

What is the most stable oxygen vacancy in $\beta\text{Ga}_2\text{O}_3$?

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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 \rightarrow 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	$\alpha = 90.0000^\circ$
b = 3.04000 Å	$\beta = 103.7000^\circ$
c = 5.80000 Å	$\gamma = 90.0000^\circ$
V = 209.5042 Å ³	

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1 Introduction

In my master thesis I will look at n-type dopant diffusion in the semiconductor β -Ga₂O₃. This diffusion is believed to be oxygen vacancy aided and dependent. In this project the three different oxygen vacancies in β -Ga₂O₃ was studied with density functional theory.

We started with convergence tests of the primitive unit β -Ga₂O₃, 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 -Ga₂O₃.

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 -Ga₂O₃.

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 and electron density isosurfaces was used to investigate the oxygen vacancy further.

2 Theory

2.1 The material, β -Ga₂O₃

The primitive unit cell of β -Ga₂O₃ is base-centered monoclinic with the unit cell parameters listed in Table 2.1, which is in the space group C2/m. 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 three-fold coordinated, while O(III) is fourfold coordinated (see 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 2.4 shows which gallium atoms the 'different' oxygens are bonded to and the length of the bonds. The lengths are from the relaxed super cell.

Table 2.1: This is the unit cell parameters for the β -Ga₂O₃ primitive unit cell.

$a = 12.23000 \text{ \AA}$	$\alpha = 90.0000^\circ$
$b = 3.04000 \text{ \AA}$	$\beta = 103.7000^\circ$
$c = 5.80000 \text{ \AA}$	$\gamma = 90.0000^\circ$
$V = 209.5042 \text{ \AA}^3$	

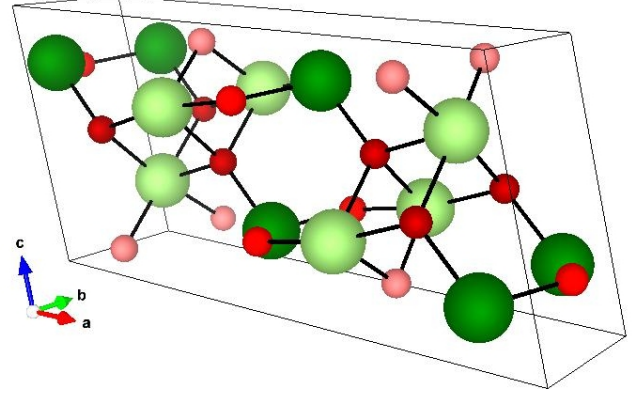


Figure 2.1: This figure shows the primitive unit cell of β -Ga₂O₃.

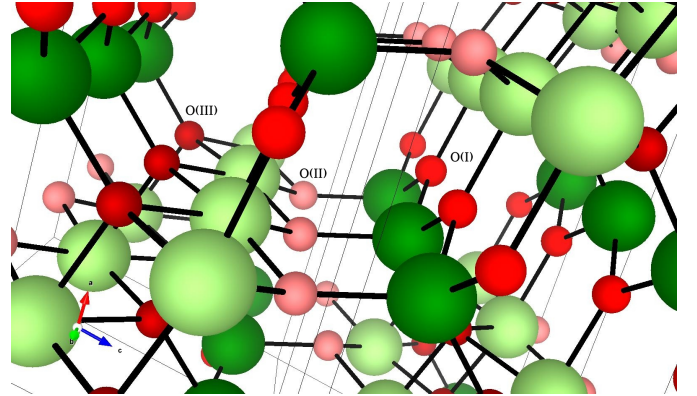


Figure 2.2: This figure shows the inequivalent oxygens in the unit cell. There are three different oxygen sites, they are color coded and named.

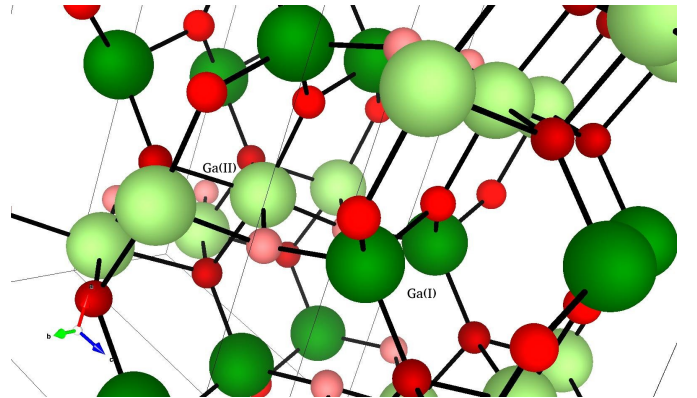


Figure 2.3: This figure shows the inequivalent gallium sites in the unit cell.

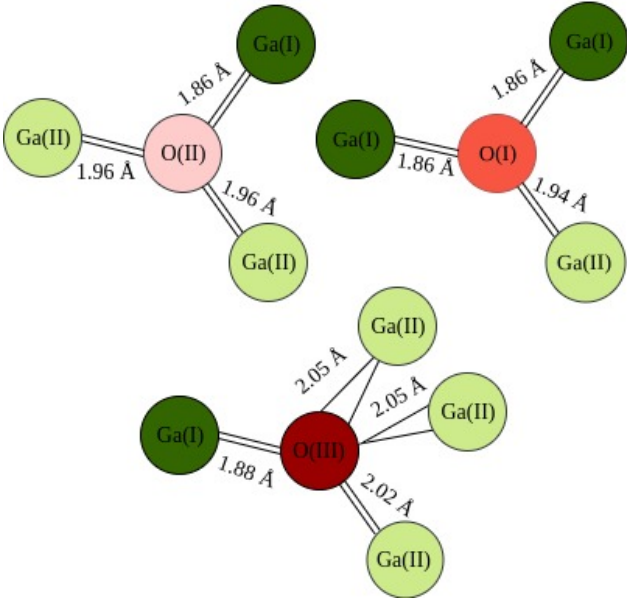


Figure 2.4: This figure shows the distances at the different oxygen sites in the relaxed super cell. We assume that the distances are similar for all equivalent sites in the super-cell, because these are the distances for a three specific ones.

