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# WS14/15 Condensed Matter Physics I
# Exercise 1. Crystal Lattices & diffraction

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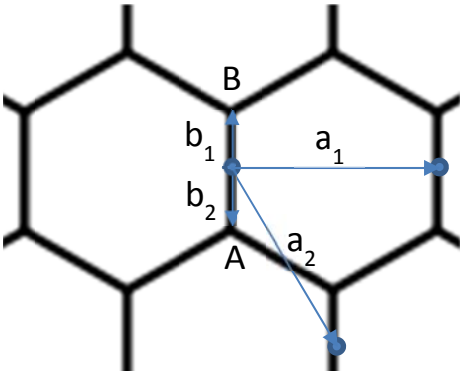
**Notice**: *In solving the proposed exercises clearly motivate the passages to reach the result. The use of clear and compact notation is greatly encouraged, as well as the systematic use of dimensional checks of the expressions and results. When you are asked to "evaluate" something this means to provide a numerical evaluation of the expression. In this case, at times, it might be necessary to indicate a parametrer whose explicit numerical value is not provided, i.e.* $\omega_c = 1.76\ H$ *(Gauss) Hertz. Otherwise specified, all the evaluations are to be given with 3 significant figures.*

## 1.1 Honeycomb lattice. (10 pts)

Let us consider the 2D honeycomb lattice (see Figure 1). Let us indicate the atomic position at the base and the top of the vertical side of the hexagon as A and B.

1. The honeycomb lattice is a Bravais with basis. Which Bravais is that? Choose and indicate the Bravais primitive vectors ($\mathbf{a}_1$ and $\mathbf{a}_2$).

   [The corresponding Bravais lattice is the triangular lattice with a particularly symmetric two-atom basis. If a is the AB distance then the Bravais primitive vector is:




   $a_1 = \left(\sqrt{3}a, 0\right)$ and $a_2 = \left(\sqrt{3}a/2\,, 3a/2\right)$; the two-atom basis is $b_1 = (0, a/2)$, and $b_2 = (0, -a/2)$.]

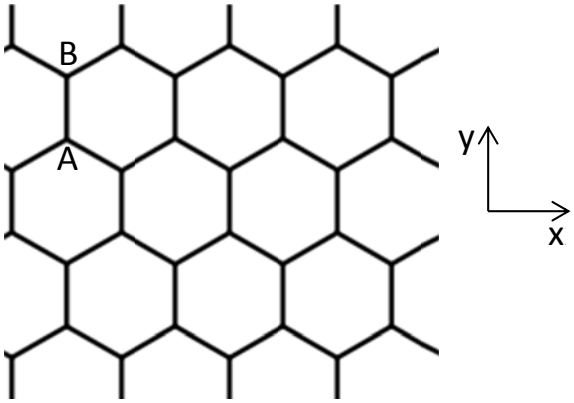



**Figure 1**: Honeycomb lattice.

2. Give the reciprocal of the Bravais lattice and its primitive vectors ($\mathbf{g}_1$ and $\mathbf{g}_2$).

   [the reciprocal lattice is again triangular; using the formula

   $$\mathbf{a_i} \cdot \mathbf{g_i} = 2\pi\delta_{ij}$$

   we obtain $\mathbf{g}_1 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, -\frac{1}{3}\right)$ and $\mathbf{g}_2 = \frac{2\pi}{a}\left(0, \frac{2}{3}\right)$. ]

3. Calculate the geometric form factor $F(\boldsymbol{G})$ relative to the generic reciprocal lattice vector $\boldsymbol{G} = n_1\mathbf{g}_1 + n_2\mathbf{g}_2$. Indicate with $f_A$ and $f_B$the atomic form factors (consider them to be real numbers).

