

Weekly Report

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July 15, 2020 - July 22, 2020

1 Introduction

This week I finally find some ways to use VASP, but the usage is still limited. After discussion with Yujie, I decide to study some other small systems and he will do the part of 'Martrix Figures'.

2 Progress

I think it's helpful to start with the systems which suffer direct to indirect band gap transitions, so I choose three questions which will be elaborated in the following.

1. Transition by lattice constant in GaP
2. Transition by structure in AlSb
3. Transition happens in Group II-VI compounds

2.1 GaP

According to Ref [1](#), zinc-blende GaP would suffer a indirect to direct band gap transition when we increase the lattice constant. Here I set lattice constant from 5.15Å to 5.75Å (intervals of 0.1Å) and calculate their band structure. From Figure [1](#) We can see that GaP changes from Γ -X indirect band gap to Γ - Γ direct band gap. From the trend I found that Γ , X, L points play a very important role. Therefore, I extract specific energy data of these three points during the enlargement of lattice constant, which are showed in Figure [2](#). When energy in Γ point is the lowest among these three points GaP turns to direct band gap semiconductor.

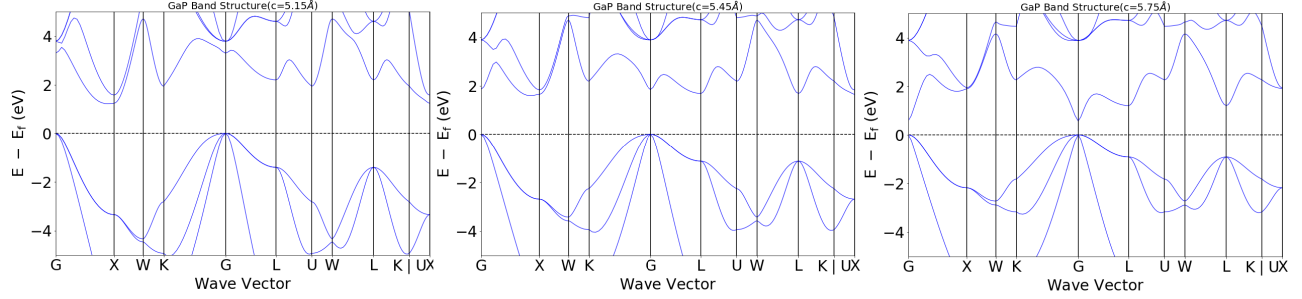


Figure 1: Band structure of GaP in different lattice constant

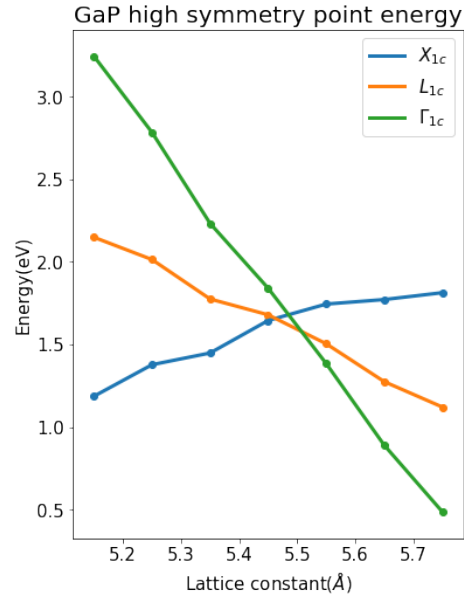


Figure 2: Energies of the CB Γ , X and L valleys as a function of the change of the lattice constant (In reality GaP lattice constant = 5.506 Å)

The further explanation of hybridization can be found in Ref 1. My idea is that we may find some ways to let GaP be stable in larger lattice constant, such as strain, special temperature and doping. In this way maybe GaP would has some applications in semiconductor industry like GaAs.