2.2 DFT Convergence

The first thing one does when doing DFT calculations are convergence tests. This is important because it gives data one can use to consider how accurate the resulting properties will be, compared to how costly the calculations are. The more accurate results, the higher cost in CPU time. A convergence test will also show if numerical noise gives a limit to the accuracy of the result.

The convergence of a relative change in energy, relative change in force and relative change in pressure versus energy cut-off and k-point density is checked. The energy cut-off is a value that represent the limit of the infinite sum over G-vectors (see Equation 1). We cannot sum an infinite sum, so we have to choose a limit that is sufficient for the accuracy we want to achieve. Because it is a sum over G-vectors, the energy cut-off has to be big for localized states. Oxygen has localized states and that indicates that this material need a high energy cut-off for good accuracy.

$$E_{cut-off} = \sum \frac{1}{G} \quad (1)$$

The k-point density is related to the k-point mesh of the numerical integral over k-vectors. Because

it involves k-vectors it is related to more unlocalized states and metallic materials might need high k-point density because of their electrons delocalized states. β -Ga₂O₃ is a semiconductor though and might not need a high k-point density.

The properties are chosen to be the relative change because it is easier to converge and the total energy from DFT calculations are not that interesting physically because it is not a physical number. It is simply a numerical one. The relative change in energy is interesting though because then one can compare different situation. The comparison is physically interesting because it is independent of the real total value.

After choosing a convergence criteria, the accuracy one wants or settles at, the energy cut-off and the k-point density can be used to relax the structure. When relaxing the structure, the program minimizes the maximum force felt by the the atoms in the structure and, if one chooses to, minimizes the pressure. The energy cut-off and the k-point density is used for all the calculations; relaxation, the total energy and density of states calculations.

2.3 DFT Formation Energy

When comparing total energies from DFT calculations, it is important to compare the energy for the same amount of atoms. That means that if one compares the energy of a material with the energy of the material with a vacancy, as we will do in this project, one has to add the energy of the atom giving the vacancy in vacuum. In this case the vacancy is an oxygen vacancy and the energy of an oxygen molecule in vacuum also has to be calculated. This difference will give the formation energy of the oxygen vacancy.

The formation energy of the oxygen vacancy is actually also dependent on the temperature, pressure and the charge of the vacancy. The equation for calculating the formation energy is given in Equation 2 where E_{vac} is the total bulk energy with the vacancy, E_b is the total bulk energy without the vacancy, P is the pressure, μ_O is the chemical potential of oxygen given by Equation 3. $E_{tot}^{O_2}$ is the total energy of the oxygen molecule in vacuum, $\tilde{\mu}_{O_2}$ is the difference from $T = 0$ K at the reference pressure, P_0 , and can be found in tables, $kT \log(\frac{P}{P_0})$ represents the difference in

pressure, P , from the reference pressure and the last term represent the impact of a charged vacancy where q is the charge, ϵ_f is the Fermi level (or energy ??) and ϵ_{VBM} is the maximum of the valence band.

$$E_f = (E_{vac} + \sum_i N_i \mu_i) - E_b + q(\epsilon_f + \epsilon_{VBM}) \quad (2)$$

$$\mu_O = \frac{1}{2}\mu_{O_2} = \frac{1}{2} \left(E_{tot}^{O_2} + \tilde{\mu}_{O_2} + kT \log\left(\frac{P}{P_0}\right) \right) \quad (3)$$

In this project the setup is simple, the temperature is 0 K and the sample is assumed to be in oxygen rich conditions and in vacuum (how can it be in both o-rich and vacuum ??). This makes the chemical potential of O_2 , $\mu_{O_2} = E_{tot}^{O_2}$. The oxygen vacancy is also made to be neutral, not charged. A changed oxygen vacancy is a donor in the semiconductor, but if it is neutral the Fermi level is not changed and the term $q(\epsilon_f + \epsilon_{VBM}) = 0$. That is why the formation energy is simply given by Equation 4 where μ_O is simply given by Equation 5.

$$E_f = (E_{vac} + \mu_O) - E_b \quad (4)$$

$$\mu_O = \frac{1}{2} E_{tot}^{O_2} \quad (5)$$

3 Method

3.1 Set up

Type of GGA. VASP. PDE?

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:

$$ENCUT = 600$$

$$\text{makekpoints -d 5} \rightarrow (3 \times 11 \times 6)$$

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

4 Result

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

$$|\Delta E_{rel}^i| = |(E_a^{i+1} - E_a^i) - (E_b^{i+1} - E_b^i)| \quad (6)$$

We started with the energy convergence. Figure 4.1 shows the plot of the change in relative energy (Equation 6) 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.

