EXPERIMENT 1 – LAB GUIDE
Bravais Lattices, Crystal Structures and X-Ray Diffraction Simulations

1. INTRODUCTION

1.1 Bravais Lattice and Primitive Unit Cells

One of the fundamental concepts in the description of a crystalline solid is the **Bravais lattice**, which specifies how the basic component units (atoms, groups of atoms or molecules) are repeated periodically throughout the crystal.

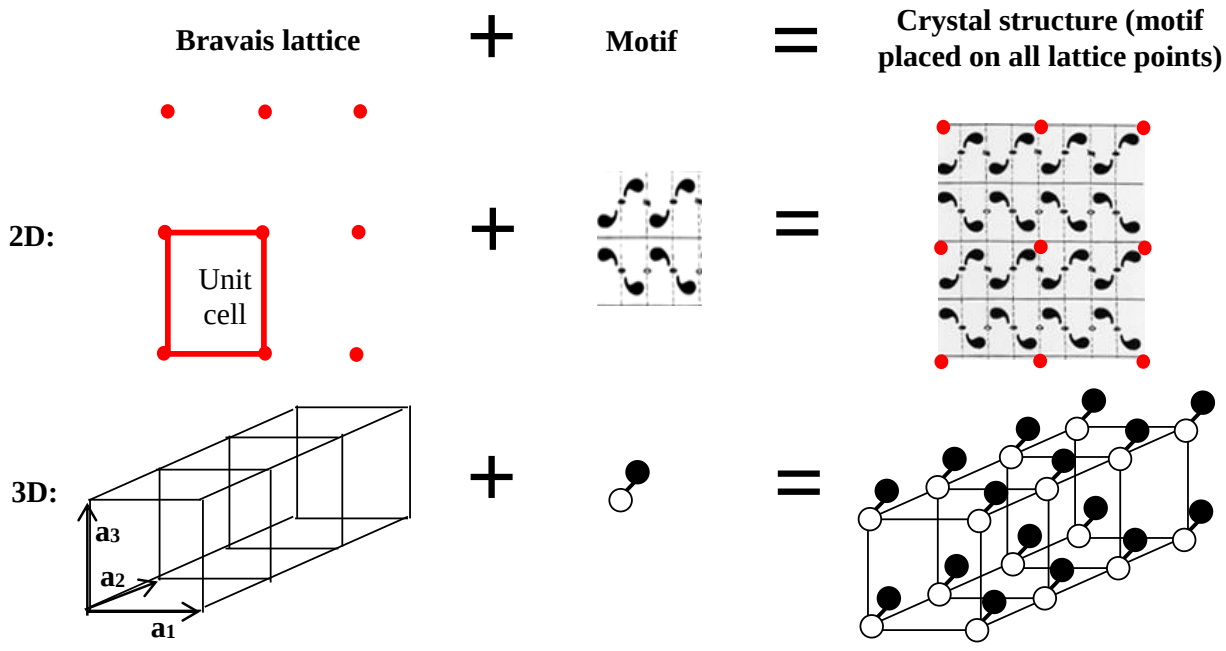
A Bravais lattice is the set of all points whose position vector is of the form $\mathbf{R} = n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3$ where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are three linearly independent vectors and n_1, n_2 and n_3 are integers.

The $\mathbf{a}_i$ vectors are called primitive vectors or fundamental translations of the Bravais lattice. When a Bravais lattice is translated by a vector of the form $\mathbf{R} = n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3$, it coincides with itself. The translational invariance of the Bravais lattice is its most important characteristic.

A **primitive unit cell** of a Bravais lattice is a volume of space such that, when repeated on all of the lattice points, it fills the entire space without gaps and without overlapping. This condition implies that a unit cell contains only one lattice point. However, there is an infinite number of arbitrary primitive cells, all of which have the same volume.

It is always possible to choose a region (which may contain more than one lattice point) which, translated by a subset of grid vectors, fills the space without gaps or overlaps. Such (non-primitive) unit cells can be chosen so that they better reflect the symmetry of the grid and are easier to work with.

The structure of a real crystal is described by two things: 1) the underlying **Bravais lattice**, and 2) the distribution of atoms within the primitive cell (also known as the **motif**). The crystal lattice thus consists of copies of the same fundamental unit (or motif) located at all points of the Bravais lattice as shown below:



1.2 Symmetry Operations

In addition to translation symmetry, which is common to all Bravais lattices, a lattice may remain invariant in other types of transformations. The most important of these are:

- **Rotation around an axis**: a lattice has an *n*-fold axis of symmetry when it coincides with itself when rotated by an angle $2\pi/n$ around this axis. Due to the requirements of translational symmetry, only two-fold (2), three-fold (3), four-fold (4) and six-fold (6) axes are possible in a Bravais lattice.
- **Reflection with respect to a plane**: a lattice has a plane of symmetry when it coincides with its mirror image with respect to this plane.
- **Inversion with respect to a point**: a lattice has a centre of inversion when it coincides with its inverted image with respect to a point.

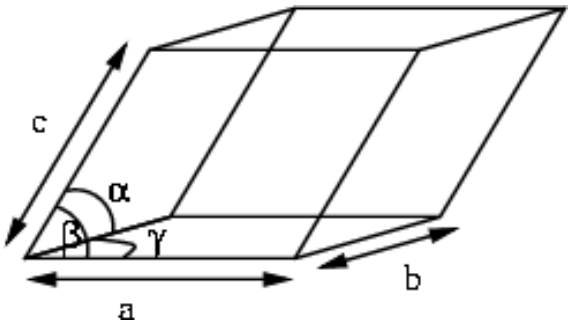
Some lattices can be invariant when subjected to a combination of two symmetry operations without being invariant in respect of either of them individually.

There are other transformations resulting from the combination of two of the above or of one of the above together with a translation that does not belong to the Bravais lattice:

- **Screw axis**: the lattice is invariant to an *n*-fold *rotation* followed by a *translation* not belonging to the Bravais lattice.
- **Glide plane**: the lattice is invariant to a *reflection* with respect to a plane followed by a *translation* not belonging to the Bravais lattice.

The set of symmetry transformations that leave **all points** of a Bravais lattice invariant is called the **space group** of the lattice. The set of symmetry transformations that leave the lattice invariant while keeping **a single point** of the lattice fixed is called the **point group** of the lattice.

Depending on the symmetry of the unit cell, Bravais lattices have more or fewer additional symmetry elements. There are 7 crystalline systems, each with a specific point group. There can be different Bravais lattices with the same point group, with a total of 14 crystalline Bravais lattices. If we characterise each lattice by its unit cell, which is a parallelepiped with sides a, b, c and with angles between edges α, β, γ, the different systems can be obtained, going from the cube (cell with maximum symmetry) to the irregular parallelepiped:



CRYSTAL SYSTEM	DIMENSIONS	BRAVAIS LATTICE*
Cubic	a=b=c $\alpha=\beta=\gamma=90^o$	Primitive (P) or Simple (S) Body-centred(I) Face-centred (F)
Tetragonal	a=b≠c $\alpha=\beta=\gamma=90^o$	Primitive (P) or Simple (S) Body-centred(I)
Orthorhombic	a≠b≠c $\alpha=\beta=\gamma=90^o$	Primitive (P) or Simple (S) Body-centred(I) Face-centred (F) Base-centred (C)
Rombohedral (also known as Trigonal)	a=b=c $\alpha=\beta=\gamma\neq90^o$	Primitive (P) or Simple (S)
Hexagonal	a=b≠c $\alpha=\beta=90^o$ $\gamma=120^o$	Primitive (P) or Simple (S)
Monoclinic	a≠b≠c $\alpha=\beta=90^o$ $\gamma\neq90^o$	Primitive (P) or Simple (S) Base-centred (C)
Triclinic	a≠b≠c $\alpha\neq\beta\neq\gamma\neq90^o$	Primitive (P) or Simple (S)

*Primitive (P) and Simple (S) are equivalent. Different sources use different names.

If the symmetry of the crystal structure motif itself is introduced (so far, we have only referred to the Bravais lattice), up to 32 point groups and 230 space groups can be counted.

1.4 X-ray Diffraction

Since the wavelengths of X-rays are similar to the interatomic distances, when X-rays interact with crystalline solids, a diffraction phenomenon occurs. The resulting diffraction pattern allows us to study the crystal structure (i.e., repeating atomic arrangement) of the crystalline solids.

1.4.1 Bragg's Law.

In 1913, the Braggs[1] observed that crystalline solids diffracted X-rays, producing patterns characterised by very intense peaks in particular directions. In their interpretation of this phenomenon, the Braggs assumed that a crystal must consist of parallel planes of atoms separated by an interplanar spacing, *d*. The Braggs' key idea was that the X-rays *reflected* from these parallel planes and then optically interfered with each other. The optical path difference (shown in pink in the figure below) between two rays reflected from adjacent planes will be $2d\cdot\sin\theta$, where θ is the angle of incidence. When the optical path difference is equal to an integer number, n, of wavelengths, λ, the interference is constructive, and a diffraction peak is observable. The condition for constructive interference is therefore Bragg's Law:

$$2d\cdot\sin\theta = n\lambda. \qquad [1.1]$$

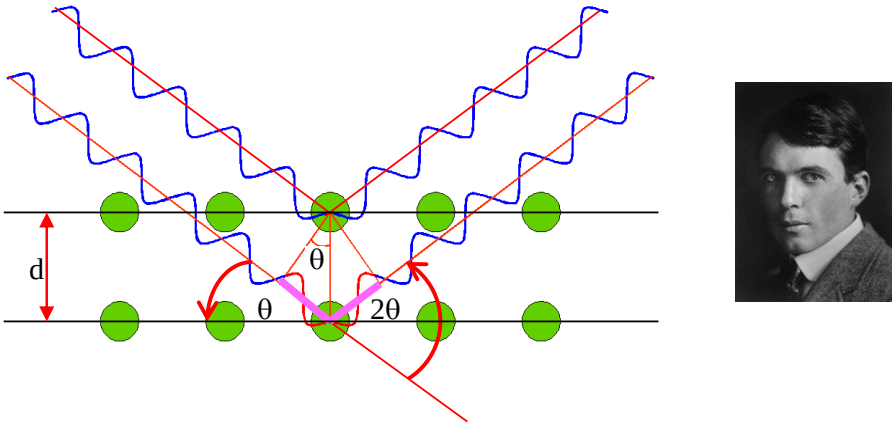


Figure 1.1: Bragg's model. Photo: W. L. Bragg who won the Nobel Prize in 1915 at the age of only 25.

1.4.2 The Laue equations

In order to explain the phenomenon of X-ray diffraction, Von Laue thought instead that the electrons of each atom in the crystal, when subjected to X-ray radiation, become emitters of X-rays of the same frequency (and wavelength) in all directions, i.e., each atom elastically scatters the X-rays. There will be directions in which the scattered rays are in phase, leading to constructive interference and an observable peak. Let's imagine two different atoms (shown in figure 1.2). Let **n** be the unit vector in the incident direction and **n'** be the unit vector in the direction corresponding to a diffraction peak.

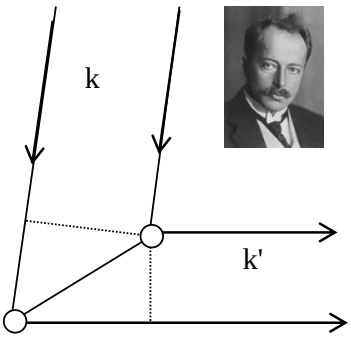


Figure 1.2

[1] The father and son team of W. H. Bragg and W. L. Bragg.

Evidently, the wave vector will be: $\vec{k} = \frac{2\pi}{\lambda}\vec{n}$; $\vec{k'} = \frac{2\pi}{\lambda}\vec{n'}$

The condition for the interference to be constructive is, in this case:

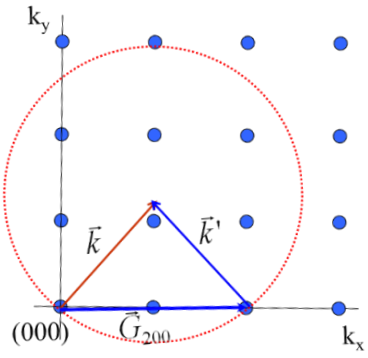
$$d\cos\theta + d\cos\delta = m\lambda \qquad \left(\frac{2\pi}{\lambda}\vec{n'} - \frac{2\pi}{\lambda}\vec{n}\right)\cdot\vec{d} = 2\pi m$$

$$\vec{n'}\cdot\vec{d'} - \vec{n}\cdot\vec{d} = m\lambda \qquad \text{or equivalently} \qquad \left(\vec{k'} - \vec{k}\right)\cdot\vec{d} = 2\pi m \qquad [1.2]$$

For the set of atoms, the vector ***d*** will take as values all the vectors of the **direct lattice, *R***. (The *direct lattice* is the *real space lattice*, where *d* is the inter-planar spacing.) Therefore, for there to be constructive interference, the relation (***k***' - ***k***)·***R*** = 2πm must be satisfied for all ***R***. This condition is equivalent to saying that ***k***' - ***k*** must be a vector of the **reciprocal lattice**.

Since there is a correspondence between **reciprocal lattice vectors** and **families of crystal planes**, both formulations are equivalent.

1.4.3 Ewald's Sphere



There is a geometrical construction (the Ewald sphere, shown above) which makes it possible to predict which diffraction peaks will appear for a given crystal and a given incident radiation (X-ray wavelength). The above figure shows the reciprocal lattice and the wave vector ***k*** of the incident radiation, which is plotted from the origin. From its end a sphere of radius equal to its modulus is drawn. If this sphere contains a point ***G*** of the reciprocal lattice, there will be a peak in the X-ray spectrum in the direction ***k***'= ***G***-***k***.

