

Exam

1. INITIAL STRUCTURE SETUP AND CONVERGENCE OF THE RELEVANT INPUT PARAMETERS

I am group 16, therefore I have to calculate NaS. This lattice has a space group number of 225, which represents "Fm-3m", it is an FCC lattice with a basis of two atoms, with wickoff positions 4a and 4b, respectively, the multiplicity for both of them is 4, as indicated in the table in Bilbao Crystallographic Server, and evidenced by the fact that in the conventional cell, there are 4 of each atom in an fcc lattice. The point group for both of them (because 4b is just a translation of 4a) is "m-3m". The space groups are a combination of two symmetries, the bravais lattice translations, and the local point groups, which include rotations, reflections, etc.

My estimated lattice constant will be

$$5.64\text{\AA} \cdot \frac{1}{190 + 79 \text{ pm}} \cdot (190 + 88 \text{ pm}) = 5.83\text{\AA} = 11.01 \text{ a.u.}$$

The input file for the SCF simulation is "NaS_scf.scf.in", and the following is the resulting lattice plotted with VESTA.

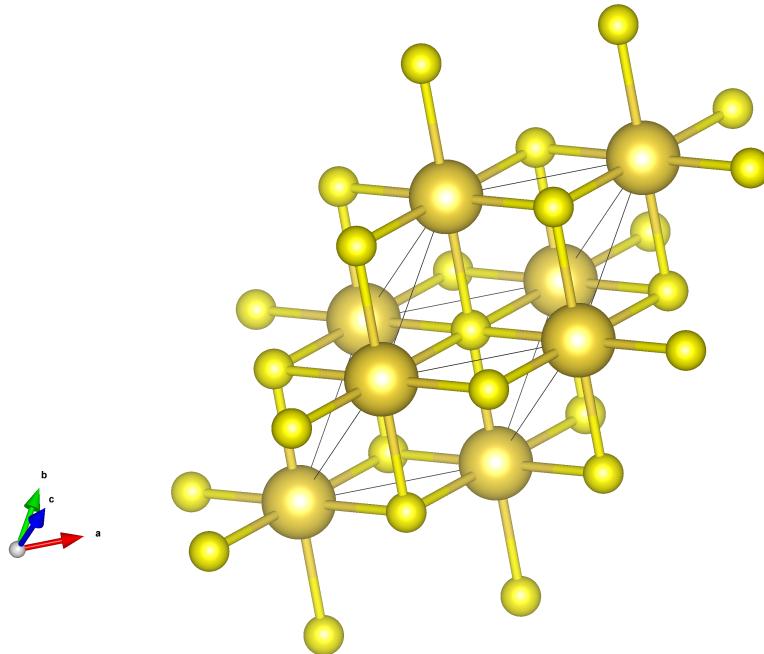


FIGURE 1. NaS structure.

I made two convergence tests, the first, plotted on Figure 2, on the energy cutoff (k cutoff) of the number of basis functions, with a fixed kpoints of 10. To achieve a precision of 10 meV per atom, we need to go to 100 Ry, though it's not very visible in the plot, the difference between 80 and 100 is 0.4 meV. On Figure 3, we are testing for the number of kpoints that we sample in the Brillouin zone, for a fixed $ecut = 100$ Ry, and we quickly see that at 10 it has converged very well.

2. STRUCTURAL RELAXATION

Structural relaxation is a technique which consists on changing the lattice parameters in order to find the configuration of least energy, the "relaxed" state, which is the state in which the net force on the system is 0, therefore we use minimizations algorithms like "bfsgs" in order to iteratively find the zero-force

