Difração de Raios X

Principais aplicações

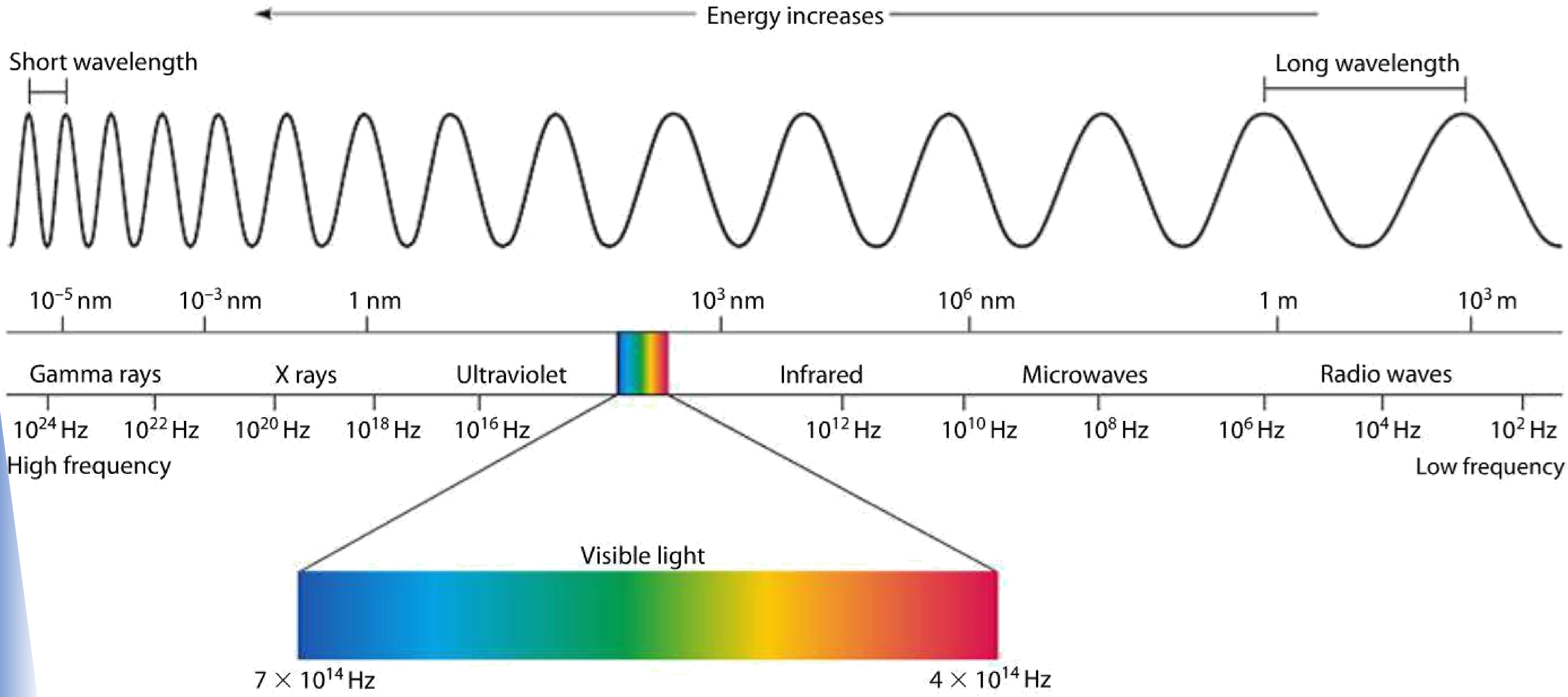
- Identificação de materiais
- Análises químicas
- Análise de estruturas cristalinas
- Determinação da estrutura cristalina
- Distinção das diferentes estruturas alotrópicas de elementos químicos
- Quantificação de fases
- Caraterização do material
(ex: tamanho das cristalites)

X-ray diffraction

Main applications

- Identification of materials
- Chemical analyses
- Analysis of crystalline structures
- Determination of the crystalline structure
- Distinction of the different allotropic structures of chemical elements
- Quantification of phases
- Characterization of the material
(ex: crystallite size)

Espetro da radiação eletromagnética
Spectrum of electromagnetic radiation



Descoberta da radiação X
Discovery of Radiation X

Wilhelm Conrad Röntgen (1845-1923), em 1895, com uma foto tirada com raios X mostrando a mão e o anel da esposa. A descoberta da radiação X valeu-lhe o prémio Nobel da Física em 1901.

Wilhelm Conrad Röntgen (1845-1923), in 1895, with a photo taken with X-rays showing his wife's hand and ring. The discovery of X-radiation earned him the Nobel Prize in Physics in 1901.

Equipamento radiológico de hospital
Hospital Radiological Equipment

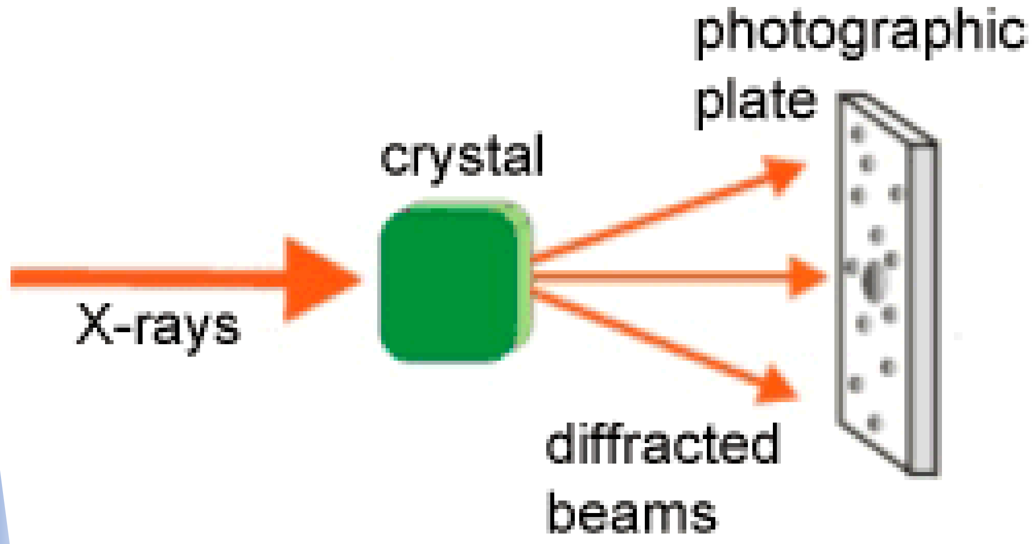
Difração de Raios X   X-Ray diffraction

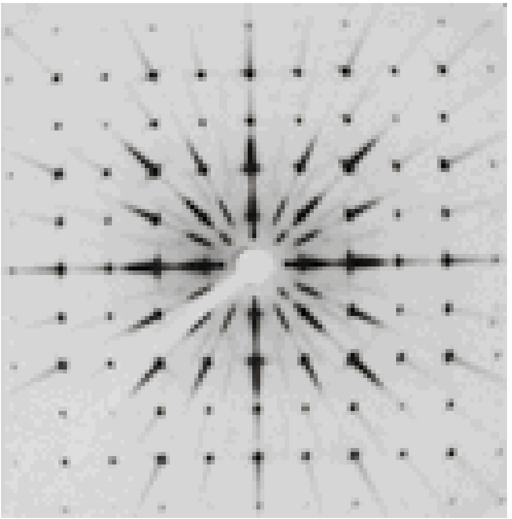
Alguns anos após a descoberta da radiação X em 1895, Max von Laue, em 1912, revoluciona as áreas da Física, Química e Biologia com uma nova descoberta.

A few years after the discovery of X-radiation in 1895, Max von Laue, in 1912, revolutionized the fields of Physics, Chemistry and Biology with a new discovery.

Max von Laue
(1879-1960)

O fenómeno da difracção   The diffraction phenomenon





difraction pattern

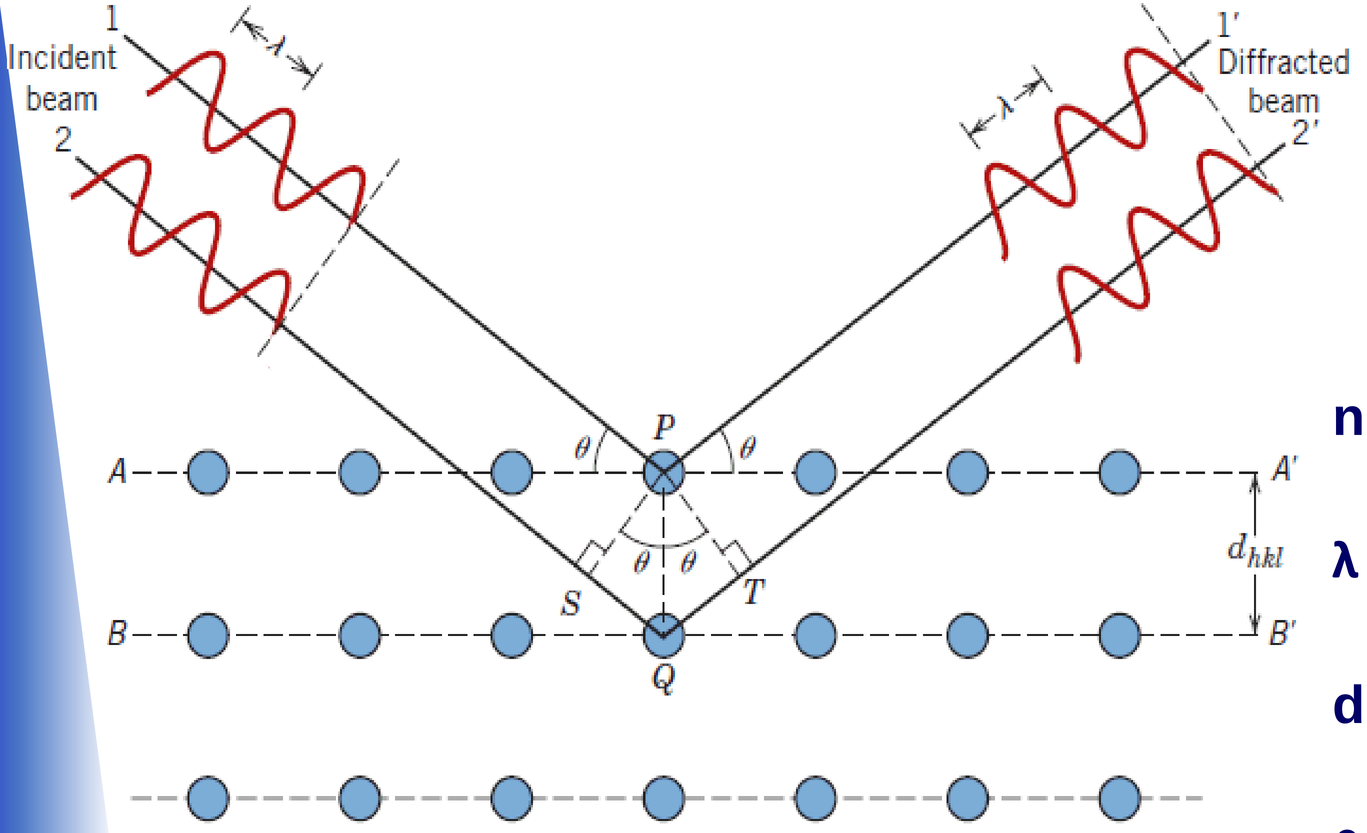
von Laue placed copper sulfate crystals in the X-radiation path and obtained a characteristic diffraction pattern. For his discoveries, he won the Nobel Prize in Physics in 1914.