2.2 AlSb

In previous report I mentioned that zinc-blende AlSb has indirect band gap while hexagonal AlSb has direct band gap. Here I'd like to use VASP to acquire some orbital contribution to see if I can get some inspiration. Figure 3 shows

that Zinc-blende AlSb has Γ -L indirect band gap and Hexagonal AlSb holds Γ - Γ direct band gap.

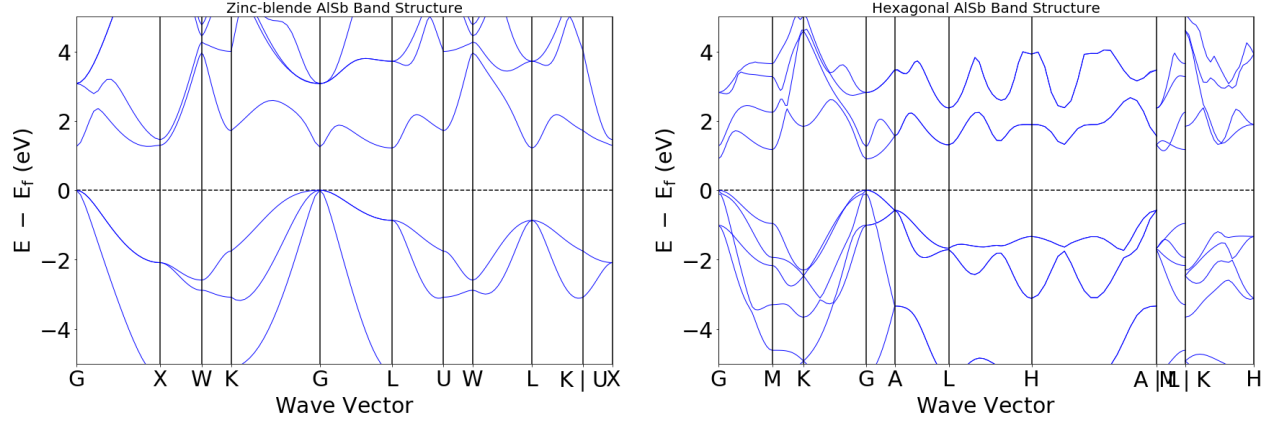


Figure 3: Band structure of different structure AlSb

Orbital contribution could be found in Figure 4 and 5

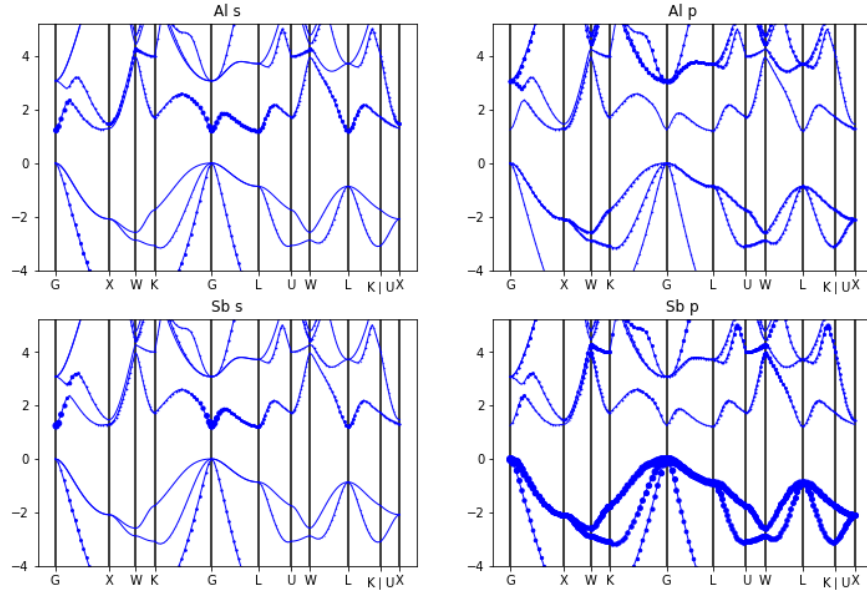


Figure 4: Orbital contribution of zinc-blende AlSb

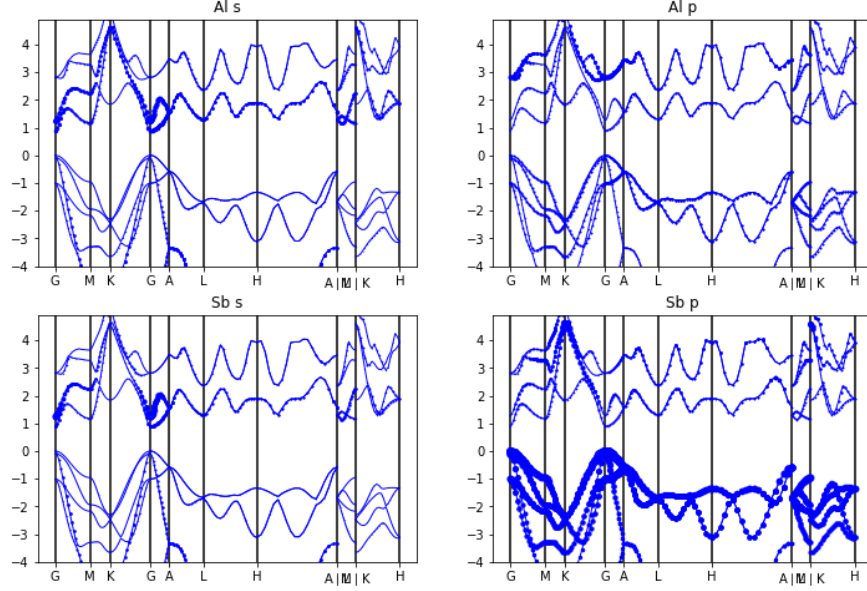


Figure 5: Orbital contribution of hexagonal AlSb

The interesting thing happens along Γ -L high symmetry line. In both structure they are dominated by Al and Sb s orbitals. Compared with zincblende structure hexagonal structure has a relatively higher energy in CBM L point which is the key to the different band gap feature. What does this imply? My hypothesis is that the two L points holds different symmetry, so maybe certain type of hybridization could happen in one L point but couldn't happen in the other one. However, I haven't figure out how to do such analysis by VASP results up to now(I guess COHP analysis would be helpful but I just finish installing Lobster on virtual machine and haven't totally handled it). Next week I will keep working on this.

2.3 Group II-VI compounds

Compared with Group III-V semiconductors, Group II-VI compounds are usually insulators so they don't attract much attention. However, they holds simpler band structure and suffer interesting direct to indirect band gap transition so I think they may also be a good way to start with. Here I choose MgO, CaO, SrO and BaO for studying. Figure 6 shows the bandstructure of them.

