Towards the development of a mathematical model for prediction of the magnetic and structural properties of iron ferrites obtained by mechanosynthesis.

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Table of Contents

Introduction

In the search of materials with very specific properties, both chemical and physical, many synthesis methods have been proposed, so that they are formed from known materials through chemical reactions.

Important parameters in these methods are:

- The energy necessary for starting or activating the chemical reactions that happens thanks to mechanicals forces.

- The specific conditions used to perform the mechanosynthesis process.

This talk is approached from different perspectives: historical, methodological and thrown by the procedure results.

Objectives

- To present magnetic nanoparticles and know some of their physical properties.
- To take a look at the mechanochemical or mechanosynthesis process.
- To show the instrumental setup.
- To show some theoretical approaches to the milling process.
- To make a projection about possible work fronts in the investigation being the title of this talk.

What is a nanoparticle?

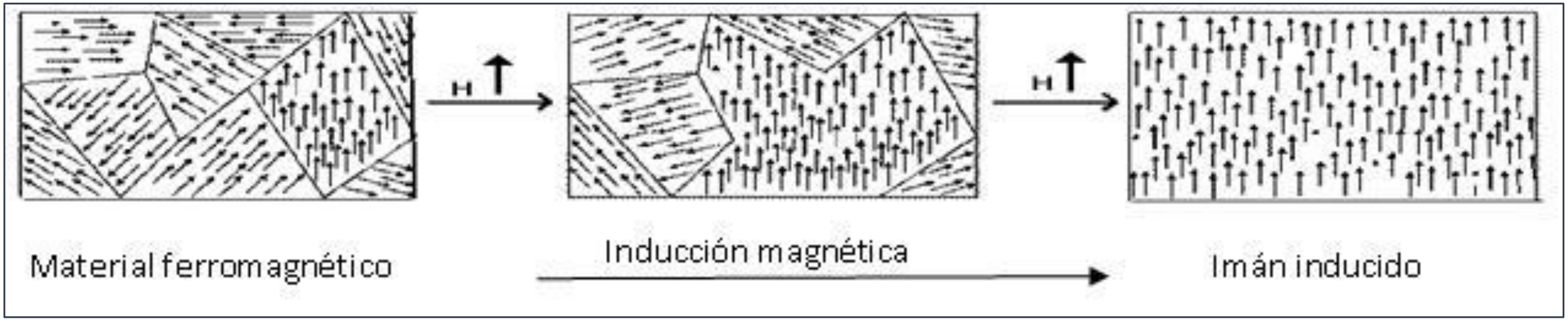
A nanoparticle is a particle whose dimensions are of the order of nanometers (from 1 to 100 nm)

This particle has its own characteristics, it presents magnetic, electrical and chemical properties very different from those presented by particles in higher scales.

- Neuberger T. et al. (2005)
- Taken from: http://avancesnanotecnologia.euroresidentes.com/2005/04/nanoparticulas-para-detectar-y-tratar.html

Bases of magnetism and crystallography

Origin of magnetism



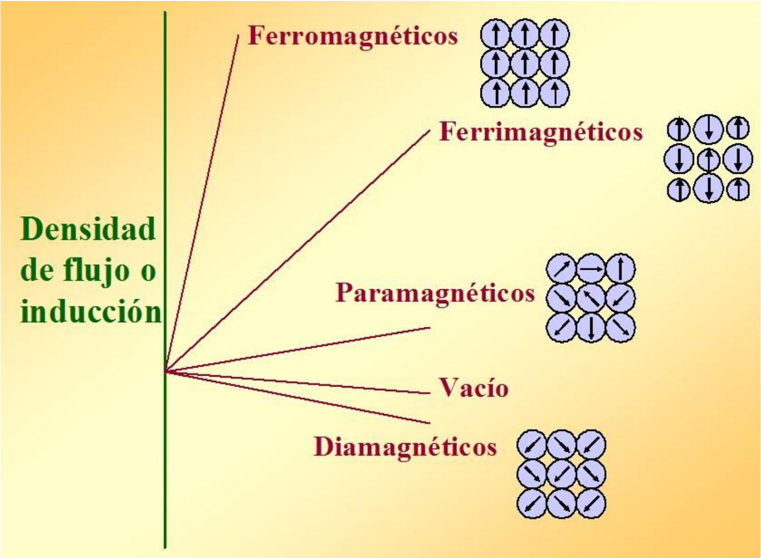
Taken from: http://www.datuopinion.com/dominio-magnetico

Domains in a ferromagnetic or ferrimagnetic material

Dimensions of the domains ≈ 10 000 – 100 000 nm

Dimensions of the walls ≈ 100 nm

Magnetization of matter



Taken from: http://www.upv.es/materiales/Fcm/Fcm10/trb10_2.html

	Magnetic material	Permeability μ	Example
(a)	Diamagnetic Paramagnetic	$\mu < \mu_0$ $\mu > \mu_0$	Gold Manganese
(b)	Ferromagnetic	$\mu >> \mu_0$	Iron
(c)	Antiferromagnetic	$\mu > \mu_0$	Hematite
(d)	Ferrimagnetic	$\mu > \mu_0$	Ferrites (magnetite)

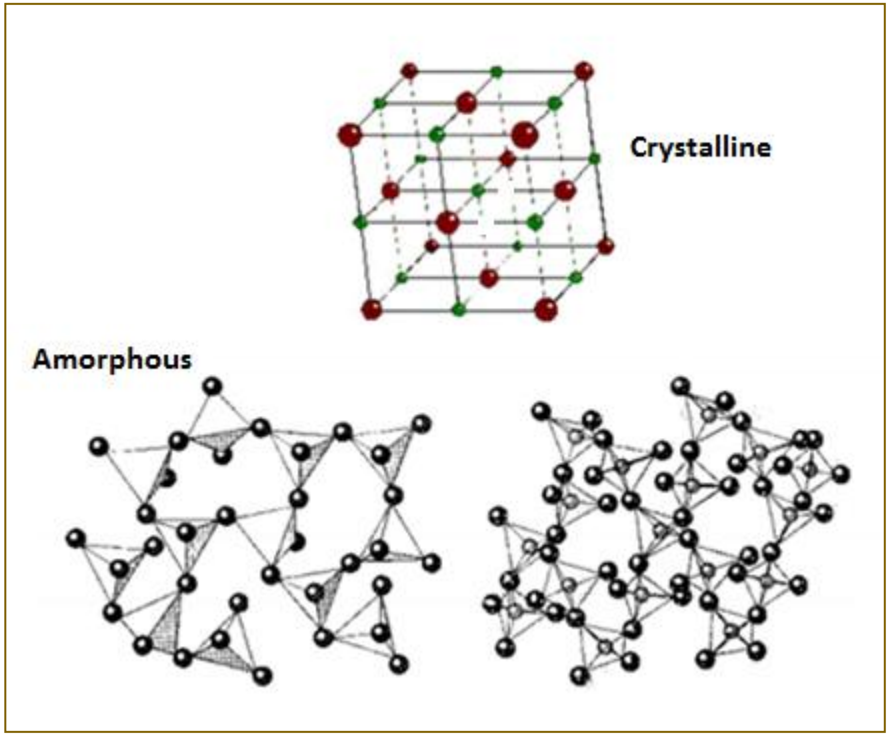
$$\vec{B} = \mu \vec{H}$$

Where:

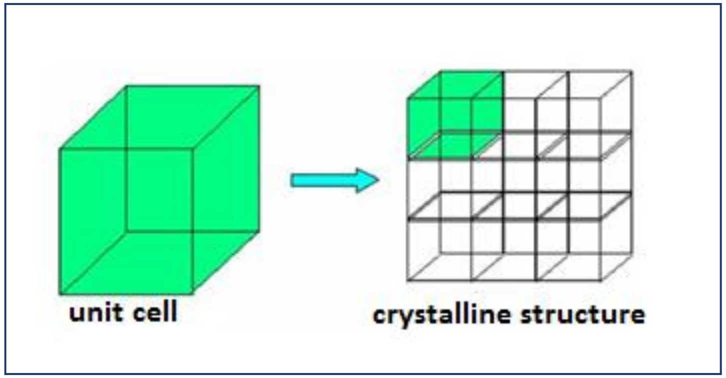
B: Magnetic induction
H: magnetic field strength