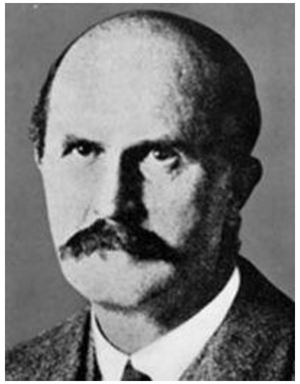
von Laue colocou cristais de sulfato de cobre no caminho da radiação X e obteve um padrão de difração característico. Pelas suas descobertas ganhou o Prémio Nobel da Física em 1914.

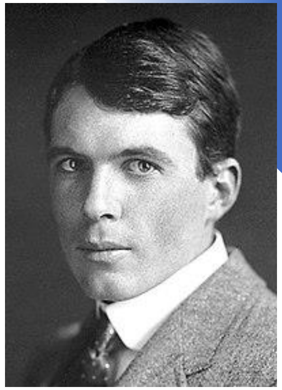
Difração de Raios X
X-ray diffraction

Lei de Bragg   Bragg's law

$$n\,\lambda = 2\,d\,\text{sen}\theta$$







W.H. Bragg (1862-1942)   W.L Bragg (1890-1971)

Pai e filho receberam o Prémio Nobel da Física em 1915, pela descoberta de que sólidos cristalinos produziam padrões de reflexão de raios X.

Father and son were awarded the Nobel Prize in Physics in 1915 for the discovery that crystalline solids produced X-ray reflection patterns.

n – número inteiro de comprimento de onda
integer number of wavelenghts

λ – comprimento de onda da radiação X (1.54 Å)
wavelenght of radiation X (1.54 Å)

d_{hkl} – distância entre planos atómicos
distance between atomic planes

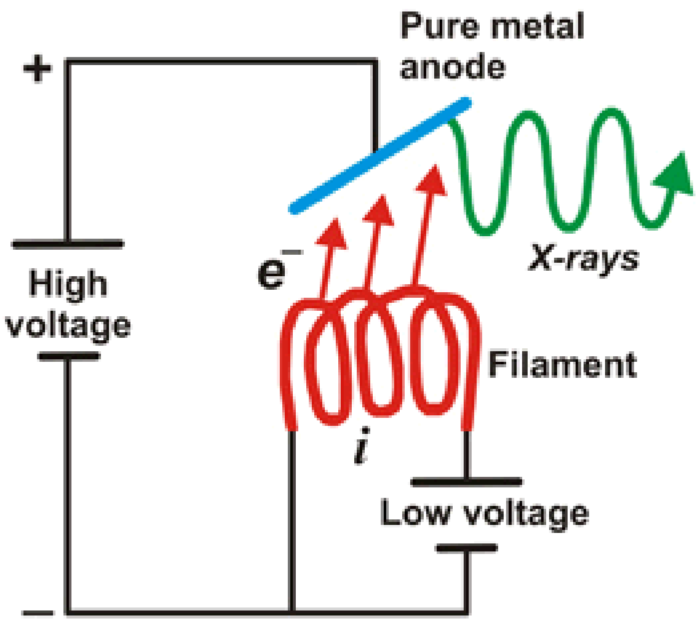
θ – ângulo de Bragg / Bragg's angle

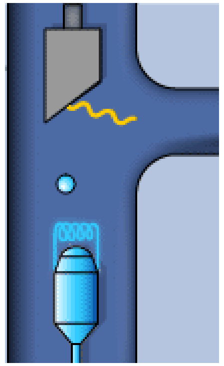
Difração de Raios X

X-ray Diffraction

Origem da radiação X

Origin of radiation X



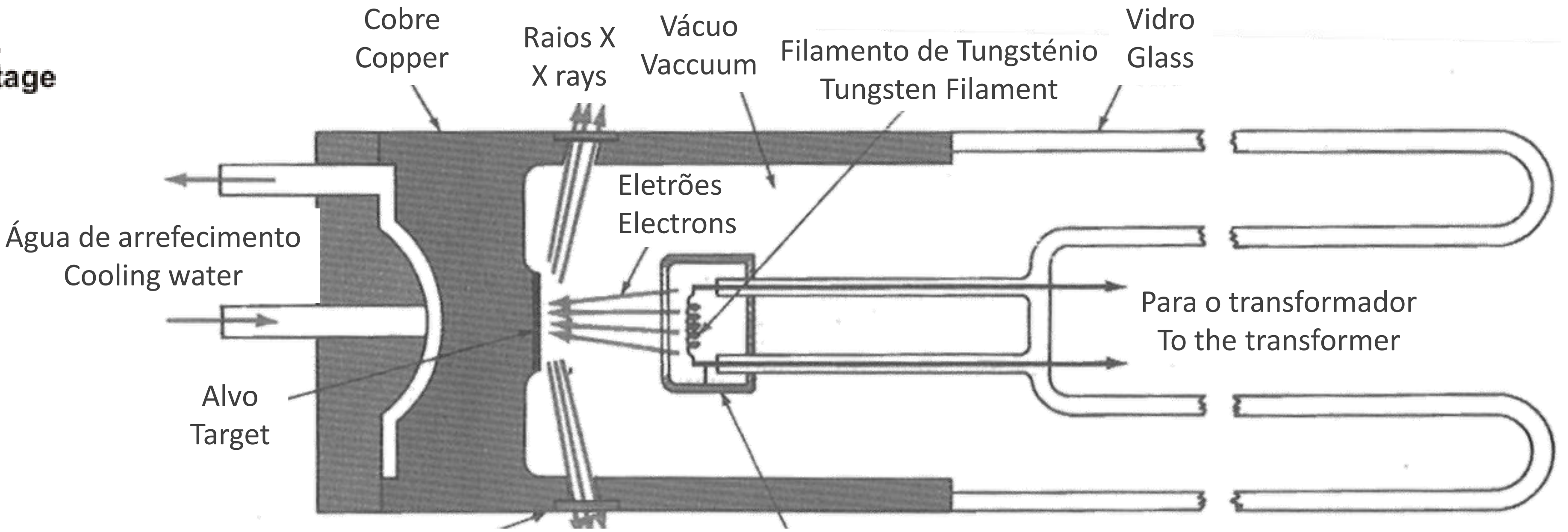


Ampola para produção de radiação X

Ampoule for production of radiation X

Um filamento aquecido emite electrões por efeito termiónico, que são acelerados por um potencial eléctrico muito elevado (~40 kV)

A heated filament emits electrons by thermionic effect, which are accelerated by a very high electrical potential (~40 kV)

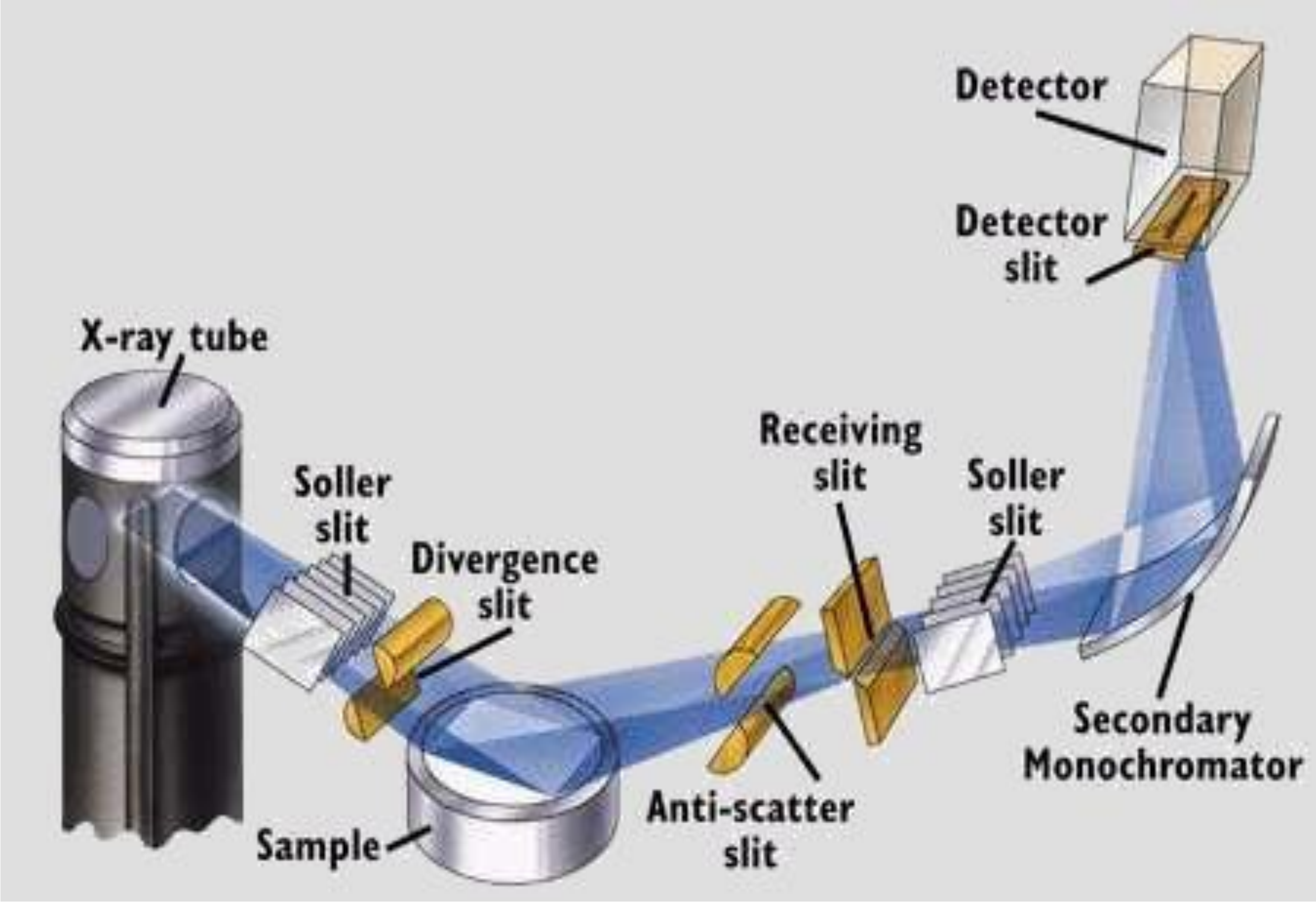


Difração de Raios X   X-Ray diffraction

Os **difratómetros** em geral são constituídos por:

