Elementi di teoria elettronica della materia

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1 Sommario degli argomenti trattati

1. Reticoli cristallini [AM, Cap. 4]
2. Il reticolo reciproco [AM, Cap. 5, sezioni: *Definitions and Examples*; *First Brillouin zone*]
3. Classificazione dei reticoli di Bravais [AM, Cap. 7, sezione *The classification of Bravais lattices*]
4. Il teorema di Bloch [AM, Cap. 8]
5. Elettroni in un debole potenziale periodico [AM, Cap. 9, sezioni: *Energy bands in one dimension*; *Energy-wave-vector curves in three dimensions*; *The energy gap*; *Geometrical structure factor in monatomic lattices with bases*]
6. Metodi per calcolare la struttura a bande [AM, Cap. 11, sezioni: *Orthogonalized plane-wave method*; *Pseudopotentials*].
7. Il lavoro di Cohen e Bergstresser sugli pseudopotenziali empirici [CB]
8. Conoscere e saper modificare i due programmi discussi a lezione per il calcolo delle bande di energia degli elettroni liberi in un reticolo fantasma e per il calcolo delle bande dei semiconduttori semplici con gli pseudopotenziali empirici.

2 Bibliografia

[AM] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, ISBN: 978-0-03-083993-1.

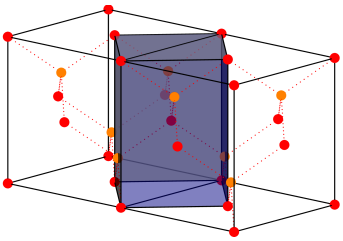
[CB] M.L. Cohen and T.K. Bergstresser, Phys. Rev. **141**, 789 (1966).

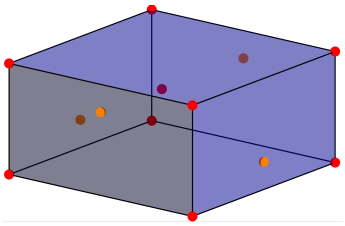
3 Problemi

Problem 1: Band structure and Fermi surface of white tin

Alpha tin (or gray tin), the low temperature structure of tin, has the diamond structure. You can find in the Cohen and Bergstresser (CB) paper the form factors of alpha tin and plot its electronic band structure using the code distributed in the lectures. At 13.6 °C the unit cell changes and tin becomes white tin, the room temperature phase. In this exercise we plot its band structure and its Fermi surface.

The structure of white tin (also known as beta tin) can be described by a centered tetragonal lattice with two atoms per cell. In order to visualize the unit cell, we can start from the tetragonal cell of alpha tin shown in the figure on the left:





The c/a ratio of this tetragonal cell is $c/a = \sqrt{2}$ ($a = a_{fcc}/\sqrt{2} = 4.59$ Å). Beta tin (shown in the figure on the right) can be obtained by decreasing c and increasing a until $c/a = 0.55$ and $a = 5.80$ Å. The simple tetragonal cell shown in the figure contains four atoms, but using a centered tetragonal Bravais lattice we can describe the structure with a unit cell with two atoms. The primitive lattice vectors are:

$$\begin{aligned} \mathbf{a}_1 &= \frac{1}{2}(-a, a, c), \\ \mathbf{a}_2 &= \frac{1}{2}(a, -a, c), \\ \mathbf{a}_3 &= \frac{1}{2}(a, a, -c). \end{aligned}$$

The position of the two atoms that in alpha tin were at $\mathbf{d}_{1,2} = \pm a_{fcc}(1/8, 1/8, 1/8)$ are strained uniformly and in beta tin are at $\mathbf{d}_{1,2} = \pm(a/4, 0, c/8)$ (with respect to the figure the origin is shifted in the center of the line that join the two atoms).

