Utrecht University
Exam Solids and Surfaces
Tuesday, February 1st, 2022
Time: 13:30 - 16:30

Name and student number: ______________________________

Good luck!

- Write your name on each answer sheet.
- Please pay attention to your hand-writing. If we cannot read your answers, we cannot award points.
- In your answers, do not immediately start with equations. Also draw conclusions from the calculations you have done.
- You can answer in English or in Dutch.
- Please note that you can earn a maximum of 61 points.
- Not each question is worth the same number of points.
- The following relations might be helpful:

$$\begin{aligned}\cos(2a) &= 2\cos^2 a - 1\\ \cos(a+b) + \cos(a-b) &= 2\cos(a)\cos(b)\\ \cos(a+b) &= \cos(a)\cos(b) - \sin(a)\sin(b)\\ \cos(a-b) &= \cos(a)\cos(b) + \sin(a)\sin(b)\\ e^{ik} + e^{-ik} &= 2\cos(k)\\ \sin(x) &\approx x \text{ (for small } x)\end{aligned}$$

Question 1: **Geometric structure of surfaces** .... *11 points*

(a) (3 points) Copper has an FCC crystal structure. The surface energy of the Cu(111) surface is 1.97 eV. Compute the surface energy of the Cu(100) **AND** Cu(110) surfaces.

Answer: Use the broken-bond ratio (1 point). Atoms in the (111), (100) and (110) plane have 9, 8 and 6 neighbors, respectively. Hence, 3, 4, and 6 bonds are broken. The broken-bond ratio gives the following surface energies: Cu(100): $\frac{4}{3}\gamma_{(111)} = 2.63$ eV and for Cu(110): $\frac{6}{3}\gamma_{(111)} = 3.94$ eV. 1 point for each correct answer.

(b) (2 points) Arrange these copper surfaces in the order of ascending work function. Explain.

Answer: Cu(111), Cu(100), Cu(110). More open surfaces have lower work function due to charge smoothening. 1 point for the correct order, 1 point for the explanation.

(c) (4 points) Determine the equilibrium shape of a Cu crystal using the planes indicated above and the surface energies you determined above. If you did not determine the surface energies, please use $\gamma_{100} = 2.5$ eV and $\gamma_{110} = 4$ eV. **IMPORTANT:** It is not essential that your drawings are exactly to scale.

Answer: This can be done using the Wulff construction (1 point). Drawing of the 100 plane, with ¡100¿ and ¡110¿ directions: $\gamma_{110} > \sqrt{2}\gamma_{100}$, and hence the 110 planes do not play a role. Drawing of the 110 plane with all three vectors: again, the γ_{110} is too large to play a role. Since the energy of the (111) is the lowest, most of the surface area of the crystal should have this plane (1 point). You get a truncated octahedron (1 point).

(d) (2 points) Name two surface preparation techniques that can be used to prepare this atomically flat and clean surface.

Answer: Sputtering/annealing or epitaxial growth (2 points).

Question 2: **Tight Binding calculations** .... *24 points*

Consider the crystal shown in Fig. 1. The black circles indicate the positions of the atoms. In this question, you will perform a tight-binding calculation of this structure. Each atom contributes one electron and one s-type orbital. Only interactions with nearest neighbors have to be taken into account.

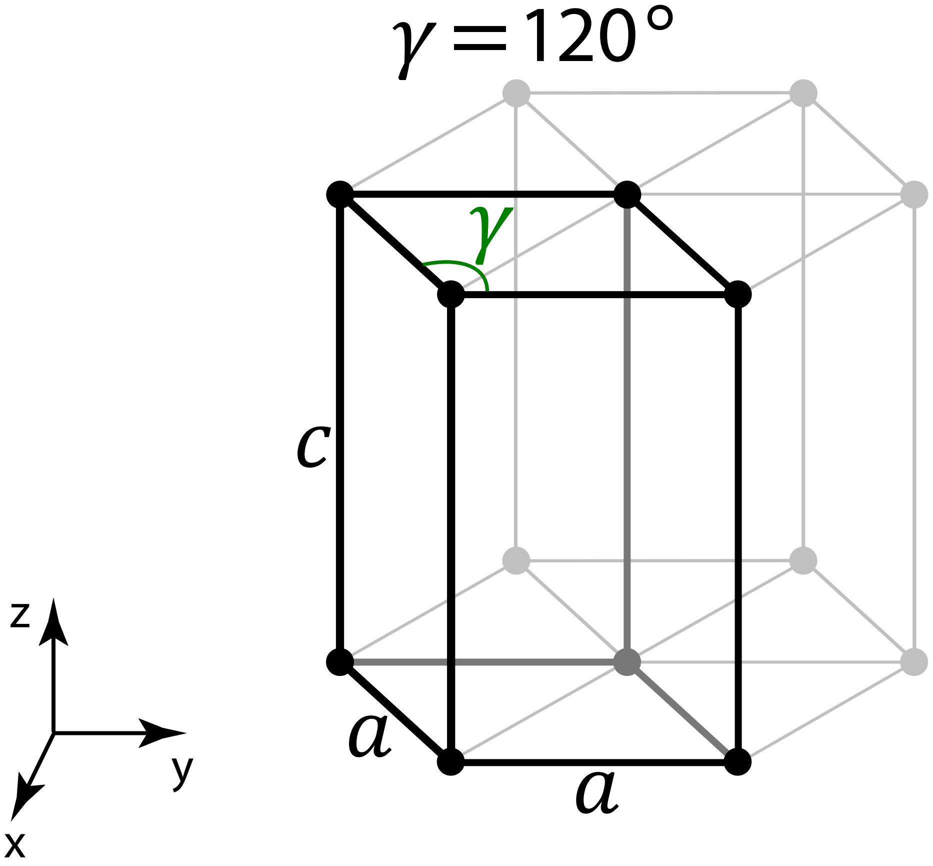

Figure 1: Hexagonal lattice. Note the orientation of the spatial directions x, y and z.