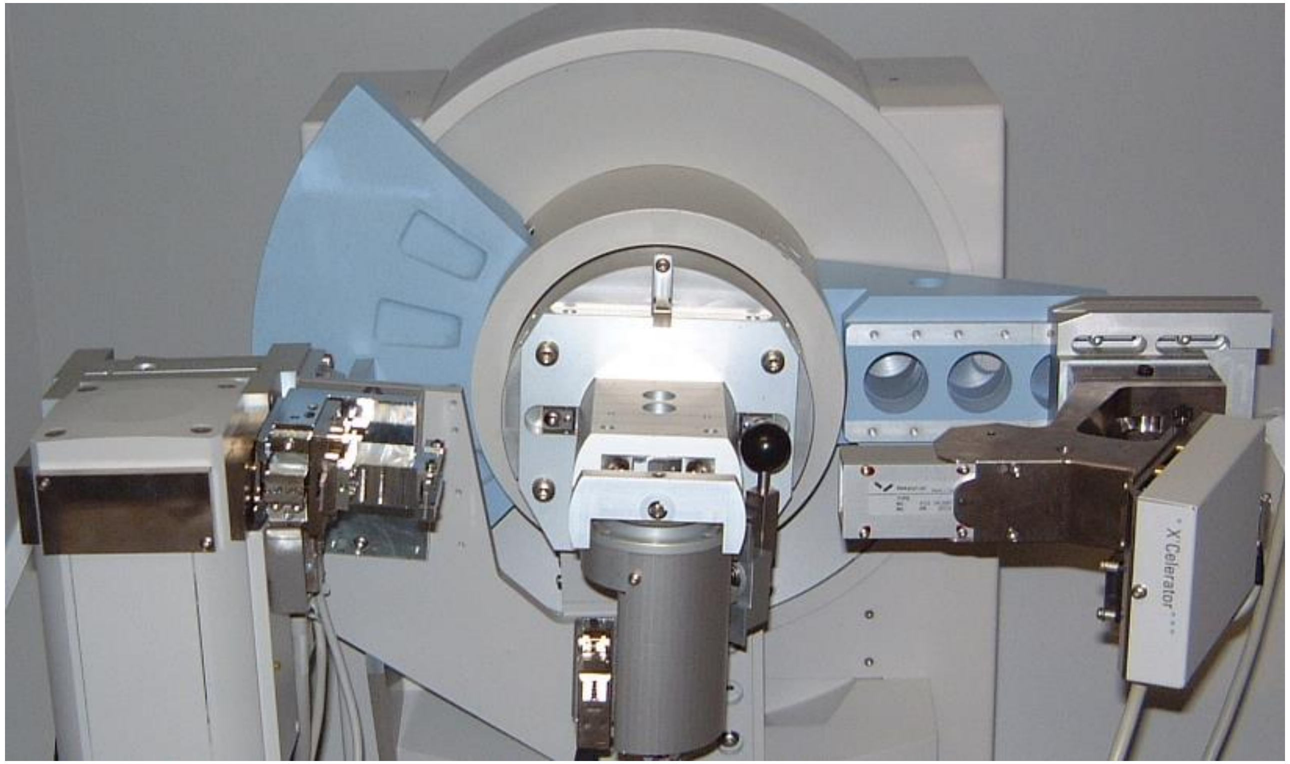
Diffractometers in general consist of:

- ❖Refrigerador / Refrigerator
- ❖Fonte de eletricidade / Electricity source
- ❖Tubo gerador de Raio X / X-Ray Generator Tube
- ❖Câmara da amostra / Sample Chamber
- ❖Detetor da intensidade de Raio X / X-ray Intensity Detector
- ❖Goniómetro / Goniometer
- ❖Computador(es) / Computer(s)



Difração de Raios X   X-Ray diffraction

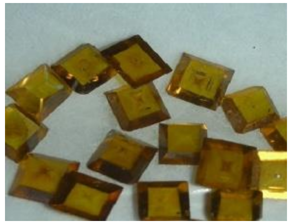
Difratómetros   Difractometers



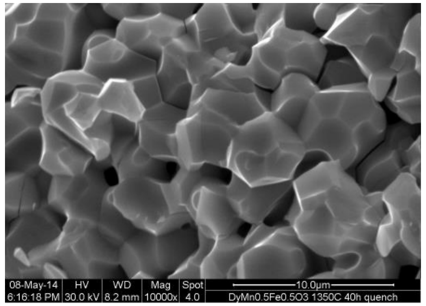
Difração de Raios X   X-Ray diffraction

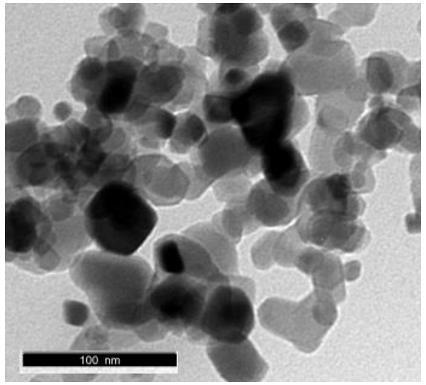
Materiais cristalinos e não cristalinos   Crystalline and non-crystalline materials

Materiais monocristalinos
Monocrystalline materials



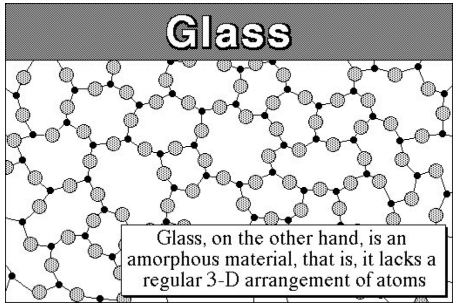
Materiais policristalinos
Polycrystalline materials





Materiais nanocristalinos
Nanocrystalline materials

Materiais amorfos
Amorphous materials



Difração de Raios X

X-Ray diffraction

Acerca da amostra a analisar

- Conhecemos a composição química?
- A amostra é pura ou é uma mistura?
- A amostra é um pó, um pedaço de metal/liga, um filme?
- A amostra pode ser moída, ou tem de ser analisada como está?
- A amostra tem fases amorfas?
- A amostra contém nanopartículas?
- Que quantidade de amostra temos?
- Para que servem os resultados obtidos?

About the sample to be analysed

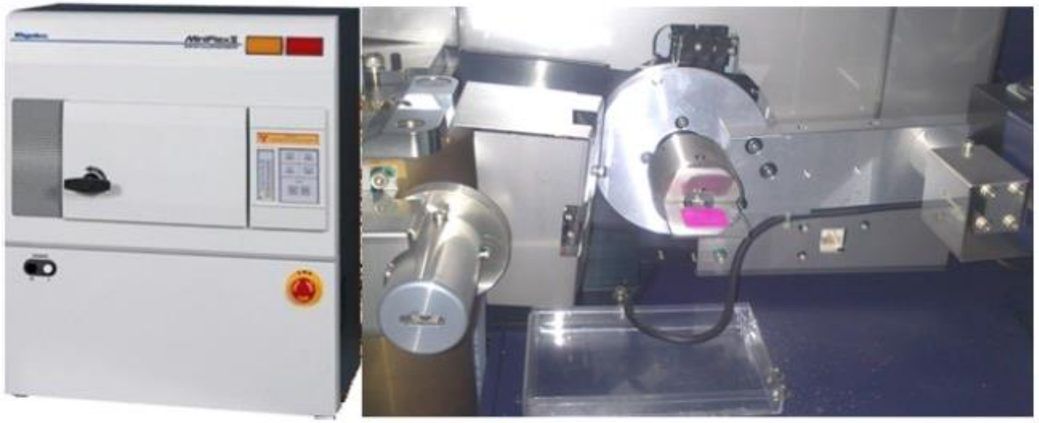
- Do we know its chemical composition?
- Is the sample pure or is it a mixture?
- Is the sample a powder, a piece of metal/alloy, a film?
- Can the sample be ground, or does it have to be analysed as is?
- Does the sample have amorphous phases?
- Does the sample contain nanoparticles?
- What quantity of sample do we have?
- What are the results for?

Equipamento disponível no DQ/FCT
Equipment available at DQ/FCT

https://sites.fct.unl.pt/labanalises/biocv

- XRPD - X-Ray Powder Difraction

Equipment



Benchtop X-Ray Diffractometer RIGAKU, model MiniFlex II with:

Cu X-ray tube (30KV/15 mA) Scanning range: 3~ +145° (2θ)

Scanning speed: 0,01~ +100°/min (2θ)

Minimum step width: 0,01° (2θ).