μ: magnetic permeability of the medium
μ_0: magnetic permeability of vacuum

Types of solids: crystalline and amorphous

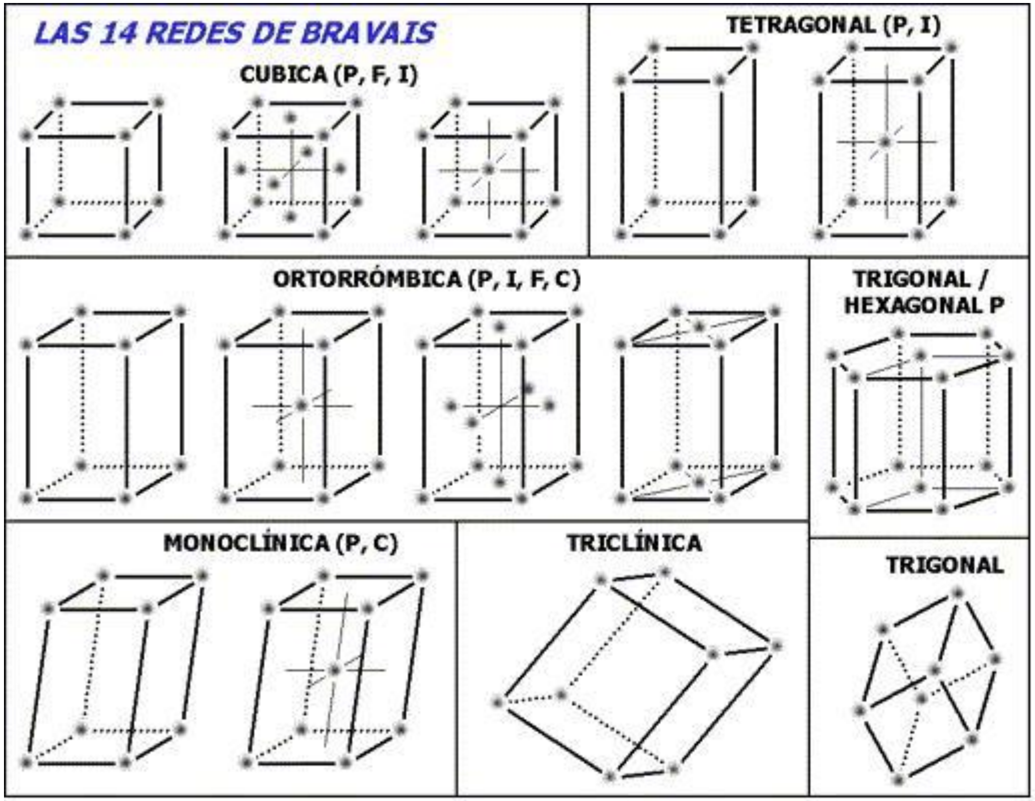


Taken from: http://www.eis.uva.es/~macromol/curso05-06/pp/cristalinos_y_amorfos.htm

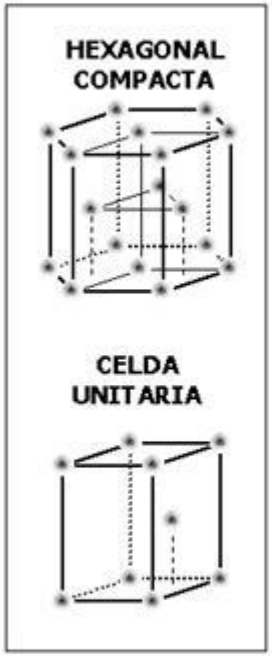


Taken from: http://datateca.unad.edu.co/contenidos/256599/256599%20Materiales%20Industriales/124_estructura_de_los_materiales.html

Crystalline structure



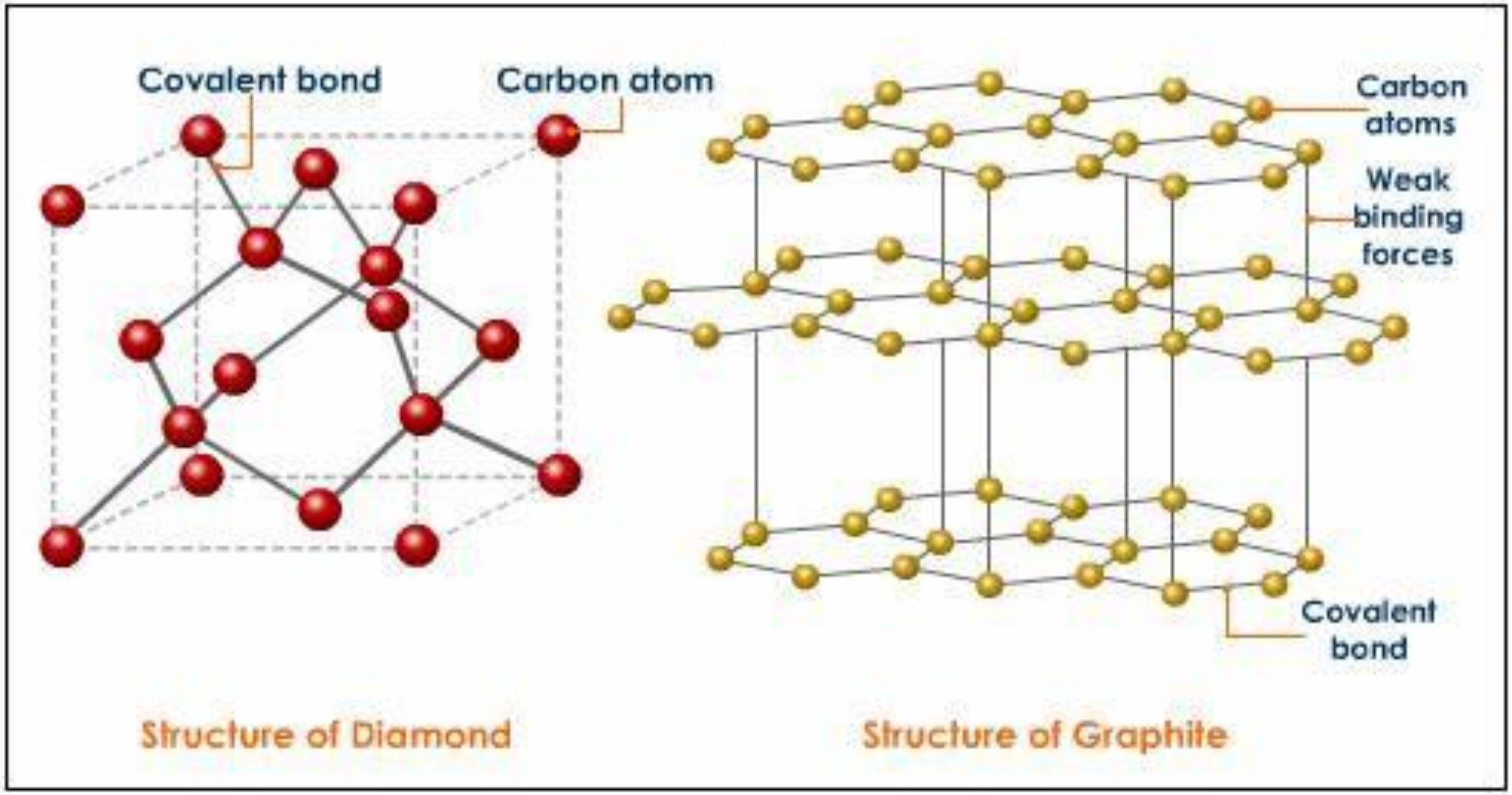
Taken from: http://neetescuela.com/solidos-cristalinos-y-amorfos