Naturally, for arbitrary radiation travelling in an arbitrary direction, it is unlikely that this condition will be fulfilled, but this construction suggests several methods of achieving it.

Thus, in the rotating crystal method (also known as the angle-dispersive method), monochromatic radiation is used, but the angle of incidence is varied, causing the crystal to rotate about itself along a given axis. Effectively, in terms of Ewald's construction, rotating the crystal rotates the reciprocal lattice about an axis passing through the origin. Diffraction peaks will appear corresponding to those points whose circumference of rotation intersects the Ewald sphere.

In the **Debye-Scherrer method**, a sputtered sample is used. The X-ray beam and the crystal remain fixed, but the crystals in the sample are randomly oriented. In this case, when using the Ewald sphere, each point of the reciprocal lattice will originate a sphere centred at the origin. Diffractions corresponding to the vectors whose sphere intersects the Ewald sphere will be observed. Since the

intersection is a circle, diffraction is observed in the directions determined by the centre of the Ewald sphere and that circle. Each point of the reciprocal lattice therefore corresponds to a cone of diffracted beams centred on the sample, the axis of which will be the incident beam, which is detected as a circle.

In an X-ray diffraction experiment, what we measure is the angle between the incident ray and the diffracted ray, that is, the angle formed by $\boldsymbol{k}$ and $\boldsymbol{k}'$, 2θ. Once the wavelength of the X-ray is known, the Bragg formula allows us to obtain the spacing of the family of planes that originates the diffraction peak. We can also use Laue's equations to determine the modulus and direction of the corresponding reciprocal lattice vector. From the sequence of spacings obtained in this way, it is possible to deduce the crystal structure of the solid.

To determine the structure, recall that the distance d_{hkl} between planes of the Miller index family (*hkl*) is given by:

$$d_{hkl} = \frac{2\pi}{G_{hkl}} \quad , \qquad [1.3]$$

where $\vec{G}_{hkl} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$ is a vector of the reciprocal lattice of the crystal. The following table shows the values of $1/d_{hkl}$ in the cases of some common structures (a, b, c = lattice parameters):

Simple cubic	$\frac{1}{d_{hkl}} = \frac{1}{a}\sqrt{h^2 + k^2 + l^2}$
Hexagonal	$\frac{1}{d_{hkl}} = \sqrt{\frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}}$

Table 1.1. Interplanar spacing, d_{hkl}, as a function of Miller indices (*hkl*) for some common crystal structures. **The indices for face-centred and body-centred cubic lattices usually refer to the simple cubic cell.**

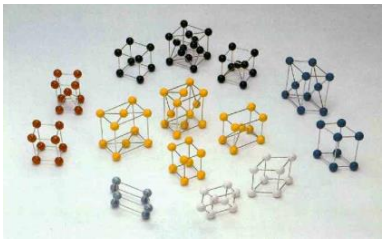
In order to correctly determine the structure of a solid, we must remember that, due to the complex structure of the motif of most crystalline solids, it is possible that the radiation diffracted by the atoms contained in the unit cell interferes destructively, resulting in the absence of reflections corresponding to certain families of crystal planes. In this case, a **systematic absence** (or **extinction**) of certain diffraction peaks is said to occur. Assuming that the motif of a crystal consists of *N* atoms, whose positions inside the unit cell are given by the vectors $\vec{r}_i = x_i\vec{a}_1 + y_i\vec{a}_1 + z_i\vec{a}_1$, then for a given diffraction peak, corresponding to a family of planes associated with the vector $\vec{g}_{hkl}$ of the reciprocal lattice, the contribution of the atoms in the cell is given by the following expression:

$$F(h,k,l) = \sum_{i=1}^{N} f_i e^{i\vec{r}_i \cdot \vec{G}} = \sum_{i=1}^{N} f_i e^{i2\pi(hx_i + ky_i + lz_i)} \qquad [1.4]$$

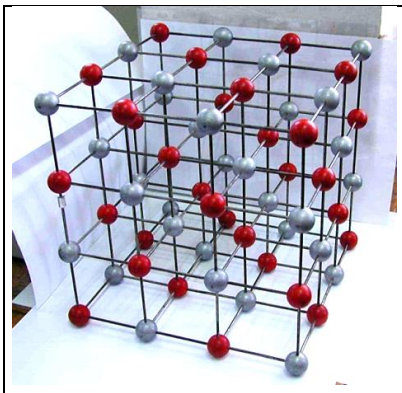
where f_i is the dispersive power of the atom *i* known as the atomic form factor. *F* is known as the **structure factor**, and it is a central concept in crystallography. For each reciprocal lattice point there is a unique structure factor. The experimentally observed intensity, *I*, of a diffraction peak is proportional to the square of the structure factor: $I \propto F^2$.

2. EQUIPMENT

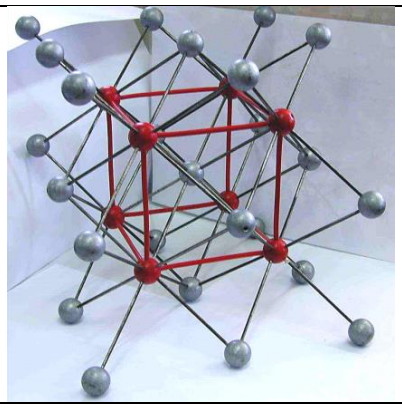
2.1 An assortment of models of unit cells from the 14 possible Bravais lattices:



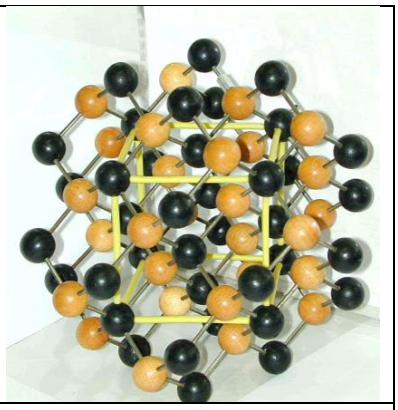
2.2 An assortment of crystal structure models:



NaCl
Characteristic of salts (KCL, AgBr, KBr, PbS) and oxides (MgO, FeO)

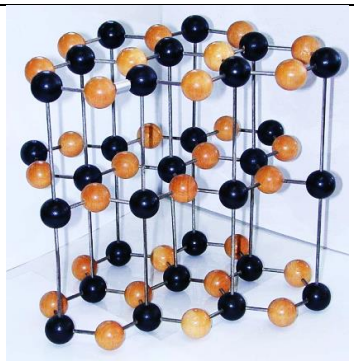


CsCl
Intermetallic compounds and salts CsCl, or AlNi, CuZn



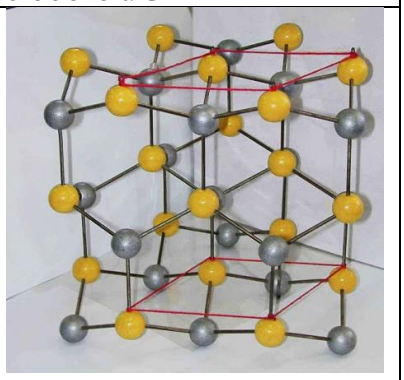
Sphalerite (Zincblende)
III-V semiconductors (GaAs, GaP, InSb, InP). Diamond, if there is only one element: C

Plan view (view from above)

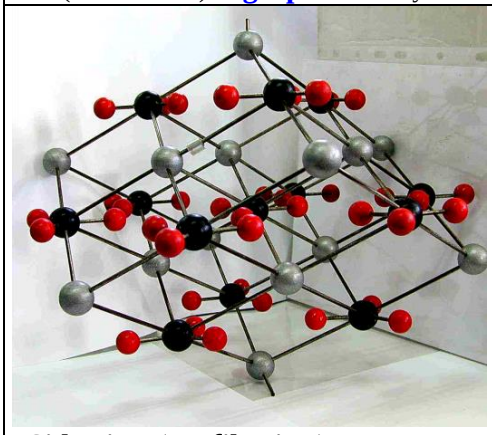


Side view (profile view)

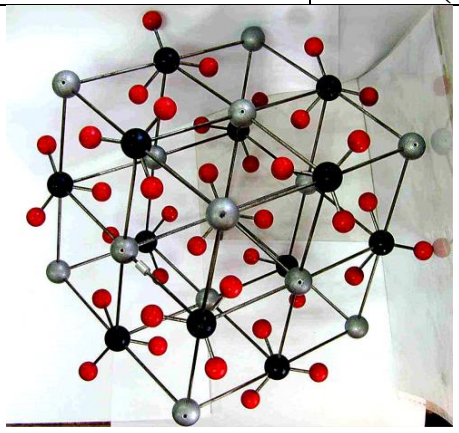
BN (Borin nitride) or **graphite** if only carbon



Wurtzite (CdS, ZnS)



Side view (profile view)



Plan view (view from above)

Calcite (CO_3Ca)

2.3 The *SIMULX* simulation program

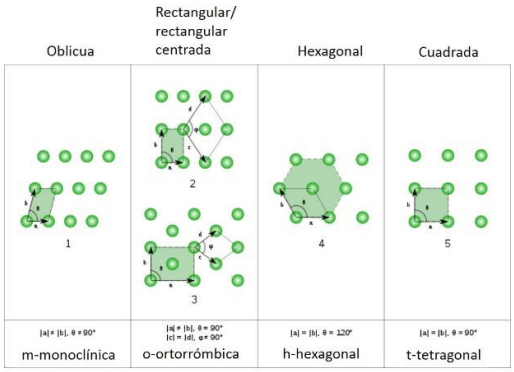
The X-ray diffraction simulation program SIMULX can be downloaded for practice at home from the following site:
http://www.uv.es/~elecfis/fisol/Fisol.htm

To simulate X-ray diffraction, the program calculates the X-ray intensity diffracted in a given direction from a crystal consisting of a number of atoms sufficient to show the effects of translational symmetry, but small enough to keep the calculation time reasonably short. **The program assumes an X-ray wavelength corresponding to the K_α line of copper, $\lambda = 1.5418$ Å.**

In the program, the window is divided into two. The upper part shows a model of what would be a semi-cylindrical camera with a photographic film on its surface. The glass would be located in the centre of the camera. The radiation is incident from the left and, when a sweep is launched, the crystal is rotated as it would be in a real experiment. When the Bragg condition is fulfilled, a diffracted beam appears and hits the photographic plate. If the glass is rotated by an angle of θ, the diffracted beam appears at an angle of 2θ to the direction of incidence. The mouse pointer can be used to mark the peaks, whose intensity and angular position appear in the two boxes to the left of the spectrum.

To perform a simulation, the crystal parameters are first entered using the *Parámetros* command in the *Cristal* menu. The simulation is performed on flat crystals, so only three parameters are required: the two basis vectors, a and b, and the angle they form, ϕ. There are five planar (2D) Bravais lattices:

- Square: a=b, $\phi = 90^o$
- Rectangular: a≠b, $\phi = 90^o$ (simple and centred)
- Hexagonal: a=b, $\phi = 60^o$
- Monoclinic (oblique): a≠b, $\phi \neq 90^o$



The program also supports the input of a motif of up to four atoms with different atomic factors. If more than one atom is entered, the first atom is assigned the coordinates (0,0). The coordinates are entered in units of the basis vectors, therefore they have values between 0 and 1.

The designed lattice can be visualised with the command *Mostrar estructura* in the *Cristal* menu. For the calculation it is assumed that the crystal is initially oriented in the direction [1,0]. In the window opened by this option, the different families of planes can be displayed by entering the Miller indices and rotating the crystal so that the chosen family is parallel to the plane of the X-ray beam at the start of the scan. Using the command *Girar* in the *Cristal* menu, the orientation of the crystal can be arbitrarily changed (the angles do not accumulate).

The commands in the *Barrido* menu allow you to start the data acquisition, stop the data acquisition or change the wavelength of the X-radiation.

The *Fichero* menu commands allow the calculated spectra to be saved to disk or loaded back into memory. The ASCII files consist of 403 records, the first one corresponding to the detector gain, the next two to the initial and final angles and the rest to the diffracted intensities for four hundred regularly spaced angles between the initial and final angles. To store spectra in the computer's memory, three registers are available for comparing spectra without having to store them on disk, and they are accessed by means of the commands in the *Registros* menu.

The commands in the *Gráfica* menu allow the calculated spectrum to be deleted or redrawn, as well as some simple numerical processing of the spectrum.

3.-TASKS TO BE COMPLETED

The specific tasks to be completed are detailed in the corresponding Lab Report sheet.

NAME: GROUP:
DATE:

EXPERIMENT 1 - LAB REPORT
Bravais Lattices, Crystal Structures and X-Ray Diffraction Simulations

TASKS TO COMPLETE [1]

For each question you should briefly explain what you did in the experiment and show any calculations. (You should watch this introductory video before coming to the lab session: https://mmedia.uv.es/html5/u/cr/cros/64226_fes_p1_c.mp4.)

1. Lattices and Crystal Structures (1 hour)

1.1 Identify the 14 Bravais lattices and classify them by crystal system. Take photos and label them accordingly in the space below.

1.2 Express the basis vectors of the primitive unit cell of your model **in terms of those of the non-primitive unit cell of the same crystallographic system** for 4 Bravais lattices. Draw the structure showing the basis vectors of the primitive unit cell you use.

Lattice:	Lattice:	Lattice:	Lattice:

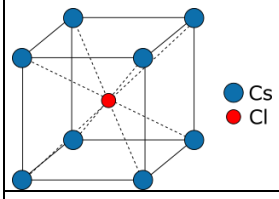
1.3 The non-primitive unit cell (the cell represented by the model available in the laboratory) contains points whose coordinates **with respect to the primitive basis vectors of the same crystallographic system** are not integers. Determine these coordinates for the lattices in the previous section. Use the same basis vectors as in the previous section and show the structures.