Samples

Samples in dry powder form and homogeneous. The samples should be supplied of the sample plate.

https://sites.fct.unl.pt/labanalises/AnalyticalFields/MaterialsCharacterization

Responsável/Responsible: Nuno Costa

(ver/watch video)

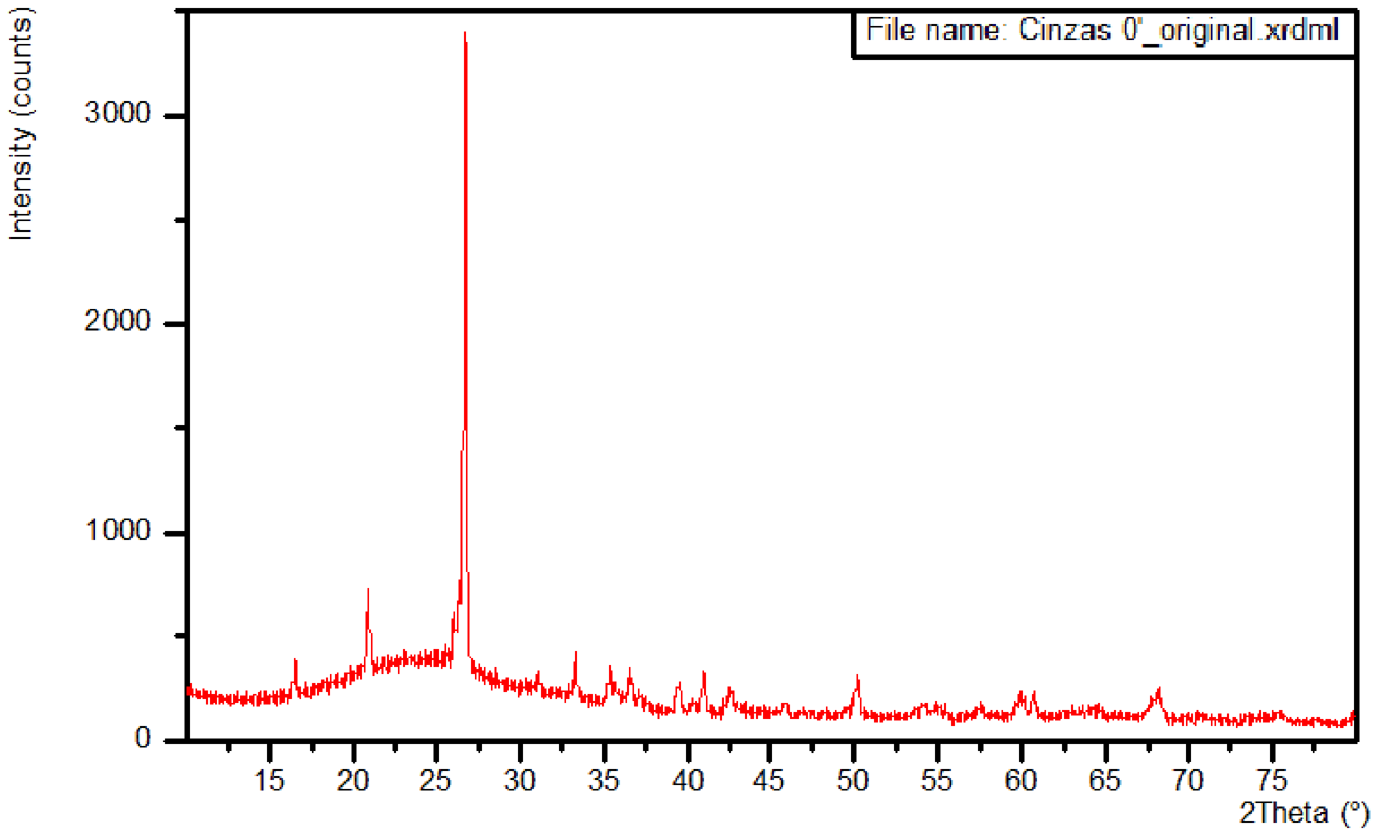
Difração de Raios X X-Ray diffraction

Preparação da amostra
Sample preparation

Difração de Raios X X-Ray diffraction

Obtenção do difratograma Obtaining the diffractogram

Sempre que um plano cristalográfico da amostra satisfaz a lei de Bragg, obtém-se uma difração que se traduz num pico de radiação X captado pelo detetor. No gráfico representa-se o número de contagens (de radiação X) obtidas em função do ângulo 2θ.



Whenever a crystallographic plane of the sample satisfies Bragg's law, a diffraction is obtained that translates into a peak of X-radiation captured by the detector. The graphic shows the number of counts (of X-radiation) obtained as a function of the 2θ angle.

Difração de Raios X

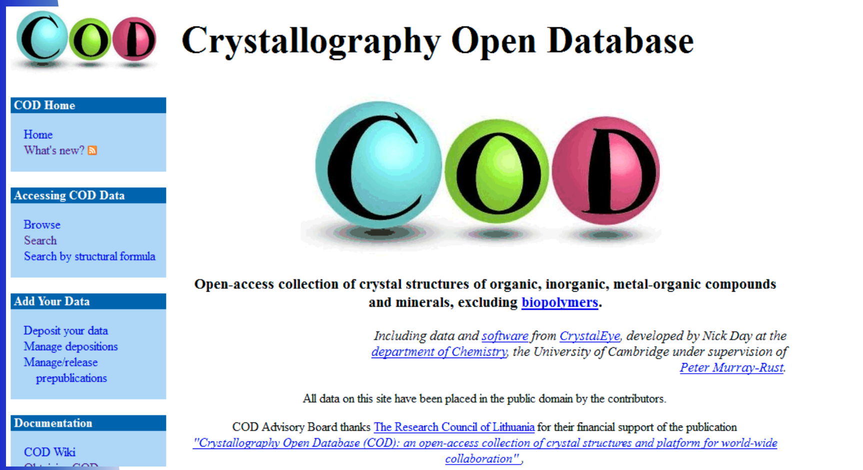
X-Ray diffraction

Identificação dos picos

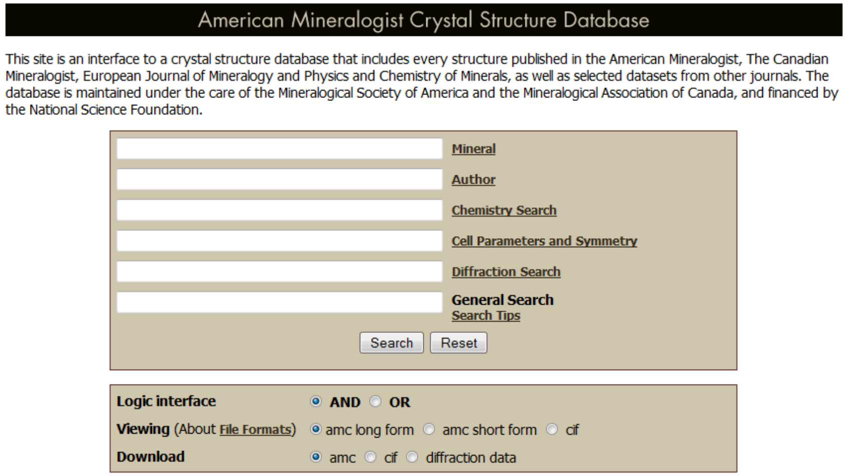
Peak identification

A interpretação é efetuada comparando o espetro obtido (posição e intensidade dos picos de difração) com estruturas cristalográficas de bases de dados (ex: fichas ASTM – American Society of Testing Materials, bases de dados online – algumas gratuitas)

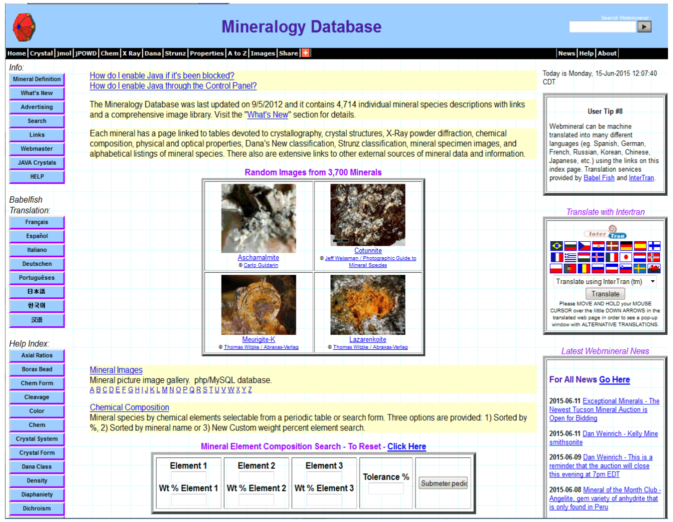
The interpretation is performed by comparing the obtained spectrum (position and intensity of diffraction peaks) with crystallographic structures from databases (e.g. ASTM – American Society of Testing Materials sheets, online databases – some free)



COD
Crystallography Open Database
http://www.crystallography.net/



American Mineralogist Crystal Structure Database
http://rruff.geo.arizona.edu/AMS/amcsd.php



Mineralogy Database
http://webmineral.com/

Difração de Raios X

Identificação dos picos

❖Havendo conhecimento prévio da natureza química dos compostos a identificar, usa-se uma lista de substâncias por ordem alfabética.
(d_{hkl} e I_{hkl} das fichas ASTM, têm que coincidir com as do composto a identificar).

❖**Método das 3 riscas mais intensas**
A risca mais intensa permite selecionar um grupo de substâncias e depois passa-se sucessivamente às menos intensas até se chegar a um número reduzido de substâncias.
Consultam-se as fichas ASTM com todos os valores de d e hkl idênticos.