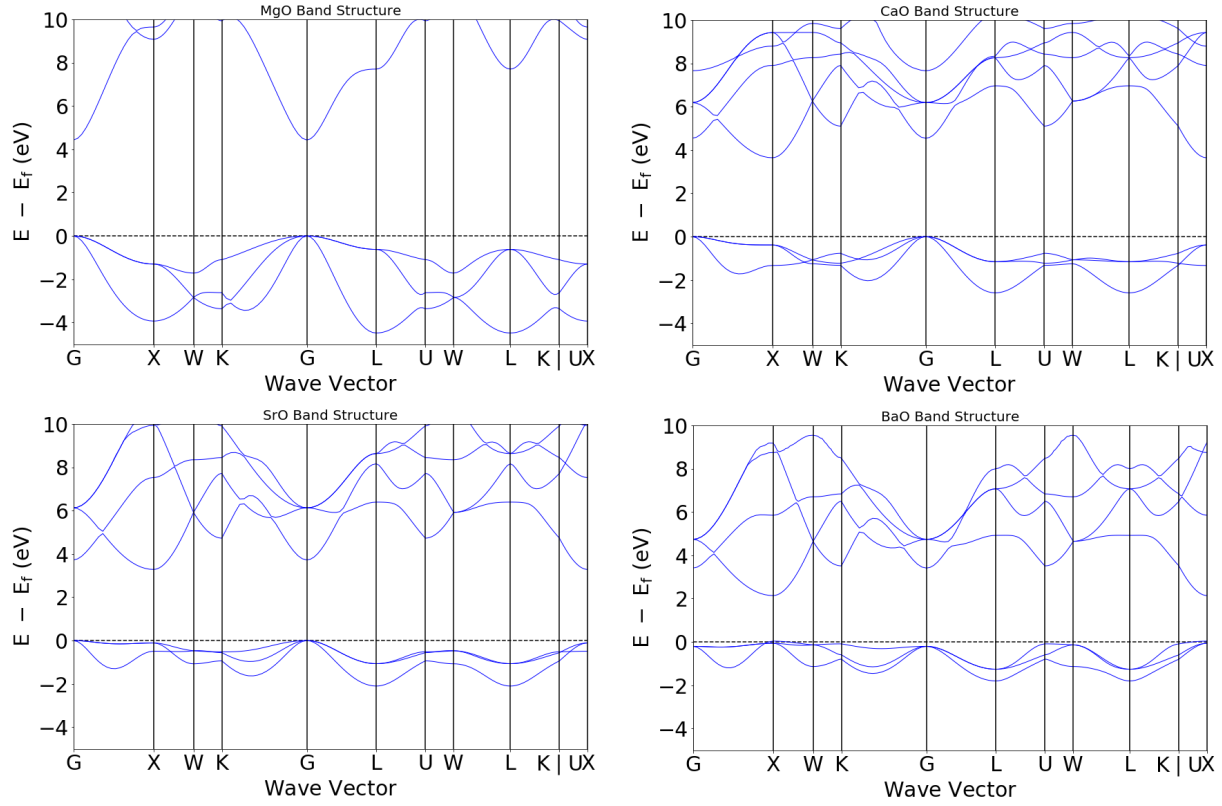


Figure 6: Zinc-blende band structure of Group II oxide

MgO has simple Γ - Γ direct band gap. CaO and SrO has Γ -X indirect band gap. Surprisingly BaO has X-X direct band gap. From orbital contributions [7](#) we can see that due to unoccupied d orbitals(especially d_{yz}), Group II oxide would form a X valley in CB. Mg don't have occupied d orbitals so MgO is a simple insulator. BaO is kind of strange because its VBM is in X points and orbital contribution(Figure [8](#)) doesn't reveal much information.

