

# Experimental problem (20 points)

### Polycrystals and monomolecular layers

Experimental problem suggests you that using only one calibrated measuring instrument – a stopwatch – and a few other simple objects and devices, to determine various characteristics of polycrystalline gold, of the monolayers of stearic acid, of the carbon atom and to estimate the value of a fundamental physical constant.

Fill corresponding boxes in attached answers sheets with results of all your taken measurements and all your answers to work tasks.

#### Experimental apparatus

To solve experimental problem, you may use:

- 1. A stopwatch
- 2. A sheet of paper marked with a grid (marked lines are equidistant but the distance between them is unknown).
- 3. A sheet of clear plastic that is marked with the same kind of grid as the paper.
- 4. A plummet.
- 5. A plate of expanded polystyrene that can be fixed on the work table.
- 6. A pin.
- 7. An electron diffraction image obtained for a polycrystalline layer of gold.
- 8. Two test tubes, one of which contains a solution. Do not drink the liquid in the tube!
- 9. Pipette
- 10. A sheet of transparent plastic.
- 11. Several sheets of white paper.
- 12. Marker.
- 13. Wipes.
- 14. A vessel for collection of waste liquids

#### It is forbidden the use of tools or measurement tools that are not included in the above list.

#### Do not drink the liquid in the tube!

It is not required an error calculation for none of working tasks.

### 1. Task A

Task A suggests you to use some of the items available, to determine the distance in millimeters between the lines on the paper sheet (2) and the plastic sheet (3). This distance is called hereinafter arbitrary unit of length, a.u.. The gravitational constant value is  $g = 9.8 m \cdot s^{-2}$ .

#### 1.1. Requirements for task A

**A.1.** Designs an experiment to determine, in millimeters, the distance between the lines on the paper sheet (2) and the plastic sheet (3) using some of the available items. Fill the appropriate box in the answer sheet with a brief description of the experimental method that you propose.

**A.2.** Make measurements as in proposed method, and record measured data in the appropriate tables in the answer sheet.

**A.3.** Use a suitable processing of data obtained from measurements and determine (in mm.) the value of arbitrary unit of length - the distance between lines on the sheet of paper and plastic sheet. In the appropriate box in the answer sheet, specify the method that you have chosen for processing data, describe the calculations for determining the value of a.u. in millimeters and write the result in the format #, # mm.



In the following you will use grid of paper sheet and plastic sheet for measuring the distance in the next working tasks.

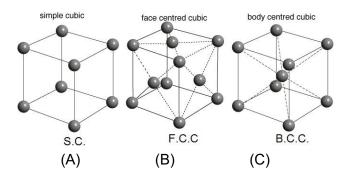
### 2. Task B

In this task it is proposed to analyze diffraction image which you were made available and to respond to the requirements of this part of the experimental problem.

We recommend you to carefully read the paragraph 2.1.

#### 2.1. About polycrystals's electron diffraction image.

For crystalline substances, which are stable solids, arrangement of the constituents (atoms or molecules) is characterized by an orderly position in space. Regular structure of a crystalline solid is characterized by the existence of a periodicity that manifests itself by reproducing its structure after equal distances along any straight line passing through atoms or molecules belonging crystal. A parallelepiped built on three fundamental vectors  $\vec{a}_i$  is called a unit cell of the crystal lattice. By translating with any combination of fundamental vectors of the unit cell can reconstitute the entire crystal lattice. Between the crystal lattices, some have a cube as elementary cell. Side of the cube, *a*, is called network constant.



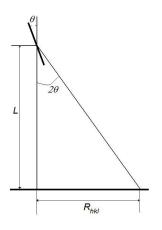
In the above figure they are shown three types of elementary cubic cells. Cell of Simple Cubic network, S. C., (A), has atoms at the apexes of a cube of side a. Cell of Face Centered, F.C.C., (B), has atoms in the apexes of cube (as S.C.) plus six atoms in the centers of the cube's faces. Cell of body centered cube, B.C.C., (C), has atoms arranged in apexes of a cube of side a - as S. C. plus an atom at the intersection of volume diagonals.

Most metals crystallize into one of three cubic structures described above. Inside a crystal can be considered different crystal planes. These are parallel planes, identical filled with atoms (or molecules), separated by equal distances – the interplanar spacing (interplanar distance).