X-Ray diffraction

Peak identification

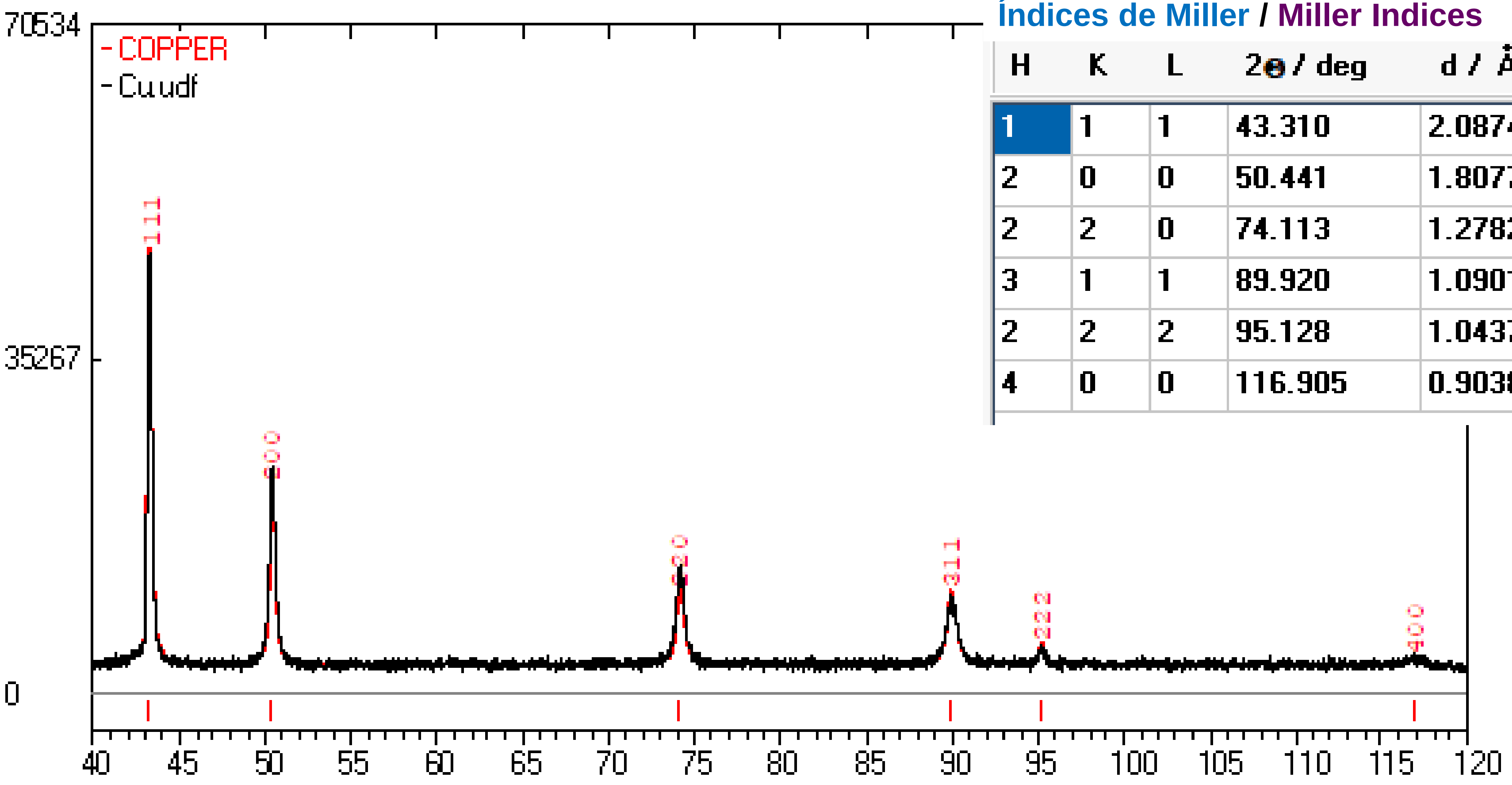
❖If there is previous knowledge of the chemical nature of the compounds to be identified, a list of substances is used in alphabetical order.
(d_{hkl} and I_{hkl} of the ASTM sheets, must match those of the compound to be identified).

❖**Method of the 3 most intense lines**
The most intense line allows to select a group of substances and then move on to the less intense ones until reaching a small number of substances.
The ASTM sheets with all the identical d and hkl values are consulted.

Difração de Raios X X-Ray diffraction

Exemplo de difratograma obtido experimentalmente **COBRE**

Example of an experimentally obtained diffractogram **COPPER**

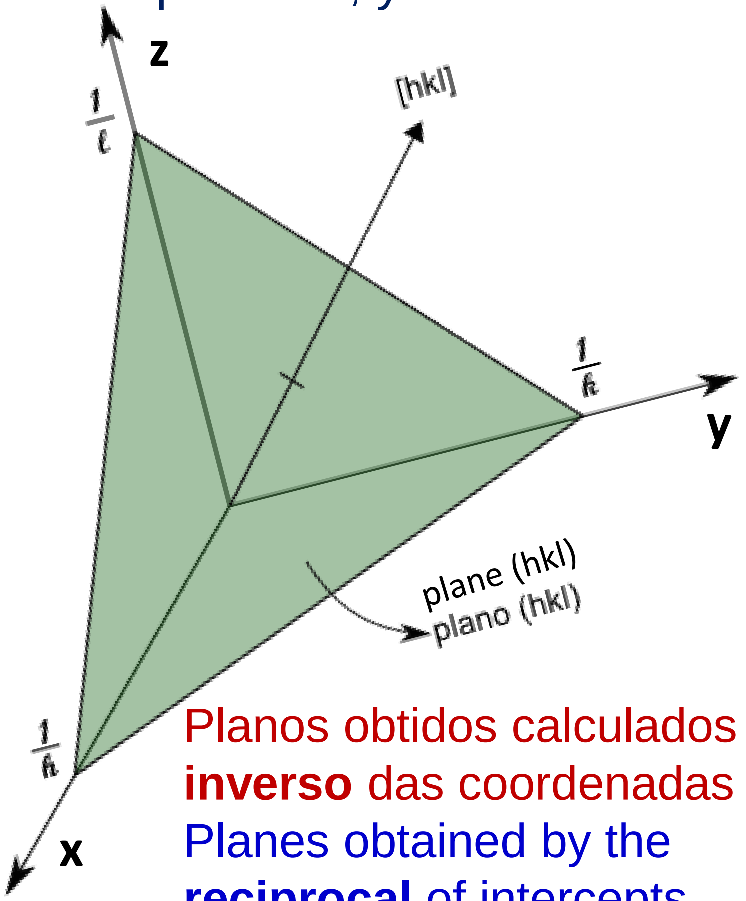


Índices de Miller / Miller Indices

H	K	L	2θ / deg	d / Å	I / rel
1	1	1	43.310	2.08743	100.00
2	0	0	50.441	1.80777	47.38
2	2	0	74.113	1.27829	28.20
3	1	1	89.920	1.09013	33.85
2	2	2	95.128	1.04372	10.12
4	0	0	116.905	0.90389	6.51

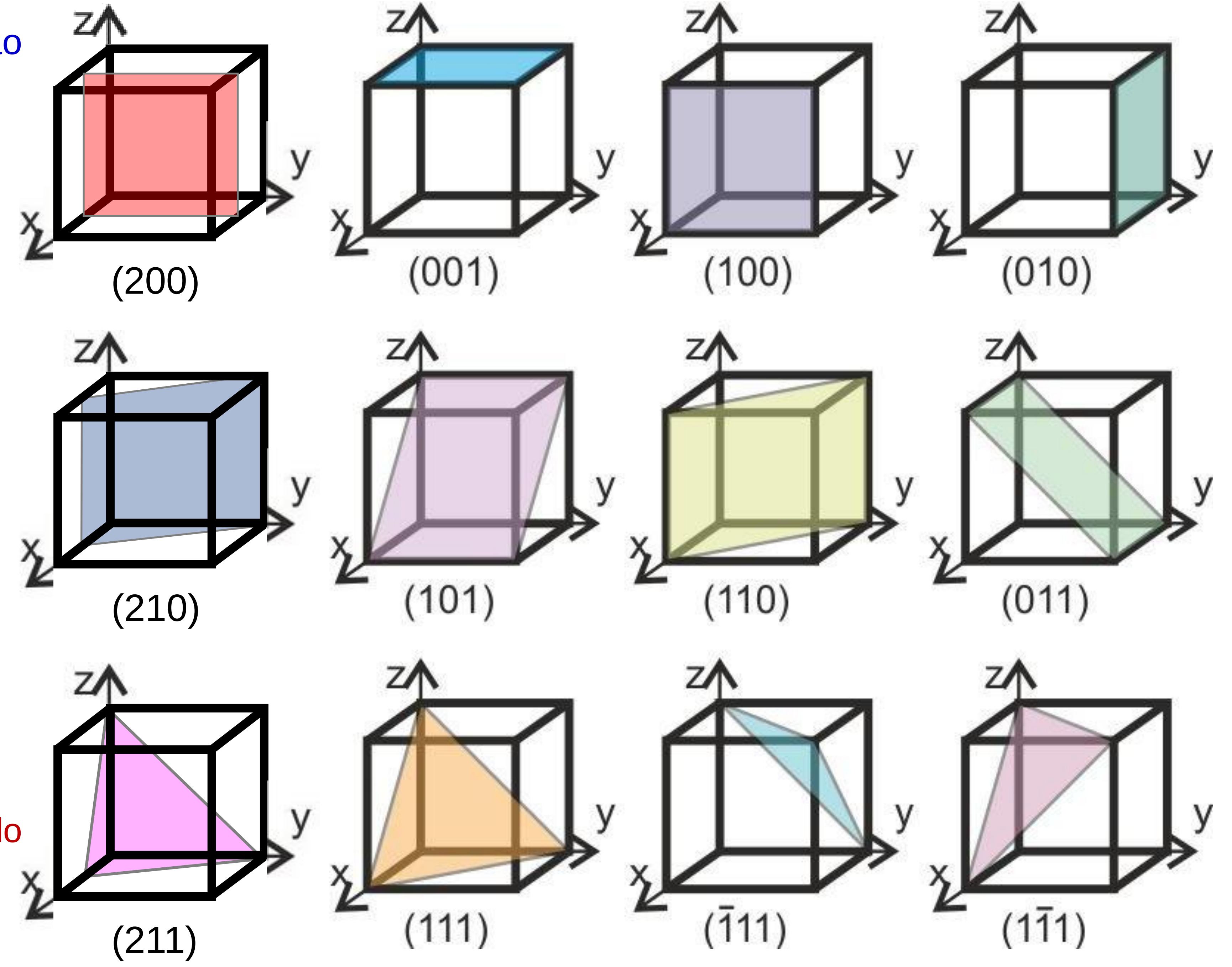
Os **planos cristalinos** são dados pelos **índices de Miller** (hkl) que são coordenadas nas quais o plano interceta os eixos x, y e z

Crystal planes are specified by the **Miller indices** (hkl) that are coordinates at which the plane intercepts the x, y and z axes