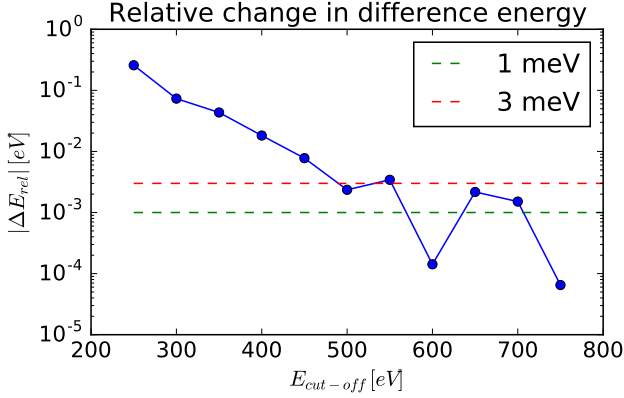


Figure 4.1: This is a plot of the difference between change in energy for Ga_2O_3 with and without a oxygen vacancy. We can see from the plot that a cut-off energy of 600 eV is sufficient.

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.

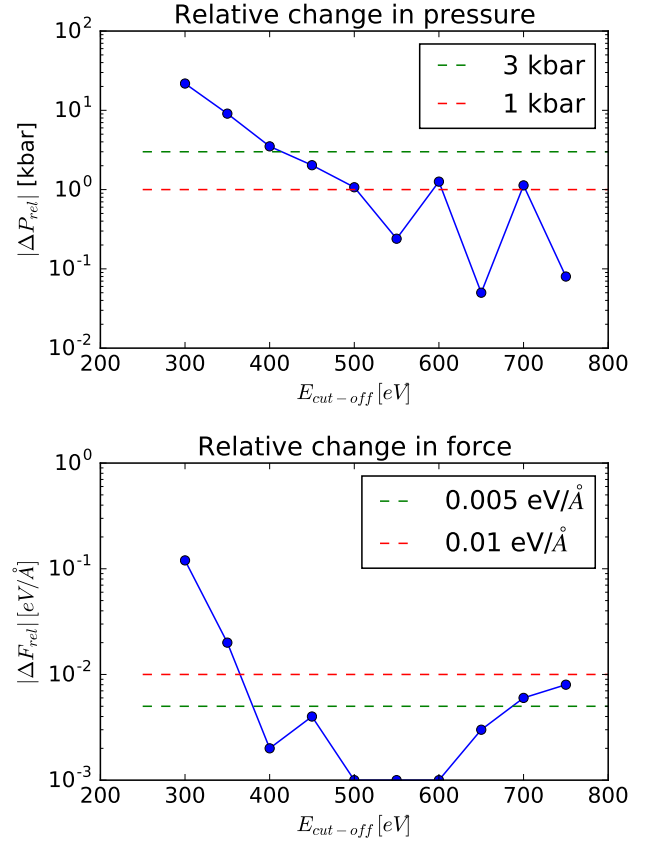


Figure 4.2: This is a plot of the difference between change in both force and pressure for Ga_2O_3 with and without a oxygen vacancy. We can see from the plot that with respect to pressure and force 600 eV is more than sufficient. The change in force increases, but it is still small.

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 set 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.

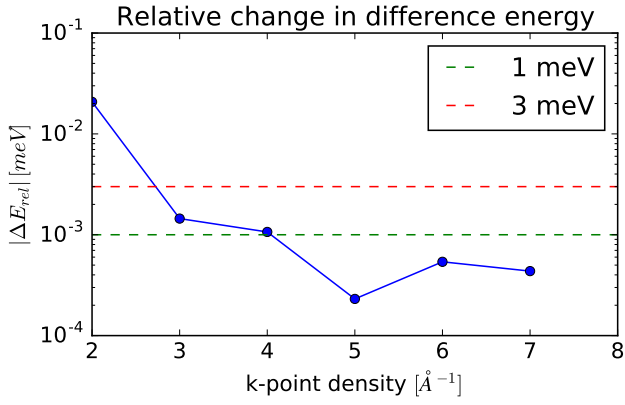


Figure 4.3: This is a plot of the difference between change in energy for Ga_2O_3 with and without a oxygen vacancy. We can see from the plot that a k-point density of 5 \AA^{-1} is sufficient.

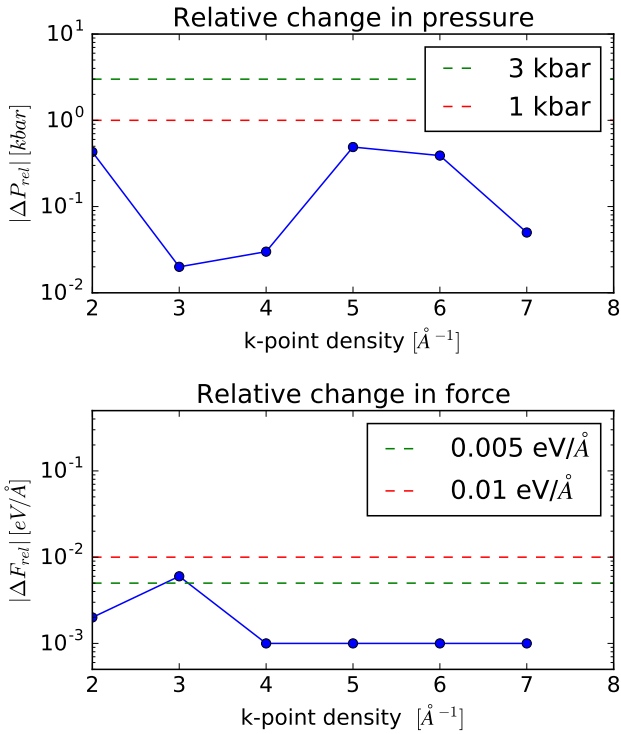


Figure 4.4: This is a plot of the difference between change in both force and pressure for Ga_2O_3 with and without a oxygen vacancy. All the k-point densities gives good convergence.