Interplanar spacing is a characteristic of crystalline planes family. Interplanar distances for the cubic networks have expression  $d_{hkl} = a/\sqrt{h^2 + k^2 + l^2}$ ; in expression h, k, l are three integers - indices of crystalline planes family. When it is irradiated with radiation having a wavelength comparable to the interplanar distance, the regular structure of crystalline planes, produces diffraction directions separated from the incident radiation direction by angles  $2\theta$  as shown in Figure 1. Due to geometric properties, certain combinations of plane indices lead to the cancellation of the amplitude of diffracted radiation; accordingly, the respective planes family do not give maximum of diffraction. Thus, in the diffraction image of a substance which crystallized in the structure B.C.C. exists diffraction maximum only of families of planes whose indices sum is an even number: (0,1,1), (2,0,0), (2,1,1), (2,2,0), etc. In the diffraction image of a substance which crystallized in the structure F.C.C. exists diffraction maximum only of families of planes whose indices have the same parity (all odd or all even: (1,1,1), (2,0,0), (2,2,0), (3,1,1), etc. In the diffraction image of a substance which crystallized in the structure S.C. it exists diffraction maximum for all families of planes whatever indices they have: (1,0,0), (1,1,0), (1,1,1), (2,0,0), etc.



Above, the sets of crystalline indices were given in order of decreasing of corresponding interplanar distances.



#### Figure 1: The formation of the electron diffraction image of the crystal plane of indices (hkl)

Using electron microscope only as generator of an electron beam, can be done the diffraction of electrons on thin conductive polycrystalline layer. Scheme of diffraction experiment is shown in Figure 1. Monoenergetic electron beam represented by the vertical line, falls on a thin layer composed of numerous small crystalline grain oriented chaotic. If the beam falls on one of the crystals at the appropriate angle for diffraction on crystalline plane having indices (h,k,l) (represented in the figure by short, thickened, oblique), then on the direction that makes angle  $2\theta$  with the direction of the incident radiation a diffracted beam appears. Diffraction directions due to planes family (h,k,l) from all the small crystals determines a cone of  $2\theta$  angle. In the experiment, at the distance *L* from the sample studied and perpendicular to the initial direction of the electron beam is arranged a photographic plate. The cone of directions of diffraction causes the apparition on the photographic plate of a circle of radius  $R_{hkl}$ . Obvious,  $tg(2\theta) = R_{hkl}/L = D_{hkl}/(2L)$ . In expression,  $D_{hkl}$  is the diameter of the circle appeared on the photographic plate due to diffraction determined by the planes family of indices (h,k,l) from small crystals in the sample.



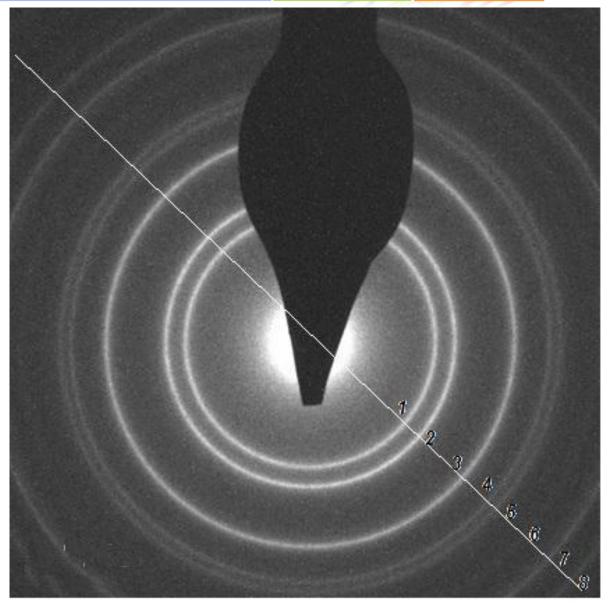


Figure 2: Electron diffraction image of a polycrystalline thin gold foil. Diffraction circles are numbered.

#### 2.2. Requirements for task B

For each of the requirements in this task, write all the answers in the appropriate boxes in the Answer Sheet.

**B.1**. Calculate the de Broglie wavelength  $\lambda_e$  of the electrons in the beam diffracted; acceleration voltage of electrons is U = 100 KV. You can use the following values of physical constants: the rest mass of the electron  $m_e = 9,11 \times 10^{-31} kg$ , the electric charge of the electron  $e = 1,60 \times 10^{-19} C$ , the speed of light in vacuum  $c = 3,00 \times 10^8 m \cdot s^{-1}$ , the Planck constant  $h = 6,63 \times 10^{-34} J \cdot s$ .