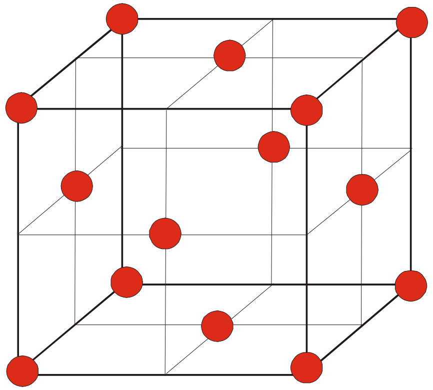


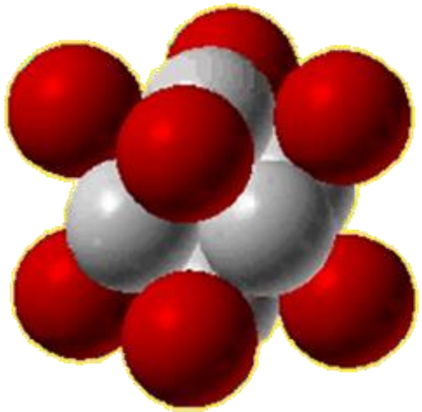
Planos obtidos calculados pelo **inverso** das coordenadas

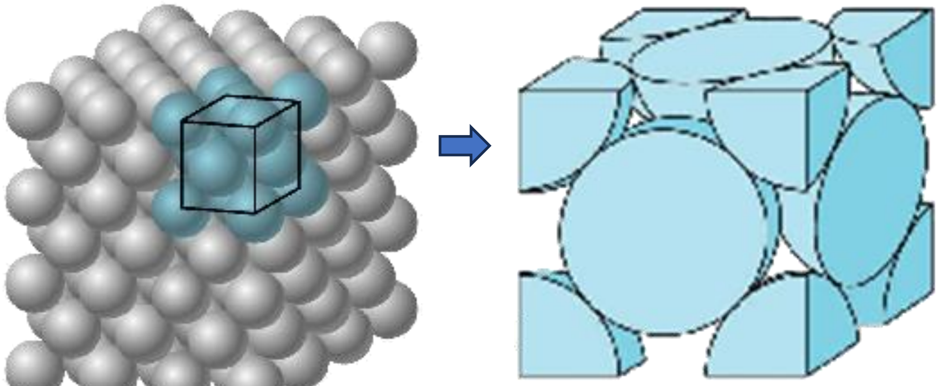
Planes obtained by the **reciprocal** of intercepts



Ex: Face centred cubic (fcc) crystal structure



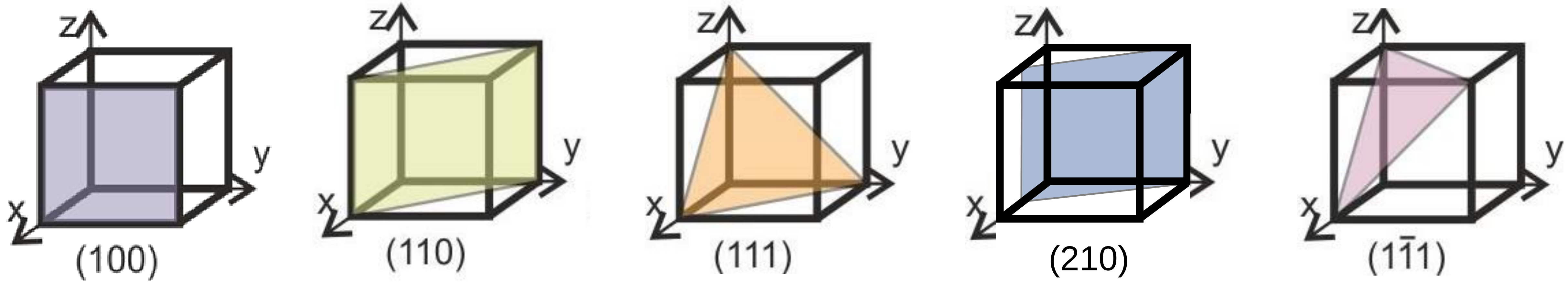


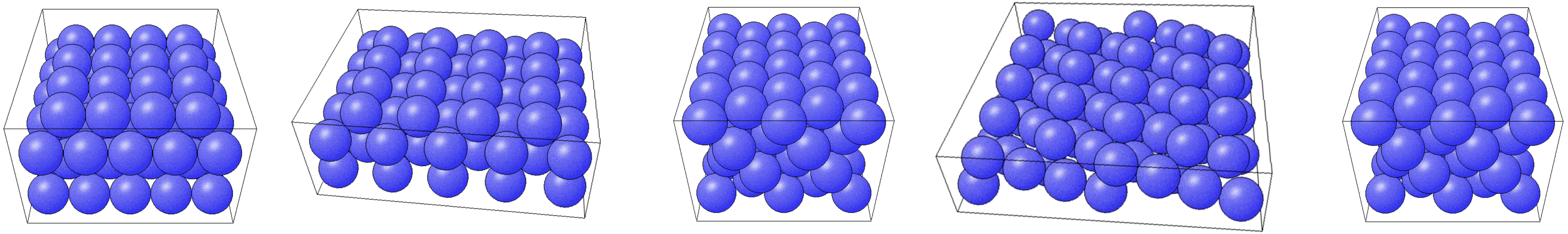


Célula unitária / Unit cell

Images from:

NIST Surface Structure Database [*http://www.fhiberlin.mpg.de/th/personal/hermann/SSDpictures.html#A*](http://www.fhiberlin.mpg.de/th/personal/hermann/SSDpictures.html#A)



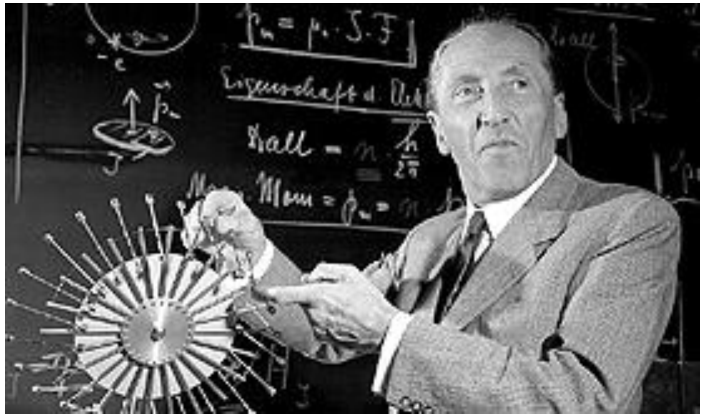


Surfaces generated with Surface Explorer: [*http://surfexp.fhi-berlin.mpg.de/*](http://surfexp.fhi-berlin.mpg.de/)

Difração de raios X X-Ray diffraction

Fórmula de Scherrer Scherrer's formula

$$dp = \frac{\beta\ \lambda}{b\ \cos\theta} = \frac{6\ y}{\rho\ S_M}$$



Paul Scherrer (1890-1969)

dp – **diâmetro das cristalites / crystallite diameter**

β – constante que depende da forma das cristalites (em geral = 1)
constant that depends on crystallite shape (in general = 1)

λ – comprimento de onda da radiação X (1.54 Å)
wavelenght of radiation X (1.54 Å)

π rad = 180º

b – largura a meia altura do pico mais intenso (em radianos)
full width at half maximum of the most intense peak (in radians)

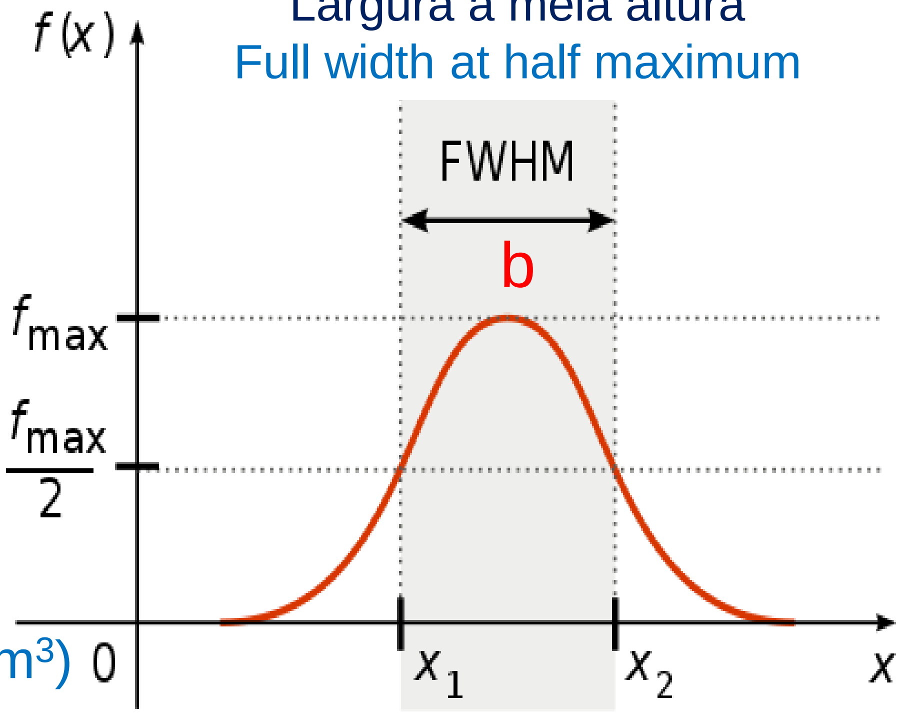
θ – ângulo de Bragg (em radianos) / Bragg's angle (in radians)

y – fração ponderal do metal no catalisador /
weight fraction of metal in catalyst

ρ – massa volúmica da fase (g/cm^3) / volumetric mass of phase (g/cm^3)

S_M – área específica da fase (m^2/g$_{cat}$) / specific área of phase (m^2/g$_{cat}$)

Largura a meia altura
Full width at half maximum



Difração de raios X   X-Ray diffraction

Fórmula de Scherrer   Scherrer's formula

$$dp = \frac{\beta \ \lambda}{b \cos\theta} = \frac{6 \ y}{\rho \ S_M}$$

dp – diâmetro das cristalites / crystallite diameter

β – constante que depende da forma das cristalites (em geral igual a 1)
constant that depends on crystallite shape (in general equal to 1)

λ – comprimento de onda da radiação X (1.54 Å)
wavelenght of radiation X (1.54 Å)