Lattice:	Lattice:	Lattice:	Lattice:

[1] The digital version of this document can be edited later at home to add space and information as required.

NAME: GROUP:
DATE:

1.4 Identify the crystal structures of 2 of the models available in the laboratory. Express the basis vectors with the unit vectors $\vec{\imath},\vec{\jmath},\vec{k}$ and the minimum interatomic distances (nearest neighbours), according to the example in the first line.

Crystal Structure	Bravais Lattice	Unit Cell Parameters	Primitive Unit Cell (Basis Vectors)	Motif (atoms and their coordinates)
CsCl *d=distance Cs-Cl*  	*Simple cubic*	$a=b=c=\frac{2d}{\sqrt{3}}$	$\vec{a}_1 = \frac{2d}{\sqrt{3}}\vec{\imath}$ $\vec{a}_2 = \frac{2d}{\sqrt{3}}\vec{\jmath}$ $\vec{a}_3 = \frac{2d}{\sqrt{3}}\vec{k}$	*An atom of Cs on the lattice point (0,0,0)* *An atom of Cl on the lattice point* $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$

1.5 At home, search the Internet and describe other structures (using the same elements as in the previous question). Insert a picture of the structure.
(Examples: perovskite structure, delafossite structure, β-tin structure, fluorite structure, etc.)

Crystal Structure	Bravais Lattice	Unit Cell Parameters	Primitive Unit Cell (Basis Vectors)	Motif (atoms and their coordinates)

NAME: GROUP:
DATE:

2. X-ray Diffraction Simulations (2 hours)

2.1 Two-dimensional monoatomic lattice. (Minimum 2)

How to start:

- Define the parameters of the 2D lattice indicated in each section.
- Examine its appearance with the *Mostrar Estructura* command in the *Cristal* menu.
- Obtain the positions of the diffraction peaks.
- The *Girar* option allows us to reorient the crystal to observe the peak corresponding to each family of planes. We can also reorient it using the Miller indices of the plane we want to study.

Obtain the spacing of different crystallographic planes (**at least 3**) for each of the lattices defined from the X-ray simulation. Indicate, with appropriate diagrams or formulae, how you obtain the spacing. **The use of the reciprocal lattice is recommended.**

a) Square 2D lattice. Chosen parameters: a = [, b] = [, γ] = [ ]

→For each orientation, plot $n = \frac{2d_{hk}}{\lambda}\sin\theta$ to obtain the value of d_{hk} that is extracted from the data and attach the fit you make.

Include screenshots of your crystal structures and the corresponding diffraction images.

Orientation 1 = 0º, (*h*,*k*) = (0,1)

d_{family} (theory) = [ ]

Diffractogram

2θ					

d_{hk} (simulation) = [ ]

Orientation 2= [ ], (*h*,*k*) = [ ]

d_{family} (theory) = [ ]

Diffractogram

2θ					

d_{hk} (simulation) = [ ]

Orientation 3= [ ], (*h*,*k*) = [ ]

NAME: GROUP:
DATE:

d_{family} (theory) = ____

Diffractogram

2θ					

d_{hk} (simulation) = ____

b) Non-square 2D lattice. Chosen parameters: a = ____ , b = ____ , γ = ____ .

Orientation 1 = 0º, (*h*,*k*) = (0,1)

→For each orientation, plot $n = \frac{2d_{hk}}{\lambda}\sin\theta$ to obtain the value of d_{hk} that is extracted from the data and attach the fit you make.

d_{family} (theory) = ____

Diffractogram

2θ					

d_{hk} (simulation) = ____

Orientation 2= ____, (*h*,*k*) = ____

d_{family} (theory) = ____

Diffractogram

2θ					

d_{hk} (simulation) = ____

Orientation 3 = ____, (*h*,*k*) = ____

d_{family} (theory) = ____

Diffractogram

2θ					

d_{hk} (simulation) = ____

NAME: GROUP:
DATE:

2.2 2D (square or rectangular) lattice with more than one atom per unit cell.

For one of the above lattices, introduce a motif (two atoms) with different atomic factors. Analyse the effect of the positions in the cell and the atomic factor on the intensity of the diffraction peaks. **Design a lattice in which systematic extinctions are observed.**

Unit Cell 1. Chosen Parameters: a = , b = , γ =

Position and atomic factors of the atoms in the motif:

$(x_1,y_1) = (0,0)$ $f_1 = 1$

$(x_2,y_2) = (\ ,\ )$ $f_2 =$

$(x_3,y_3) = (\ ,\ )$ $f_3 =$

Chosen Orientation =

(h,k) =

Diffractogram of the chosen diatomic lattice

2θ					
$\mathbf{I_{hk}}$ (*)					

(*) $\mathbf{I_{hk}}$ is the value of the intensity of the diffraction peak.

Compare the above results with those of the diffractogram generated from the same unit cell but with only 1 atom in the motif:

2θ					
$\mathbf{I_{hk}}$					

Are there differences in the diffractogram intensities? For which vectors (h,k)? Why?

Explain what you observe by calculating the expected structure factor F(h,k) for the diatomic lattice, applying the expression [1.4].

$F(h,k)$ = 1 +

For which values of (h,k) does the structure factor equal zero?

3. Discussion of Results and Conclusions

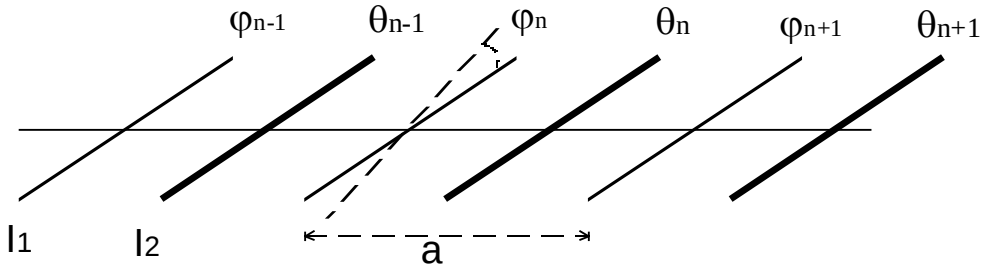
Evaluate and comment on the results with respect to what was expected, drawing conclusions about the experiment.

EXPERIMENT 2 – LAB GUIDE
Vibrations of a Linear Chain: Acoustic and Optical Modes

1. INTRODUCTION

The vibrations of the atoms in a crystal lattice can, under certain conditions, be compared to the vibrations of a series of coupled harmonic oscillators. This is because, at equilibrium, the lattice energy is minimal, so that for small displacements the energy variations are always quadratic with respect to the displacement. The restoring forces are therefore linearly dependent on the displacement. Thus, to study the vibrations of a crystal lattice, we replace the atoms by point masses connected by springs characterised by an elastic constant. This is known as the **harmonic crystal** approximation. A linear chain of coupled oscillators with lattice parameter *a* would be the simplest model. By alternating two types of atoms with different masses *M* and *m*, acoustic and optical modes can be observed.

In this experiment, the coupled oscillator system will be a series of transverse rods connected to an elastic steel shaft. Bronze and aluminium rods of the same length and diameter are alternated. In the vibrations we are going to study, the rods rotate with respect to the shaft and the restoring force is generated by the twisting of the wire. The dynamic coordinate will be the angle of rotation of each rod in unit cell *n*, φ_n y θ_n for rods 1 and 2 respectively. Its position along the chain (the rod) is given by *na* for rod 1 and $\left(n+\frac{1}{2}\right)a$ for rod 2.



If we call the torsion constant of the steel shaft, τ, the equations of motion of this system will be formally identical to those of a chain of atoms connected by springs, except that here the moments of inertia appear instead of the masses and the angles of rotation instead of the displacements:

$$I_1\frac{d^2\varphi_n}{dt^2} = -\tau(2\varphi_n - \theta_n - \theta_{n-1}) \qquad I_2\frac{d^2\theta_n}{dt^2} = -\tau(2\theta_n - \varphi_n - \varphi_{n+1}) \qquad [2.1]$$

Since we are looking for solutions that propagate as harmonic waves, these will be of the form:

$$\varphi_n = \varphi_0 e^{inak}e^{-i\omega t} \qquad \theta_n = \theta_0 e^{i\left(n+\frac{1}{2}\right)ak}e^{-i\omega t} \qquad [2.2]$$

where *k* is the wave vector (2π/ λ) and the angles φ_0 y θ_0 are the vibration amplitudes of both types of rod. Substituting into equation 2.1, we obtain:

$$-I_1\omega^2\varphi_0 e^{inak}e^{-i\omega t} = -2\tau\varphi_0 e^{inak}e^{-i\omega t} + \tau\theta_0\left(1+e^{-ika}\right)e^{i\left(n+\frac{1}{2}\right)ak}e^{-i\omega t}$$

$$-I_2\omega^2\theta_0 e^{i\left(n+\frac{1}{2}\right)ak}e^{-i\omega t} = -2\tau\theta_0 e^{i\left(n+\frac{1}{2}\right)ak}e^{-i\omega t} + \tau\varphi_0\left(1+e^{-ika}\right)e^{i\left(n+\frac{1}{2}\right)ak}e^{-i\omega t} \qquad [2.3]$$

Eliminating the time dependency that appears in both terms and rearranging leaves:

$$(2\tau - I_1\omega^2)\varphi_0 - \tau\left(1+e^{-ika}\right)e^{\frac{1}{2}ika}\theta_0 = 0$$

$$\tau\left(1+e^{ika}\right)e^{-\frac{1}{2}ika}\varphi_0-(2\tau-I_2\omega^2)\theta_0=0$$

Such a homogeneous system only has a solution if its determinant is zero:

$$(2\tau-I_1\omega^2)(2\tau-I_2\omega^2)=\tau^2\left(1+e^{-ika}\right)\left(1+e^{ika}\right)$$

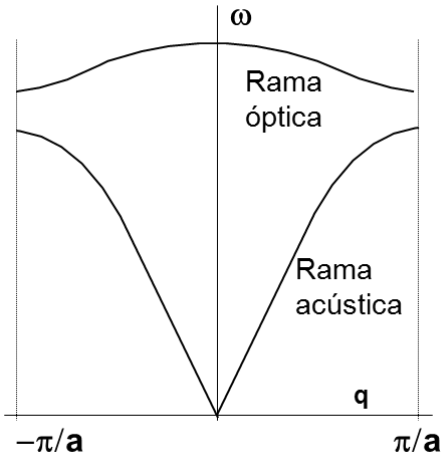
By rearranging the terms, we obtain a second degree equation in ω^2:

$$I_1I_2\omega^4-2\tau(I_1+I_2)\omega^2+2\tau^2(1-\cos ka)=0$$

whose solution indicates how the vibration frequencies depend on the wave vector through the following **dispersion relations**:

$$\omega^2=\tau\frac{I_1+I_2}{I_1I_2}\pm\sqrt{\left(\tau\frac{I_1+I_2}{I_1I_2}\right)^2-2\frac{\tau^2}{I_1I_2}(1-\cos ka)}=\frac{\tau}{I_r}\pm\sqrt{\left(\frac{\tau}{I_r}\right)^2-2\frac{\tau^2}{I_1I_2}(1-\cos ka)} \qquad [2.4]$$

where we have defined a reduced moment of inertia, I_r, of the two rods as: $I_r=I_1I_2/(I_1+I_2)$. The possible modes of vibration of the linear chain of atoms are thus classified into two main groups, corresponding to the + and - signs in the solution. The figure below shows the dispersion relation for both + and - solutions.



To see what the difference between them is, let us study what happens for $k \to 0$, i.e., for wavelengths much larger than the interatomic distances. Approximating the cosine with a Taylor series we get:

$$\omega^2=\frac{\tau}{I_r}\left(1\pm\sqrt{1-\frac{I_r^2}{I_1I_2}k^2a^2}\right)$$

Taking the positive sign gives:

$$\omega_+^2=\frac{\tau}{I_r}\left(2-\frac{I_r^2}{2I_1I_2}k^2a^2\right)\approx\frac{2\tau}{I_r}$$

and the negative sign gives:

$$\omega_-^2=\frac{\tau}{2(I_1+I_2)}k^2a^2 \qquad [2.5]$$

We see that the solution branch ω_- corresponds to a type of wave whose frequency increases linearly with the wave vector, for long wavelengths. This solution is characteristic of sound waves and is therefore called the acoustic branch. Taking the square root of equation [2.5] gives the dispersion relation for small values of k:

$$\omega_-=\sqrt{\frac{\tau}{2(I_1+I_2)}}ka$$

The propagation velocity of these waves will therefore be: $v_s = \sqrt{\frac{\tau a^2}{2(I_1+I_2)}}$

It should be noted that there is a maximum frequency, above which there are no acoustic modes of vibration. This frequency corresponds to k = π/a, or, in other words, a wavelength of 2a. Obviously, this is because the shortest wavelength that can propagate in the lattice corresponds to the mode of vibration in which the rods of two adjacent cells vibrate in phase opposition.

The branch described by ω_+ corresponds to waves whose frequency tends to a constant value for long wavelengths, a value that depends on the reduced moment of inertia and the torsion constant of the shaft. It corresponds to the frequency of oscillation of two rods of moments I_1 and I_2 connected by an axis of constant 2τ. It is the branch that corresponds to what is called the optical branch in a solid, because these modes of vibration interact strongly with electromagnetic radiation in the far infrared range. It is easy to see that in the optical branch, where k tends to zero, all the rods of each type vibrate in phase and in each cell, the two rods would vibrate out of phase, with relative amplitudes given by $\varphi_0 I_1 + \theta_0 I_2 = 0$. Between the edge of the acoustic branch and that of the optical branch there is a frequency interval in which there are no allowed modes.