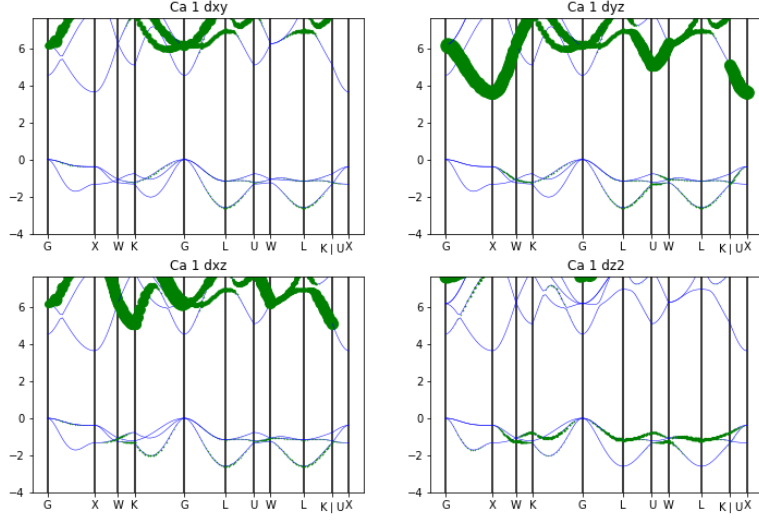


Figure 7: Orbital contribution of CaO

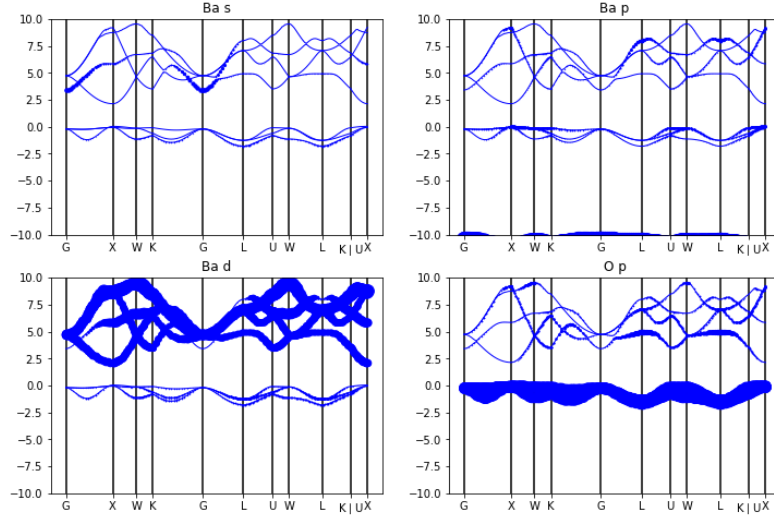


Figure 8: Orbital contribution of BaO

To make further inquiry, first I try to set the lattice constant of CaO and SrO equal to BaO and see how their bandstructure change accordingly and weird things happened. CaO and SrO both turn to Γ - Γ direct band gap and CB X point valley lifts up(showed in Figure 9).

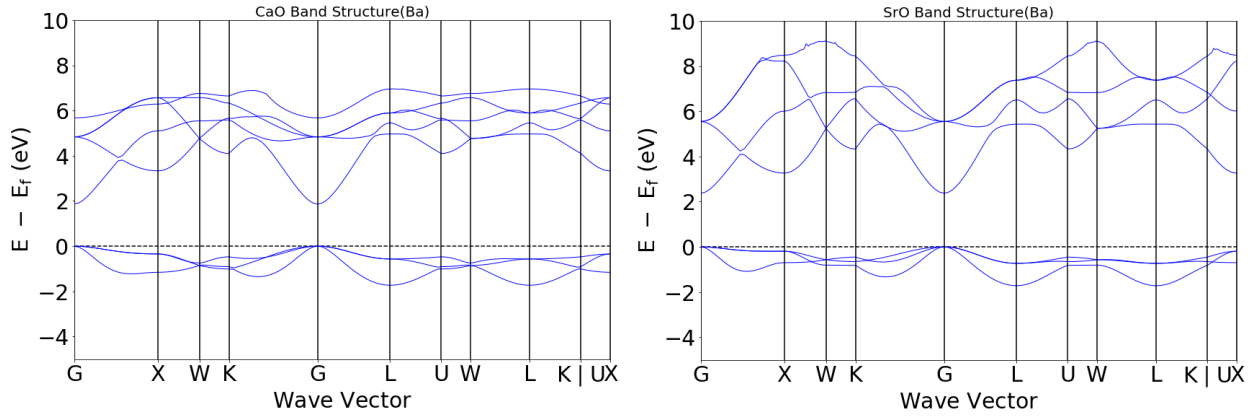


Figure 9: Cao and SrO band sturcture in BaO's lacttice constant

I have checked the final structures and they are correct. Now I have no idea why this situation happened. If the band structureares are right, perhaps it's because they are sensitive to bond length? But I don't think it makes sense since Group III-V compounds don't show such features under lacttice constant change.