The k-point density was changed to 3 k-points per \AA , 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
\vdots	\vdots	\vdots	\vdots	\vdots
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 $\frac{E_{tot}}{\# \text{ of atoms}} = \frac{\text{m}}{\text{m}}$ 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.

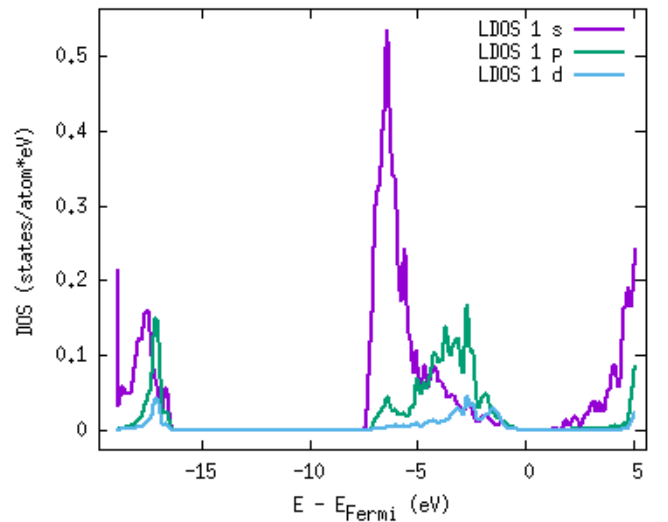


Figure 4.5: This is a plot of local density of state at the Ga(I) site.

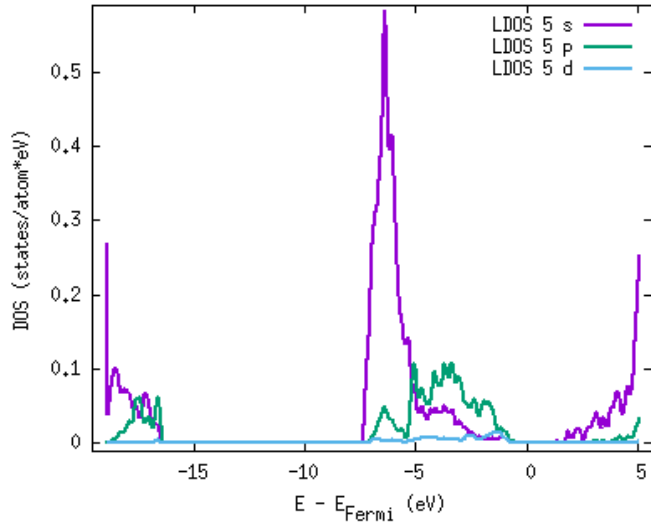


Figure 4.6: This is a plot of local density of state at the Ga(II) site.

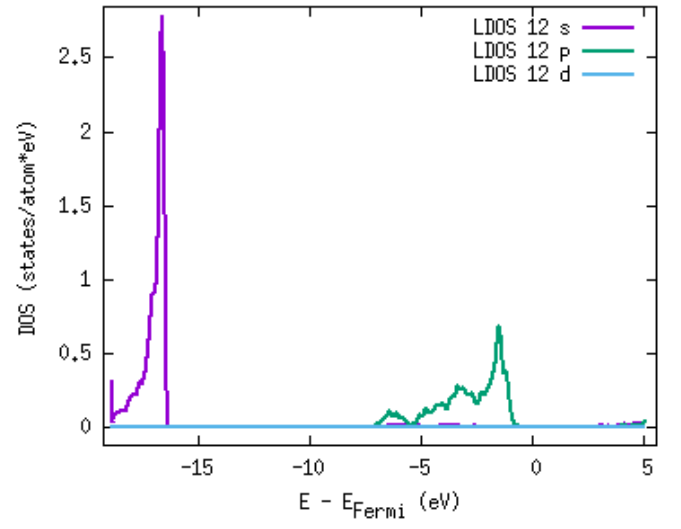


Figure 4.8: This is a plot of local density of state at the O(II) site.

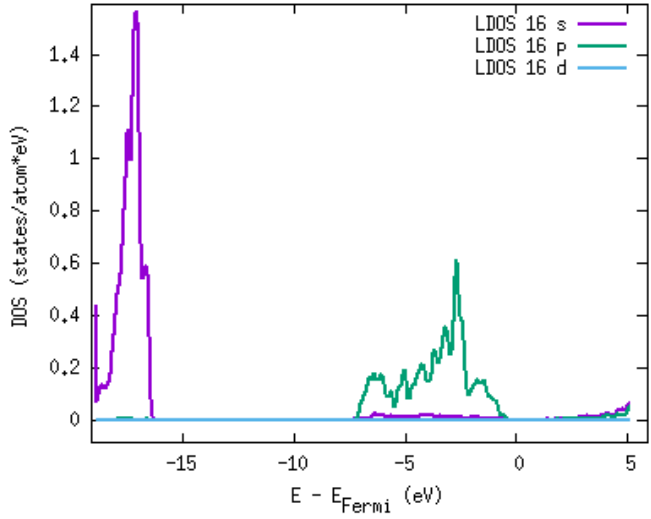


Figure 4.7: This is a plot of local density of state at the O(I) site.

