbitals below -17 eV, but it is very small for the gallium atoms.

4.2.2 Band structure

Should do INCAR$_{dos}$ again with ISMEAR -5?

At last we plotted the band structure of β-Ga_2O_3 the band gap was found to be 1.8051 eV which is way to small, but a too small band gap is a common error with the simple functionals we are using in this project. Figure 4.11 shows the band structure we plotted after our calculations. Figure 4.12 shows the band structure from an article where they used hybrid functionals and other tricks to get the correct band gap [1].

The band structure in Figure 4.11 shows that the lowest point in the conduction band is at the Γ-point (G), and this corresponds with the result in Figure 4.12. The highest point in the valence band on our band structure is difficult to set, but in the other it is either at the M-point or the Γ-point.

There seems to be something wrong at the M-point in our calculations because it looks very different form the other one. The band gap of β-Ga_2O_3 is indirect, but the difference in the valence band between the Γ-point and the M-point is so small, that it is practically direct.

Some more stuff in the discussion?

Figure 4.11: This is a plot of the band structure of β-Ga_2O_3 form our density of states calculations.

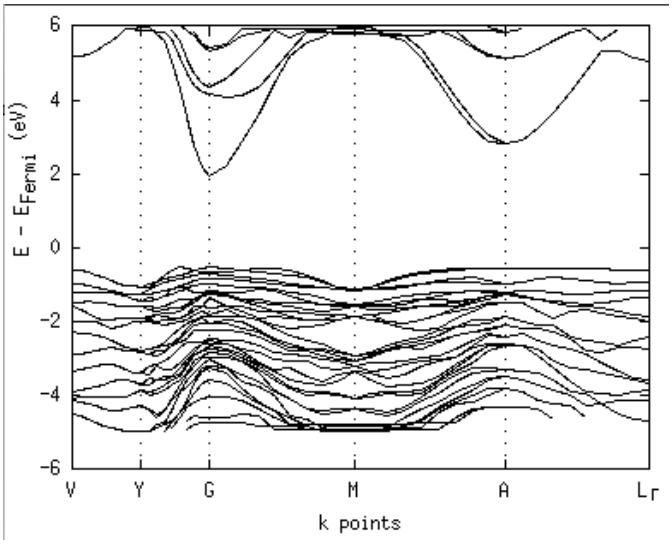
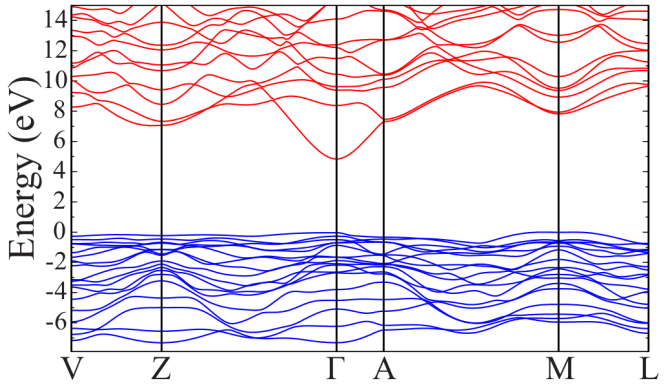


Figure 4.12: This is a plot of the band structure taken from an article that did DFT on β-Ga_2O_3 with hybrid density functionals [1].



4.3 Supercell

4.3.1 Relaxation and energy

Energy cut-off: 600 eV

K-mesh: 3x4x3

EDIFFG = -0.05

ISIF = 2

Table 4.2: The ionstep - relaxation of supercell with convergence result.

F_{max}	$\#_{atom}$	P	Drift	E_{tot}
0.443	49	134.07	0.023	-718.260
⋮	⋮	⋮	⋮	⋮
0.009	25	109.22	0.023	-718.913
CPU	time:	3546.421 s		≈ 59 min

Energy calculation after:

Table 4.3: The energy output after relaxation of supercell.

F_{max}	P	Drift	E_{tot}
0.045	0.023	2.63	**??**

4.3.2 Changed convergence criteria

To have less CPU time with super cell I lowered the criteria to:

Energy cut-off: 500 eV

K-mesh: 2x3x2 (density 3)

EDIFFG = -0.01

ISIF = 3

Table 4.4: The ionstep - relaxation of supercell with convergence result.

F_{max}	$\#_{atom}$	P	Drift	E_{tot}
0.427	49	136.09	0.023	-717.821
⋮	⋮	⋮	⋮	⋮
0.006	49	0.03	0.024	-720.914
CPU	time:	1763.585 s		≈ 29 min

Energy calculation after:

Table 4.5: The energy output after relaxation of supercell.