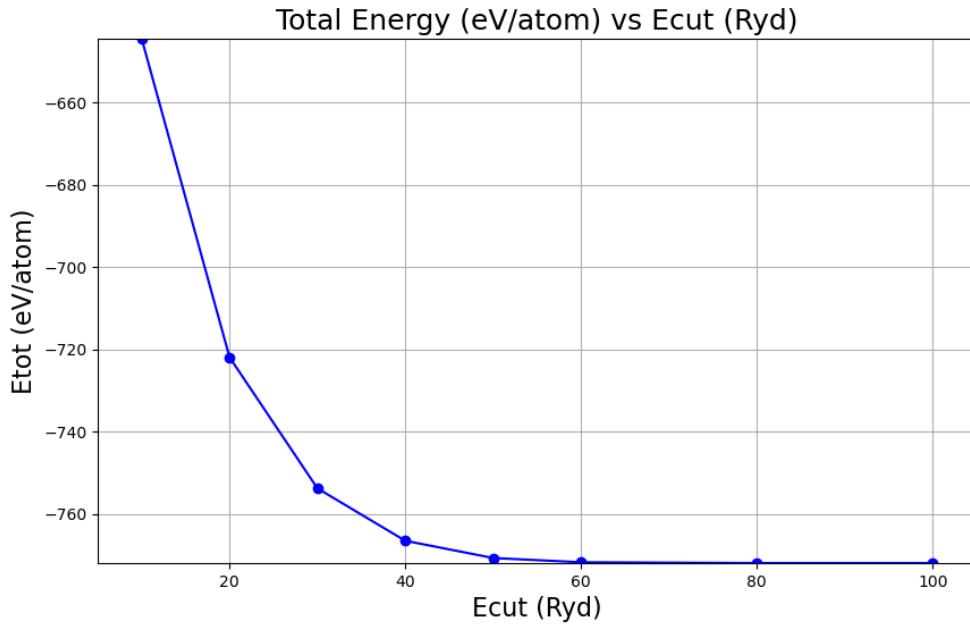


FIGURE 2. Convergence test on Ecut.

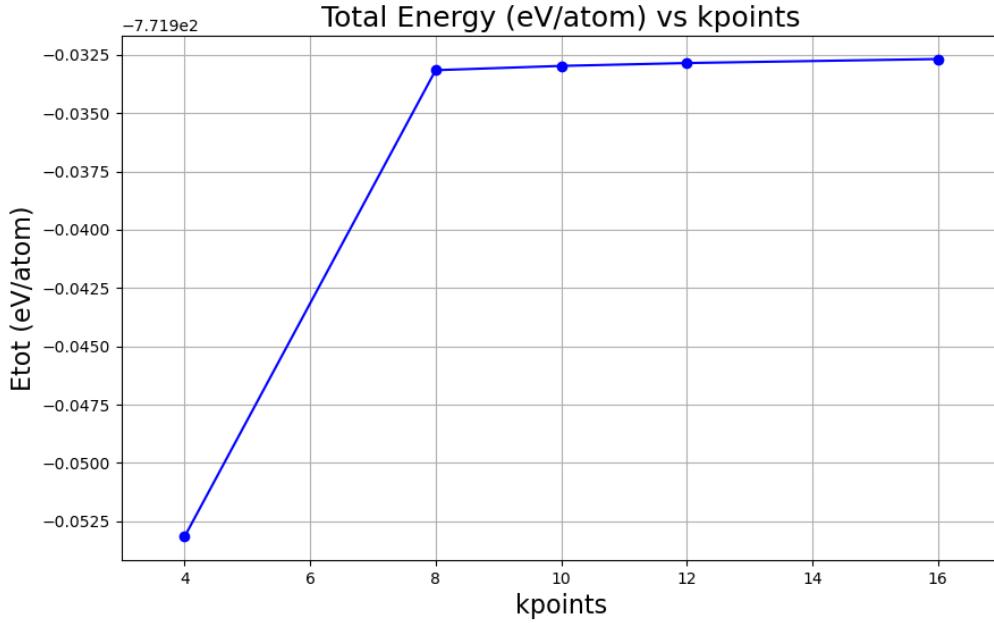


FIGURE 3. Convergence test on K-point discretization of the brillouin zone.

state. To compute the force, Quantum Montecarlo uses the Hellmann–Feynman theorem, which tells us that derivatives of the energy of the system (like the forces, derivativatives with respect to the positions of the ions) can be computed as the following integrals

$$\frac{dE_\lambda}{d\lambda} = \left\langle \psi_\lambda \left| \frac{d\hat{H}_\lambda}{d\lambda} \right| \psi_\lambda \right\rangle$$