The possible values of the wave vector are determined by imposing a boundary condition. Usually, in solid physics, cyclic boundary conditions are imposed, i.e., if we have a total of N atoms, we impose $u_n=u_{n+N}$, which is equivalent to assuming that the chain closes in on itself. In that case, equation (1) leads immediately to discrete values of the wave vector given by k= 2πm /L = (2π/a) (m/N), where L=Na is the total length of the chain.

In our model the ends are fixed, so the amplitude would be zero at both ends. Since e^{ikNa} has modulus of 1, the solution cannot be a propagating wave, only a stationary wave. For the amplitude to cancel at the origin and at the end it must be proportional to sin(kx). Therefore, sin(kNa)=0 must be satisfied, i.e. kNa=mπ, k= mπ/(Na), or, as a function of the wavelength: m(λ /2)=Na=L. The wavelength must be such that an integer number of half-wavelengths fit in the total length.

The set of oscillators can be considered as a system with different modes of vibration. If the system is forced to oscillate at a certain frequency, the amplitude of its movement will depend on how close this frequency is to that of one of the modes of the system (maximum response at the resonant frequency). Recall the equation of the damped harmonic oscillator, with a frequency ω_0 and a damping constant γ, subjected to a harmonic force of amplitude F_0 and frequency ω:

$$m\frac{d^2x}{dt^2} = -m\omega_0^2 x - m\gamma\frac{dx}{dt} + F_0 e^{-i\omega t}$$

If we look for harmonic solutions of $x(t) = x_0 e^{-i\omega t}$, the amplitude will be given by:

$$x_0 = \frac{F_0}{m}\frac{1}{(\omega_0^2 - \omega^2) - i\gamma\omega}$$

The complex expression determines the modulus and the phase shift with respect to the force. The modulus will be:

$$|x_0| = \frac{F_0}{m}\frac{1}{\sqrt{\left(\omega_0^2-\omega^2\right)^2+\gamma^2\omega^2}},$$

which has a maximum when $\omega=\omega_0$. The maximum is more pronounced when the dampening coefficient, γ, is smaller. As for the phase difference, it is obtained as follows:

$$\tan\phi = -\frac{\gamma\omega}{\omega^2 - \omega_0^2}$$

where, as we pass through the resonance, there will be a 180° phase shift.

2. EQUIPMENT

2.1 A frame with 15 aluminium and 15 bronze rods, alternating, connected to a steel shaft, with an average centre distance of 31 mm. The length of the rods is 30 cm and their diameter 8 mm. Density of Al: 2.7 g/cm^3. Density of bronze: 8.5 g/cm^3.

2.2 An excitation system for the network modes consisting of:

- A low frequency oscillator
- Vibration detection system:
  - Magnets that can be attached to the end of the bars.
  - Detection coil
  - Oscilloscope

Bringing the coil close to a vibrating magnet will generate an induced electromotive force in the coil, which can be observed on the oscilloscope and compared with the excitation signal.

3.-TASKS TO BE COMPLETED

The specific tasks to be completed are detailed in the corresponding Lab Report sheet.

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EXPERIMENT 2 - LAB REPORT
Vibrations of a Linear Chain: Acoustic and Optical Modes

TASKS TO COMPLETE[1]

The aim of the experiment is to illustrate the harmonic crystal model by means of a network of coupled oscillators and to search for the dispersion relation of the vibration modes. To do this, we have to search for these modes by exciting them with forced oscillations. The excitation frequency is given by the digital counter of the oscillator.

1. Mode detection:

To detect the modes, the frequency should be varied starting from 1 Hz, taking care to ensure that the vibration amplitude used is small. The low frequency modes can be observed with the naked eye when a standing wave is formed. The corresponding frequency and the number of nodes N_v observed in the standing wave should be recorded. The wavelength of the mode is $\lambda=2L/N_v$, where L is the length of the axis.

The oscilloscope can be used to detect the modes for frequencies above 10 Hz. The magnets and the coil make it possible to accurately determine both the frequency of the mode (frequency at which the induced EMF is at a maximum) and the wavelength by observing whether or not certain rods vibrate in phase.

1.1. Measure the characteristics of acoustic and optical vibration modes*

Order (N_v) (number of modes)	Frequency (Hz)	λ $(2L/N_v)$	k $(2\pi/\lambda)$	ω (rad/s)

[1] The digital version of this document can be edited later at home to add space and information as required.

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Acoustic-zone edge (15)				
Optical-zone edge (15)				
Optical-zone centre				

* In the case of the optical branch, due to the proximity of the modes and their large damping, only the frequencies corresponding to the centre and the edge of the first Brillouin zone can be determined. For the optical-zone edge mode, it is necessary to gradually increase the frequency from the forbidden zone between the two branches. For the centre-zone mode, the frequency must be gradually decreased from that of a high-frequency evanescent mode. In both cases, when the resonant frequency of the optical modes is reached, the number of vibrating rods increases.

1.2 Verify the existence of a cut-off frequency by checking that above a certain frequency, only evanescent modes are excited (i.e. modes that only excite the rods close to the one being forced to vibrate), both in the acoustic and in the optical branches.

2. Dispersion relation

2.1 Represent the dispersion relation $\omega(k)$ of the vibration modes (optical and acoustic) in the first Brillouin zone.

2.2 Calculate the speed of sound corresponding to this dispersion relation taking into account the acoustic modes obtained in the linear zone (low-order modes).

3. Vibration structure

Draw schematically the motion of the rods for the acoustic and optical modes at the centre and at the edge of the zone. Compare in each case the motion of the rods in a unit cell with those in an adjacent cell.

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4. R**esonance curves**

Determine the amplitude-frequency excitation curves for several modes. (Select at least 2 different modes with frequencies between approximately 8 and 20 Hz.

Mode 1		**Mode 2**		**Mode 3**		**Mode 4**	
ν (Hz)	**A(mV)**	**ν (Hz)**	**A(mV)**	**ν (Hz)**	**A(mV)**	**ν (Hz)**	**A(mV)**

Note: The numbering of modes in the table refers only to the order in which they are measured in this section, not to the order of the mode (number of nodes) defined in section 1.

Plot the amplitude-frequency curves measured in the previous section. Determine the full width at half-maximum, FWHM, of the peaks. You can use a Lorentzian or Gaussian fit, or analyse the graph numerically. Do you find any correlation between mode frequency and peak width? Comment on your results.

5. Discussion of results and conclusions

Evaluate and comment on the results with respect to what was expected, drawing conclusions about the experiment.

EXPERIMENT 3 – LAB GUIDE
The Heat Capacity of Solids

1.- INTRODUCTION

1.1 The Debye Model

The **heat capacity** of a solid is the heat required to raise the temperature of a given amount of material by one degree (measured in Joule/ºC or J/K):

$$C = \frac{\delta Q}{\delta T} \qquad [3.1]$$

It is common to use the **molar heat capacity** (J/°C mol or J/ K mol), where the amount of matter considered is one mole. The **specific heat** is the heat capacity of the sample divided by its mass (J/°C kg or J/ K kg).

The heat capacity of any material depends on the existence in that material of mechanisms for the accumulation of energy through the excitation of vibrations of the atoms or the excitation of electrons to higher energy levels. For most solids (with the exception of very low temperature metals), the heat capacity is essentially determined by the energy that the solid can accumulate in the form of vibrations of its constituent atoms about their equilibrium positions.

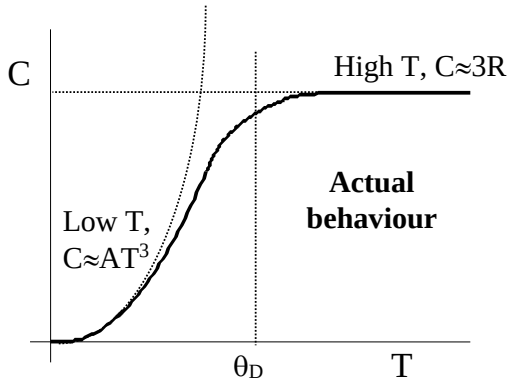

Figure 3.1

In the classical theory of specific heat capacity, the average energy at a given temperature is calculated by taking into account all possible energies and calculating the average value using Boltzmann statistics. Each degree of freedom of the particles in the system corresponds to an average energy when calculating the average energy of $k_BT/2$ (this is the so-called equipartition of energy theorem). Thus, in monoatomic gases, where each particle has three degrees of freedom, the average energy per particle would be $3k_BT/2$. The internal energy per mole would be:

$$U(T) = N_A \frac{3}{2} k_B T \qquad [3.2]$$

where N_A is Avogadro's number. With respect to temperature, the corresponding molar heat capacity would be $C=(3/2)k_BN_A$. In a solid, taking into account the independent vibrations of the atoms, all at the same frequency, and considering three degrees of freedom, we obtain an average molar energy of value $3N_Ak_BT$, from which we derive a molar specific heat capacity of $\mathbf{3N_Ak_B=3R.}$ In 1819 Dulong and Petit found that most solids have a molar heat capacity of about 25 J/mol K at room temperature. This was consistent with the predictions of the previous model and was a triumph for classical kinetic theory. However, deviations were soon observed at lower temperatures, and it was realised that 25 J/mol K was in fact an upper limit: **below a certain temperature characteristic of each solid, called the Debye temperature (θ_D), the heat capacity decreases and tends to zero proportionally to the cube of the temperature for temperatures close to absolute zero, as shown in figure 3.1.**

According to Debye's model (1912), the origin of this behaviour is to be found both in the quantum statistics that the excitation of vibrations in a solid obeys and in the fact that these vibrations are

distributed in modes (acoustic and optical, Experiment 2). In the Debye approximation, the dispersion relation is $\omega = v_s k$, where v_s is the speed of sound. This relationship is valid for small values of ω (corresponding to small values of k, i.e., very long wavelengths). Acoustic waves that can propagate in a solid in all directions in space are those with a value of k contained in a sphere of radius k_{MAX}. The number of possible waves with values of k in the range from k to k+dk is proportional to the volume between the spheres of radius k and k+dk. If we call *g* the constant of proportionality, this number will be:

$$dN = g4\pi k^2 dk = \frac{4\pi g}{v_s^3}\omega^2 d\omega \qquad [3.3]$$

Taking into account that the excitation of vibrations obeys Bose-Einstein statistics, we can calculate the total energy associated with the excitation of elastic waves in a solid. To do this, we multiply the energy associated with a wave of frequency ω, (ħω), by the number of phonons excited at a given temperature, (n(ω), which is given by statistics, and by the total number of possible waves with frequency between ω y ω+dω, and integrate between zero and maximum frequency:

$$U(T) = \frac{4\pi g}{v_s^3}\int_0^{\omega_{MAX}} \frac{(\hbar\omega)\omega^2 d\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} = \frac{4\pi g\hbar}{v_s^3}\int_0^{\omega_{MAX}} \frac{\omega^3 d\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \qquad [3.4]$$

Let's make the change of variable $u = \hbar\omega/k_B T$, and let's put everything in terms of u:

$$\omega = \frac{k_B T}{\hbar}u \qquad d\omega = \frac{k_B T}{\hbar}du \qquad [3.5]$$

Substituting in the expression for U(T), we obtain:

$$U(T) = \frac{4\pi g k_B^4}{v_s^3\hbar^3}T^4\int_0^{u_M} \frac{u^3 du}{e^u - 1} \qquad [3.6a]$$

where the limit of the integral in the variable u will be $u_M = \hbar\omega_{MAX}/k_B T = \theta_D/T$, where θ_D is the Debye temperature. The volume of the sphere of radius k_{MAX} is $4\pi k_{MAX}^3/3$, and this quantity multiplied by g is the total number of modes, which can also be written as 3 (of the three degrees of freedom of vibration of each atom) times the number of atoms N. Also taking into account the Debye definition of temperature, the above expression can also be written as follows:

$$U(T) = 9Nk_B T\left(\frac{T}{\theta_D}\right)^3\int_0^{u_M} \frac{u^3 du}{e^u - 1} \qquad [3.6b]$$

In the low temperature range, $k_B T << \hbar\omega_{MAX}$ ($T << \theta_D$) and therefore u_M is very large and can be considered infinite, so the integral does not depend on the temperature and is equal to $\pi^4/15$:

$$U(T) = 9Nk_B T\left(\frac{T}{\theta_D}\right)^3\frac{\pi^4}{15} \qquad [3.7]$$

and, therefore, the heat capacity will be:

$$C(T) = \frac{dU(T)}{dT} = \frac{12\pi^4 k_B N}{5}\left(\frac{T}{\theta_D}\right)^3 = AT^3 \qquad [3.8]$$

This corresponds to the experimental result at low temperatures.

In the high temperature range ($T >> \theta_D$), $k_B T >> \hbar\omega_{MAX}$, and therefore u_M is much smaller than 1 over the whole range of integration, so we can develop the exponential $e^u \approx 1+u$, so that the denominator of the integral is u and the integrand is equal to u^2. We can then obtain:

$$U(T) = 9Nk_B T\left(\frac{T}{\theta_D}\right)^3 \int_0^{u_M} \frac{u^3 du}{e^u - 1} \approx 9Nk_B T\left(\frac{T}{\theta_D}\right)^3 \int_0^{u_M} u^2 du = 9Nk_B T\left(\frac{T}{\theta_D}\right)^3 \frac{u_M^3}{3} \qquad [3.9]$$

and, substituting the value of u_M,

$$U(T) = 3Nk_B T\left(\frac{T}{\theta_D}\right)^3 \left(\frac{\theta_D}{T}\right)^3 = 3Nk_B T \qquad [3.10]$$

Therefore, the heat capacity will be constant and coincides with the classical Dulong-Petit value (by considering the molar capacity, i.e. $N=N_A$):

$$C = \frac{dU(T)}{dT} = 3N_A k_B = 3R \qquad [3.11]$$

So this model is able to explain the heat capacity behaviour of solids at both low and high temperatures (figure 3.1).