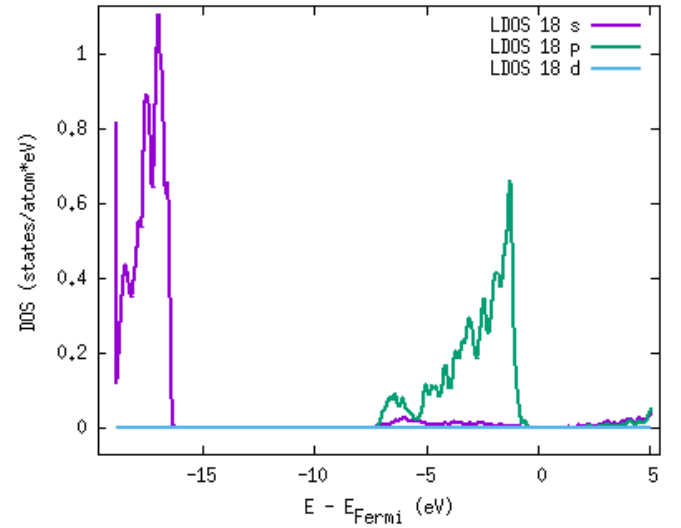


Figure 4.9: This is a plot of local density of state at the O(III) site.

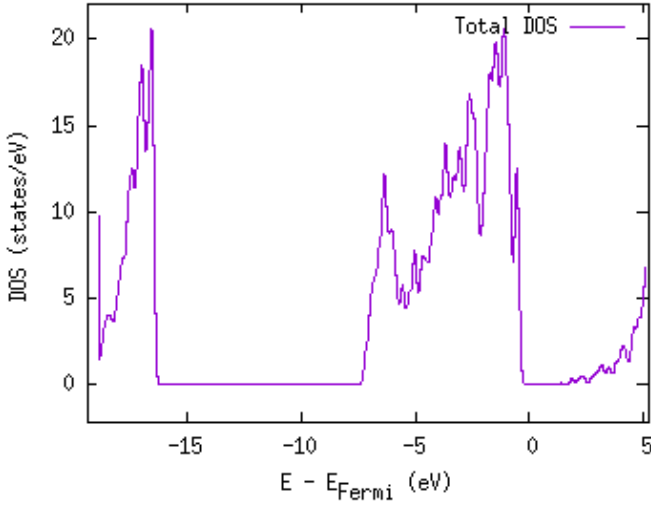


Figure 4.10: This is a plot of density of state of the primitive unit cell.

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, $E - E_{Fermi}$, from -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 `INCARdos` again with `ISMEAR -5`?

At last we plotted the band structure of β -Ga₂O₃ 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 -Ga₂O₃ 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 -Ga₂O₃ form our density of states calculations.

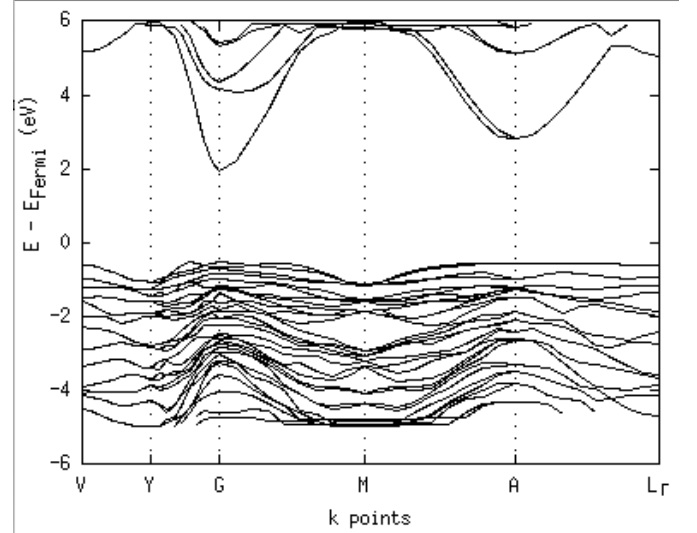
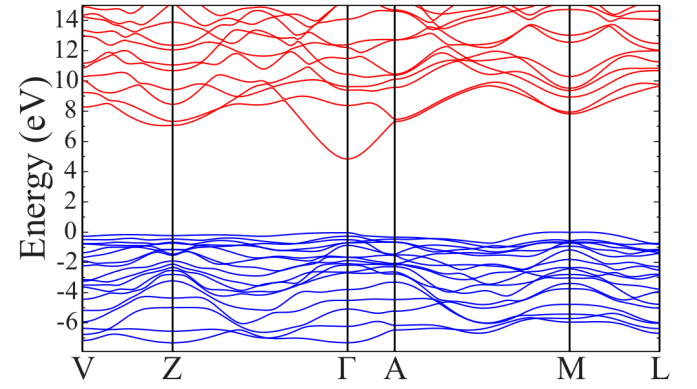


Figure 4.12: This is a plot of the band structure taken from an article that did DFT on β -Ga₂O₃ with hybrid density functionals [1].



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
\vdots	\vdots	\vdots	\vdots	\vdots
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
\vdots	\vdots	\vdots	\vdots	\vdots
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 O₂ 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
\vdots	\vdots	\vdots	\vdots	\vdots
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
\vdots	\vdots	\vdots	\vdots	\vdots
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
\vdots	\vdots	\vdots	\vdots	\vdots
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

$$E_f = (E_{vac} + \sum_i \Delta n \mu_i) - E_b = (E_{vac} + \mu_O) - E_b$$

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

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

5 Discussion

5.1 Why the O(I) vacancy?

5.1.1 Total density of states

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

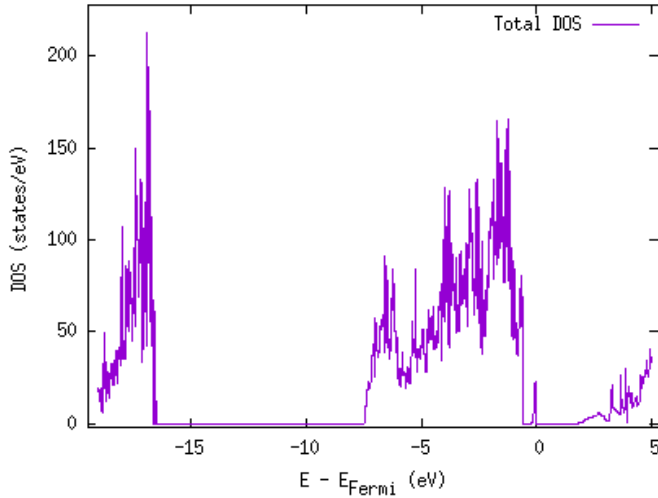


Figure 5.1: This is a plot of the density of state of the super cell with a O(I) vacancy.