Then, I try to set BaO's lacttice constant equal to CaO or SrO. It turns out that this feature remains and BaO would even become metal when its lacttice constant equals to CaO(Figure 10)

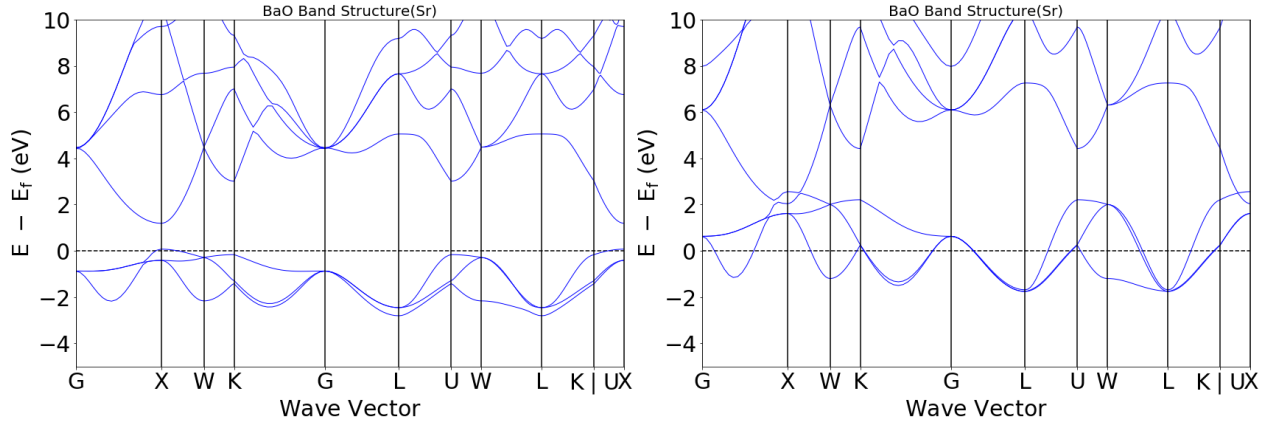


Figure 10: BaO band sturcture When setting lacttice constant equal to SrO(left) and CaO(right)

I think to solve this question we should make some oribital hybridization analysis, so it goes back to the usage problem I mention above.

2.4 Fermi surface analysis

Up to my understanding, Prof. Sun's idea is that modulating the structure would change the BZ, so maybe the electron filling process would change due to Fermi surface's transition corresponding to BZ. Ideally, the situation that a structural transition results in the intersection between Fermi surface and BZ would be a good study case. This week I tried to draw some Fermi surface by Xcrysden, but only when the system is metallic can Xcrysden work. I haven't figured out the reason and further learning is needed. Figure 11 is the metallic BaO which I mention in the former section.

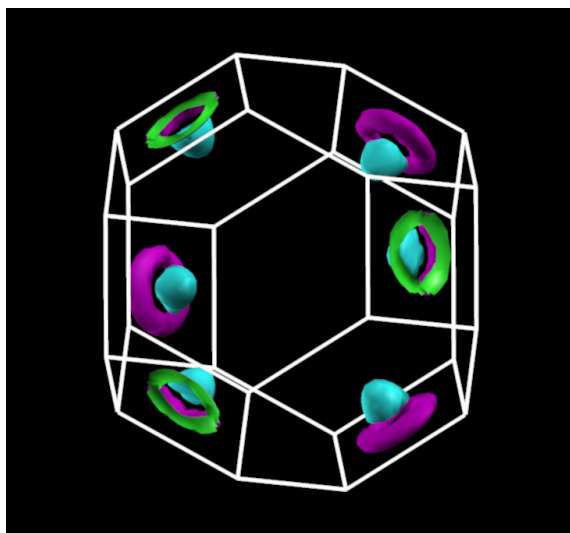


Figure 11: 'Metallic' BaO Fermi surface

3 Summary

This week I finally managed to do some VASP analysis. The next step is solving the above-mentioned questions and learning the relationship between Mott insulators (charge transfer transition metal compounds) and indirect band gap.

4 Reference

1. Lin-Ding Yuan, Hui-Xiong Deng, Shu-Shen Li, Su-Huai Wei, and Jun-Wei Luo, Unified theory of direct or indirect band-gap nature of conventional semiconductors, PHYSICAL REVIEW B 98, 245203 (2018) DOI: 10.1103/PhysRevB.98.245203 I.