   [from the definition the geometric form factor for the two atom basis is

   $$F(\boldsymbol{G}) = f_A \exp(i\boldsymbol{G} \cdot \mathbf{b}_A) + f_B \exp(i\boldsymbol{G} \cdot \mathbf{b}_B)$$

   where $\mathbf{b}_{A,B}$ are the basis vectors defined in the answer to point 1. By inserting the reciprocal lattice basis vectors we obtain

   $$F(\boldsymbol{G}) = f_A \exp[i\,(n_1 + n_2)\,\pi/3] + f_B \exp[-i(n_1 + n_2)\,\pi/3].]$$

4. Give the general expression of the vector $\boldsymbol{G}$ for which $F(\boldsymbol{G})$ is real, independently from the value of the ratio $f_A/\,f_B$ .

   [Clearly has to be $\exp[i\,(n_1 + n_2)\,\pi/3]$ real. Therefore $\sin[\,(n_1 + n_2)\,\pi/3] = 0$, that is $(n_1 + n_2)\,\pi/3 = m\pi$, with m integer.

5. Consider now $f_A = -f_B$. Are there any $\boldsymbol{G}$ for which $F(\boldsymbol{G}) = \mathbf{0}$? If so, indicate which and draw them on the reciprocal lattice.

   [In this case the structure factor reduces to

   $$F(\boldsymbol{G}) = 2f_A \sin[(n_1 + n_2)\,\pi/3]$$

   The condition is the same $n_1 + n_2 = 3m$. It is a triangular lattice of points with 90 deg rotated and double periodicity.

## 1.2 Powder diffraction on $C_{60}$ crystal. (15 pts)

The solid $C_{60}$ lattice is a face-centered cubic with conventional unit cell of side a.

1. Which is the corresponding reciprocal lattice? What is the side of its conventional unit cell?

   [The reciprocal lattice is a bcc with side $4\pi/a$. ]

2. In a powder diffraction experiment a $C_{60}$ polycristal is placed at a distance L from a flat photographic film, and a monochromatic X-ray beam of wavelength λ is directed to the sample with an initial wavevector $k_0$ perpendicular to the film (See Figure 2). The projection $\Delta\boldsymbol{x}$ of the back-diffracted beams of wavevector k´ are recorded on the film and can be easily measured.

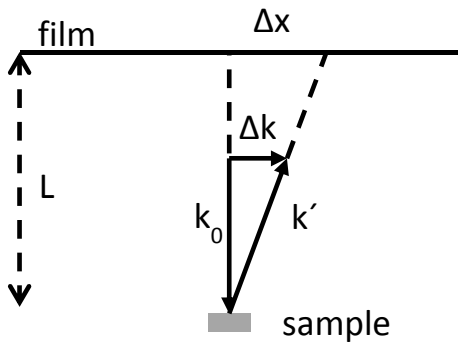



**Figure 2** : Powder diffrraction setup (schematics)

   We know that the diffraction condition prescribes $\Delta\boldsymbol{k} = \boldsymbol{k}' - \boldsymbol{k_0} = \boldsymbol{K}$ and that $|\boldsymbol{k_0}| = \boldsymbol{2\pi}/\lambda$. Consider the approximation in which $\Delta\boldsymbol{k}$ is parallel to the film. Give the formula linking $\Delta\boldsymbol{k}$, $\Delta\boldsymbol{x}$, λ and L. Verify that $2\pi/\lambda\,\Delta\boldsymbol{k} = \boldsymbol{L}/\Delta\boldsymbol{x}$.

   [By analyzing the similar triangles in figure 2 we get $2\pi/\lambda\,\Delta\boldsymbol{k} = \boldsymbol{L}/\Delta\boldsymbol{x}$. Here we approximate the Ewald sphere to the plane.