We can calculate the form factors for arbitrary values of the square modulus of the reciprocal lattice vectors $|\mathbf{G}|^2$, interpolating the form factors of alpha tin by an analytic function:

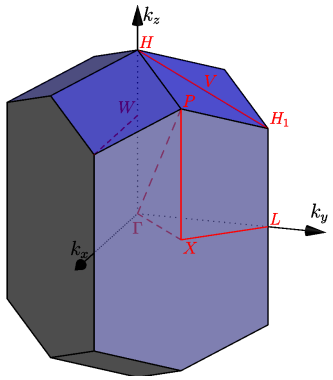
$$U(|\mathbf{G}|^2) = \frac{A_1(|\mathbf{G}|^2 - A_2)}{e^{A_3(|\mathbf{G}|^2 - A_4)} + 1}, \tag{1}$$

with $A_1 = 0.0765$, $A_2 = 2.0997$, $A_3 = 2.9779$, $A_4 = 2.6524$, and using this function also for beta tin. These parameters, and $\mathbf{G}$ vectors in atomic units (1/bohr), give the form factors in Hartree.

1. Plot the function $U(|\mathbf{G}|^2)$ and verify that, with these parameters A, it gives the same form factors of the CB paper at the corresponding $|\mathbf{G}|^2$ values.

2. Modify the program to calculate the energy bands with the CB empirical pseudopotentials to use Eq. 1. Check your changes by recalculating the band structure of alpha tin.

3. Modify the CB program and generate the reciprocal lattice vectors of the centered tetragonal lattice of beta tin. The Brillouin zone is shown in the figure. Find the coordinates of the high symmetry points Γ, X, L, H_1, V, H, P, W:



4. Plot the band structure of beta tin along the lines $\Gamma - X - L - \Gamma - W - H - L$ and along the lines $X - P - V$.

5. Borrowing the code produced by your collegue that plotted the Fermi surface of free electrons, or using the information given in that exercise, find the Fermi energy in beta tin assuming that each tin atom contributes four valence electrons and that there are two electrons (with opposite spin) in each occupied state.

6. Plot the Fermi surface on the ΓXPH and ΓLH_1H planes.

7. Compare your results with Figs. 5 and 7 in Phys. Rev. **182**, 693 (1969).

Problem 2: Free-electron Fermi surface

In this exercise we plot the free-electron Fermi surface. The free-electron Fermi surface of a system with N electrons per cell is a sphere with a volume equal to $N/2$ the volume of the Brillouin zone. The parts of the Fermi surface outside the Brillouin zone are refolded inside so that the shape of the Fermi surface depends on the Bravais lattice. We consider the face centered cubic lattice (fcc) and the body centered cubic lattice (bcc) with one atom per cell. The atom has from 1 up to 4 valence electrons.

In this exercise we want to plot the Fermi surface on a plane in reciprocal space as contours that represent the intersection of the Fermi surface with the plane. After the computation of the free-electron bands $\varepsilon_n(\mathbf{k})$ for a two dimensional mesh of $\mathbf{k}$ points on the plane we use a graphical program (such as `gnuplot`) to identify the contours $\varepsilon_n(\mathbf{k}) = \varepsilon_F$ (ε_F is the Fermi level).

1. Determine the value of the Fermi energy for a system with 1, 2, 3, or 4 electrons per cell with the fcc or the bcc lattice. Write it in units of $\left(\frac{2\pi}{a}\right)^2$ where a is the edge of the conventional cubic cell.

2. Modify the code that plots the free-electron bands to read three vectors $\mathbf{k}_0$, $\mathbf{v}_1$, $\mathbf{v}_2$ that define the plane $\mathbf{k} = \mathbf{k}_0 + \alpha\mathbf{v}_1 + \beta\mathbf{v}_2$ with $0 \leq \alpha \leq 1$, $0 \leq \beta \leq 1$. Moreover the input must read two integers N_1 and N_2, the number of points along $\mathbf{v}_1$ and $\mathbf{v}_2$ respectively.