We can also compute the stress tensor as the derivative of the energy with respect to each component of the lattice vectors, because in principle

$$P = -\frac{\partial E}{\partial V}$$

However, this derivative is very messy because the volume is a square root of the different lattice vectors squared, instead, we can calculate the pressure from the stress tensor as its trace

$$\sigma_{ij} = \frac{1}{V} \frac{\partial E}{\partial \epsilon_{ij}} \quad P = -\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

The pressure calculated by QE in the SCF simulation is -15.00 kbar, which is a relatively low value for solids, meaning we are not very far from equilibrium. The pressure is negative, meaning the system is too big and the atoms want to get closer, therefore we expect the relaxed lattice constant to be smaller, and therefore the volume will decrease. The net forces reported by quantum montecarlo are basically 0, evidence that the system is very near the relaxed state.

Because force is already almost 0 during the whole relaxation, I test the convergence of the relaxation using the pressure, and I got the following figure. We can see that on the sixth step it's already very well

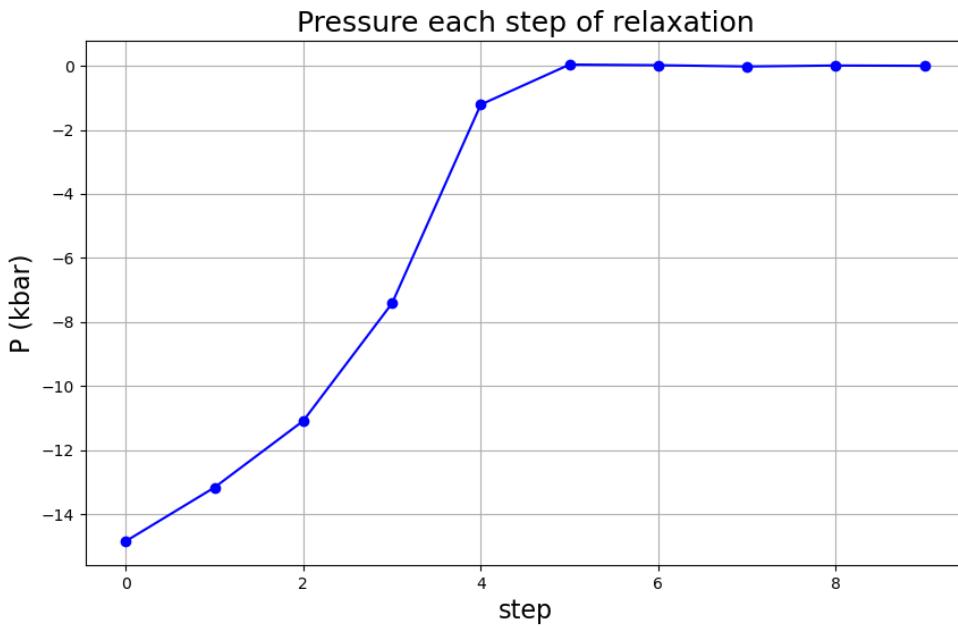


FIGURE 4. Pressure each step of the relaxation.

converged, and in the last step the pressure is exactly 0, with a difference with the previous step of 0.01 kbar. The input file of this simulation is in "NaS_scf.vcrelax.in". It took a few minutes, but I did not need to decrease the number of kpoints.

The final pressure is -0.25 kbar, which is not exactly 0 probably because some rounding error, but it's close enough, the initial volume was 333.6583 a.u 3 and the final one is 312.04877 a.u 3 = 46.24 Å 3 , and the new lattice constant is 10.766987 = a.u = 5.697641 Å.

3. ELECTRONIC PROPERTIES

The input files for these calculations are located inside the folder "bandsdos", and the results are Figure 5 and Figure 6. They have three more very flat bands below the ones I've shown with correspond with core electrons included in the pseudopotentials whose orbitals don't hybridize with other atoms, and therefore they are not very important in our case, but they are included because they may hybridize in other configurations and other atoms. For completeness I've included the full band plot in the same folder in the zip file.

Along the three core bands, we have that the fermi level rests on almost the top of three other bands, therefore we have three almost full conduction bands. The system looks like a metal, because the fermi level rests cutting some bands, however, it's very close to the top of the bands and after that we have a direct gap of ~ 4 eV, so it's probably not very hard to change the system a bit to make it semiconductor/insulator.