**B.2**. Determine the difference between the de Broglie wavelength of electrons calculated relativistic and the de Broglie wavelength of electrons calculated non relativistic.

**B.3**. Demonstrates that for attached diffraction image, between the diameters  $D_{hkl}$  of diffraction circles and interplanar spacing  $d_{hkl}$  of the crystal planes families responsible for the appearance of these maxims it is the relationship

$$D_{hkl} \cdot d_{hkl} = C \cdot \lambda_e \cdot L$$

(1)



and specify the value of constant C.

B.4. Write indices of crystalline planes responsible for the appearance of the first eight diffraction circles (in ascending order of their diameters so interplanar distances in descending order) for structures S.C., F.C.C., B.C.C.. Assume that the side length of the unit cell is *a*. For each structure calculates the ratio of the length maximum interplanar distance and length of other interplanar distance and write the results in appropriate table.

Diffraction image of a very thin film of polycrystalline gold that was made available for you, is enlarged in aria for **5.3** times. For the experiment conducted  $L = 75 \, cm$ .

**B.5.** Using paper sheet calibrated to task A, measure diameters of diffraction circles; put the results in appropriate table. Write in the appropriate column of the table in the Answer Sheet the ratio of length of measured diameter of circles and measured diameter of the smallest circle.

B.6. Analyzes the diameter sizes and relation (1), together with results achieved in the task B.4. and decides whether the crystal structure of gold is S.C., F.C.C., or B.C.C.

B.7. Plot the dependency between inverses of interplanar distances of planes producing crystalline diffraction circles (measured in units equal to constant a of network) - and actual diameters of the corresponding diffraction circles in the image made available. Keep in mind that the image you received is enlarged.

B.8. Use a graphical analysis of the experimental data set represented in the task B.7. properly using equation (1) and determines the constant network of gold  $a_{Au}$ .

### 3. Task C

This task proposes you to determine properties of droplets of solution of stearic acid in organic solvent. Spread onto the surface of water in a watch glass, these droplets form a monomolecular layer. Using a given data set, you will determine the properties of monolayers.

For each of the requirements in this task, write all the answers in the appropriate boxes in the Answer Sheet.

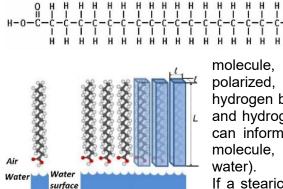
We recommend you to carefully read the paragraph 3.1.

#### 3.1. About the formation of a monomolecular layer.

Stearic acid is a saturated fatty acid consisting of a chain of 18 carbon atoms. It is a "waxy solid" with the chemical formula C<sub>17</sub>H<sub>35</sub>CO<sub>2</sub>H. The Lewis structure of stearic acid (a diagram showing the bonds between the molecule's atoms) is presented below. Lines indicate covalent bonds. Each line represents

> н н

> > ċ-н



a pair of electrons which the two atoms are "sharing". The acidic character of the substance, and thus the name of "acid", is due to the presence of the carboxylic group COOH at the left end of its chain. This part of the

molecule, which we can informally call its "head", is electrically polarized, and can therefore attach to water molecules through hydrogen bonds. Thus, it is called hydrophilic. The long chain of carbon and hydrogen atoms that form the right part of the molecule, which we can informally call the "tail" of the molecule, is the fatter part of the molecule, which is non-polarizable and thus hydrophobic (repelling water).

If a stearic acid molecule is placed on the water surface, its polarized head will attach to the water molecules, while the rest of the stearic acid

molecule - its non-polarizable "tail" - will not be attracted by the water molecules, but rather by the neighboring stearic acid molecules. Therefore, these interactions cause the stearic acid molecules to align on the water surface, with their "heads" on the water's surface and their non-polarized "tails" facing upwards, away from the water surface. The picture on the left illustrates the combined effect of the forces acting between the hydrophobic "tails" of the molecule and the forces acting between the



hydrophilic "heads" and the water molecules. These two effects produce a preferential configuration of the stearic acid molecules on the surface of water, forming a monomolecular layer.