1.2 Measurement of Specific Heat

If we supply the solid of heat capacity C with a power W, and we assume that the solid emits heat proportionally to the temperature difference, with a constant of proportionality K, the differential equation that determines the heating would be:

$$C\left.\frac{d(\Delta T)}{dt}\right|_{cal} = W - K\Delta T \qquad [3.12]$$

If the specific heat were constant, the temperature as a function of time would be given by:

$$\Delta T(t) = \frac{W}{K}\left(1 - e^{-\frac{K}{C}t}\right) \qquad [3.13]$$

On the other hand, once the maximum temperature has been reached, $\Delta T_M = W/K$, if energy is no longer supplied to the solid, the cooling equations would be:

$$C\left.\frac{d(\Delta T)}{dt}\right|_{enf} = -K\Delta T \qquad [3.14]$$

Again, if the specific heat were constant, the temperature as a function of time as the solid cools would be given by:

$$\Delta T(t) = \frac{W}{K} e^{-\frac{K}{C}t} \qquad [3.15]$$

From the maximum temperature and the time constant we could determine both C and K. **If the specific heat is not constant**, knowing the experimental heating and cooling curves, the specific heat can be calculated from them. If we take the slopes of the heating and cooling curves at a given temperature to be $m_C = \frac{d(\Delta T)}{dt}\Big|_{cal}$ and $m_E = \frac{d(\Delta T)}{dt}\Big|_{enf}$, it is easy to see, by subtracting both differential equations, that the heat capacity at that temperature will be given by:

$$C(\Delta T) = \frac{W}{m_C - m_E} = \frac{W}{m_C + |m_E|} \qquad [3.16]$$

Since the heating resistor has a mass comparable to that of the samples, the heat capacity to be measured, C, is the sum of that of the sample C_M and that of the resistor C_R.

2. EQUIPMENT

Figure 3.2 shows the circuit of the experimental device, with the heating resistor connected in series with a second resistor R ~1Ω (the value of R can be calculated from the current and V_R).

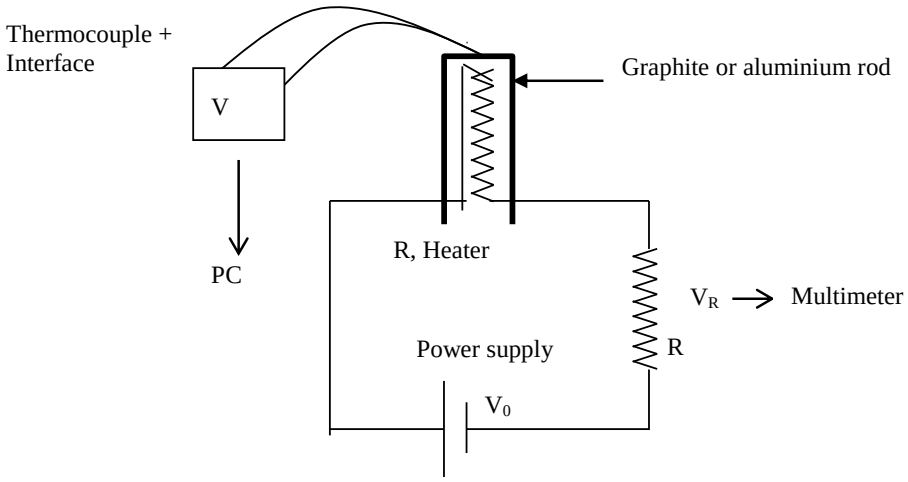

Figure 3.2

a) One heating resistor (mass 4.6 g) mounted on an aluminium support.
b) An aluminium cap (0.5 g) which is used to attach the thermocouple to the heating element.
c) An aluminium sample (8.2 g) and a graphite sample (5 g) in the form of hollow cylinders which are placed over the heating element and have a small hole for fixing the thermocouple.
d) A calibrated Cromel-Alumel thermocouple (type K). A power supply unit with an indicator for the applied voltage, V_0, and the current, I, in the circuit.
e) A computer with a National Instruments USB-TC01 interface for thermocouple measurement acquisition.
f) A cylindrical shield to minimise convective losses. AVOID AIR CURRENTS (turn off air conditioning, close windows and try not to move in the vicinity of the sample while acquiring data).

3.-TASKS TO BE COMPLETED

The specific tasks to be completed are detailed in the corresponding Lab Report sheet.

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EXPERIMENT 3 - LAB REPORT
The Heat Capacity of Solids

TASKS TO COMPLETE[1]

1. **Heating and cooling curves of the *heating resistor*.**

In this first part of the experiment, use the heater alone without the sample. Place the aluminium cap on top to attach the thermocouple. Apply a voltage of **10 V**. The total acquisition time is optional but is usually around 1000 seconds. Record and save a heating and cooling curve using the acquisition program "**TC01 Launcher P3**". To do this, go to "Temperature Logger". Press "Start Logging" to start recording the data. Press "Stop Logging" to stop recording the data once the sample has cooled down sufficiently (near room temperature).

CAUTION: NEVER EXCEED 10 W OF POWER WITH THE HEATING ELEMENT ALONE. **DO NOT EXCEED 220ºC**

The power supplied to the heating resistor at each instant can be calculated from **the current in the circuit (I)**, indicated in amperes on the generator; **the applied voltage (V_0),** indicated in volts on the generator; and **the voltage at the measuring resistor (V_R),** which is determined by the multimeter. The potential difference in the heating resistor is $V_C=V_0 - V_R$, so the power will be $W= (V_0 - V_R)I$.

2. **Heating and cooling curves of the *samples*.**

Mount the sample and record and record a heating and cooling curve for the different samples with an applied voltage of **18 V** and a similar acquisition time.

ATTENTION: NEVER EXCEED 25 W OF POWER WITH THE SAMPLES. **DO NOT EXCEED 220ºC**

The heating power is obtained following the same procedure as in the previous section. This part must be carried out on the aluminium and graphite samples.

3. **Study of heat capacity, specific heat and molar heat capacity as a function of temperature.**

In this part the temperature dependence of the experimentally obtained molar heat capacity in relation to the Debye model should be examined. Therefore, following the method described in section 1.2 of the lab guide, it will be necessary to obtain the value of the heat capacity as a function of temperature **from the gradients of the heating and cooling** curves for various temperature values. The calculation of the slope dT/dt of the cooling and heating curves can be carried out in several ways. You only need to choose one:

Method 1: This method consists of dividing the curve into sections using constant temperature intervals then determining the gradient of each section. This procedure is shown below in the figure showing temperature as a function of time.

[1] The digital version of this document can be edited later at home to add space and information as required.

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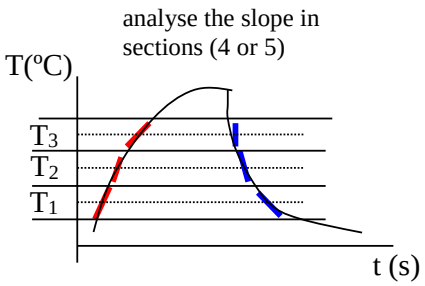


Note: If, for example, intervals of 20°C have been chosen, for a maximum temperature of about 200°C, 9 intervals will be obtained. If you want to increase the number of points for the T-dependence of heat capacity, simply use intervals of 10°. This would give a series of interleaved values whose T-dependence should be consistent with that obtained above.

Method 2: Fit the upward and downward curves, separately, to a 5^{th} degree polynomial. Although this polynomial function does not make physical sense, once the fit has been made, it allows us to obtain the derivative of the data very easily: all we need to do is to derive the polynomial. This way we obtain a value of the slope at each temperature point. Of course, the result will only be physically valid in the range in which the function fits the data well.

In either method, for the calculation of the heat capacity it is necessary to take into account that, for each value of the heat capacity, **the slopes of heating and cooling must correspond to the same temperature.**

Complete the data in the tables or provide similar tables (e.g., an Excel file). Do not forget to include the units of the different magnitudes. Briefly explain the procedure you have followed to obtain the results.

Heating Element Only

W	T	Gradients		C_R (J/ K)	c (J/g K)
		m_C	m_E		

NAME: GROUP:
DATE:

ALUMINIUM

W	T	Gradients m_C	Gradients m_E	C_{R+Al} (J/ K)	$C_{R+Al} - C_R$ (J/ K)	c (J/g K)	C_m (J/molK)

GRAPHITE

W	T	Gradients m_C	Gradients m_E	C_{R+Gr} (J/ K)	$C_{R+Gr} - C_R$ (J/ K)	c (J/g K)	C_m (J/molK)

Compare the experimental variation of the heat capacity obtained with that expected according to the Debye model (figure 3.1 in the lab guide). You should plot the molar heat capacity against T or T/θ_D and place the experimental values on this curve, checking how close they are to the Dulong-Petit value (3R) and observing if the Debye temperature of the material is consistent with this value. Codes written for Python, Mathematica and Matlab can be found on the internet. Another option is to digitise a heat capacity vs. T/θ_D curve and include your data on it.

4. Discussion of Results and Conclusions

Evaluate and comment on the results with respect to what was expected, drawing conclusions about the experiment.

EXPERIMENT 4 – LAB GUIDE
Transport Properties of Semiconductors: Resistivity and Hall Effect Measurements

1. INTRODUCTION

1.1 The Drude Model for Semiconductors

The Drude model is the simplest model for interpreting the transport properties of a solid. It consists of assuming that the charge carriers (electrons or holes in a band) interact with the lattice defects and vibrations in such a way that, on average, they have one collision every certain time interval, which is called the **relaxation time**. This time is assumed to be independent of the electron energy.

If we assume that the energy gained by the electron in one collision is transferred to the ion lattice in the next collision, this is equivalent to introducing a dissipative force which is proportional to the velocity. The damping constant will be proportional to the inverse of the relaxation time τ. The equation of motion in the presence of a uniform electric field would be:

$$m^* \frac{d\vec{v}}{dt} = -e\vec{E} - m^* \frac{\vec{v}}{\tau} \qquad [4.1]$$

Here, m^* is the effective mass of the electrons, since their mass is modified by their interaction with the ionic lattice.

In steady state, the velocity will be constant.:

$$\vec{v} = -\frac{e\tau}{m^*}\vec{E} = -\mu\vec{E} \qquad [4.2]$$

This velocity corresponds to the excess velocity that each electron gains between collisions when the electric field is applied. The constant of proportionality between the velocity and the field, or in other words, the velocity of the electrons in an electric field unit, is called **electron mobility**. If the energy band is occupied by *n* electrons per unit volume, the charge density per unit volume is *-en*. Remembering from *Electromagnetismo I* the relationship between velocity and charge density, we can obtain the relationship between current density and electric field, i.e., **Ohm's law** in Drude's model. This will allow us to obtain the conductivity σ of the semiconductor:

$$\vec{J} = -en\vec{v} = \frac{e^2 n\tau}{m^*}\vec{E} = \sigma\vec{E} \quad \rightarrow \quad \sigma = \frac{e^2 n\tau}{m^*} = en\mu \qquad [4.3]$$

Resistivity ρ is defined as the inverse of conductivity, ρ =1/σ.

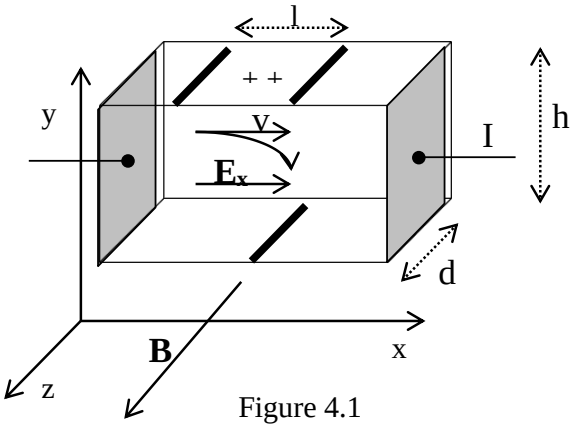


Figure 4.1

Suppose now that we subject a semiconductor sample to mutually perpendicular electric and magnetic fields. Assume that the applied electric field is directed in the x-axis direction and the magnetic field in the z-axis direction. The magnetic force will deflect the electrons in the direction perpendicular to both (Y-axis direction). If the sample is finite, the electrons will tend to accumulate on one of the surfaces, leaving an uncompensated positive charge on the other surface. **This leads to the appearance of an**

electric field in the Y-axis direction, as shown in Figure 1. This field is the **Hall field**, E_H, whose value is easy to deduce: since in the stationary situation there will be no current in the Y-axis direction, the Hall field must compensate for the action of the magnetic field, so that E_H=vB, Since, on the other hand, v=J/*en* (Eq. [4.3]), E_H=BJ/*en*, the Hall field is proportional to the current density and the magnetic field. The proportionality constant is called Hall's coefficient, R_H= 1/*en*, and is **usually expressed in cm^3/Coulomb**.

1.2 Temperature Dependence

In a semiconductor, the temperature dependence of electron mobility is determined by the type of dominant scattering mechanism, which we will not discuss in detail in this course. However, we need to know the temperature dependence of these mechanisms in order to interpret the results of the experiment. At low temperatures (well below room temperature), when the lattice vibrations are not excited, the scattering processes are dominated by the interaction of electrons with defects and ionised impurities. The temperature dependence of this type of scattering processes is: μ = Cte $T^{3/2}$. At high temperatures, which is the range we will study in our experiment, the dominant mechanism is scattering by longitudinal acoustic phonons, which gives rise to a dependence of the type μ = Cte $T^{-3/2}$.