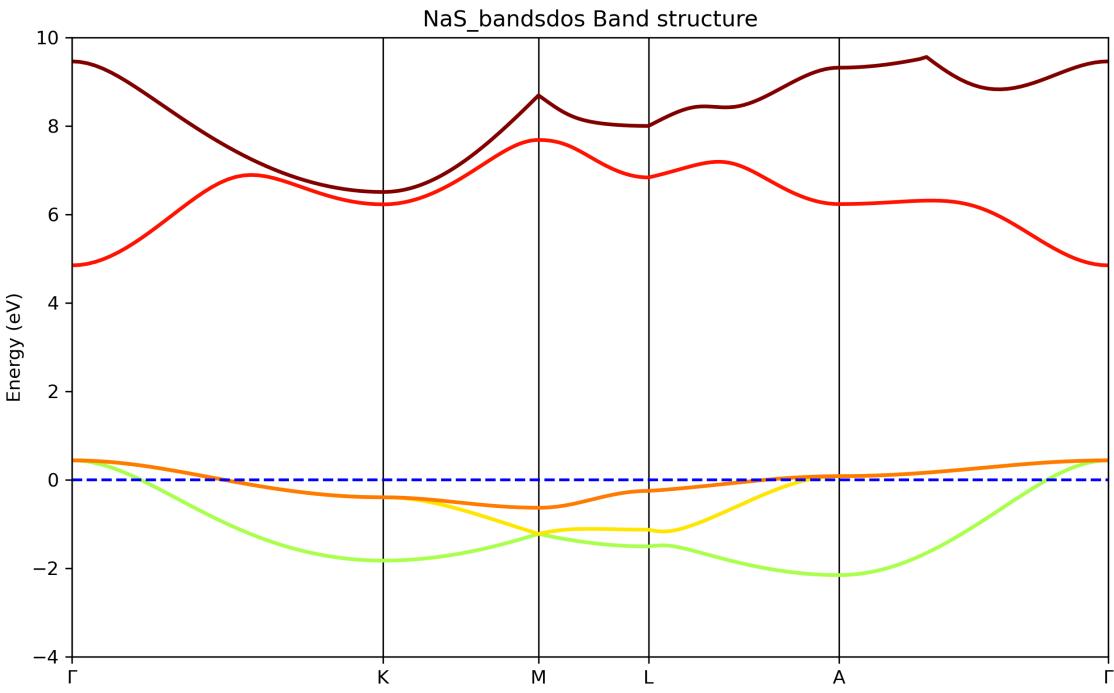


FIGURE 5. Band structure of NaS.

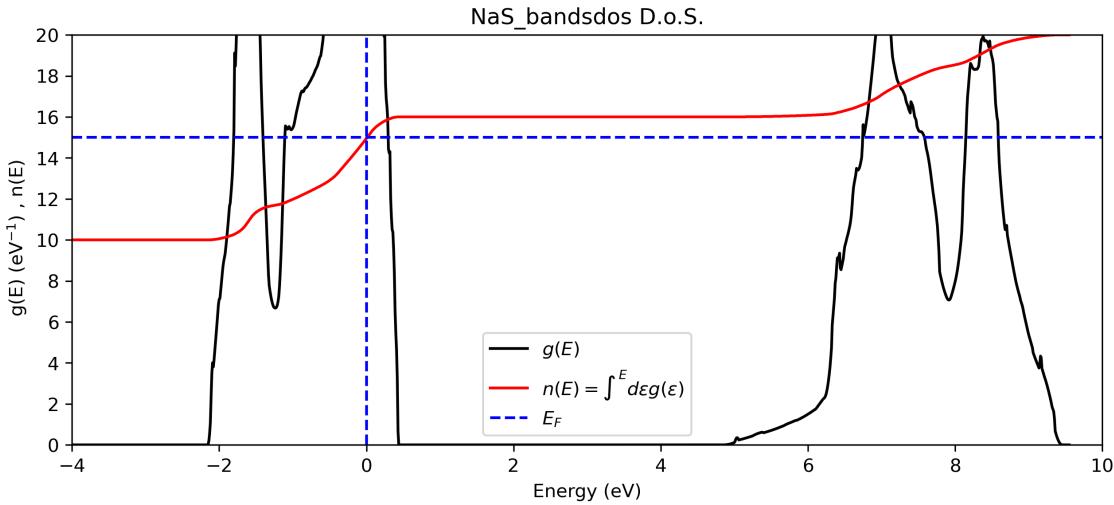


FIGURE 6. D.o.S. of NaS.