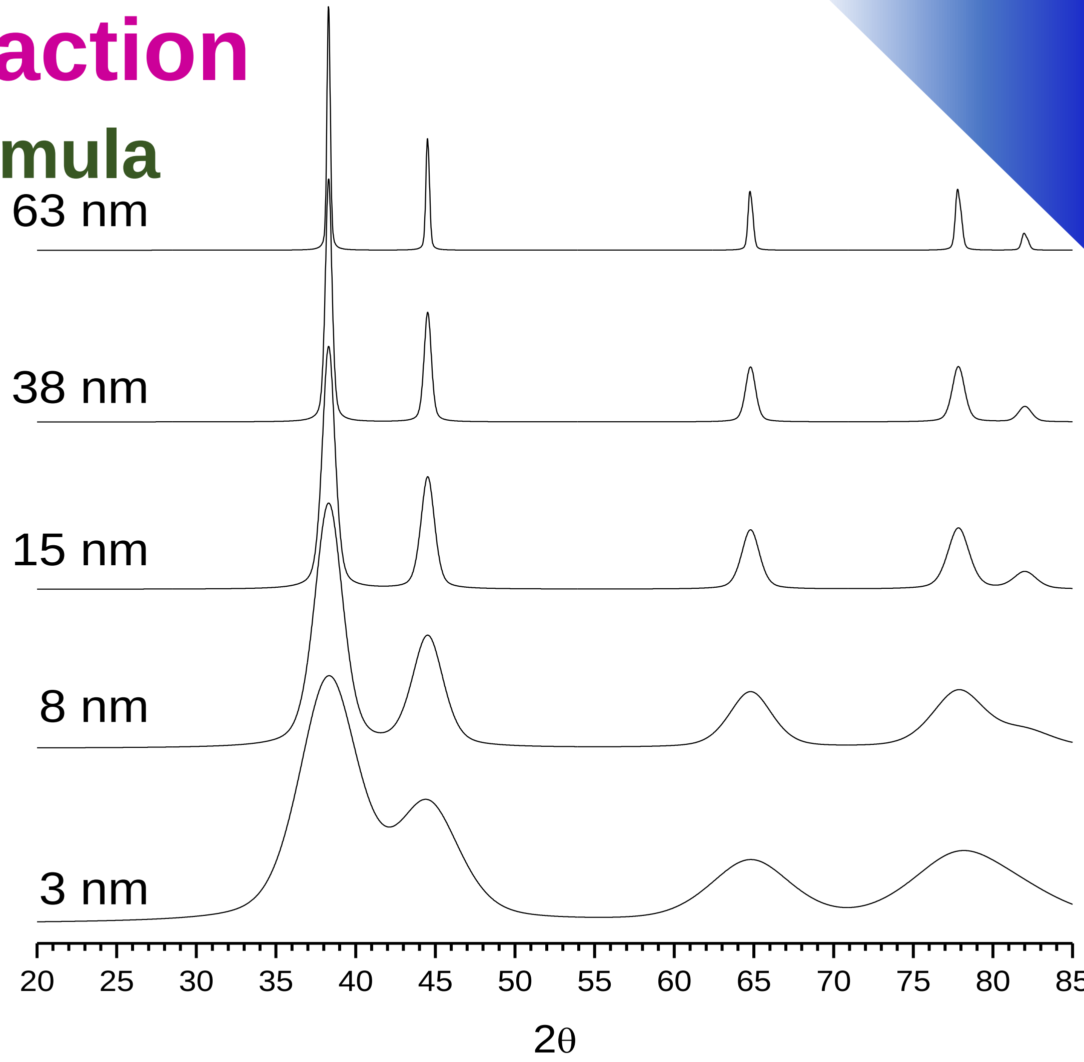
b – largura a meia altura da banda de difração de raios X (em radianos)
full width at half maximum (in radians, π rad = 180º)

θ – ângulo de Bragg (em radianos) / Bragg's angle (in radians)

y – fração ponderal do metal no catalisador
weight fraction of metal in catalyst

ρ – massa volúmica da fase (g/cm^3) / volumetric mass of phase (g/cm^3)

S_M – área específica da fase (m^2/g_{cat}) / specific área of phase (m^2/g_{cat})



Picos altos e estreitos → partículas maiores
Tall and narrow peaks → larger particles

Picos baixos e largos → partículas menores
Small and broad peaks → smaller particles

Difração de raios X X-Ray diffraction

Outros cálculos Other calculations

Sabendo, S_M, a **dispersão D_M** é dada por:

Knowing, S_M, the **dispersion D_M** is given by:

$$D_M = \frac{S_M \; n_s}{N \, y \, / \, M}$$

D_M é adimensional
D_M is dimensionless

S_M – área específica da fase (m^2/g_{cat}) / specific área of phase (m^2/g_{cat})

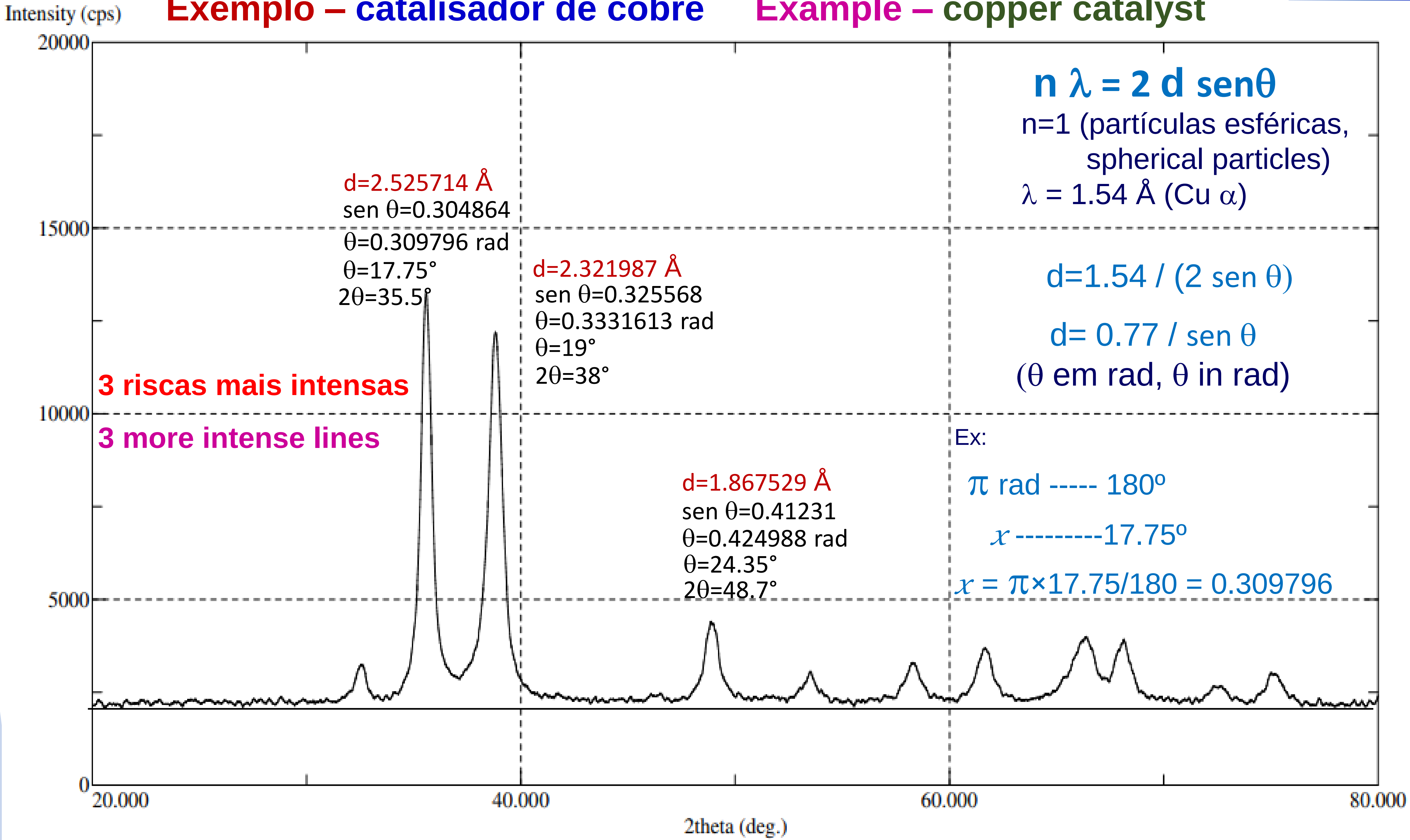
n_s – número tabelado de átomos na superfície por unidade de área (átomos/m^2)
tabulated number of atoms on the surface per unit area (atoms/m^2)

N – número de Avogrado / Avogrado's number (6.023×10^{23} átomos/mol)

y – fração ponderal do metal no catalisador / weight fraction of metal in catalyst

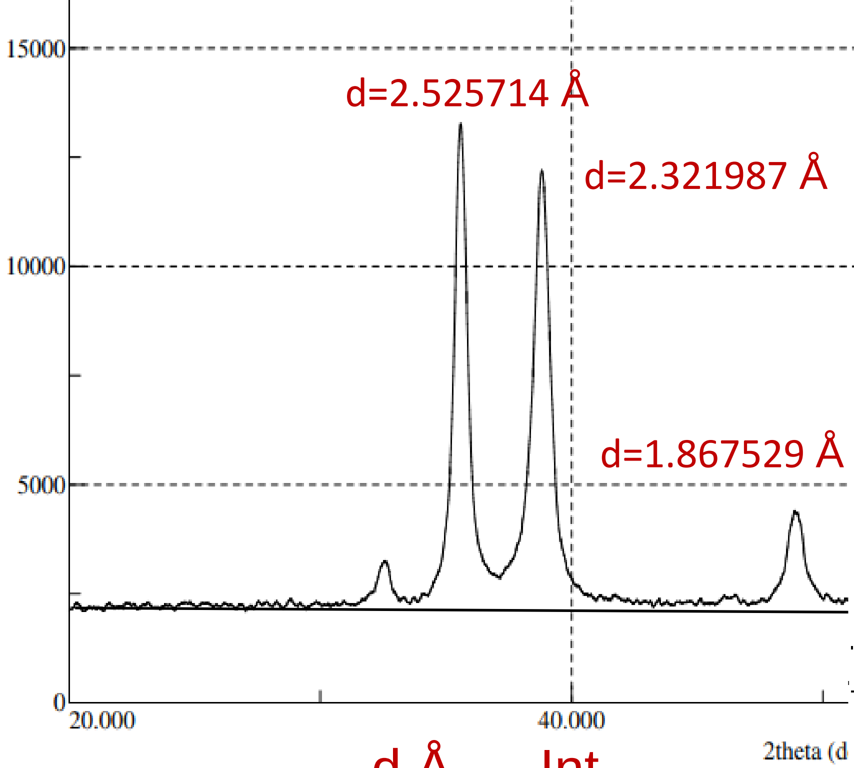
M – massa atómica de cada fase (g/mol) / atomic mass of phase (g/mol)

Exemplo – catalisador de cobre   Example – copper catalyst



Exemplo – catalisador de cobre
Example – copper catalyst

Tentativa de identificação   Atempt of identification



d Å	Int.
2.465	100

d Å	I/I_1	hkl
3.020	9	110
2.465	100	111
2.135	37	200
1.743	1	211
1.510	27	220

5-0667 MINOR CORRECTION

d	2.47	2.14	1.51	3.020	Cu_2O
I/I_1	100	37	27	9	Copper (I) Oxide (Cuprite)

Cu_2O, copper (I) oxide (cuprite)

Rad. $CuK\alpha_1$ λ 1.5405 Filter Ni
Dia. Cut off Coll.
I/I_1 G. C. Diffractometer d corr. abs.?
Ref. Swanson and Fuyat, NBS Circular 539, Vol. II 23 (1953)

Sys. Cubic S.G. O_h^4 - Pn3m
a_0 4.2696 b_0 c_0 A C
α β γ Z 2
Ref. Ibid.