3. The diffractogram of the sample of $C_{60}$ is recorded in Figure 3. We see they form a square lattice. Assume that it records the diffraction spots relative to the $\boldsymbol{K} = (h, k, 0)$ plane of the fcc reciprocal lattice, with h and k even. Indicate $l_{K_0}$ as the spacing of the observed square lattice, corresponding to the reciprocal lattice spacing of $K_0 = 4\pi/a$. Use the result found in the preceding point to obtain a relation linking $l_{\Delta\boldsymbol{k}}$ and a. By directly measuring on Figure 3 the value of $8l_{K0}$ with a ruler evaluate lattice constant a with its uncertainity. Compare your result with the accepted value of a=14.11±0.02 Å. Consider L=6 cm, λ=1,542 Å and that the diameter of the film in Figure 3 is 12 cm.

   [By direct measurement the diameter and the $8l_{K_0}$ lenght with a ruler and rescaling we obtain a value of $8l_{K_0} = 10.4 \pm 0.4$ cm. The total uncertainity is the double of the measurement uncertainty for each of the experimental uncertainities of the two measurements. In turn, that is given by the sensitivity of the ruler (1 mm) and the experimental uncertainty associated to the width of the diffraction spots (about 1 mm).

By doing the calculations and propagating the error we get $K_0 = 0{,}88 \pm 0.03$ Å$^{-1}$. Given that $K_0 = 4\pi/a$ we obtain finally $a = 14.2 \pm 0.5$ Å. This compares well with the accepted value. Of course the uncertainity is about 25 time greater, partly due to the crude measurement method adopted.]

4. Why it is suggested to measure 8 times $l_{K0}$ and not just $l_{K0}$? Which feature of the difractogram ultimately limits the uncertainity of the lattice constant?

   [To reduce the relative uncertainity of the measure, which doesn't depend on the measurement itself. The spot width is the ultimate limit in the uncertainity, although it can be greatly reduced by employing high resolution photography and fitting the spot shape by determining precisely their position. ]

5. At a closer look at Figure 3 we see that the (2,0,0) diffraction peak is very weak. Assume that the charge distribution of a fullerene ball is represented by a surface charge on a sphere of radius R=3.5 Å: $\rho(\mathbf{r}) = A\delta(r - R)$. Here $r = |\mathbf{r}|$. After finding the value of the constant A in units of the electron charge e, calculate the form factor of the $C_{60}$ molecule in this approximation. Show that the form factor of the (2,0,0) peak is indeed much less than that of the (2,2,0) peak. ( *Hint: to solve the integral consider transforming in spherical coordinates* )

   [By normalizing in spherical coordinates anre remembering the property of the delta function we obtain $A = Q/4\pi R^2$ Q=6x60=360e.
   The form factor is:

$$F(\mathbf{k}) = A\int \delta(r-R)e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r} = 2\pi A\int_{-1}^{1} d\cos\phi \int_{0}^{+\infty} dr r^2\,\delta(r-R)\,e^{ikr\cos\phi}$$

$$= 4\pi A R^2 \frac{\sin kR}{kR}$$

   Here we consider that the z axis is parallel to k (always possible). We see that for k=(2,0,0) kR=3.1, i.e. close to pi, a node for sin. whereas for k=(2,2,0) we obtain kR=4.4. the ratio of the two form factor is about 0.02.]

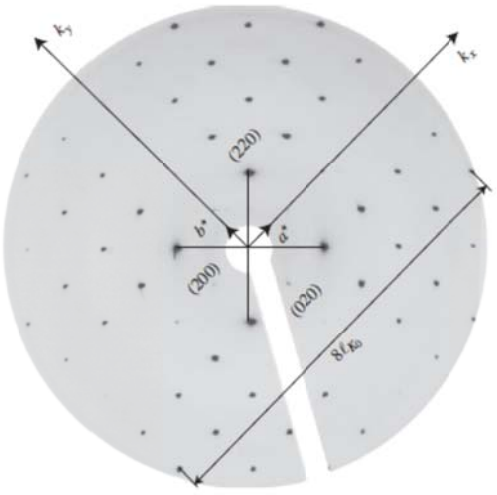



**Figure 3:** Powder diffractogram of $C_{60}$. The real diameter of the film is 12 cm.

## 1.3 Stripe order in a cuprate compound. (8 pts)

The common building block for most high temperature (high Tc) superconductors are copper oxide layers, as depicted in Figure 3(a). Considering a single isolated layer, assume the distance between copper atoms (filled circles) is a. In first approximation the layers have a fourfold symmetry; the crystal is tetragonal.