4. VACANCIES

The lattice constant will be the same, when you tell QE to make an fcc, it takes the size of the conventional cubic cell, which is what we are building now, because there are 4 times the atoms of the primitive cell in the conventional cell, we'll have 8 atoms in total, and the volume will be 4 times the volume of the primitive cell, $1248.19 \text{ a.u}^3 = 184.96 \text{ \AA}^3$. The positions of the atoms are in the next page, the sodium are just the corner and the three face atoms closest to it without repeating, I choose the ones that had negative coordinates with respect to the corner, and then the sulfur atoms are just the sodium atoms displaced by $a(1/2 \ 1/2 \ 1/2)$ the same way we did in the primitive basis. Each atom has 6 nearest neighbours pf the other type, independently of their type, and the distance between any of them is just $a/2 = 2.85 \text{\AA}$.

site n.	atom	positions (alat units)
1	Na	tau(1) = (0.0000000 0.0000000 0.0000000)
2	Na	tau(2) = (-0.5000000 0.0000000 -0.5000000)
3	Na	tau(3) = (-0.5000000 -0.5000000 0.0000000)
4	Na	tau(4) = (0.0000000 -0.5000000 -0.5000000)
5	S	tau(5) = (0.5000000 0.5000000 0.5000000)
6	S	tau(6) = (0.0000000 0.5000000 0.0000000)
7	S	tau(7) = (0.0000000 0.0000000 0.5000000)
8	S	tau(8) = (0.5000000 0.0000000 0.0000000)

Doing the SCF simulation, I get an energy of 771.47 eV per atom, and with the primitive lattice I got 771.64 eV per atom, it's not exactly the same but close enough. I get the following structure in VESTA, the same as before. I had to change the occupation of the Brillouin zone from tetrahedra to smearing, because tetrahedra did not converge.

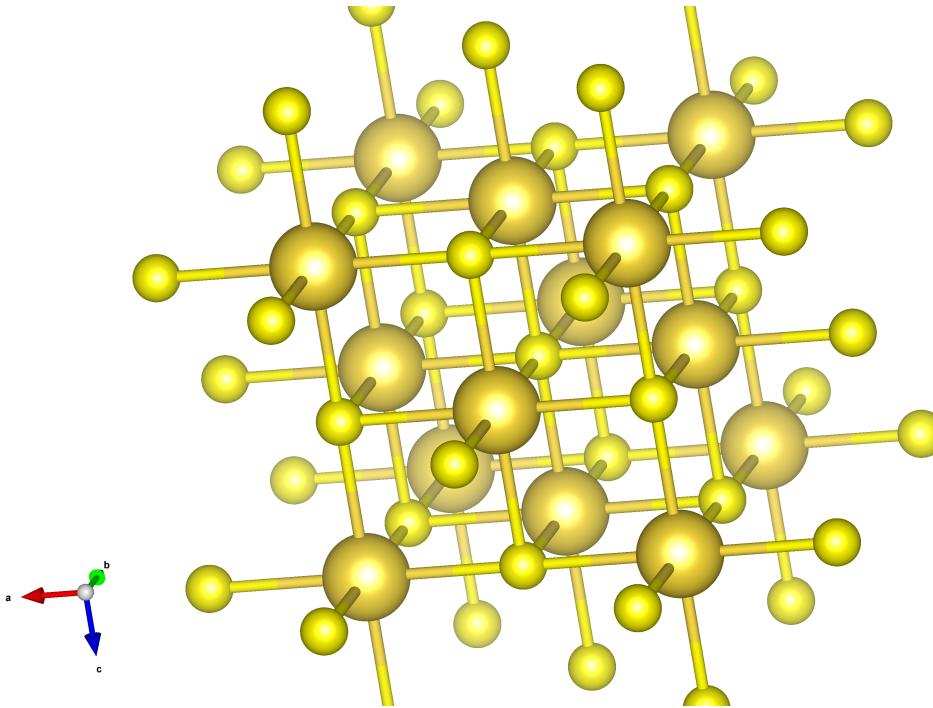


FIGURE 7. Structure of the conventional cell of NaS.