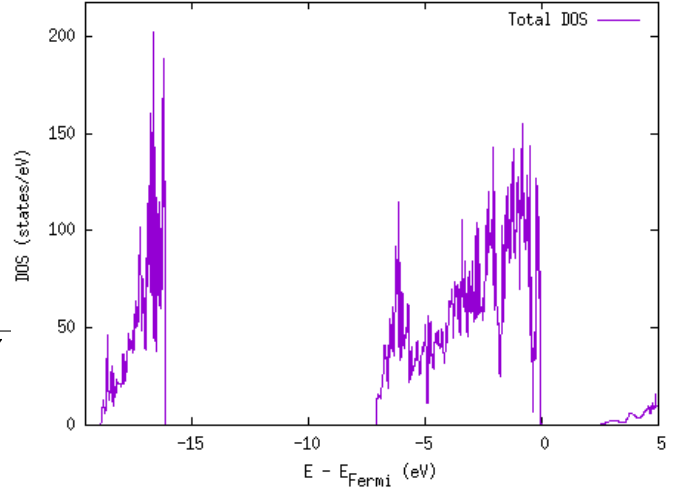


Figure 5.2: This is a plot of density of state of the general supercell.

5.1.2 Isosurfaces

Figure 5.3 shows the structure around the O(I) vacancy with different electron density isosurface levels. When the isosurface level is set to 0.04, an electron density is visible between the two Ga(I) atoms the O(I) atom should have been bonded to and when the isosurface level is 0.03, the isosurface shows a bond between them (Figure 5.4).

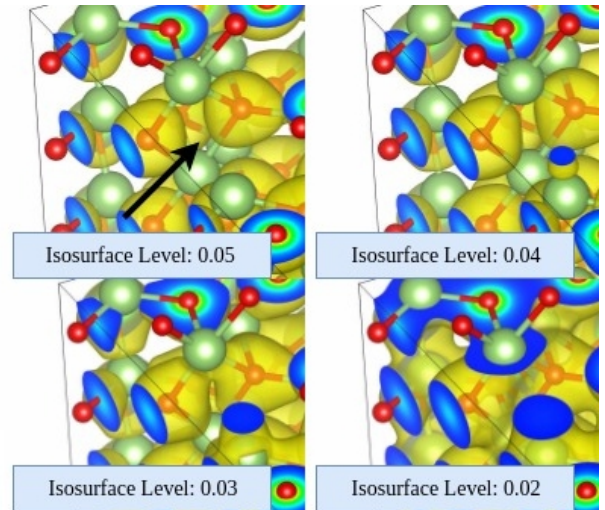


Figure 5.3: This figure shows the O(I) vacancy with different electron density isosurfaces. The black arrow points to the O(I) vacancy. When the isosurface level is lowered, a bond appears between the two Ga(I) atoms the O(I) should have been bonded to (Figure 5.4).

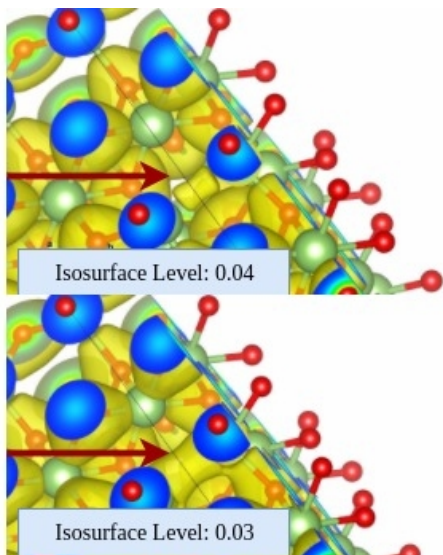


Figure 5.4: This figure shows the oxygen vacancy with different isosurfaces. In this figure the bond between the two Ga(I) atoms shows clearly. The isosurface goes from one atom to the other at the isosurface level 0.03.

Figure 5.5 shows the O(II) vacancy with different isosurfaces, when the isosurface level is lowered, the electron density around the Ga(I)-atom shows. The 'blob' shows the dangling bonds at the Ga(I) atom, but there is no 'blob' at the Ga(II) atoms. With the O(II) vacancy the isosurface level needs to be 0.02 for there to be a connection with the other Ga(II) atoms.