F_{max}	P	Drift	E_{tot}
0.045	0.023	2.63	-721.081

4.4 O_2 in vacuum

Describe the INCAR file - what is different in this then the other ones? In theory?

Table 4.6: The energy output of oxygen in vacuum.

F_{max}	P	Drift	E_{tot}
0.088	0.000	-0.22	-9.883

4.4.1 Chemical potential

$$\mu_O = \frac{1}{2}\mu_{O_2} = \frac{1}{2} \cdot (-9.883) = -4.942$$

4.5 Different oxygen vacancies

4.5.1 O(I) vacancy

Table 4.7: The ionstep - relaxation of super cell with O(I) vacancy.

F_{max}	$\#_{atom}$	P	Drift	E_{tot}
2.666	19	133.08	0.142	-708.492
⋮	⋮	⋮	⋮	⋮
0.032	63	-0.03	0.465	-712.142
CPU	time:			5127.663 s
				≈ 1 t 25 min

4.5.2 O(II) vacancy

Table 4.8: The ionstep - relaxation of super cell with O(II) vacancy.

F_{max}	$\#_{atom}$	P	Drift	E_{tot}
2.391	20	135.21	0.010	-708.256
⋮	⋮	⋮	⋮	⋮
0.013	60	-0.01	0.143	-711.709
CPU	time:			5061.359 s

4.5.3 O(III) vacancy

Table 4.9: The ionstep - relaxation of super cell with O(III) vacancy.

F_{max}	$\#_{atom}$	P	Drift	E_{tot}
1.873	1	135.42	0.141	-707.966
⋮	⋮	⋮	⋮	⋮
0.017	73	-0.00	0.145	-711.463
CPU	time:			5115.230 s

4.5.4 Total Energy

Table 4.10: The energy output after relaxation of supercell with oxygen vacancies.

Vacancy	F_{max}	P	Drift	E_{tot}
O(I)	0.107	0.146	2.29	-712.283
O(II)	0.067	0.198	2.39	-711.860
O(III)	0.087	0.221	2.13	-711.603

4.5.5 Formation Energy

$$E^f = E_d - E_h - \sum_i \Delta n \mu_i = E_d - E_h - \mu_O$$

Table 4.11: This is the calculated formation energies for the diffrent oxygen vacancies at oxygen rich conditions.

Vacancy	E_b - (E_{vac} + μ_O) = E_f
O(I)	-721.081 - (-712.282 -4.942) = -3.857
O(II)	-721.081 - (-711.860 -4.942) = -4.279
O(III)	-721.081 - (-711.603 -4.942) = -4.536

4.6 Why the O(I) vacancy?

4.6.1 Total density of states

Notice the new level in the band gap - defect level - filled.

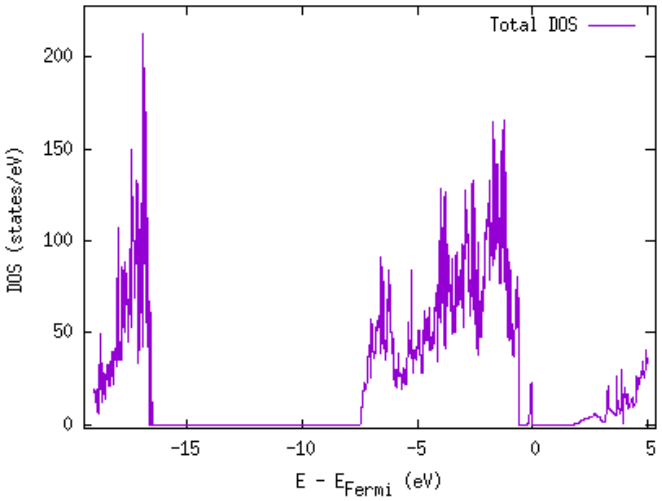


Figure 4.13: This is a plot of the density of state of the super cell with a O(I) vacancy.

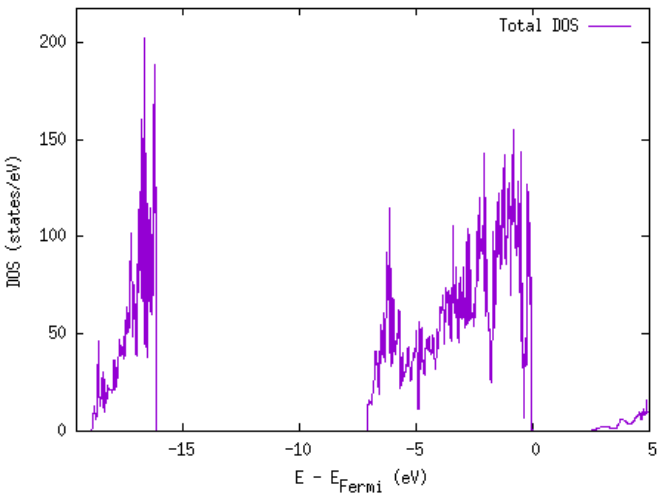


Figure 4.14: This is a plot of density of state of the general supercell.