As for the carrier concentration, if the semiconductor is **intrinsic**, (*i.e.*, an undoped semiconductor in which electrons are thermally excited from the valence band to the conduction band, leaving behind vacancies) the temperature dependence is given by the expression:

$$n_i = \sqrt{N_C N_V}\, e^{-\frac{E_g}{2k_B T}} = 2\left(\frac{k_B T}{\pi h^2}\right)^{\frac{3}{2}} (m_e^* m_h^*)^{\frac{3}{4}} e^{-\frac{E_g}{2k_B T}} \qquad [4.4]$$

where E_g is the bandgap of the semiconductor and $m_{e,h}^*$ is the effective mass of the electrons/holes.

When the semiconductor is **extrinsic** (*i.e.*, the electrons originate from impurities), three temperature ranges (in increasing order of temperature) can be identified:

a) Extrinsic Range A: temperature range in which impurities in the donor level are being ionised. (Electrons from that level pass into the conduction band.) The temperature dependence of the carrier concentration is given by:

$$n = \sqrt{\frac{N_C N_D}{2}}\, e^{-\frac{\Delta E_D}{2k_B T}} \qquad [4.5]$$

where N_D is the concentration of donor impurities and ΔE_D is their ionisation energy.

b) Extrinsic Range B: temperature range in which the impurities are all fully ionised, but there are still few electrons moving into the conduction band. In this range $n=N_D$, i.e., the electron concentration coincides with the concentration of donor impurities and does not vary with temperature.

c) Intrinsic Range: temperature range in which the increase in n is due to electrons coming from the valence band ($n=N_D+n_i$, N_D constant). In this range, the electron concentration increases with temperature according to n_i (equation [4.4]).

1.3 Resistivity and Hall Effect Measurements

What we measure with electrical instruments are currents and voltages, so we are interested in knowing the relationship between the measured currents and voltages and the quantities we have just defined above. **To measure resistivity, it is necessary to make four contacts on the sample**: a current, I, is introduced through two of them (for example, the faces perpendicular to the X axis in Figure 1). If d is the thickness and h is the height of the specimen, the current density J is given by $J = I/S = I/dh$. Between the other two contacts, placed on a face parallel to the current flow, the potential difference is measured, V_ρ. (Since the voltmeter has infinite impedance, no current flows across these contacts, therefore there is no voltage drop across the contacts themselves and the voltage measured corresponds to the ohmic potential drop across the sample.) The potential difference between the two contacts is given by $V_\rho = IR = I\rho l/hd$. **These measurements allow us to obtain the resistivity of the material with the known dimensions of the sample:**

$$\rho = \frac{V_\rho}{I}\frac{dh}{l} \qquad [4.6]$$

To measure the carrier concentration, we will apply a magnetic field to the sample and determine the Hall coefficient, R_H. The Hall voltage is the change in the potential difference between the two faces parallel to the current axis when a magnetic field is applied. The Hall voltage will therefore be given by: $V_H = h\,E_H = h\,R_H BJ = R_H BI/d$, therefore:

$$R_H = \frac{V_H d}{IB} \qquad [4.7]$$

From the resistivity and Hall's coefficient, we obtain the mobility, $\mu = R_H/\rho$ and the concentration of carriers, $n = 1/eR_H$.

Usually, as is the case in this experiment, a sample with the geometry of Figure 1 is not used, but a square sample of thickness d with four contacts, one at each vertex. To determine the electrical properties of the sample, the so-called **Van der Pauw method** is then used. To determine the resistivity with Van der Pauw's method, voltage and current measurements are made in two different configurations. Let us call the four contacts A, B, C and D. Current is passed through two adjacent contacts, for example A and B (I_{AB}) and the voltage drop across the other two contacts, C and D (V_{CD}), is measured. From this data, the resistance is determined, $R_1 = V_{CD}/I_{AB}$. This type of measurement is shown schematically in Figure 4.2.

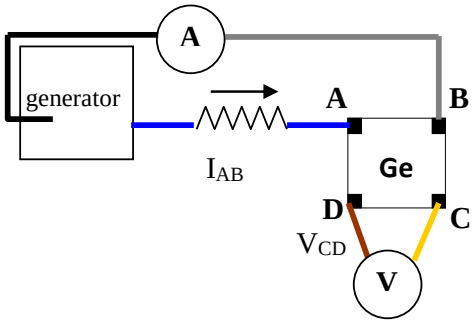


Figure 4.2 a)

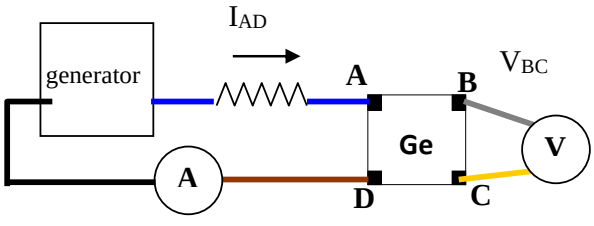


Figure 4.2 b)

Then the contacts are changed, repeating the previous measurements with the other pair of adjacent contacts [Figure 2 (b)]: the current will flow through B-C (I_{BC}) and the voltage will be measured

between A and D, (V_{AD}). From the data obtained, the corresponding resistance is calculated, $R_2=V_{AD}/ I_{BC}$. The resistivity is obtained by using both resistance values, from the expression:

$$\rho = \frac{d\pi}{ln2}\frac{R_1+R_2}{2}F\left(\frac{R_1}{R_2}\right) \qquad [4.8]$$

In this equation the function $F(R_1/R_2)$ takes a value of 1 when R_1 and R_2 are very close, which is the case for samples of almost square shape, as in our case.

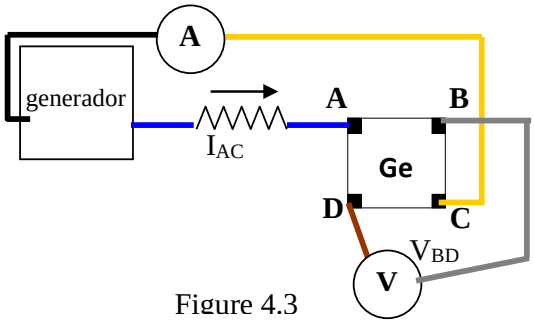
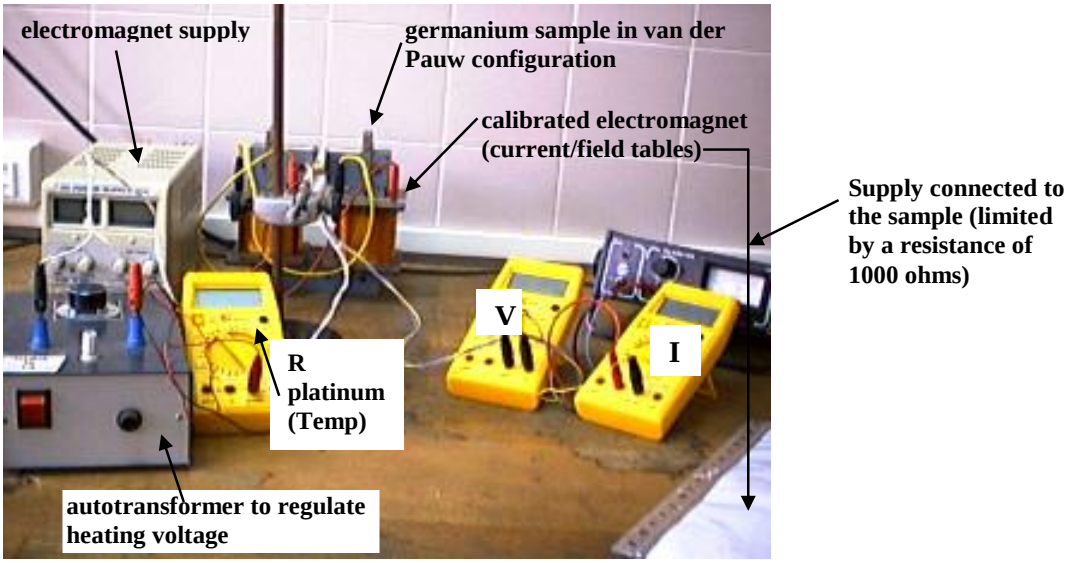


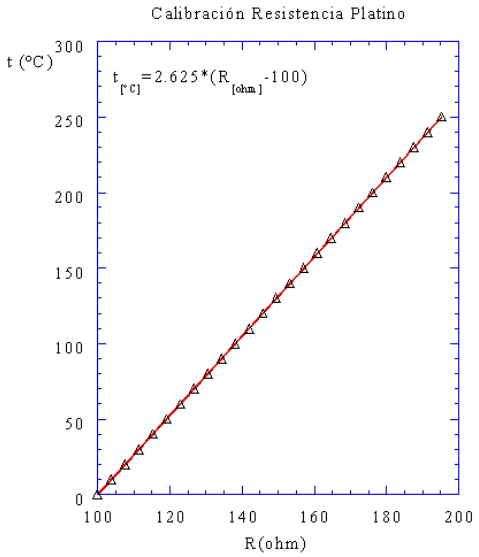
Figure 4.3

The contacts must be changed for the Hall effect measurement: current is passed through two opposite contacts (A and C, for example, obtaining I_{AC}) and the variation of the potential difference between the other two (B and D) is measured, applying the magnetic field, $V_{BD}(B)$, and no field, $V_{BD}(0)$ (because there may be a remnant field effect). The **Hall voltage**, V_H is therefore given by the difference between the two values: $V_H = V_{BD}(B)-V_{BD}(0)$.

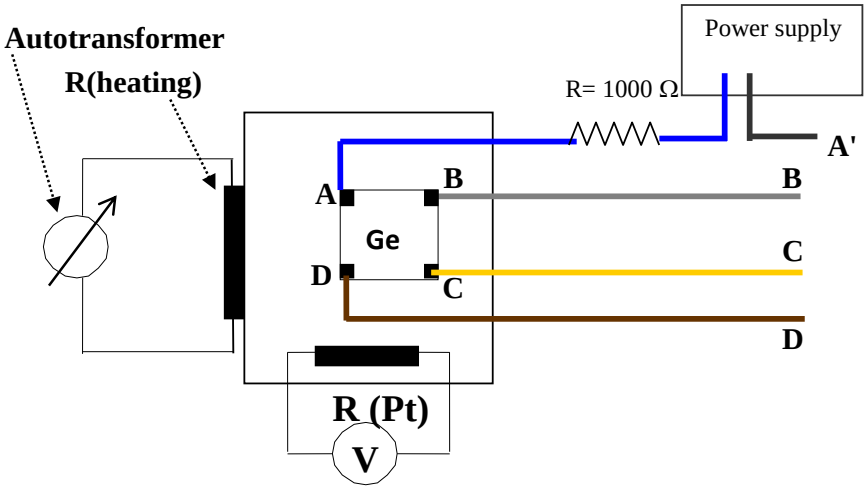
2. EQUIPMENT



In the experiment, a square sample of **germanium**, **0.5 mm** thick, will be studied. The sample is mounted on a heating system consisting of: a resistor, a sample holder and a platinum resistor embedded in the sample holder. The platinum resistor acts as a temperature sensor. Eight wires come out of the system: two from the heating resistor (**thick**), two from the platinum resistor (**black and red**) and four from the sample (**A: blue; B: grey; C: yellow and D: brown**).



The platinum resistance must be measured with a multimeter (connect the black and red wires to the multimeter). Knowing the dependence of the platinum resistance on the temperature we can obtain T (**it should be recorded in Kelvin**). The calibration of the platinum resistance is shown in the attached figure. **Note that in this graph the temperature is expressed in degrees Celsius.**



Since the blue wire (A) is connected to the power supply, it is the wire coming out of the power supply (A') that must always be used for current measurements, together with any other wire to be considered (ammeter in series). That is, regardless of the wire configuration chosen for voltage and current measurements by the van der Pauw method, **THE WIRE COMING OUT OF THE POWER SUPPLY (A') MUST <u>ALWAYS</u> BE CONNECTED TO THE CURRENT MEASUREMENT MULTIMETER.**

3.- TASKS TO BE COMPLETED

The specific tasks to be completed are detailed in the corresponding Lab Report sheet.

NOMBRE: GRUPO:
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EXPERIMENT 4 – LAB REPORT
Transport Properties of Semiconductors: Resistivity and Hall Effect Measurements

TASKS TO COMPLETE[1]

1. At room temperature:

1.1 Verify that the relationship between the potential V_{CD} and the current I_{AB} is linear. Repeat the measurements for V_{BC} and I_{AD}.

I_{AB}	V_{CD}	I_{AD}	V_{BC}

1. Plot V_{CD} versus $I_{AB,}$ and V_{BC} versus I_{AD}. Determine the resistance corresponding to each configuration. Compare their values and discuss whether it is a square sample. Calculate the resistivity of the sample at room temperature. Are the approximations made for this calculation adequate?

1.3 Switch the connections to measure the Hall voltage (swap the yellow and grey wires). By setting the value of the applied magnetic field (approximately 2-4 kG), measure the Hall voltage ($V_H = V_{BD}(B) - V_{BD}(0)$) as a function of the current through the sample (I_{AC}).

ATTENTION: Turn on the electromagnet ONLY when the VBD(B) measurement is taken. Refer to the laboratory tables for electromagnet calibration.

I_{AC}	V_{BD} (0)	V_{BD} (B=)	V_H

[1] The digital version of this document can be edited later at home to add space and information as required.