3. Generate the two dimensional mesh $\mathbf{k}_{n_1,n_2} = \mathbf{k}_0 + \frac{n_1-1}{N_1-1}\mathbf{v}_1 + \frac{n_2-1}{N_2-1}\mathbf{v}_2$. Compute the bands $\varepsilon_n(\mathbf{k})$ on this grid and write them on output files: one band per file. For the fcc lattice you can consider the plane $k_z = 0$ and a size sufficient to contain the Brillouin zone, the plane $k_z = 1$ parallel to the first, and a third plane with $\mathbf{k}_0 = (0,0,0)$, $\mathbf{v}_1 = (1,1,0)$, $\mathbf{v}_2 = (0,0,1)$ in units $\frac{2\pi}{a}$. For the bcc lattice consider the plane $k_z = 0$ and a size sufficient to contain the Brillouin zone, and a plane with $\mathbf{k}_0 = (0,0,0)$, $\mathbf{v}_1 = (1/2,1/2,0)$, $\mathbf{v}_2 = (0,0,1)$ in units $\frac{2\pi}{a}$.

4. Plot the contours of the Fermi surface on these planes. For each lattice show separately the contours of the Fermi surface for 1, 2, 3, and 4 valence electrons.

5. Compare your results with the figures reported in: Phys. Rev. **118**, 1190 (1960) and Ashcroft and Mermin, Solid State Physics (Chap. 9). Describe the main features of the free-electron Fermi surfaces in the fcc and bcc lattices.

In real solids, the Fermi energy must be determined numerically. Having the bands $\varepsilon_n(\mathbf{k})$ in a uniform three dimensional mesh of $\mathbf{k}$ points, such as the one used to plot the density of states, we can use the following relationship (valid at zero temperature):

$$f(\varepsilon_F) = \frac{2}{N_{\mathbf{k}}} \sum_{\mathbf{k},n} \theta(\varepsilon_F - \varepsilon_{\mathbf{k},n}) - N = 0 \tag{2}$$

where N is the number of electrons per cell, $N_{\mathbf{k}}$ is the total number of $\mathbf{k}$ points and $\theta(x)$ is the step function: $\theta(x) = 1$ if $x > 0$, $\theta(x) = 0$ if $x < 0$. The factor two accounts for spin degeneracy. ε_F can be determined searching the zero of $f(\varepsilon_F)$. You can use the bisection method or another method of your choice to find the zero of a function. The bisection method is described in Wikipedia, or in many numerical methods books. See for instance: Press, Teukolsky, Vetterling, and Flannery, Numerical Recipes.

6. Modify the free-electron code that computes the density of states and add a routine that computes the Fermi level. Compute the Fermi level of an fcc lattice with 3 electrons per cell and compare with the analytic result.

7. Study the convergence of the calculated Fermi level as a function of the size of the $\mathbf{k}$-point mesh. Start by implementing the function $\theta(x)$ with a step function and compare with the results that you obtain by approximating $\theta(x)$ as $\tilde{\theta}(x) = \int_{-\infty}^{x} \tilde{\delta}(y)dy$ where $\tilde{\delta}(x)$ is the Gaussian introduced to calculate the density of states. Study the convergence of the Fermi energy with the value of the smearing σ and of the $\mathbf{k}$-point mesh size. (Note that the integral of a Gaussian can be computed with the help of the `erf` function provided by some `fortran` compilers — such as `gcc` — or easily found on the web.

8. Calculate the Fermi level of an fcc and of a bcc lattice with 1, 2, 3, or 4 electrons and compare with the exact result.

Problem 3: Band structure of Arsenic

Elemental arsenic is a metal with a rhombohedral unit cell and two atoms per cell. In this exercise we plot the electronic band structure of metallic arsenic using the empirical pseudopotential method of Cohen and Bergstresser (CB).

The arsenic structure can be described in comparison with the diamond structure. Starting from the fcc lattice of diamond where the side of the conventional cubic cell is a_{fcc} and stretching the cube along a diagonal we obtain a rhombohedral lattice described by the primitive vectors:

$$\begin{aligned} \mathbf{a}_1 &= a_0(\epsilon, 1, 1), \\ \mathbf{a}_2 &= a_0(1, \epsilon, 1), \\ \mathbf{a}_3 &= a_0(1, 1, \epsilon). \end{aligned}$$

When $\epsilon = 0$ and $a_0 = a_{fcc}/2$ we have the fcc lattice of diamond. In arsenic $\epsilon \neq 0$ and $a_0 = 5.510$ a.u.. The positions of the atoms in the unit cell are $\mathbf{d}_{1,2} = \pm u\mathbf{d}$ where $\mathbf{d} = \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$. In diamond $u = 1/8$ while in arsenic $u = 0.226$.