Iron Ferrite
Their unit-cell is BCC

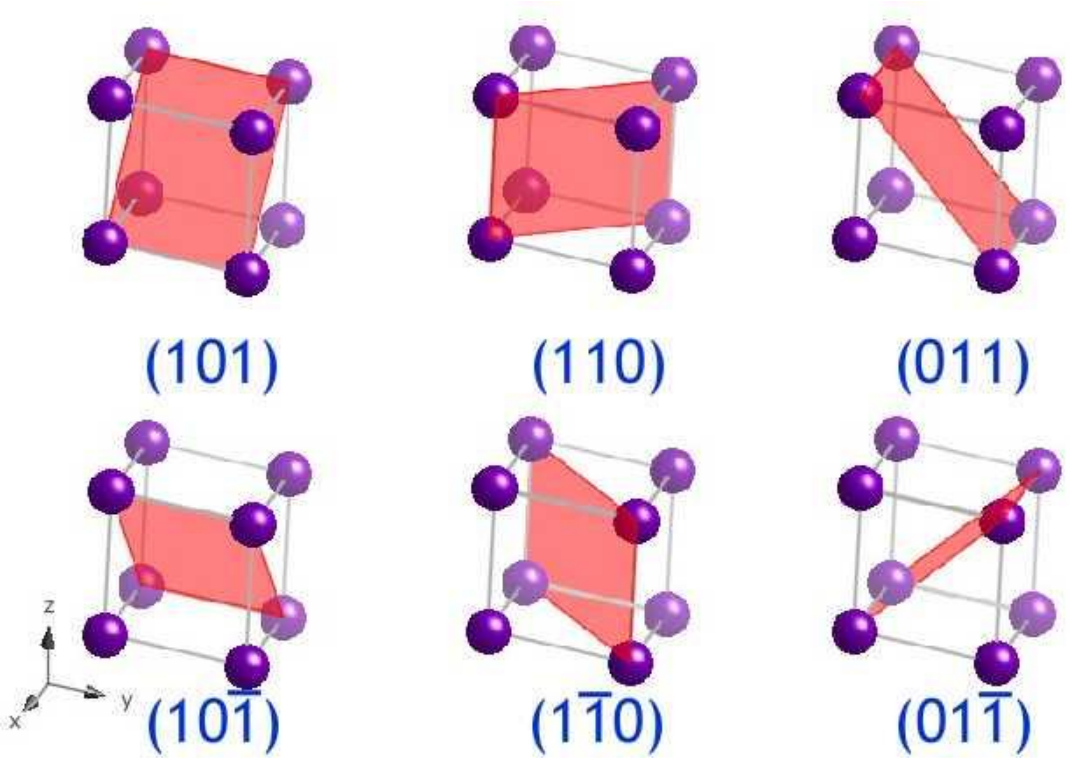
Hematite
Their unit-cell is hexagonal

The structures for (a) diamond and (b) graphite



Taken from: https://www.pinterest.com/pin/412642384579376064/?from_navigate=true

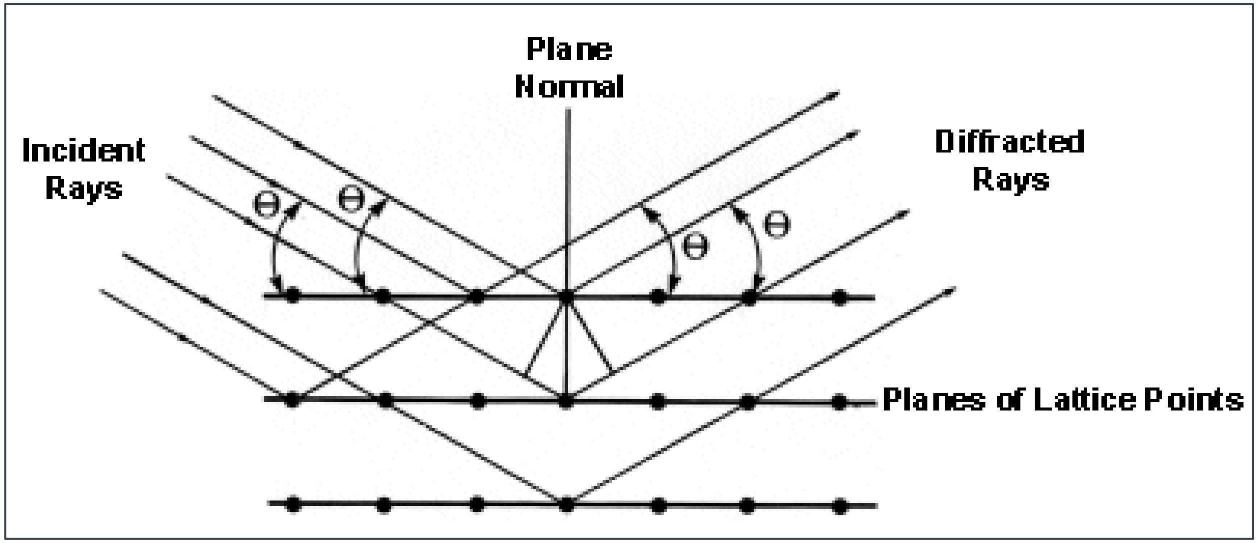
Six different lattice planes in the simple cubic structure characterized by their Miller indices



Taken from: http://materialesbuap2013.weebly.com/iacutendices-de-miller.html

X-ray diffraction

X-rays are electromagnetic waves whose wavelength is 10^{-10} m. They have the same size of the atom.

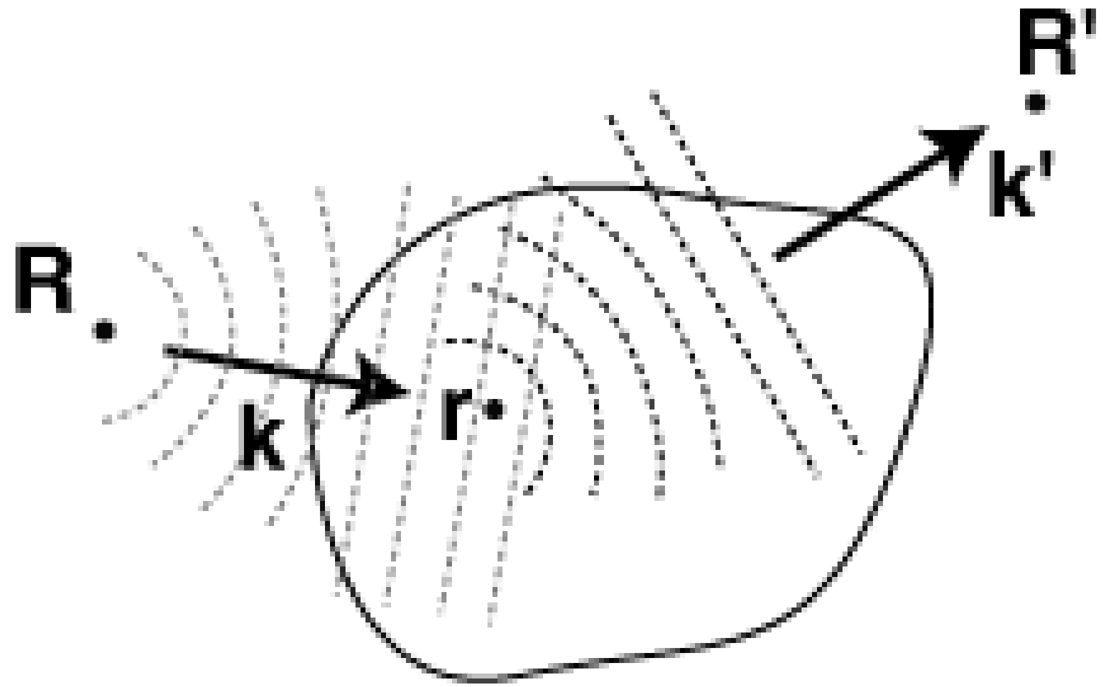


Taken from: http://wesharepics.info/imagexgkl-x-ray-diffraction.asp

The horizontal lines represent the lattice planes, which are separated by a distance *d*

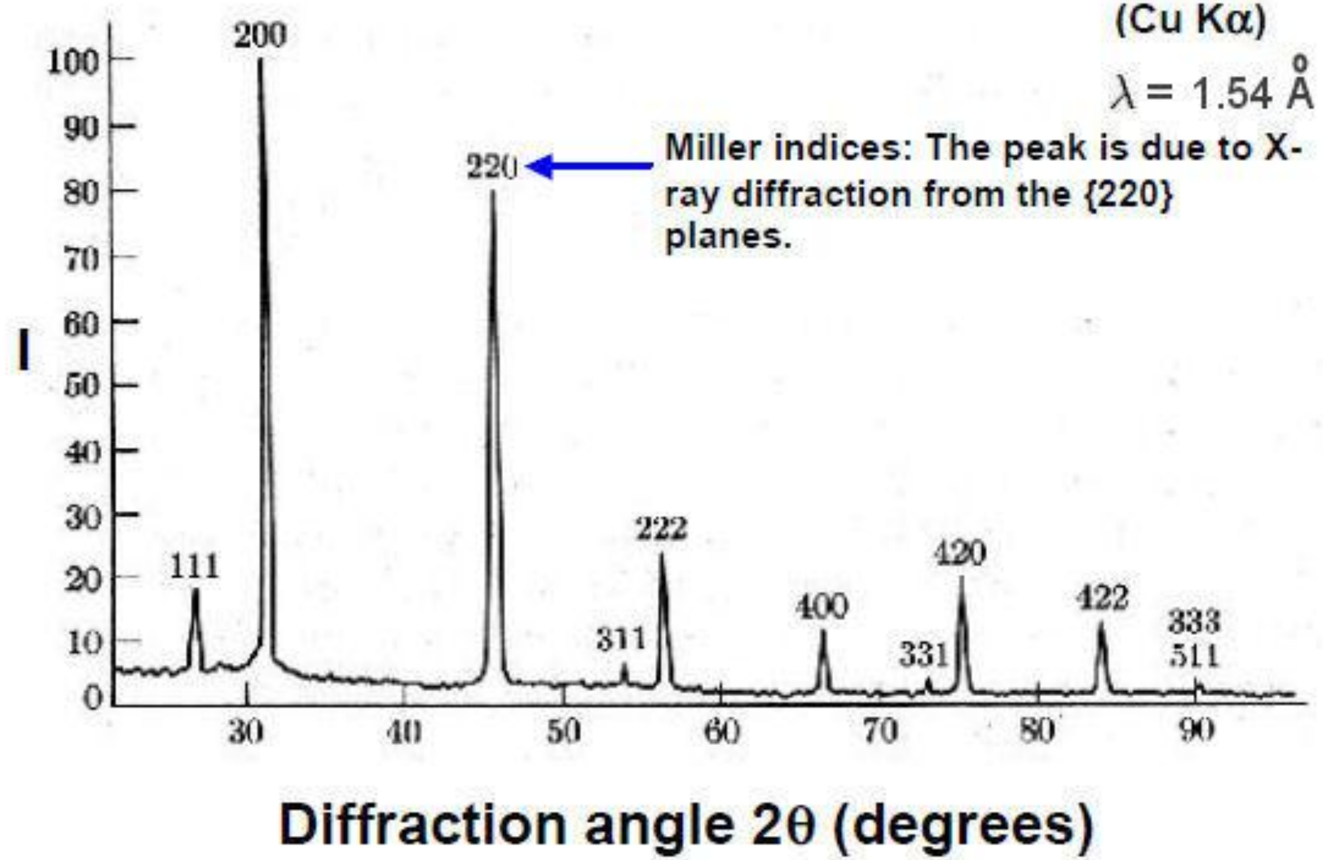
Illustration of x-ray scattering from a sample

The source and detector for the X-ray are placed at **R** and **R’**, respectively.