4.6.2 Isosurfaces

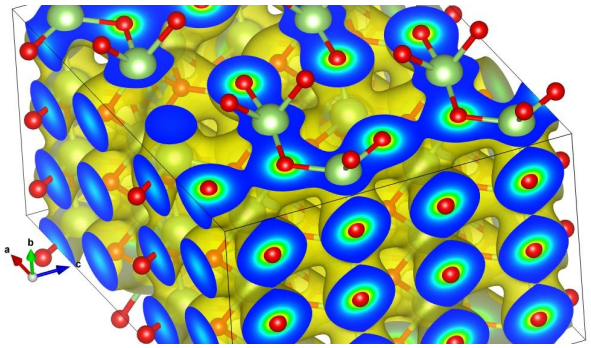


Figure 4.15: This figure shows the oxygen vacancy with different isosurfaces.

O(I)

O(I)

O(II)

4.6.3 Local DOS Ga(II)

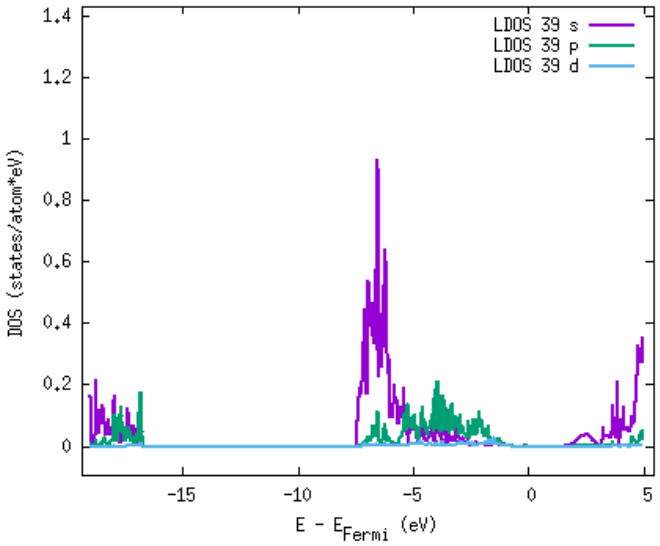


Figure 4.16: This is a plot of local density of state at the Ga(II) site next to the O(I) vacancy in the super cell.

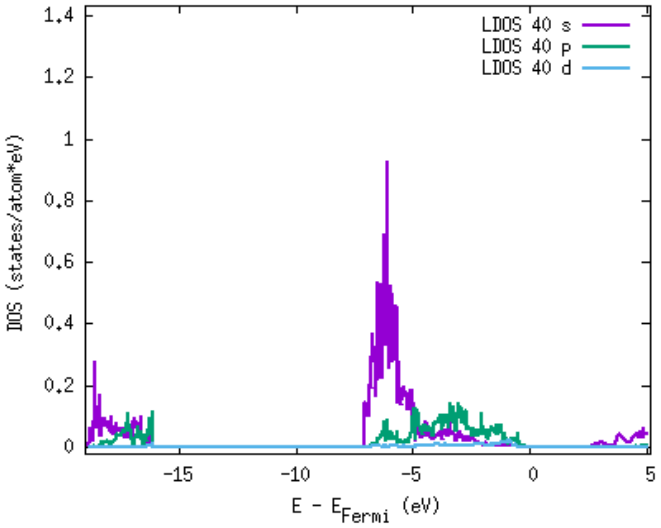


Figure 4.17: This is a plot of local density of state at the Ga(II) site in the general supercell.

4.6.4 Local DOS Ga(I)$_1$

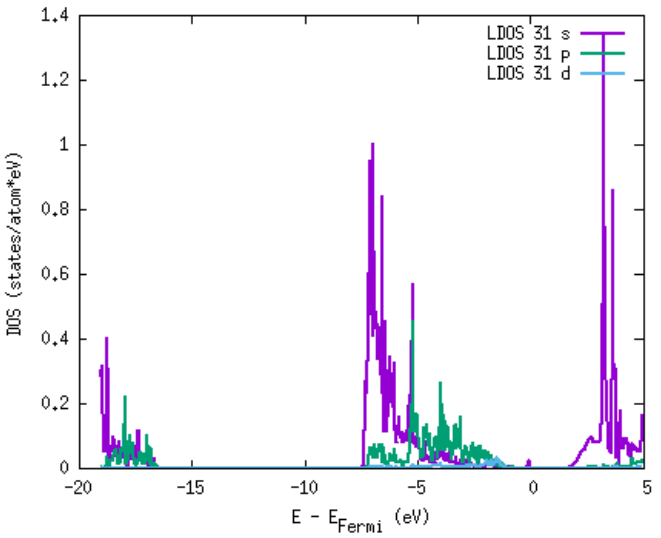


Figure 4.18: This is a plot of local density of state at the Ga(I) site next to the O(I) vacancy in the super cell.