The picture presents a 3-D representation of stearic acid molecules. The small circles represent individual atoms (black circles represent carbon atoms, white circles represent hydrogen atoms, and red circles represent oxygen atoms), while the lines represent bonds between the atoms. As presented in the picture, we will consider that a stearic acid molecule occupies a  $L \times \ell \times \ell$  parallelepiped. If a few stearic acid molecules are placed on the water surface, they will form a layer with height equal to the height of one individual molecule. If, instead, many stearic acid molecules are placed on the water surface, they could pile up on top of each other, yet the first molecules will always form a monomolecular layer.

The elevation of a stearic acid molecule with respect to the water surface is equal to the length or the molecule. This length is smaller than the wavelengths of the visible spectrum. Therefore, light shone upon the layer would not interfere with the molecule, making the monomolecular layer non-visible to the human eye. However, by adding enough stearic acid molecules, and allowing them to pile up, producing a thicker layer, the thickest part of the layer can become visible. Alternatively, the layer can also be observed in the presence of floating talcum particles. The expanding stratum of stearic acid clears the talcum particles, leaving a circular area free of floating talcum particles.

You may assume the following quantities regarding the stearic acid are known: its molar mass is  $\mu_s = 284 \text{ kg}/\text{kmol}$ , density  $\rho = 941 \text{ kg}/\text{m}^3$ , the molecule's sectional surface is  $\ell^2 = 21 \times 10^{-20} \text{ m}^2$ . The concentration of the stearic acid solution in the volatile solvent is  $c = 0.02 \text{ kg}/\text{m}^3$ . The solvent's density is  $\rho_{solvent} = 878 \text{ kg} \cdot \text{m}^{-3}$ 

### 3.2. Requirements for task C

#### C.1. Measurements on droplets

From the set of tools found on the workbench you should use: paper sheet with arbitrary units, marker, pipette and two test tubes and their support. *Test tubes have not a flat base.* One of the test tubes contains the solution of stearic acid in an organic solvent, and the other is empty.

**C.1.1.** Describe, briefly, a method by which you may determine the volume of a drop delivered by pipette.

**C.1.2.** Using the objects available, determines (in  $m^3$ ) the volume  $V_p$  of a drop of solution.

**C.1.3.** Using paper sheet calibrated in task A, measure the inner diameter  $d_{pipeta}$  of the pipette tip. Using results from C.1.2. estimates value of the surface tension coefficient  $\sigma$  of the solution.

**C.1.4**. Determine (in  $m^3$ )  $V_s$  volume of stearic acid in a solution drop, whose volume  $V_p$  you have determined in task **C.1.2**.

#### C.2. Measurements on monomolecular layers

If water is placed in a watch glass and few drops of solution studied in **C.1** are spread on the surface of water, a monomolecular layer of stearic acid remains (after the solvent evaporation) on the surface of the water - whose diameter  $D_s$  can be measured. In the neighboring picture can be seen the described situation.

The table below presents data on the diameter  $D_s$  of

the layer appeared when on water surface is dripping a number  $N_s$  of drops of stearic acid.





N <sub>s</sub> (#)	5	7	9	11	13	15	17
$D_s$ (cm)	4,9	5,7	6,5	7,2	7,9	8,5	9

**C.2.1.** Properly analyzing the data in the table above determine the expression of height of the layer of stearic acid and its numerical value.

**C.2.2.** Considering that 18 carbon atoms of stearic acid molecule are equidistant and disposed vertically above the water surface, determine the expression of the height of the space occupied by a carbon atom and its numerical value.

#### C.3. Estimation of Avogadro's number

**C.3.1**. Determine the number  $N_m$  of molecules in each of the layers described in **C.2**.

**C.3.2.** Estimate numerical value of Avogadro's number.

© Problem written by:

Prof. dr. Delia DAVIDESCU Prof. dr. Ioana STOICA Prof. dr. Dan Ovidiu CROCNAN Conf. univ. dr. Adrian DAFINEI



# Answer Sheet

# Experimental Problem (20 points)

Polycrystals and monomolecular layers

1. Task A

A.1 Brief description of the experimental method proposed



A.2. Results of measurements made - tables with data collected from measurements

1.50p



### A.3. Processing method of collected experimental data

Determining the value in millimeters of arbitrary unit of length and writing the result in # # mm format.

1.50p



# 2. Task B

**B.1**. Calculation of de Broglie wavelength  $\lambda_e$  of the electrons in the diffracted beam



**B.2**. Determining the difference between de Broglie wavelength of electrons calculated relativistic and de Broglie wavelength of electrons calculated non relativistic.