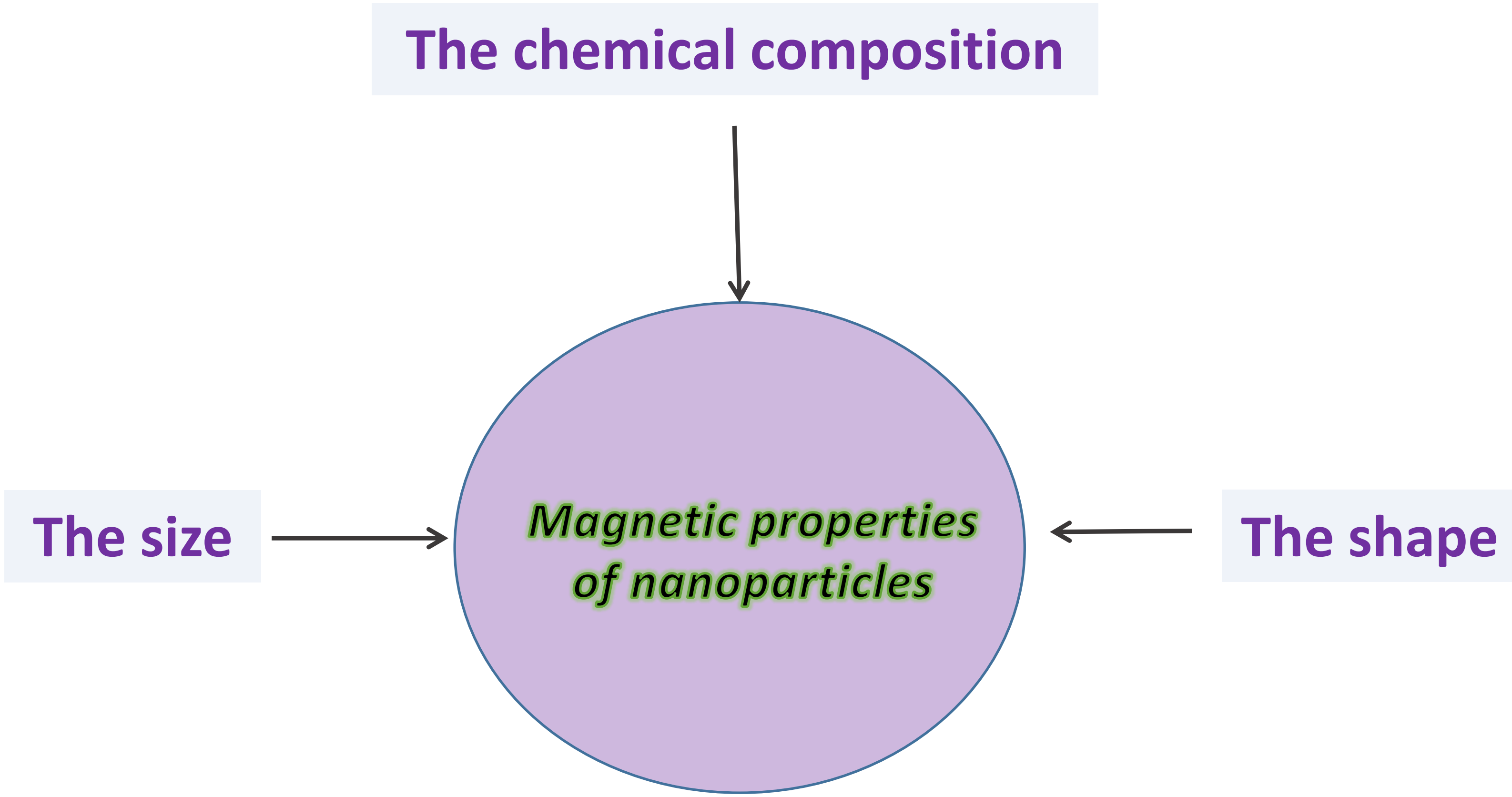


Taken from: http://users-phys.au.dk/philip/pictures/physicsfigures/physicsfigures.html

XRD Pattern of NaCl Powder



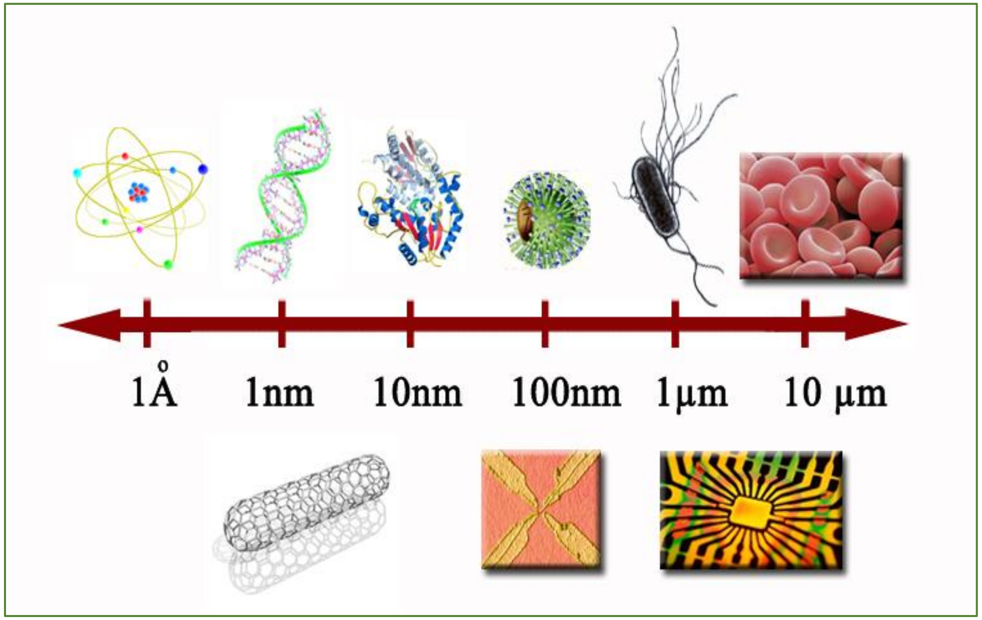
Taken from: http://subato.blogspot.com.co/2011/03/lets-do-experiment-using-xrd-how-to.html


The chemical composition
The size
Magnetic properties of nanoparticles
The shape

Some applications of magnetic nanoparticles

Nanoparticles vs biological entities

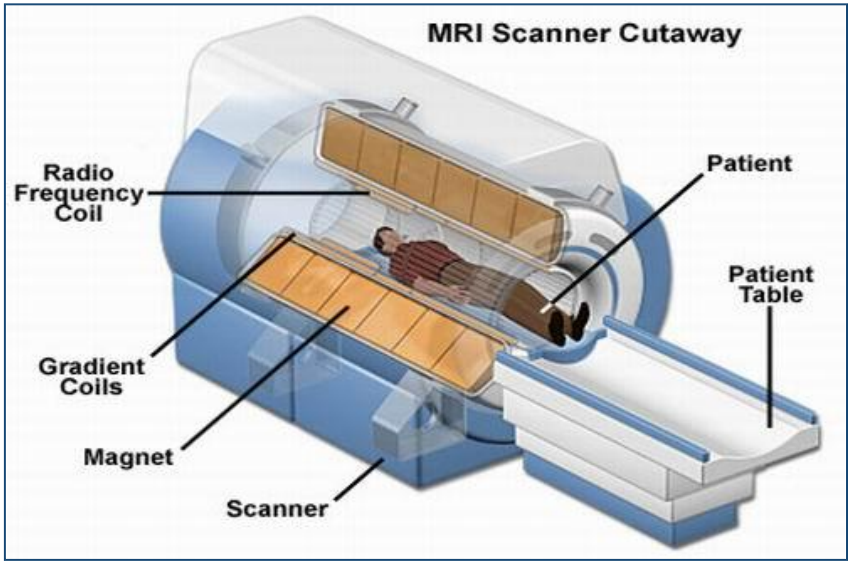
Nanoparticles	**1.0 – 100 nm**
Cell	200 nm – 100 000 nm
Virus	20 – 450 nm
Proteins	5 – 50 nm
Gene	2 nm wide
	10 – 100 nm long



Taken from: http://es.slideshare.net/luisaranguena/nanomedicina-35167076

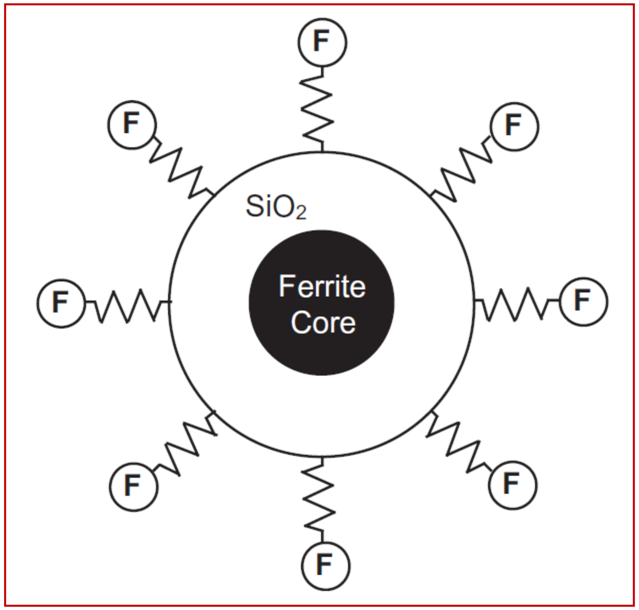
1. Diagnosis and medical treatment

Magnetic hyperthermia



Taken from:
http://www.iranreview.org/content/Documents/New_Sci_Tech_Improvements_in_Iran.htm

Functionalization



Pankhurst, Q.A. (2003, 2009)