NOMBRE: GRUPO:
FECHA:

1.4 Measure the Hall voltage by fixing the current value ($I_{AC} \approx 10$ mA) and varying the magnetic field.

ATTENTION: Turn on the electromagnet ONLY when the $V_{BD}(B)$ measurement is taken. Refer to the laboratory tables for electromagnet calibration.

B	V_{BD} (0)	V_{BD} (B)	V_H

I_{AC}=

1.5 Plot V_H versus I_{AC} and V_H versus B. Are the relationships linear? Obtain the value of Hall's coefficient for both cases. Do they coincide? Comment on your results.

2. As a function of temperature:

The temperature is varied by increasing the voltage on the heating resistor with the autotransformer control. To make the measurement, it is necessary to wait for the temperature to stabilise (i.e., for the platinum resistor to have a stable value). It is sufficient for it to be stable in the time interval of a complete measurement).

2.1 Set the current through the sample (I_{AB} at room temperature around 10 mA) as well as the magnetic field to be applied for the Hall effect measurement (2-4 kG approx.). Measure V_{CD}, I_{AB} (resistivity), I_{AC}, V_{BD} (B=0) and V_{BD} (B) (Hall effect) for 15-20 temperatures covering the range between room temperature and a **maximum of 200-210 °C** (180 ohms of the platinum resistance. **NEVER EXCEED THIS VALUE as the sample will be damaged**). You can measure all values in a single experiment by changing the wires at each temperature.

ATTENTION: Turn on the electromagnet **ONLY** when the VBD(B) measurement is taken. Consult the electromagnet calibration on the laboratory desk tables.

NOMBRE: GRUPO:
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R (plat)	V_{CD}	I_{AB}	I_{AC}	$V_{BD}(B)$	$V_{BD}(0)$	V_H	**T (K)**	**ρ**	**R**	**R_H**	**n**	**μ**

2.2 Perform the necessary calculations to obtain the absolute temperature, resistivity, resistance, Hall coefficient, carrier concentration and mobility for each temperature.

2.3 Plot the resistivity and the Hall coefficient as a function of temperature. On both plots, mark the temperature at which the semiconductor transitions from the extrinsic to the intrinsic regime and give reasons for your choice.

2.4 Plot μ against T on a double logarithmic scale. Perform a least-squares fit and determine the dominant type of dispersion. Briefly discuss your results.

2.5 Plot $\ln((nT^{-3/2})$ against 1000/T (Arrhenius diagram). Determine the energy of the forbidden band. Compare the result with a tabulated value.

2.6 Calculate the impurity concentration of the material, stating the values from which you have made the calculation and the expression you have used to derive it.

3. Discussion of results and conclusions

Evaluate and comment on the results in relation to what was expected and draw conclusions about the experiment carried out.

EXPERIMENT 5 – LAB GUIDE
Ferroelectric Materials and the Curie Temperature

1. INTRODUCTION

To understand what a ferroelectric material is, the central concepts are the dipole moment, $\vec{p}$, and vector polarisation, $\vec{P}$, (or dipole moment per unit volume), which you have already seen in the *Electromagnetismo I* and *II* courses.

A **ferroelectric** is a solid with a spontaneous polarisation, $\vec{P}$, meaning that even in the absence of an electric field the value of $\vec{P}$ is non-zero. For this to occur, the positive and negative charge centres must be different. Since real materials are made up of positive ions (cations) and negative ions (anions), in a ferroelectric material the charges must be arranged in a such a way in the crystal so that their contributions to polarisation do not cancel each other out. In a similar way to ferro*magnetic* materials (*e.g.* magnets), ferro*electric* materials have domains of defined polarisation, called Weiss domains, and there exists a temperature (the **Curie temperature**) above which the material ceases to have ferroelectric properties.

A necessary (but not sufficient) property for a crystal to be ferroelectric is that it is not centrosymmetric, *i.e.*, it must not be invariant when inverted. The inversion of a crystal transforms the position of an atom from $\vec{r}$ to -$\vec{r}$. Since the dipole moment $\vec{p}$ is given by $\vec{p} = \sum_i q_i \vec{r}_i$, when the inversion operation is applied $\vec{p}$ becomes -$\vec{p}$.

It is important to note that ferroelectric materials are also *piezoelectric*, i.e., their polarisation changes with applied pressure. Equally, the crystals deform when an electric field is applied. This phenomenon of piezoelectricity is exploited in numerous applications, for example: in quartz in watches; microphones; the manufacture of capacitors; infrared detectors; the generation and detection of ultrasound, *etc*. In the second part of this experiment, you will have the opportunity to listen to the sound generated by applying a sinusoidal potential to a piezoelectric ring.

Firstly, however, the experiment focuses on the study of another property of ferroelectric materials: *pyroelectricity*. This is the change in their polarisation through a change in temperature.

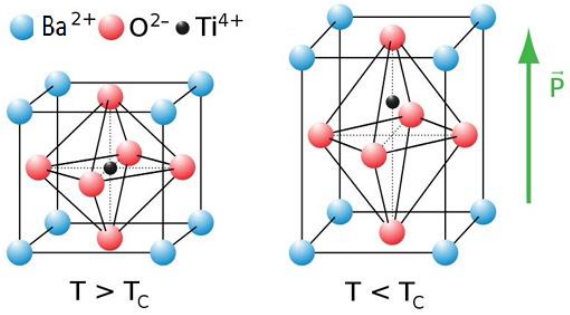


Figure 5.1

Amongst the best-known ferroelectric crystals are oxides with a **perovskite** crystal structure (ABO_3) such as barium titanate ($BaTiO_3$), whose crystal structure is shown in Figure 5.1. The main characteristic of the perovskite crystal structure is the octahedral arrangement of oxygen atoms around the titanium atom, which occupies the centre of the cell, and the barium atoms which occupy the eight vertices of the cube. This material has a non-ferroelectric phase when its structure is cubic (figure on the left). In this phase the crystal has inversion symmetry and therefore its polarisation is zero. In the ferroelectric phase (figure on the right), a tetragonal distortion occurs in which the

cations are slightly displaced in the opposite direction to the anions, meaning that there is no longer a centre of inversion. The crystal therefore acquires a permanent polarisation. Another widely used ferroelectric material is PZT (lead zirconate titanate). Its structure is similar to that of barium titanate, with lead taking the place of barium with lead and titanium and zirconium alternating in the different cells, depending on their composition.

1.1. Local field theory and ferroelectricity

The origin of ferroelectricity can be explained using the concept of the **local field**. The electric field experienced by an individual atom in a material can differ substantially from the externally applied macroscopic field. This field experienced by an atom/molecule is called the local field, E_{loc}. To calculate the local field around an atom, we can consider E_{loc} to be the sum of the external field plus the fields produced by the surrounding atoms/molecules in the crystal. This concept allows us to calculate the dielectric constant of a material by dividing the problem into two parts: 1) the area close to the local molecule, formed by the molecules contained in a sphere of radius *a*; and, 2) the rest of the dielectric, whose molecules are sufficiently far away from the local field and which can be considered to be a continuous medium whose electrical properties are represented by the dielectric constant ε. You can find a detailed calculation of the local field, for example, on page 108 of the book *Fundamentos de la Teoría Electromagnética* by Reitz, Milford and Christy. For the purpose at hand, it is sufficient to say that the field inside a uniformly polarised sphere is obtained as the sum of: the external field, *E*, plus the field inside the sphere, $\frac{P}{3\varepsilon_0}$, plus the field of the local molecules, E_{mol}, which in non-ferroelectric materials is zero.

Let us now see how to obtain the dielectric constant of a material with the local field model as a function of the dipole density, *N*, and the molecular polarisability, α. We start by calculating the polarisation, *P*. If *p* is the dipole moment of each molecule, $P=Np$. The definition of polarisability allows us to relate the molecular dipole moment to the local field: $p=\alpha E_{loc}$. Using local field theory, we write $E_{loc} = E + \frac{P}{3\varepsilon_0}$. We have not included the E_{mol} contribution because for the moment we assume that the material is not ferroelectric. This leaves:

$$P = Np = N\alpha E_{loc} = N\alpha \left(E + \frac{P}{3\varepsilon_0}\right) \qquad [5.1]$$

Dividing [5.1] by the applied external field we obtain the following relation with the susceptibility and the dielectric constant of the material:

$$\frac{P}{E} = \varepsilon_0 \chi = \varepsilon_0(\varepsilon - 1) = \frac{N\alpha}{1-\frac{N\alpha}{3\varepsilon_0}} \qquad [5.2]$$

Then, rearranging for the dielectric constant we obtain:

$$\varepsilon = \frac{1 + \frac{2N\alpha}{3\varepsilon_0}}{1 - \frac{N\alpha}{3\varepsilon_0}} \qquad [5.3]$$

According to this expression, a singularity will exist when the condition $N\alpha=3\varepsilon_0$ is fulfilled, a singularity that would lead to the appearance of a polarisation in the absence of field, i.e., to ferroelectric behaviour. The crystal deformation contributing to the increase in polarisation is energetically favourable, so that a phase change occurs. This behaviour is only really observed in particular structures where the polarisability is very large. This is the case for the perovskites

described above, which change from a cubic to a tetragonal phase. In this case the polarisation is large due to the existence of Ti-O chains.

1.2.Phase Transitions

Since the polarisability is very sensitive to temperature, around the temperature at which the condition $N\alpha=3\varepsilon_0$ is satisfied, which we will call the **critical temperature** or **Curie temperature**, small variations in the polarisability, α, give rise to enormous variations in the dielectric constant. It is this dependence of the dielectric function on temperature that we will study in the first part of the experiment. To introduce the temperature dependence into equation [5.3], we will define a parameter s of the form $s = 1 - N\alpha/3\varepsilon_0$. If we do not stray too far from the critical temperature, T_C, we can assume that this parameter changes linearly with temperature, of the form $s = \beta(T-T_C)$. Then, using equation [5.3] and eliminating polarisation, we find that the variation of the dielectric constant with temperature is given by the so-called **Curie-Weiss law**:

$$\varepsilon = \frac{3/\beta}{T - T_C} \qquad [5.4]$$

The relationship [5.4] is represented in this graph:

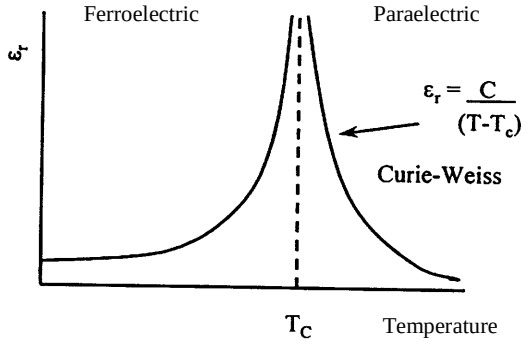


Figure 5.2

Below the critical temperature, the crystal becomes permanently polarised, changing from the paraelectric phase (T>Tc) to the ferroelectric phase (T<Tc).

Landau's theory of phase transitions allows us to predict the change of the permanent polarisation as a function of temperature in the ferroelectric phase. For this purpose, we can represent the free energy as a power series of the polarisation:

$$F(P,T,E) = -EP + g_0 + \frac{1}{2} g_2 P^2 + \frac{1}{4} g_4 P^4 + \frac{1}{6} g_6 P^6 + \ldots \qquad [5.5]$$

The equilibrium polarisation will correspond to a minimum of the free energy:

$$\frac{\partial F(P,T,E)}{\partial P} = -E + g_2 P + g_4 P^3 + g_6 P^5 + ... = 0 \qquad [5.6]$$

For a phase transition to occur, the value of g_2 must pass through zero at T_C, $g_2=\gamma(T-T_C)$, so that, below T_C, the unpolarised crystal is unstable. If g_4 is positive, neglecting g_6, the polarisation at zero field, P_s would be obtained from the equation:

$$\gamma(T - T_C) P_S + g_4 P_S^3 = 0 \qquad [5.7]$$

whose solutions are $P_s=0$ or $P_s=(\gamma/g_4)^{1/2}(T-T_C)^{1/2}$. We conclude that the permanent polarisation tends to zero continuously with increasing temperature, cancelling out at the critical temperature. This is a second order phase transition.

If g_4 is negative, the next term of the development must be taken into account, and the equilibrium polarisation would be:

$$\gamma(T - T_C) P_S + g_4 P_S^3 + g_6 P_S^5 = 0 \qquad [5.8]$$

Whose solutions are, again, $P_s=0$ and another solution which does not cancel for $T=T_C$. In this case there is an abrupt change of polarisation at the transition (first order phase transition).