1. Sketch the Bravais lattice and indicate a possible set of primitive vectors for this crystal. What is the unit cell, and what is the basis?

   [See figure 4(a). Square lattice with three atom basis.]

2. In LaCuO4 once discovers, at closer inspection, that the CuO2 lattice is actually not flat, but that the oxygen atoms are moved a small amount out of plane ("up"and "down") in an alternating fashion [in Figure 3(b) $\oplus$ means up and $\ominus$ means down), forming diagonal striped undulations. What is the primitive cell and lattice spacing for the crystal? What is the reciprocal lattice? Describe (qualitatively) what happens in the X-ray diffraction pattern as the distortion is decreased gradually to zero. (*Hint: Sketch the corresponding Reciprocal lattices*)

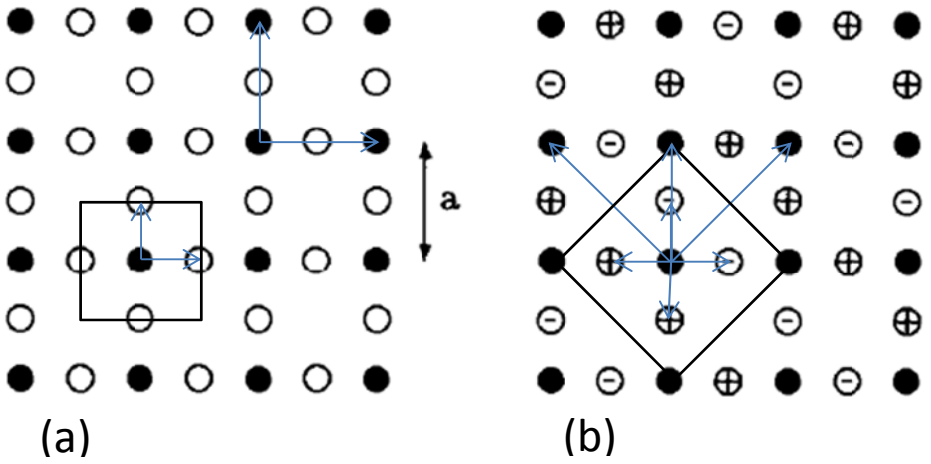
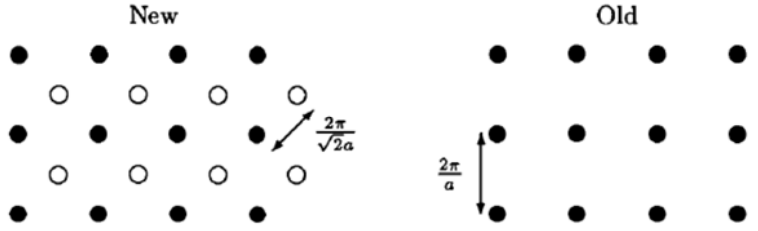



**Figure 4** (a) CuO2 lattice; (b) distorted CuO2 lattice.

[See figure 4(b). Square lattice rotated 45 degrees with respect to the undistorted one with lattice constant $\sqrt{2}a$, with fia five atom basis.



The reciprocal lattices are both square, each 45 deg rotated with respect to the direct lattice. Upon reducing the distortion the periodicity is reduced (increased) by a factor sqrt(2) in the direct (reciprocal) space. By comparing the two lattices is easy to see that the white dots will disappear. It is also possible to come to the same conclusion by calculating the geometrical form factor and imposing the same form factor for both + and – atoms. This mimics the limit of vanishing distortion.]