Iron core , shell silica (SiO_2) and functional groups

2. Environmental remediation

heavy metals in solution

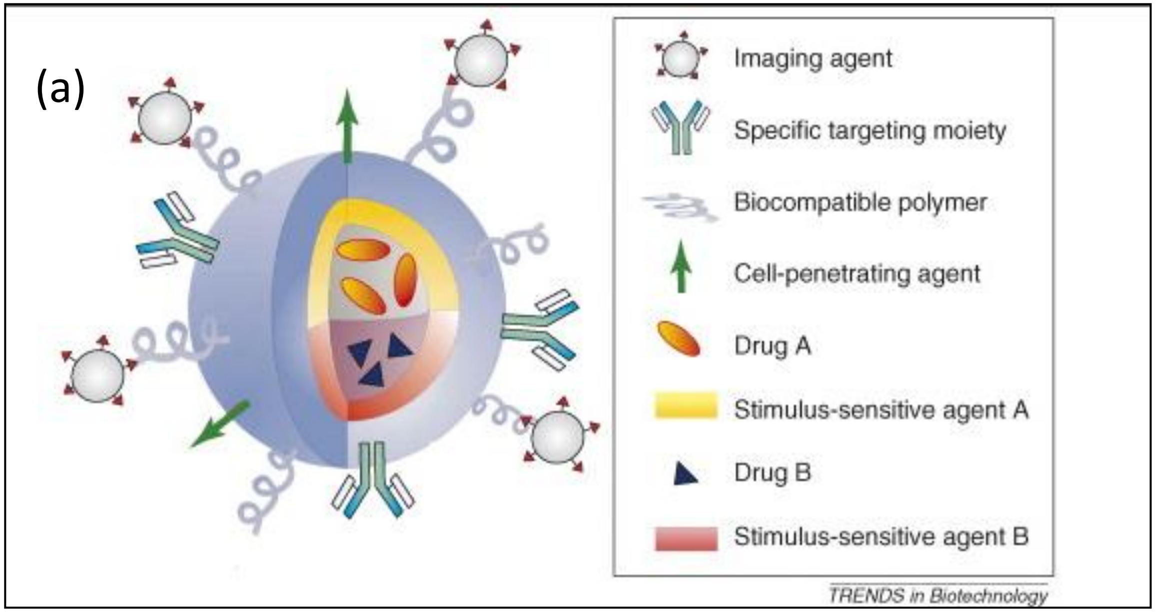
lower concentrations 1 μg/l

3. Information storage

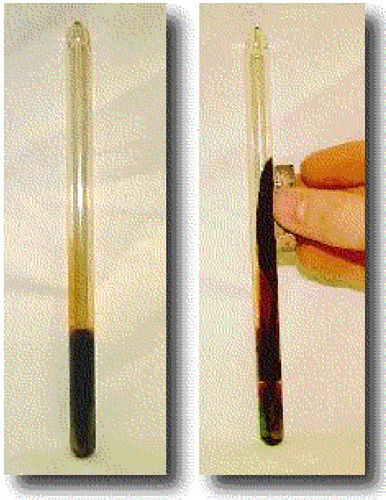
nanoparticles with sizes around 3 nm

4. Drug transport and delivery (ferrofluids)

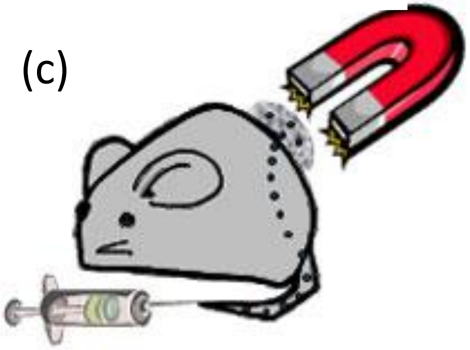
(a)



(b)



(c)



Taken from:
(a) http://www.cell.com/trends/biotechnology/fulltext/S0167-7799(08)00140-6
(b) http://www.astro.gla.ac.uk/users/plasma/ferro.html
(c) http://www.elmundo.es/elmundo/2011/10/10/nanotecnologia/1318237136.html

The ball milling process

Natural Iron Oxides

Taken from: http://marcianosmx.com/25-paisajes-surrealistas-tierra. *Petra en Jordania*.

Taken from: http://www.directindustry.es/prod/caterpillar-equipment.html

Iron oxide powders

Taken from: https://spanish.alibaba.com

Cosmetics
Iron oxide (II)

Taken from: https://spanish.alibaba.com

Ball mill

- Grinding to break up the rock (top - down approach)
- Grinding (dry - wet)
- Cement and mining
- Physical method

Ball mill for mining

Taken from: http://oruro.quebarato.com.bo/cercado/chancadoras-en-bolivia-maquinaria-para-la-mineria-molino-de-bolas__B54FD3.html

Operating Principles ball mill:

The particle size reduction occurs by different mechanisms, namely:

✓**High energy impacts between:**

- **Particle - particle**
- **Particle - ball**

✓**Friction between:**

- **Particles - ball**
- **Particles - grinding vessel wall**

✓**Compression**

- **Particles - ball**

Milling today : mechano-synthesis, mechanochemical or mechano-activation

Mechanochemical reaction:

"Chemical reaction is induced by direct absorption of mechanical energy"

Compendium of Chemical Terminology (IUPAC).

Parents of mechanochemical


Sepelák, V. et al. (2013)

Left: Matthew Carey Lea (1823-1897) ➔ separate arm of chemistry.

Right: Wilhelm Ostwald (1853 - 1932) ➔ introduced the term in the literature.

Planetary mill - pulverisette 7 brand FRITSCH

Taken from: http://www.retsch.com

Mill available in the Instrumentation and Spectroscopy Laboratory (EAFIT)

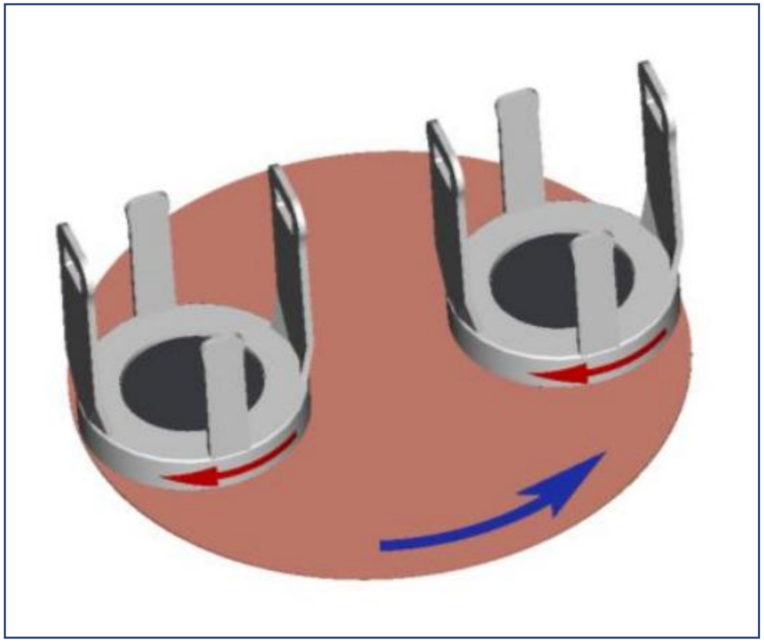
Taken from: http://www.retsch.com

__Available accessories:__

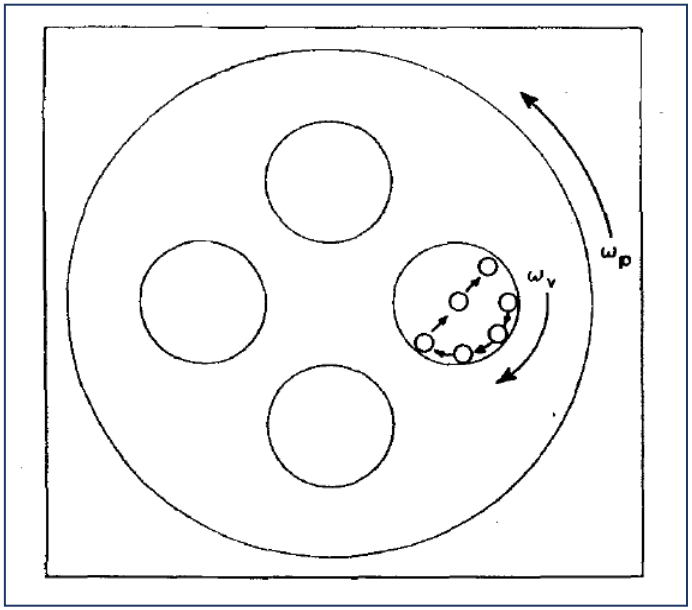
Tempered steel bowls for grinding in dry or humid environment → 80 ml

Tempered steel balls of different diameters

Ball milling: operating method



Taken from: www.fritsch-france.fr

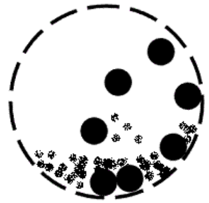


Burgio, N. et al. (1991)