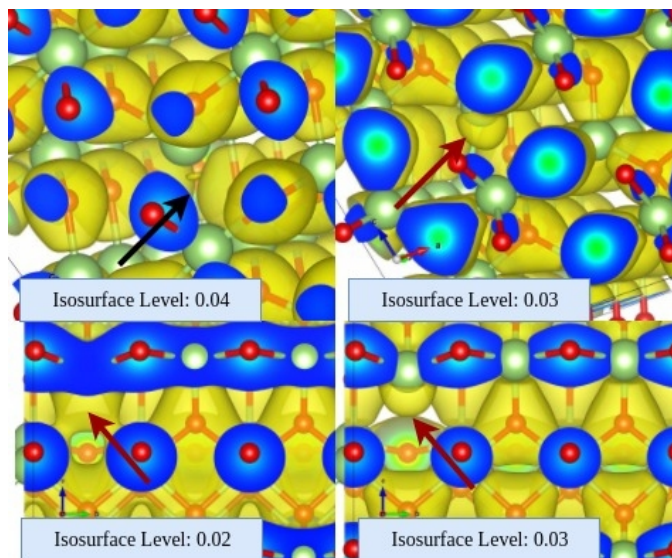


Figure 5.5: This figure shows the O(II) vacancy with different electron density isosurfaces. The figure shows the oxygen vacancy from different angles. The black arrow points to the vacancy and the red arrows point to the isosurface indicating dangling bonds at the Ga(I) atom.

Figure 5.6 shows the same for the O(III) vacancy. As in the case for the O(II) vacancy, the isosurface level needs to be 0.02 before there is a connection,

and before that there is the same 'blob' at the one Ga(I) atom, indication dangling bonds.

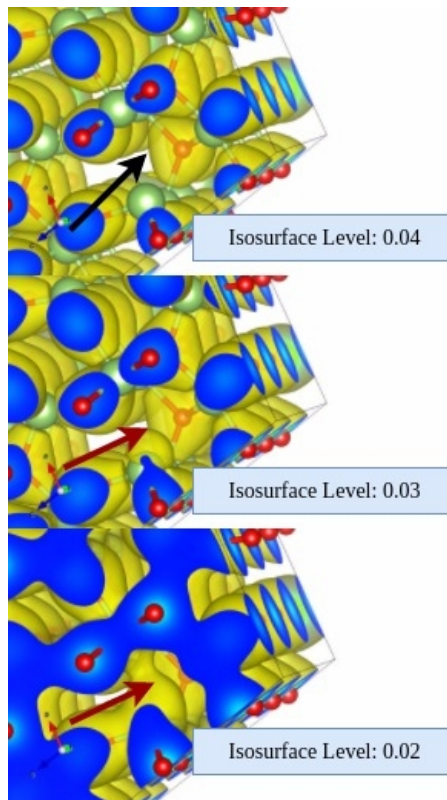


Figure 5.6: This figure shows the oxygen vacancy with different electron density isosurfaces. The black arrow points to the oxygen vacancy and the red arrows point to the dangling bond at the Ga(I) atom.

The difference between the O(I) vacancy with two Ga(I) atoms, that seems to form a covalent bond in the absence of an oxygen, and the other two vacancies, that only have one Ga(I) atom, might be a reason why the O(I) vacancy has the lowest formation energy.

The reason for the bond between two the Ga(I) atoms may come from the shorter length of the O-Ga(I) bond compared to the O-Ga(II) bond (see Figure 2.4). The 'bulb' from the isosurface always occur at the Ga(I) atom, and nothing at the Ga(II) atoms. Maybe the Ga(I) atom has dangling bonds, and the Ga(II) relocate the electrons elsewhere - is that possible? ??

5.1.3 Local DOS Ga(II)

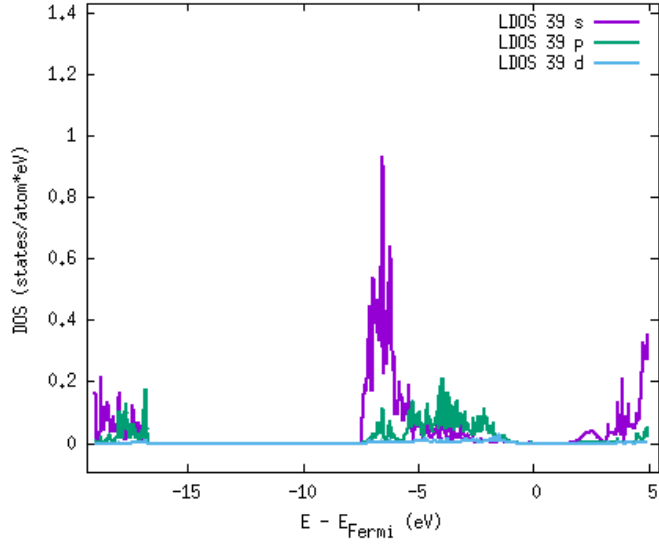


Figure 5.7: This is a plot of local density of state at the Ga(II) site next to the O(I) vacancy in the super cell.

5.1.4 Local DOS Ga(I)₁

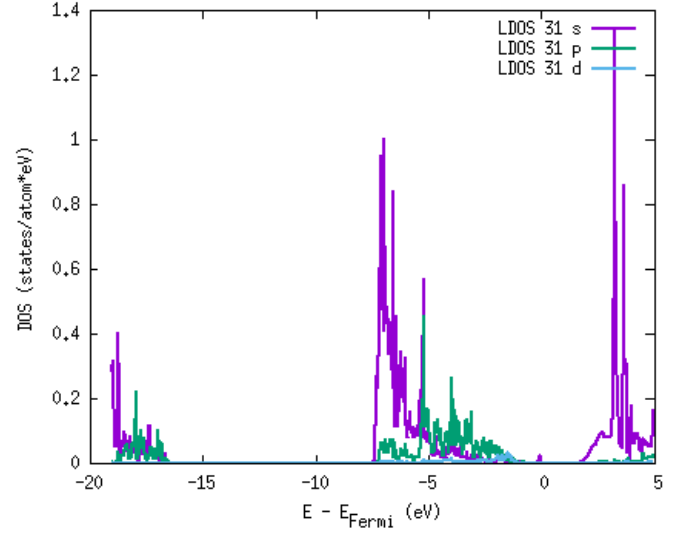


Figure 5.9: This is a plot of local density of state at the Ga(I) site next to the O(I) vacancy in the super cell.