Now we are ready to create the vacancy removing the first atom the list, this structure is represented in Figure 7, the concentration of vacancies is just 1 over the volume of the cell, that is 0.0054 \AA^{-3} . The number of electrons is 51, because we have $3 \cdot 9$ for the sodium, and $4 \cdot 6$ for the sulfur. The forces and tensions are

Forces acting on atoms (cartesian axes, Ry/au):

atom	1	type	Na	force =	0.00000000	0.00000000	0.00000000
atom	2	type	Na	force =	0.00000000	0.00000000	0.00000000
atom	3	type	Na	force =	0.00000000	0.00000000	0.00000000
atom	4	type	S	force =	0.00000000	0.00000000	0.00000000
atom	5	type	S	force =	0.00000000	0.00000000	0.00000000
atom	6	type	S	force =	0.00000000	0.00000000	0.00000000
atom	7	type	S	force =	0.00000000	0.00000000	0.00000000

Total force = 0.000000 Total SCF correction = 0.000000

Stress and pressure (kbar) P= -94.83

-94.83	0.00	0.00
0.00	-94.83	0.00
0.00	0.00	-94.83

The forces are almost 0 in these units, but we've got an (although not very big, noticeable) negative diagonal pressure, which makes sense because we have removed an atom and there's more "empty" space, so they wanna get closer. However, I would have expected bigger forces and stress considering how much we've changed the structure, I would also expect some off-diagonal terms in the stress related to the fact that now FCC is probably not the best structure and the system would like to go to a different structure. In the following picture we have a 2D slice of charge density along xy plane for both the regular NaS and

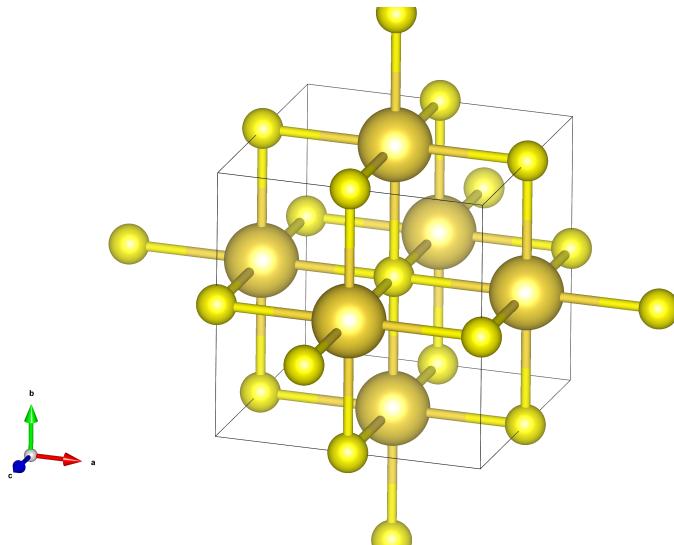


FIGURE 8. Structure of the conventional cell of NaS with vacancy.

the one with a vacancy. We can see that in the crystal without vacancies, in the origin, where we have a Sodium atom, it is very saturated with electric charge, when we introduce the vacancy, those points disappear. On the other hand, the Sulfur atoms are almost without charge, only with a small sphere of charge surrounding them. The electronegativity of Sodium (0.93) is smaller than that of Sulfur (2.58), so it looks a bit weird that most of the charge is concentrated in the sodium atoms instead of in the sulfur atoms, however, the high density of sodium atoms may be explained by the greater number of core electrons in the pseudopotential.