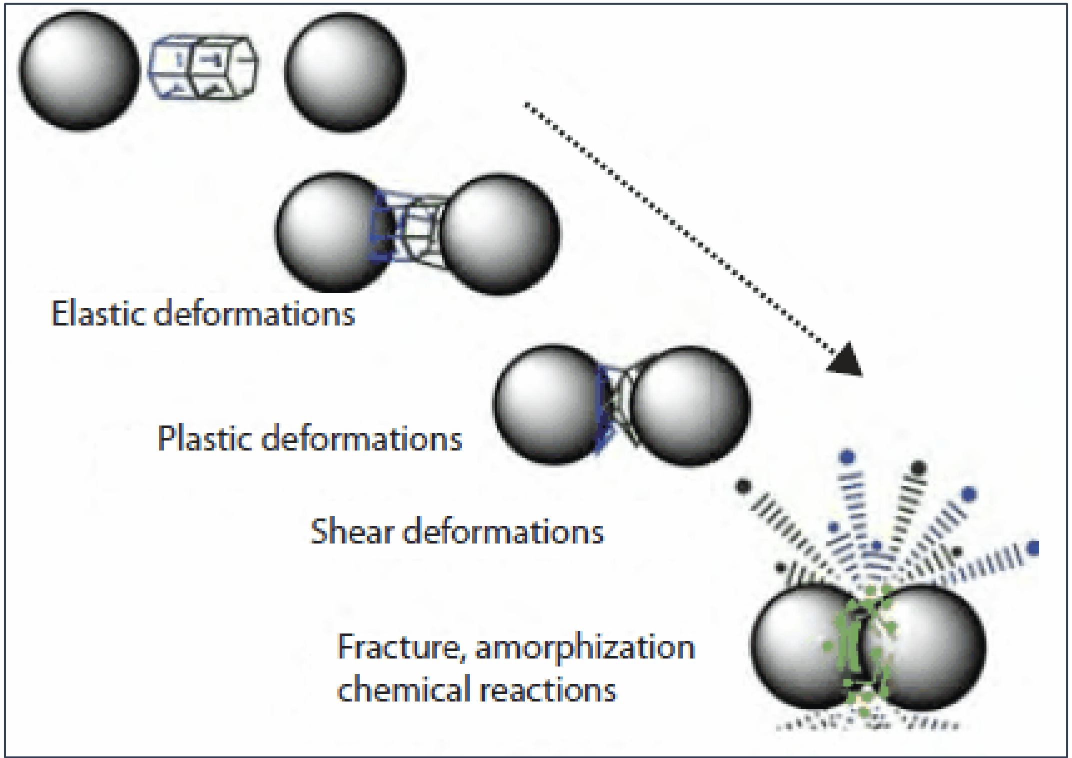
The grinding bowls are arranged eccentrically on the sun wheel.

The main wheel rotates in the opposite direction to the grinding bowls with a speed ratio of 1: 2.

Ball milling: operating method



http://www.chancadoras.org



Taken from: http://www.sigmaaldrich.com/technical-documents/articles/material-matters/mechanochemical-effect.html

The grinding efficiency depends on:

The hardness and density of the load elements.

The hardness and fracture toughness of the balls.

Fundamental condition

(Hardness and toughness) Balls >> (hardness and toughness) load elements

Benefits of Mechanochemical

- It is considered as a green chemistry because it generates less amount of waste.
- It is a low cost production method.
- You can try out new reactions.
- It is a scalable method for industrial production.

Technical specifications

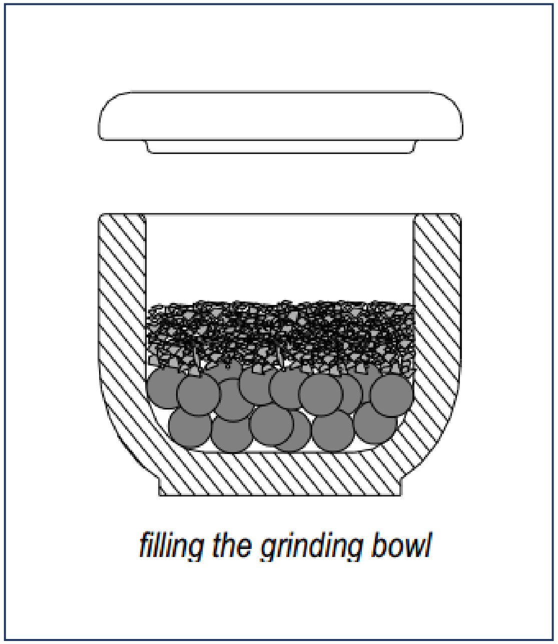
Number of balls per grinding bowl

Ball Φ (mm)	Bowl volume 80 ml
5	250-300
10	30-35
15	10
20	5
30	

Taken from: http://www.retsch.com

Filling the grinding bowl

Grinding bowl	Min. material volume	Max. material volume
80 ml	1 ml	30 ml



Taken from: http://www.retsch.com

Milling process

Milling process

Input variables

- Mass precursors
- Chemical certanty (%)
- Ratio mass powder/balls
- Diameter jars and balls
- Atmosphere
- Dry or wet millling
- And etc

milling

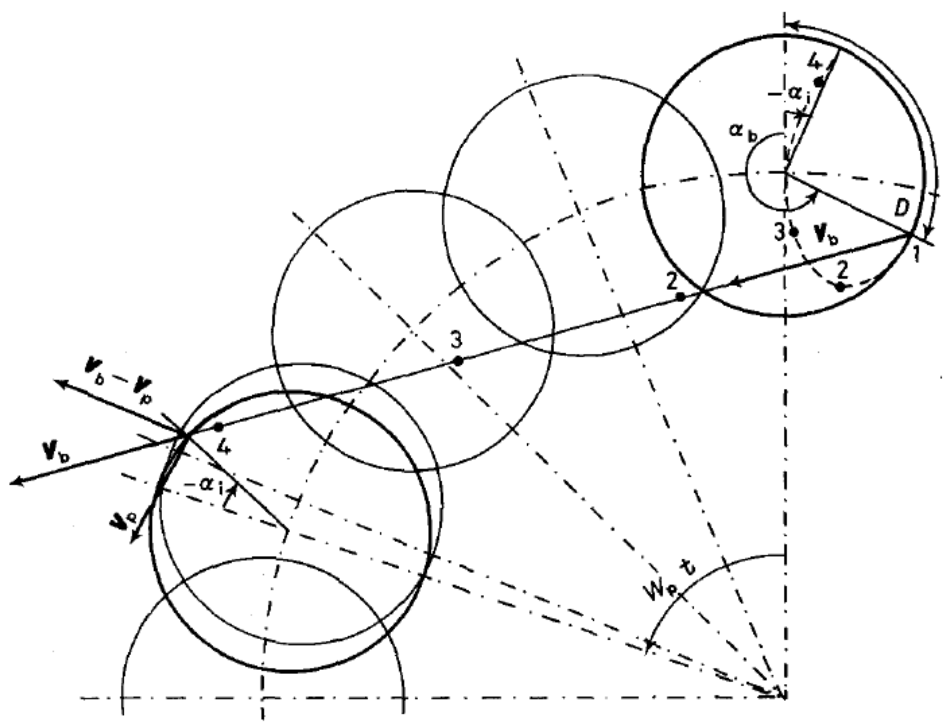
- Griding time and break
- Angular velocity of the plate and jar

Response variables

- Uniform size and shape
- Stability
- Morphology
- Magnetic properties
- And etc

Some theoretical models of the planetary mill

i) Mechanical model



Burgio, N. et al. (1991)

"The energy ΔE_b* dissipated by a ball in a system with N_b balls is proportional to the energy release ΔE_b

$$\Delta E_b^* = \varphi_b \, \Delta E_b$$

where φ_b is a filling fraction of the vial by the grinding balls, $N_{b,v}$ is the number of balls that can be contained in a simple cubic arranged, and ε is a parameter depending on the ball diameter" (Burgio, N. et al. (1991))

$$\varphi_b = \left(1 - \left(\frac{N_b}{N_{b,v}} \right)^{\varepsilon} \right)$$

The total power, P*, transferred from the mill to the system

$$P^* = -\varphi_b\, N_b\, m_b\, t\, (W_p - W_v)\left[\frac{W_v^3 (R_v - d_b/2)}{W_p} + W_p\, W_v\, R_p\right]\frac{(R_v - d_b/2)}{2\pi\, PW}$$

where:

φ_b: filling fraction of the vial by the grinding balls

N_b, m_b, d_b: Number of balls, mass and diameter of the balls

t: grinding time

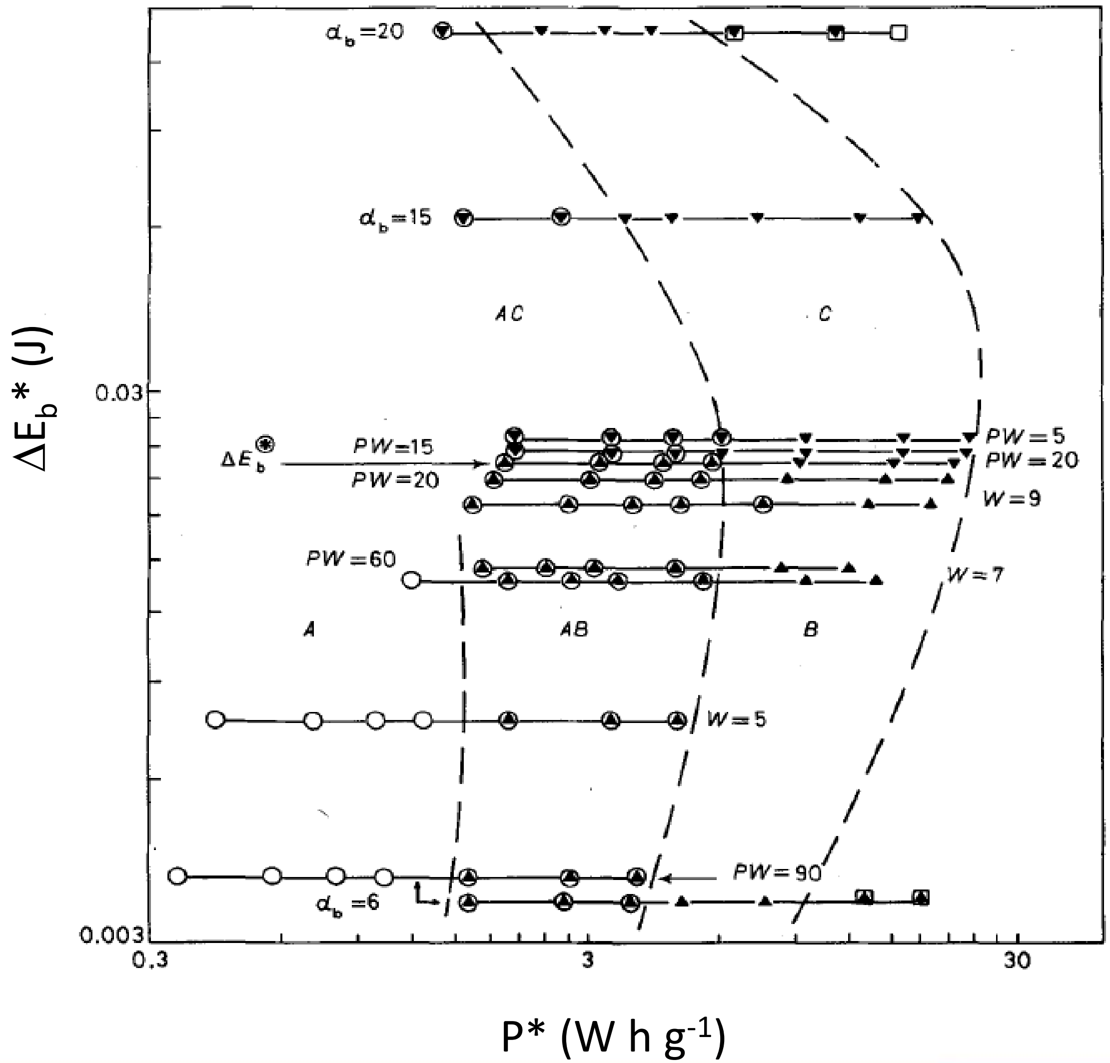
W_p, W_v: angular velocities (main plate mill and vials)

R_p, R_v: distance from the center of the mill to the center of the vial and the vial center of its periphery

PW: powder weight

Burgio, N. et al. (1991)

Energy Map ΔE_b* against P*



Parts

A: line broadening

B: Formation of amorphous phase

C: Intermetallic phase formation of amorphous

Burgio, N. et al. (1991)

ii) Mechano-thermal model

Hypothesis:
The mechano-chemical reactions occur through a process of energization

The energy of the collision

$$\Delta E = K_a \frac{m_b v^2}{2}$$

The relative impact velocity

$$v = K_b \, \omega_p \, r_p$$

where:

ΔE: the energy involved in a collision event

m_b : the mass of the ball

v: the relative impact velocity

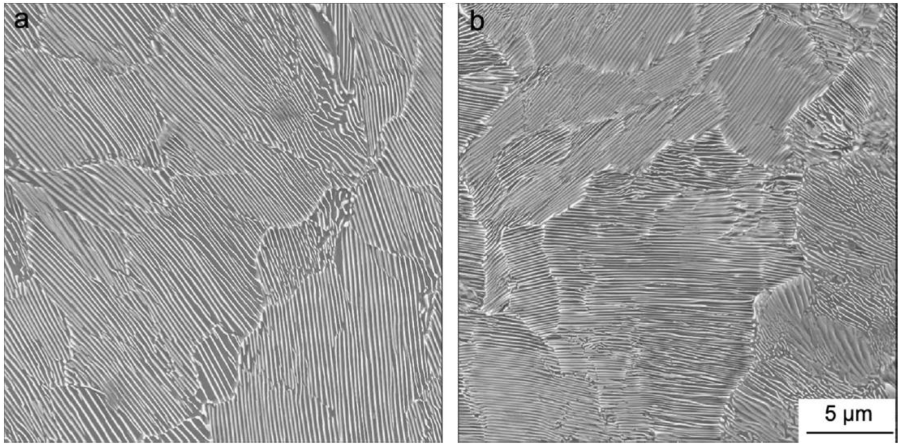
K_a: a coefficient depending on the elasticity of the collision

K_b: a constant that depends on the geometry of the planetary mill
ω_p , r_p : angular speed and radius of the planetary mill disc

Zdujic´, M. et al. (1998)

iii) Thermodynamic model

“Initial steel wire rod was machined into cylindrical samples with dimensions of 10 mm in heigth and 4 m in diameter” (Junjie, Li, Wei Liu, 2014)

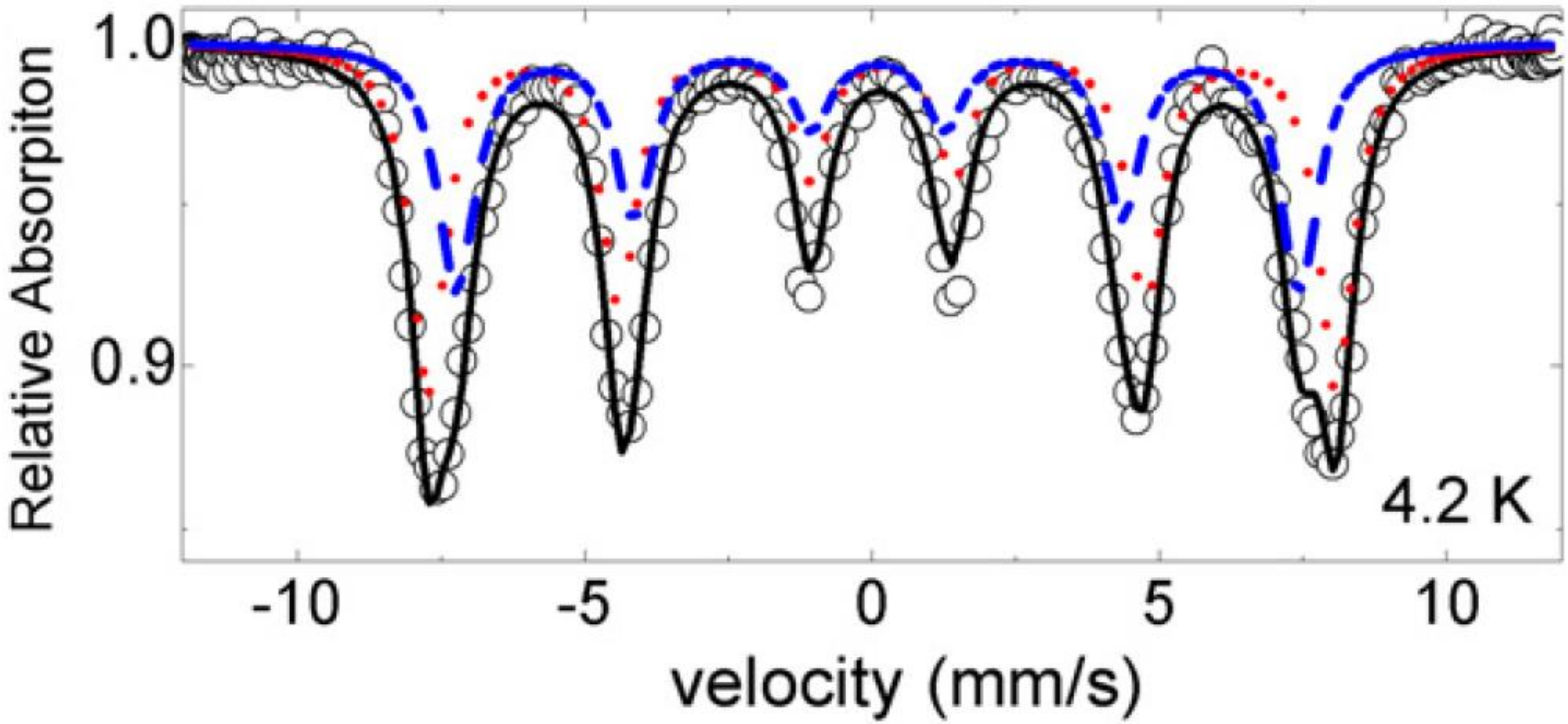


SEM images of samples transformed completely at 700 °C without (a) and with (b) magnetic field treated

$$\Delta G_M^f(T) = 1186 - 2.884T + 0.001640T^2$$

A T < 770 ºC y H = 10 T

Availability experimental production and characterization of the nanoparticles produced