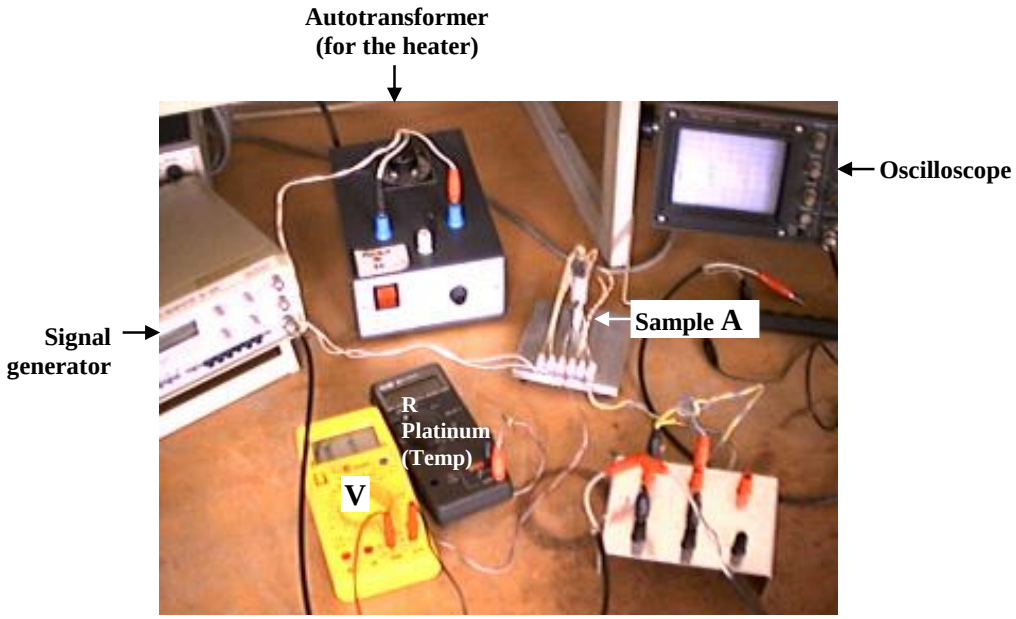


Figure 5.3

2. EQUIPMENT

2.1 Piezoelectric ceramic sample (A) (PZT8, with 80% Zr and 20% Ti) mounted on an aluminium sample holder including a heating resistor connected to an autotransformer. The temperature is measured by means of a platinum resistor as a temperature sensor, which is read with a multimeter. **The surface of the sample (which is metallised on both sides) is S = 20 mm^2 and its thickness d = 1 mm.**

2.2 Piezoelectric ceramic sample in the form of a cylinder, with electrical contacts on both surfaces (50ø ×10 ×2 mm^3), mounted on an acrylic support.

2.3 Signal generator, variable frequency.

2.4 Oscilloscope.

2.5 Autotransformer to supply the heating resistor.
2.6 Multimeter for temperature measurement (Pt resistance).
2.7 Multimeter to measure voltage.
2.8 Board for mounting the measuring circuit.

3. EXPERIMENTAL METHOD

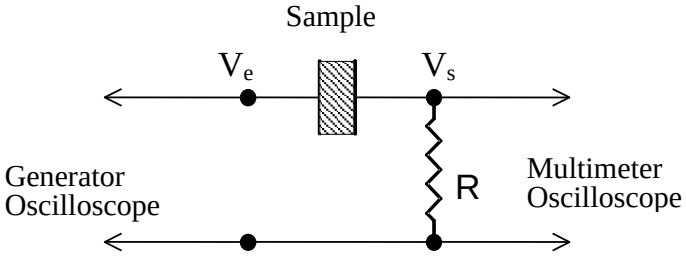


Figure 5.4

To determine the *dielectric constant* of the material, the *capacitance* of the ferroelectric sample is measured by measuring the current in the capacitor branch for an applied alternating voltage of known frequency and amplitude, according to the diagram in the figure. If we consider the sample as a capacitor of capacitance C_m, the relationship between V_e and V_s is given by:

$$\frac{V_s}{V_e} = \frac{jRC_m\omega}{1 + jRC_m\omega} \qquad [5.9]$$

so that, for low frequencies, the voltage V_s will be proportional to C_m. The capacitance of the sample can be modelled as a flat capacitor of area S and thickness d. Its value will be $C_m=\varepsilon S/d$, where ε is the dielectric constant of the material. Knowing R and measuring V_e and V_s for a given frequency, the value of ε can be determined. The values of S and d can be found in the description of the available equipment (section 2).

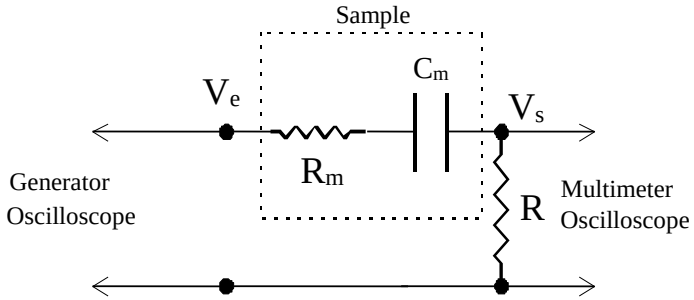


Figure 5.5

Treating the sample as a capacitor is a good approximation at low frequencies as long as the dielectric losses, and those caused by the piezoelectric effect, are negligible. Dielectric losses, which would be represented by a parallel resistor, are negligible in our assembly. When far from the resonance frequency, the losses due to the piezoelectric effect can be represented by means of a series resistor, R_m, which remains to be determined experimentally. The circuit for the experimental setup is shown in Figure 5.5. The dashed box encompasses the elements describing the electrical behaviour of our sample, the value of which we need to determine. Taking into account the impedances of each element, the ratio between the output and input voltages would be in this case:

$$\frac{V_s}{V_e} = \frac{jRC_m\omega}{1 + j(R + R_m)C_m\omega} \qquad [5.10]$$

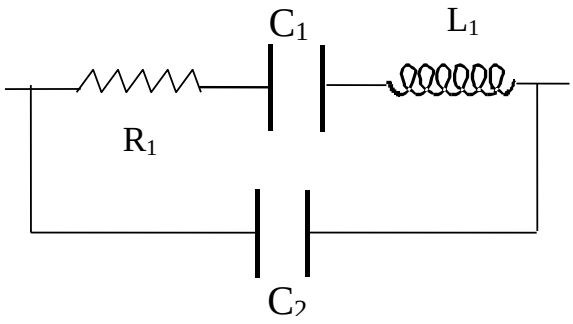


Figure 5.6

On the other hand, if the frequency of the applied voltage is close to a resonance, the equivalent circuit is more complicated. This situation will be encountered in the second part of the experiment: essentially, resonance occurs when the *excitation frequency corresponds to a mode of vibration of the ceramic sample*. These modes of vibration will depend both on the speed of propagation of the elastic waves in the material and on the size of the ceramic. The resonant frequencies are those for which a half-wavelength corresponds to one of the dimensions of the ceramic. Given that it is a hollow cylinder, we will have three fundamental resonance frequencies, one corresponding to the **length of the circumference,** another corresponding to the **length of the cylinder (its height)** and another corresponding to **the thickness of the cylinder wall**, in inverse order of the length involved in each resonance. For each resonance, the equivalent circuit would be as shown in Figure 5.6. The impedance of such a circuit and the ratio between input and output voltages will be:

$$Z = \frac{R_1 + j(L_1\omega - \frac{1}{C_1\omega})}{1 + jRC_2\omega + \frac{C_1}{C_2} - C_2L_1\omega^2} \qquad [5.11]$$

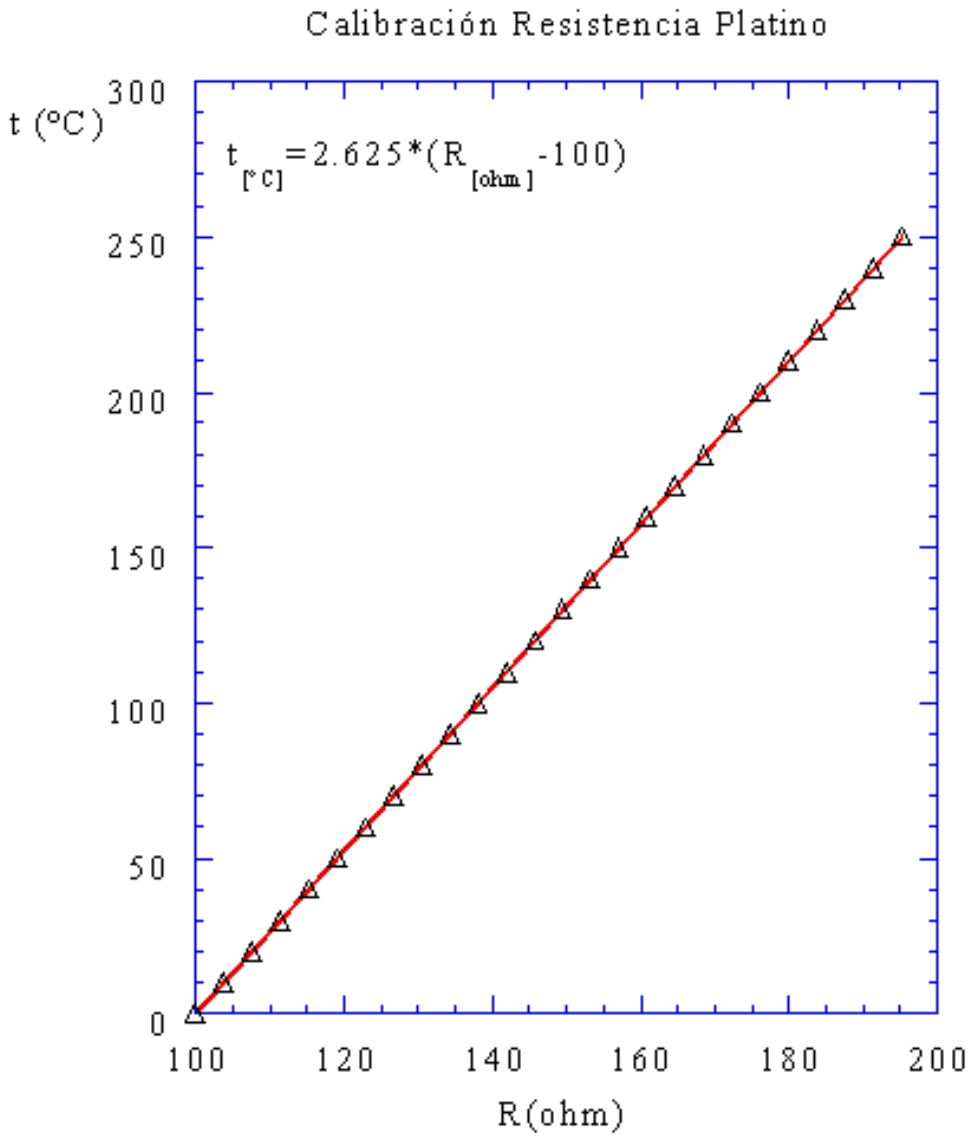
$$\frac{V_s}{V_e} = \frac{R}{R+Z} \qquad [5.12]$$

The impedance Z has a maximum and a minimum, corresponding to the resonances of L_1 with C_1 (series) and C_2 (parallel).

3.- TASKS TO BE COMPLETED

The specific tasks to be completed are detailed in the corresponding Lab Report sheet.

The calibration of the Pt resistor used for the determination of sample temperature is given on the next page:


Calibración Resistencia Platino
t (°C)
300
250
200
150
100
50
0
t [°C] = 2.625*(R [ohm] -100)
100
120
140
160
180
200
R(ohm)

NAME: GROUP:
DATE:

EXPERIMENT 5 – LAB REPORT
Ferroelectric Materials and the Curie Temperature

TASKS TO COMPLETE[1]

For each question you should briefly explain what you did in the experiment and show any calculations. You may also include photographs of the set-up. (You should watch this introductory video before coming to the lab session: https://mmedia.uv.es/html5/u/cr/cros/64825_practica5_c.mp4.)

1. Low and high frequency behaviour.

1.1 Using the setup in Figure 2 (with R=10 kΩ) and with constant Ve (Ve≈10 V) measure Vs(ω) in a frequency range from 50 Hz up to the MHz range. Use the oscilloscope for voltage measurements.

ν (Hz)	ω (rad/s)	V_s	V_s/V_e

V_e=

2.2 Plot the gain (V_s/V_e) versus ω on a double logarithmic graph. Analyse your results using equation [5.9] in the low and high frequency limit. Using a least squares fit in the low frequency range, obtain

[1] The digital version of this document can be edited later at home to add space and information as required.

the value of C_m. Calculate the value of ε and compare it with that expected for this type of material. Determine R_m from the values obtained at high frequencies.

3. Temperature-dependent behaviour.

3.1 The temperature is varied by increasing the voltage across the heating resistor with the autotransformer control. At a constant low frequency (around 100 Hz) and by fixing V_e ($V_e \approx 10$ V), measure V_s with the multimeter as a function of temperature. **WARNING: do not exceed the temperature corresponding to 210 ohms of the platinum resistor, but you will need to get quite close to it.** Note that the temperature must remain stable during the measurement. From the gain at low frequency (V_s/V_e), deduce the capacitance for each temperature, and from this the dielectric constant.

R platinum	**V_s**	**T (K)**	V_s/V_e	C_m	$\varepsilon/\varepsilon_0$

ω= V_e=

3.2 Plot the inverse of the dielectric constant versus temperature. Using equation [5.3] and the data obtained, determine the Curie temperature of this material. To do this, a least-squares fit should be made for the low temperature data.

NAME: GROUP:
DATE:

4. Resonance

4.1 Find the resonance frequencies of the piezoelectric cylinder using the circuit in Figure 5.4. Use a smaller value for the resistor R for the assembly (1 kΩ or smaller, choose in each case the most appropriate one to observe the resonance maxima and minima). These frequencies will appear as singularities in the frequency response. Measure in detail the frequency response around each of the resonances, showing, in particular, that the impedance Z has a maximum and a minimum for each resonance.

ν1 (Hz)	ω1 (rad/s)	V_s	V_s/V_e

ν2 (Hz)	ω2 (rad/s)	V_s	V_s/V_e

ν3 (Hz)	ω3 (rad/s)	V_s	V_s/V_e

NAME: GROUP:
DATE:

4.2 Plot the resonance curves (V_s/V_e vs. ω).

4.3 Taking into account that each resonance corresponds to the fundamental mode of vibration of the different dimensions of the cylinder (circumference, height and thickness of the wall), plot the frequency versus the inverse of the wavelength and deduce, by means of a linear fit, the propagation velocity of the sound waves in the medium.

5. Discussion of results and conclusions

Evaluate and comment on the results with respect to what was expected, drawing conclusions about the experiment.