0.50p



**B.3**. Demonstration of the fact that for attached diffraction image, between the diameters  $D_{hkl}$  of diffraction circles and interplanar spacing  $d_{hkl}$  of the crystal planes families responsible for the appearance of these maxima it is the relationship  $D_{hkl} \cdot d_{hkl} = C \cdot \lambda_e \cdot L$  Specification of the value of constant *C*.



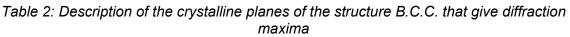
**B.4**. Fulfilling of tables of indices of crystalline planes responsible for the appearance of the first eight diffraction circles for structures S.C., F.C.C., B.C.C..

			S. C. Structu	ire.			
- ab	le 1: Descrit	otion of the crvs	talline planes of	the struct	ure S.C. that o	give diffraction	
			maxima				
۸r.	(h,k,l)	$h^2 + k^2 + l^2$	$\sqrt{h^2 + k^2 + l^2}$	$d_{_{hkl}}$	$a/d_{_{hkl}}$	$d_{100}/d_{hkl}$	
2							
3							
<u> </u>							
5							
6							
7							
8							



#### B.4. - continuation

B.C.C. structure

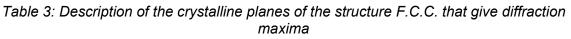


Nr.	(h,k,l)	$h^2 + k^2 + l^2$	$\sqrt{h^2 + k^2 + l^2}$	$d_{_{hkl}}$	$a/d_{hkl}$	$d_{110}/d_{hkl}$
1						
2						
3						
4						
5						
6						
7						
8						



#### B.4. - continuation

F.C.C. Structure



Nr.	(h,k,l)	$h^2 + k^2 + l^2$	$\sqrt{h^2 + k^2 + l^2}$	$d_{_{hkl}}$	$a/d_{hkl}$	$d_{111}/d_{hkl}$
1						
2						
3						
4						
5						
6						
7						
8						
		I				



**B.5.** Measuring and fulfilling of table 4 with data about diameters of diffraction circles and about ratios of length of measured diameter of circles and measured diameter of the smallest circle

4: Description	Diameter		Diameter	
number	$\langle u.a. \rangle$	Di D1	$\langle cm \rangle$	
				1.00p

B.6. Analyze of results and decision whether the crystal structure of gold is S.C., F.C.C., or B.C.C..C

	Tab	ole 5			
$d_{100}/d_{hkl}$	$d_{\scriptscriptstyle 110}/d_{\scriptscriptstyle hkl}$	$d_{\scriptscriptstyle 111}/d_{\scriptscriptstyle hkl}$	$\frac{Di}{D1}$		
CS	CVC	CFC			
				•	
					1.00p
					1.000



**B.7.** Plot of dependency between inverses of interplanar distances of planes producing crystalline diffraction circles (measured in units equal to constant a of network) - and actual diameters of the corresponding diffraction circles in the image made available.

	7	Table 6						
Nr.	$a/d_{hkl} = \sqrt{h^2 + k^2 + l^2}$	$D_{hkl}\langle cm angle$ (enlarged image)	$\begin{array}{ c c }\hline D_{hkl}\langle cm \rangle \\ \hline (real image) \end{array}$					
1								
2								
3								
04								
5								
6								
7								
8								



**B.8.** Results of usage of graphical analysis of the experimental data set represented in the task **B.7.** - properly using equation (1) and determination of the network constant of gold  $a_{Au}$ .



3. Task C

# C.1. Measurements on droplets

**C.1.1.** Brief description of method used to determine the volume of a drop delivered by pipette.

1.00p

**C.1.2.** Determination (in  $m^3$ ) of volume  $V_p$  of a drop of solution



**C.1.3.** Estimation of value of the surface tension coefficient  $\sigma$  of the solution

1.00p

**C.1.4**. Determination (in  $m^3$ ) of  $V_s$ , volume of stearic acid in a solution drop, whose volume  $V_p$  you have determined in task **C.1.2**.

1,00p



# C.2. Measurements on monomolecular layers

**C.2.1.** Determination of expression of height of the layer of stearic acid and its numerical value.



**C.2.2.** Determination of expression and of numerical value of  $H_c$ , the height of the space occupied by a carbon atom.

0.50p

### C.3. Estimation of Avogadro's number

**C.3.1**. Determination of number  $N_m$  of molecules in each of the layers described in **C.2**.

0.50p

**C.3.2.** Estimation of numerical value of Avogadro's number.

0.50p