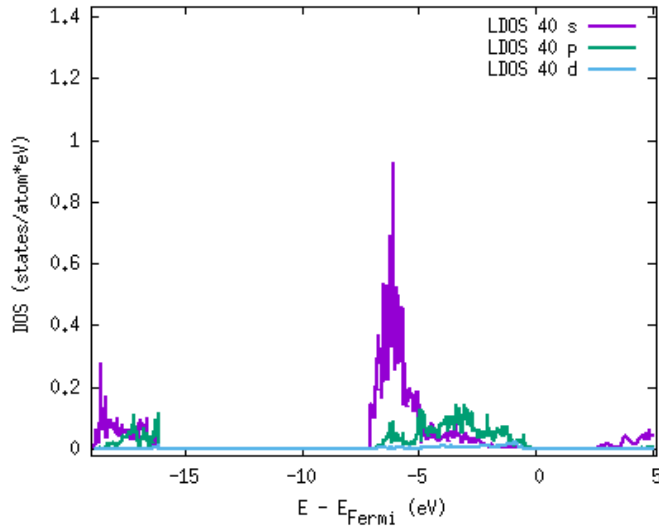


Figure 5.8: This is a plot of local density of state at the Ga(II) site in the general supercell.

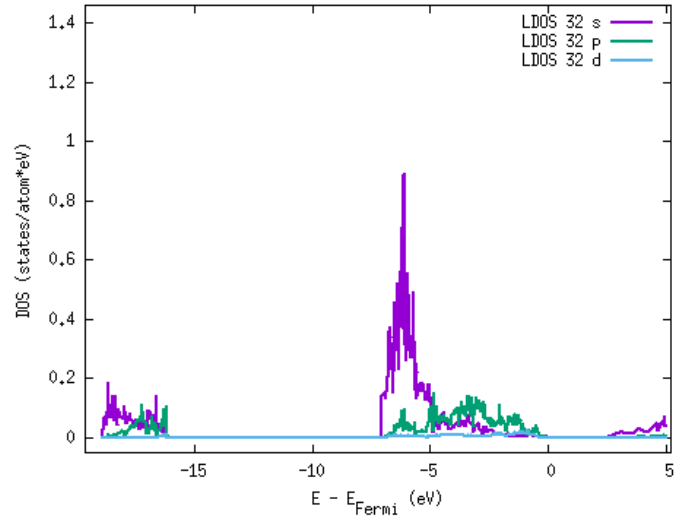


Figure 5.10: This is a plot of local density of state at the Ga(I) site in the general supercell.

5.1.1.5 Bond between Ga(I)₁ and Ga(I)₂?

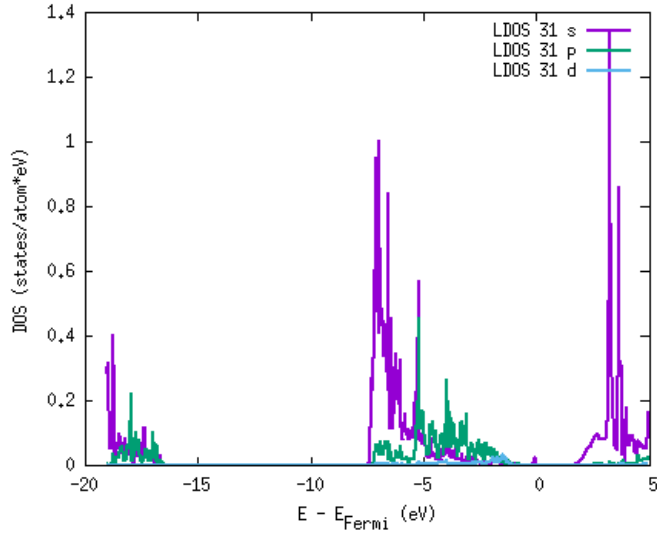


Figure 5.11: This is a plot of local density of state at the Ga(I) site next to the O(I) vacancy in the super cell.

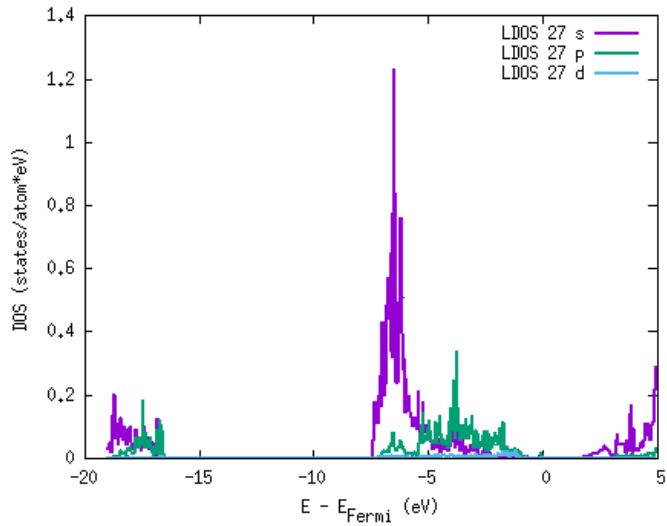


Figure 5.12: This is a plot of local density of state at the other Ga(I) site next to the O(I) vacancy in the super cell.

References

- [1] JB Varley, JR Weber, A Janotti, and CG Van de Walle. Oxygen vacancies and donor impurities in β -Ga₂O₃. *Applied Physics Letters*, 97(14):142106, 2010.

Appendix

6 Conclusion