In order to apply the empirical pseudopotential method we need the form factors for arbitrary values of the reciprocal lattice vectors $|\mathbf{G}|^2$ and we can use the function:

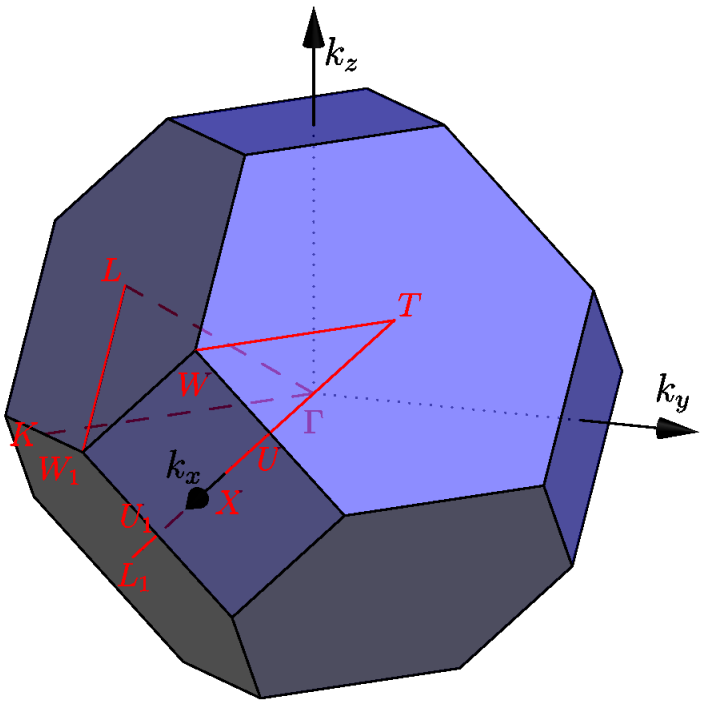
$$U(|\mathbf{G}|^2) = \frac{A_1(|\mathbf{G}|^2 - A_2)}{e^{A_3(|\mathbf{G}|^2 - A_4)} + 1} \tag{3}$$

with $A_1 = 0.0655$, $A_2 = 2.78$, $A_3 = 2.38$, $A_4 = 3.70$. With these values of the parameters and $\mathbf{G}$ in atomic units (1/bohr) the form factors are in Hartree.

1. Determine the value of ϵ using the experimental value of the angle between two direct lattice vectors: $\alpha = 54.167°$.

2. Modify the CB program in order to use Eq. 4 and to introduce the positions of the atoms inside the unit cell of arsenic.

3. Modify the CB program and generate the reciprocal lattice vectors of the rhombohedral lattice of arsenic. The Brillouin zone of this lattice is shown in the figure. Find the coordinates of the points Γ, X, L, L_1, T, W, W_1 U, U_1 and K:



(Hint: The coordinates of each vertex of the BZ can be determined analytically as the solution of a 3×3 linear system, but you can also solve the linear system numerically using, for instance, the `Lapack` routine `DGESV`).

4. Show that only the hexagonal faces perpendicular to the vector $(1, 1, 1)$ are regular, the sides of the other hexagonal faces have two different lengths that are also the sides of the six rectangles. Find these two lengths.

5. To the points found at previous point, add the point $X_1 = (0.5153, -0.5153, 0.0)$. Plot the band structure of arsenic along the lines $X_1 - K - \Gamma - T - W \equiv W_1 - L$ and along the lines $U - X - \Gamma - L_1 - U_1 \equiv U - T$.

6. An approximate value for the Fermi energy is 0.540 Ha. Put the level on the band plot and describe qualitatively the Fermi surface of arsenic.

7. Compare your bands with Fig. 2 of Phys. Rev. **137**, A871 (1965).

Problem 4: Band structure of Antimony

Elemental antimony is a metal with a rhombohedral unit cell and two atoms per cell. In this exercise we plot the electronic band structure of metallic antimony using the empirical pseudopotential method of Cohen and Bergstresser (CB).