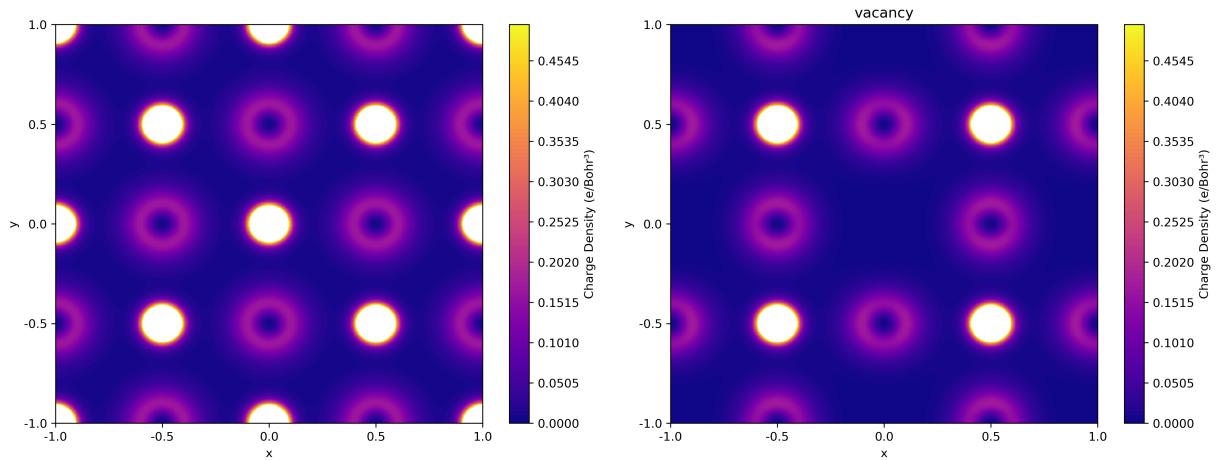


FIGURE 9. 2D slice of charge density along xy plane for regular NaS (left) and for NaS with a vacancy (right).

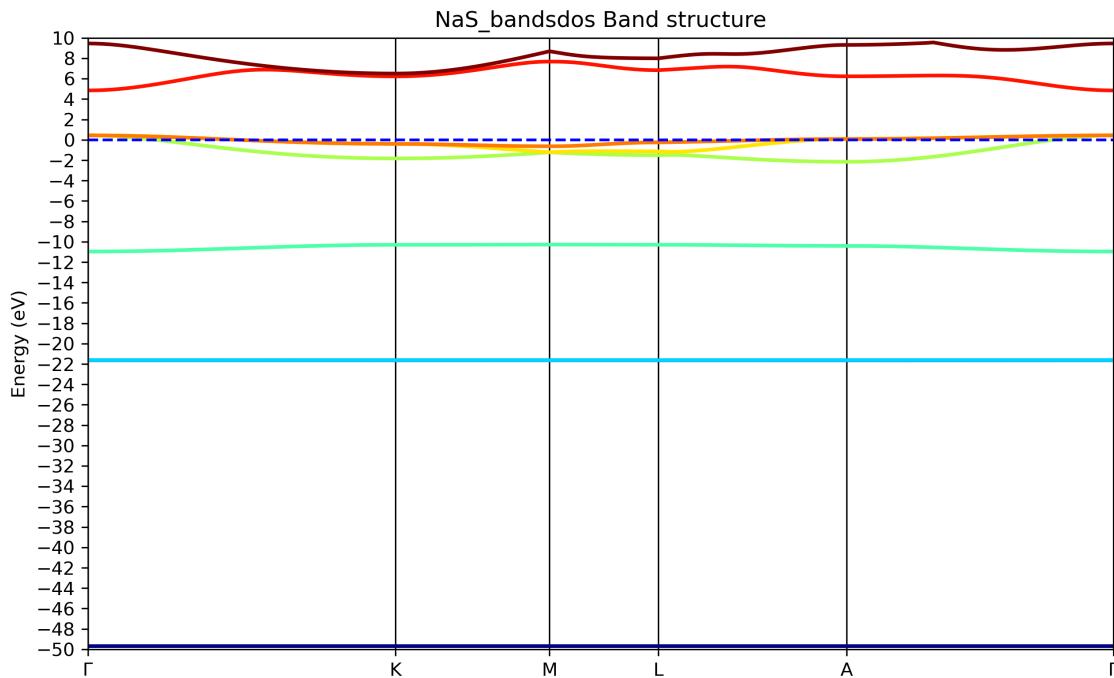


FIGURE 10. Complete band structure of NaS.

4.1. **Appendix.** ROSADOPINEADO.2183060@STUDENTI.UNIROMA1.IT