(a) (3 points) Determine the primitive unit cell vectors using the directions indicated in Fig. 1. Set $c = a$.

Answer: For the lattice shown in Fig. 1, the atomic positions are also lattice points. The unit cell vectors of the primitive cell shown in the the figure (that contains exactly one atom) are

$$\boldsymbol{a_1} = \frac{\sqrt{3}a}{2}\hat{x} + \frac{a}{2}\hat{y} \tag{1}$$

$$\boldsymbol{a_2} = a\hat{y} \tag{2}$$

$$\boldsymbol{a_3} = a\hat{z} \tag{3}$$

1 point for each correct vector.

(b) (4 points) Based on your previous answer, determine the primitive unit cell vectors of the reciprocal lattice.

Answer: The reciprocal lattice vectors are defined by:

$$\boldsymbol{b_1} = \frac{2\pi}{V}\boldsymbol{a_2} \times \boldsymbol{a_3} \tag{4}$$

with $V = |\boldsymbol{a_1} \cdot (\boldsymbol{a_2} \times \boldsymbol{a_3})| = \sqrt{3}a^3/2$ the volume of the real-space unit cell, and similar equations for $\boldsymbol{b_2}$ and $\boldsymbol{b_3}$ (1 point). We find:

$$\boldsymbol{b_1} = \frac{4\pi}{\sqrt{3}a}\hat{x} \tag{5}$$

$$\boldsymbol{b_2} = \frac{4\pi}{\sqrt{3}a}\left(-\frac{1}{2}\hat{x} + \frac{\sqrt{3}}{2}\hat{y}\right) \tag{6}$$

$$\boldsymbol{b_3} = \frac{s\pi}{a}\hat{z} \tag{7}$$

1 point for each correct vector.

(c) (9 points) Compute the dispersion relation for this material.

Answer: There is one atom per unit cell. Each atom has 8 nearest neighbors, all at the same distance, implying 9 terms (one on-site, 8 hopping terms) (2 points). Since the distance to all neighboring atoms is the same, the hopping parameter will be the same for all interactions. This is set to t below (1 point). The dispersion relation can be computed by evaluating the expectation value of the energy (1 point)

This gives rise to the following expression

$$E(\boldsymbol{k}) = \epsilon + te^{i\boldsymbol{k}\cdot\boldsymbol{a_1}} + te^{i\boldsymbol{k}\cdot\boldsymbol{a_2}} + te^{i\boldsymbol{k}\cdot\boldsymbol{a_3}} + te^{-i\boldsymbol{k}\cdot\boldsymbol{a_1}} + te^{-i\boldsymbol{k}\cdot\boldsymbol{a_2}} + te^{-i\boldsymbol{k}\cdot\boldsymbol{a_3}} + te^{i\boldsymbol{k}\cdot(\boldsymbol{a_1}-\boldsymbol{a_2})} + te^{-i\boldsymbol{k}\cdot(\boldsymbol{a_1}-\boldsymbol{a_2})} \tag{8}$$

Insert the definitions of the unit cell vectors to find

$$E(\boldsymbol{k}) = \epsilon + 2t\cos(k_y a) + 4t\cos(k_y a/2)\cos(k_x\sqrt{3}a/2) + 2t\cos(k_z a) \tag{9}$$

5 points for the correct math.

(d) (3 points) A large force is applied along the z-axis that pulls the atomic planes apart. Does this change the band structure? Explain.

Answer: If the atomic planes are pulled apart, the distance between the atomic planes increases ($c \neq a$). Consequently, the hopping integral becomes smaller ($|t_z| < |t_{x,y}$) (1 point). Hence, the dispersion in the k_z-direction decreases (1 point). The dispersion in the lateral directions is, to first order, unaffected (1 point). To second order, the value of $|t_{x,y}|$ increases (remaining bonds become stronger).

(e) (2 points) Do you expect this material to be a metal, semi-conductor, or insulator? Explain.

Answer: Metal (1 point). Each atom contributes one orbital and one electrons. Hence, the band structure will have one band that is half full. There are empty states available immediately above the Fermi level (1 point).

(f) (3 points) Assume that you want to make your calculation more accurate by including a second s-type orbital with a significantly higher on-site energy for each atom. Describe how this will change the calculation and the results (is it still a metal or not?) You do not need to do the calculation.

Answer: A second orbital would lead to a 2×2 determinant and two bands in the dispersion relation (1 point). Since the on-site energy of the two orbitals is significantly different, there will be a band gap between the two bands (1 point). Given the energy difference, the bands will not couple very strongly, meaning that to first order the second band does not influence the dispersion of the first band. Since each atom still contributes only one electron, the calculation will still predict this material to be a metal (1 point).