Antimony has the same structure as arsenic (see the text of the corresponding exercise) but here we describe it by a rhombohedral Bravais lattice whose threefold symmetry axis is along z. The rhombohedral lattice has the following primitive vectors:

$$\begin{aligned}
\mathbf{a}_1 &= a(\frac{\sqrt{3}}{2}\sin\theta, -\frac{1}{2}\sin\theta, \cos\theta), \\
\mathbf{a}_2 &= a(0, \sin\theta, \cos\theta), \\
\mathbf{a}_3 &= a(-\frac{\sqrt{3}}{2}\sin\theta, -\frac{1}{2}\sin\theta, \cos\theta),
\end{aligned}$$

where $a = 8.486$ a.u., $\cos\theta = \frac{1}{\sqrt{3}}\sqrt{1+2\cos\alpha}$, $\sin\theta = \sqrt{\frac{2}{3}}\sqrt{1-\cos\alpha}$ and $\alpha = 57.23°$. The atoms inside the unit cell are at $\mathbf{d}_{1,2} = \pm u\mathbf{d}$ where $\mathbf{d} = \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$ and $u = 0.2336$.

In order to apply the empirical pseudopotential method we need the form factors for arbitrary values of the reciprocal lattice vectors $|\mathbf{G}|^2$ and we can use the function:

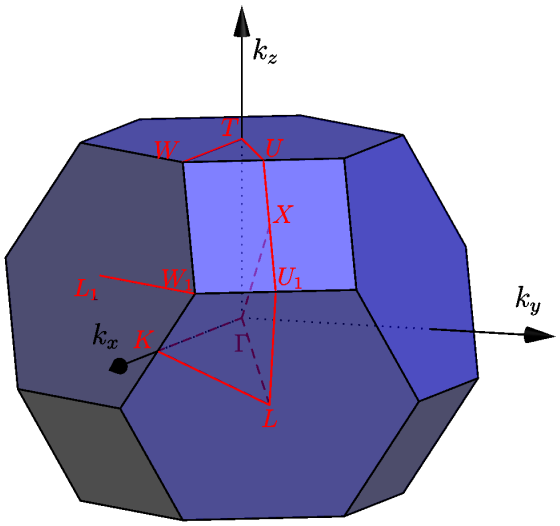
$$U(|\mathbf{G}|^2) = \frac{A_1(|\mathbf{G}|^2 - A_2)}{e^{A_3(|\mathbf{G}|^2 - A_4)} + 1} \tag{4}$$

with $A_1 = 0.0782$, $A_2 = 2.367$, $A_3 = 3.260$, $A_4 = 2.803$. With these values of the parameters and $\mathbf{G}$ vectors in atomic units (1/bohr), the form factors are in Hartree.

1. Show that the angle between any two vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ is α.

2. Modify the CB program in order to use Eq. 4 and to introduce the positions of the atoms in the unit cell of antimony.

3. Modify the CB program in order to calculate the reciprocal lattice vectors of the rhombohedral lattice of antimony. The Brillouin zone is shown in the figure. Find the coordinates of the points Γ, X, L, L_1, T, W, W_1, U, U_1 and K:



(Hint: The coordinates of each vertex of the BZ can be determined analytically as the solution of a 3×3 linear system, but you can also solve the linear system numerically using for instance the `Lapack` routine `DGESV`).

4. Show that only the hexagonal faces perpendicular to the k_z axis are regular and compute the side of the hexagon. The other hexagonal faces have sides of two different lengths that are also the sizes of the six rectangles. Find these two lengths.

5. To the points calculated before add the points $X_1 = (1.0127, 0, 0)$ and $H = (0.1542, -0.0890, 0.3534)$ (in units $\frac{2\pi}{a}$) and plot the band structure of antimony along the lines $X_1 - K - \Gamma - T - W \equiv W_1 - L$ and along the lines $U - X - \Gamma - L - U_1 \equiv U - T - H$.

6. Plot the Fermi level at 0.445 Ha and describe qualitatively the Fermi surface of antimony.

7. Compare your results with Fig. 3 of Phys. Rev. **141**, 565 (1966).