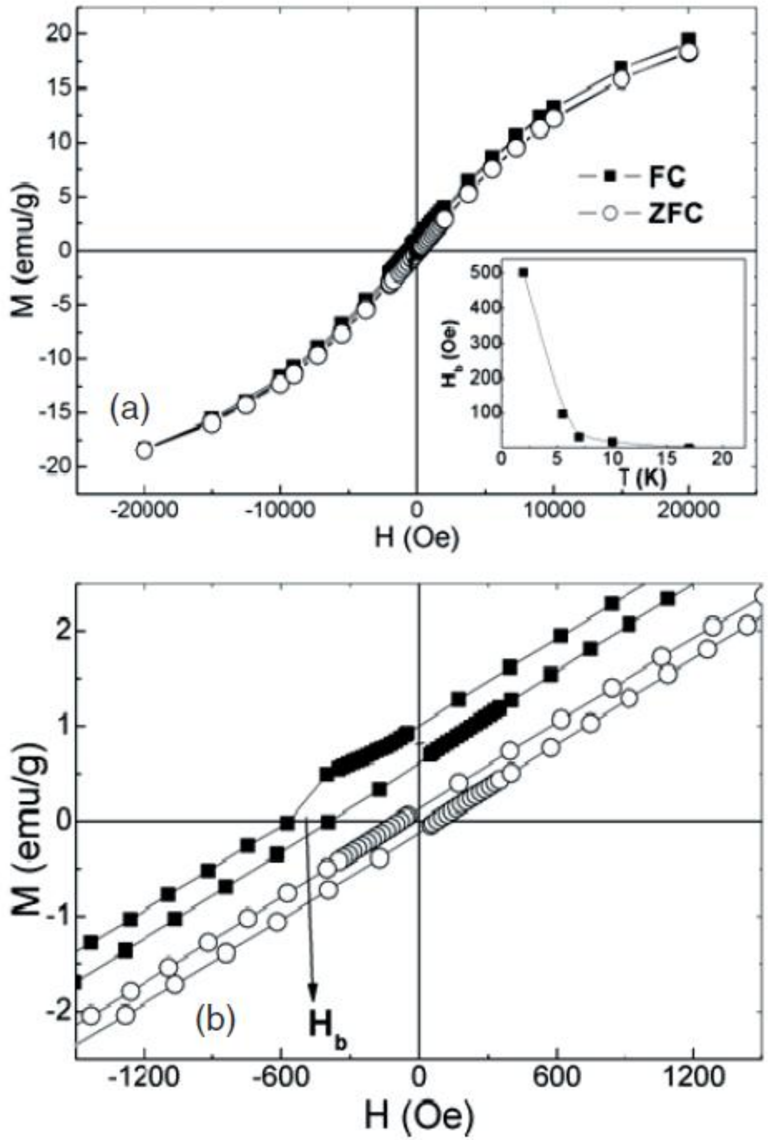


Mössbauer spectrum

Solid line: It is the expected spectrum.

Red line and blue: They refer to sites A and B respectively.

Lima, E. Jr. et al. (2009)



Isotherms of magnetization (in modes ZFC and FC) measured at T = 2K and H> 20 kOe.

FC detail cycle

Lima, E. Jr. et al. (2009)

TEM image of nanoparticles (D = 4.5 ± 0.8 nm)

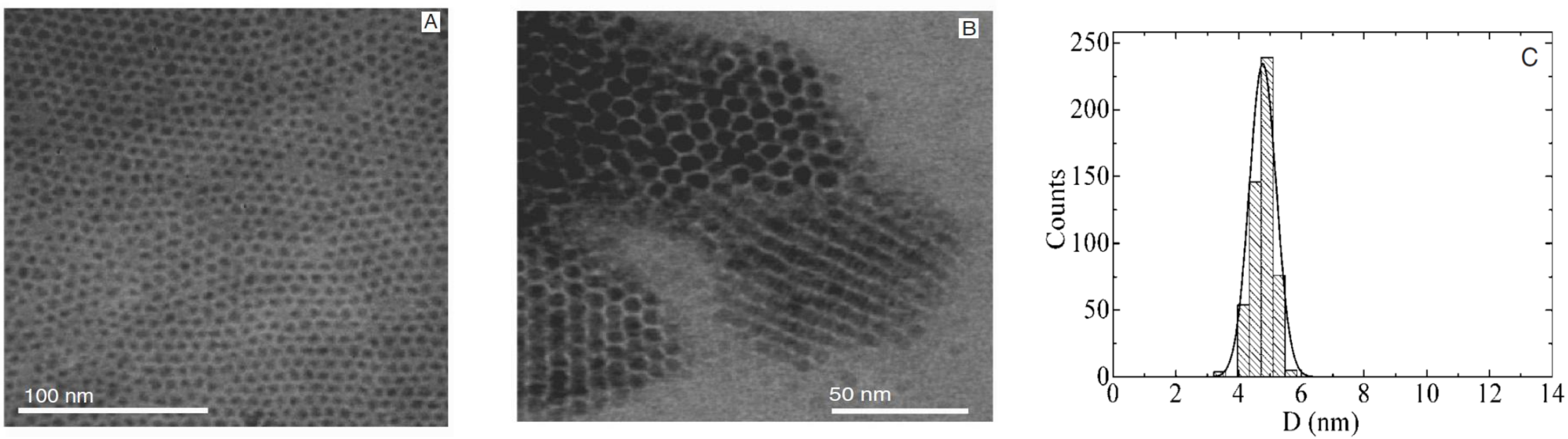


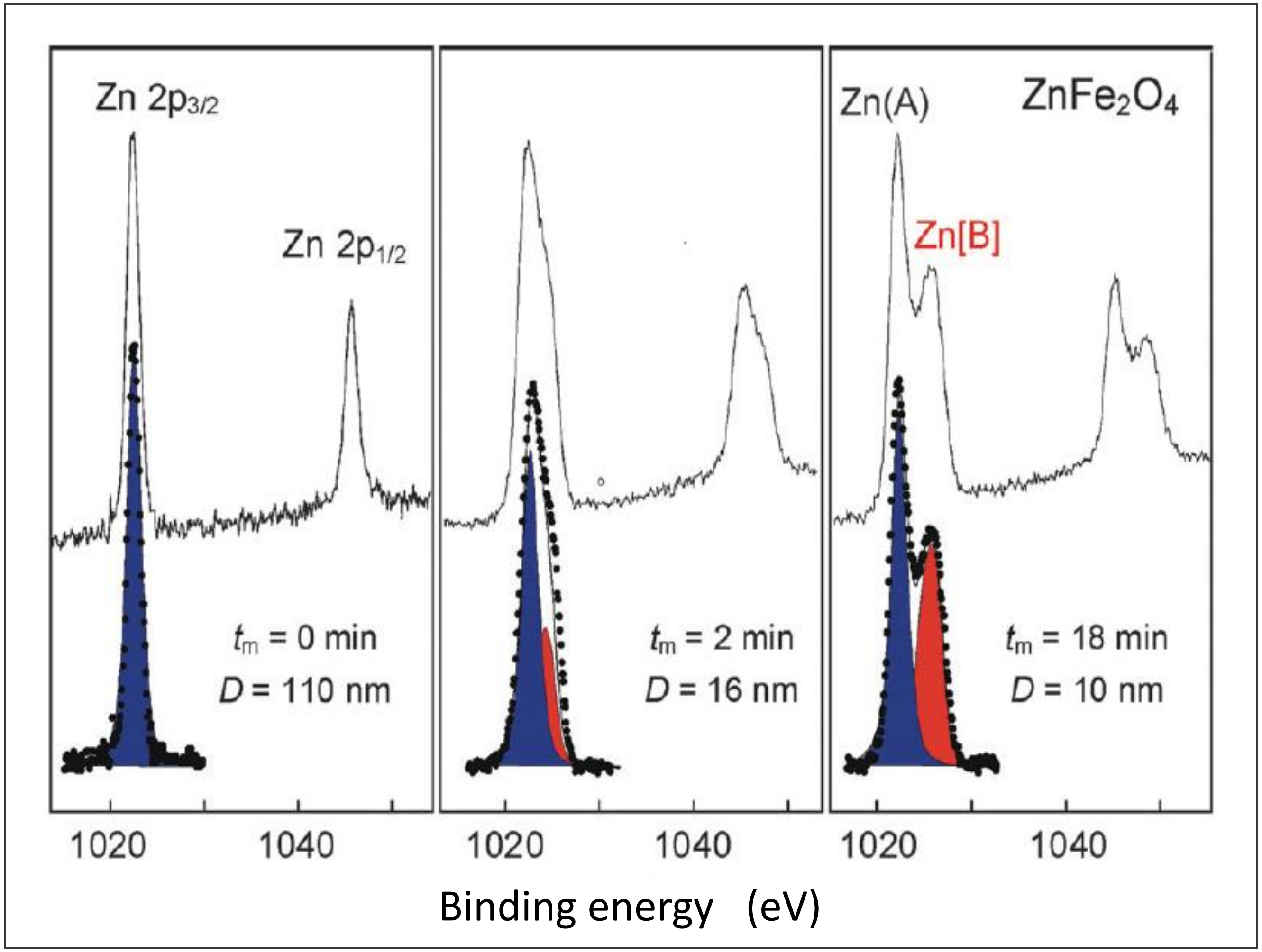
Figure A: cubic cells and size distribution very close.

Figure B: Accumulation of particles in a self assembled structure.

Figure C: Histogram distribution (were counted more than 400 particles).

Vargas, J. M. & Zysler, R. D. (2005)

XPS spectrum of zinc ferrite ($ZnFe_2O_4$)



Sepelák, V. et al. (2013)

Inspira Crea Transforma

UNIVERSIDAD EAFIT

Purposes

1. To find the critical variables of the milling process
2. To propose an equation that predicts the results of a grinding under controlled conditions
3. To achieve reproducibility and repeatability of the process
4. To produce large numbers of stable ferrites

Conclusions

1. Iron oxides such as the ferrites in bulk and nanoescala size have different magnetic behaviors and different crystal structures.

2. Mechanosynthesis is a term used to refer to milling procedures where the collision energy is enough for starting chemical reactions yilding totally different products from the precursors.

3. The grinding process is a stochastic process that requires modeling for their critical variables.

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Thank you very much