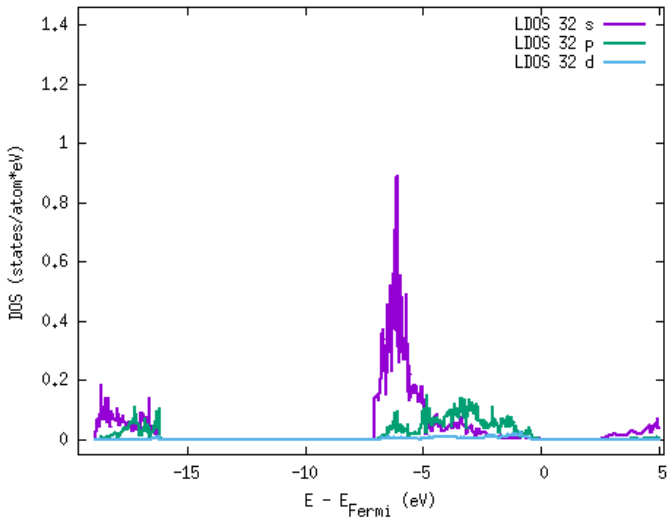


Figure 4.19: This is a plot of local density of state at the Ga(I) site in the general supercell.

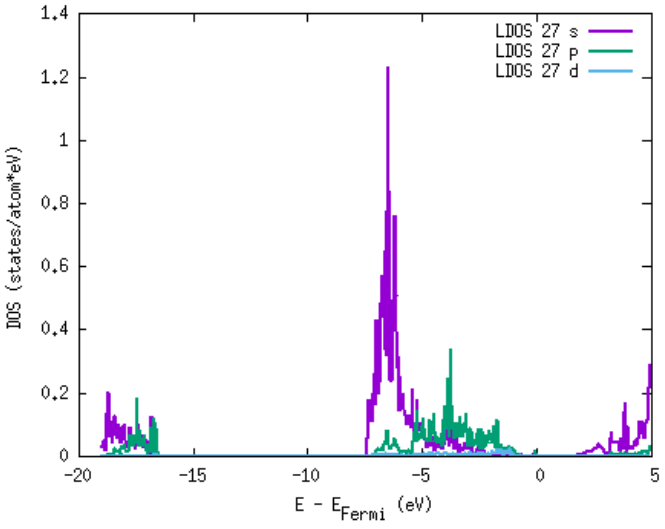


Figure 4.21: This is a plot of local density of state at the other Ga(I) site next to the O(I) vacancy in the super cell.

4.6.5 Bond between $Ga(I)_1$ and $Ga(I)_2$?

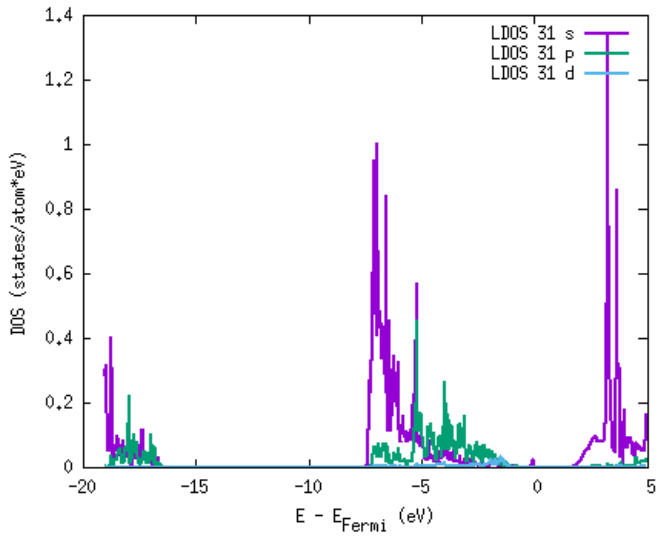


Figure 4.20: This is a plot of local density of state at the Ga(I) site next to the O(I) vacancy in the super cell.

5 Conclusion

References

[1] JB Varley, JR Weber, A Janotti, and CG Van de Walle. Oxygen vacancies and donor impurities in β-Ga_2O_3. *Applied Physics Letters*, 97(14):142106, 2010.

Appendix