εα nωβ εγ Sign
2V D_x 6.100 mp Color
Ref.

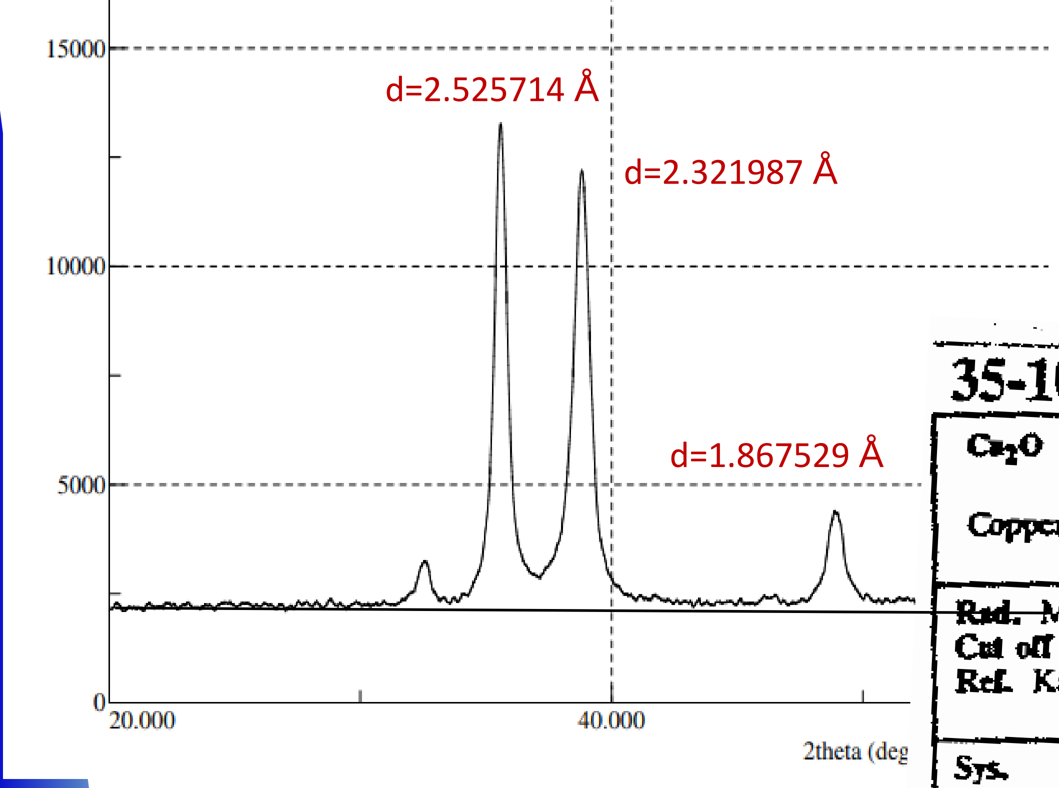
Sample prepared at the NBS. Spect. anal.: <1% Ca,Si; <0.1% Al,Mg; <0.01% Ag,B,Ba,Fe,Ti; <0.001% Mn,Pb,Sn.
X-ray pattern at 26°C.

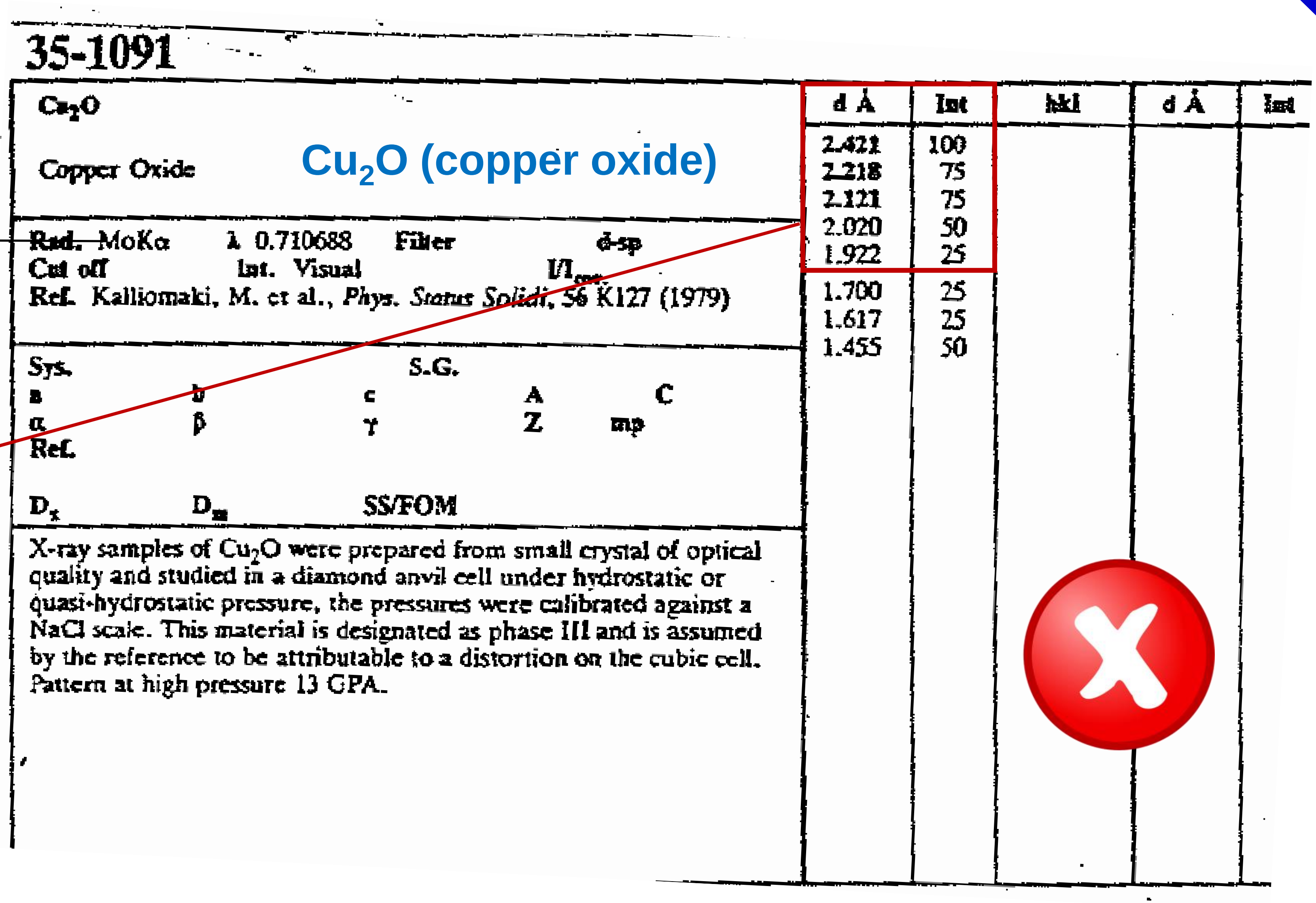
Replaces 1-1142, 2-1067, 3-0892, 3-0898

d Å	I/I_1	hkl	d Å	I/I_1	hkl
3.020	9	110			
2.465	100	111			
2.135	37	200			
1.743	1	211			
1.510	27	220			
1.287	17	311			
1.233	4	222			
1.0674	2	400			
0.9795	4	331			
.9548	3	420			
.8715	3	422			
.8216	3	511			

Exemplo – catalisador de cobre
Example – copper catalyst

Tentativa de identificação **Atempt of identification**





35-1091

Cu_2O

Copper Oxide

d Å	Int	hkl	d Å	Int
2.421	100			
2.218	75			
2.121	75			
2.020	50			
1.922	25			
1.700	25			
1.617	25			
1.455	50			

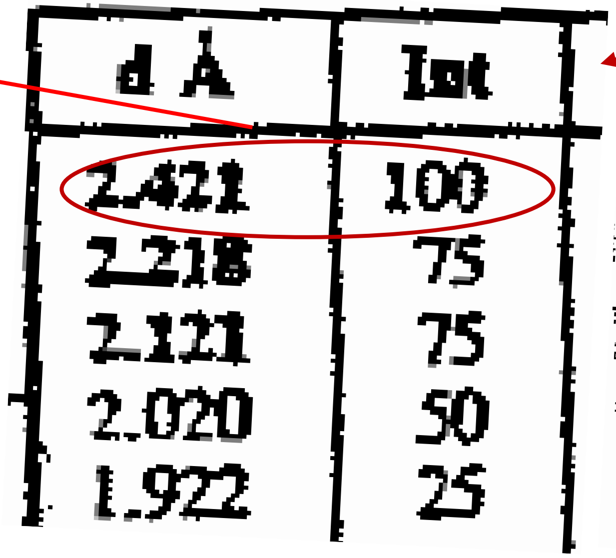
Rad. MoKα λ 0.710688 Filter d-sp
Cut off Int. Visual I/I_{cor}
Ref. Kalliomaki, M. et al., *Phys. Status Solidi*, 56 K127 (1979)

Sys. S.G.
a b c A C
α β γ Z mp
Ref.

D_x D_m SS/FOM

X-ray samples of Cu_2O were prepared from small crystal of optical quality and studied in a diamond anvil cell under hydrostatic or quasi-hydrostatic pressure, the pressures were calibrated against a NaCl scale. This material is designated as phase III and is assumed by the reference to be attributable to a distortion on the cubic cell. Pattern at high pressure 13 GPA.

Cu_2O (copper oxide)

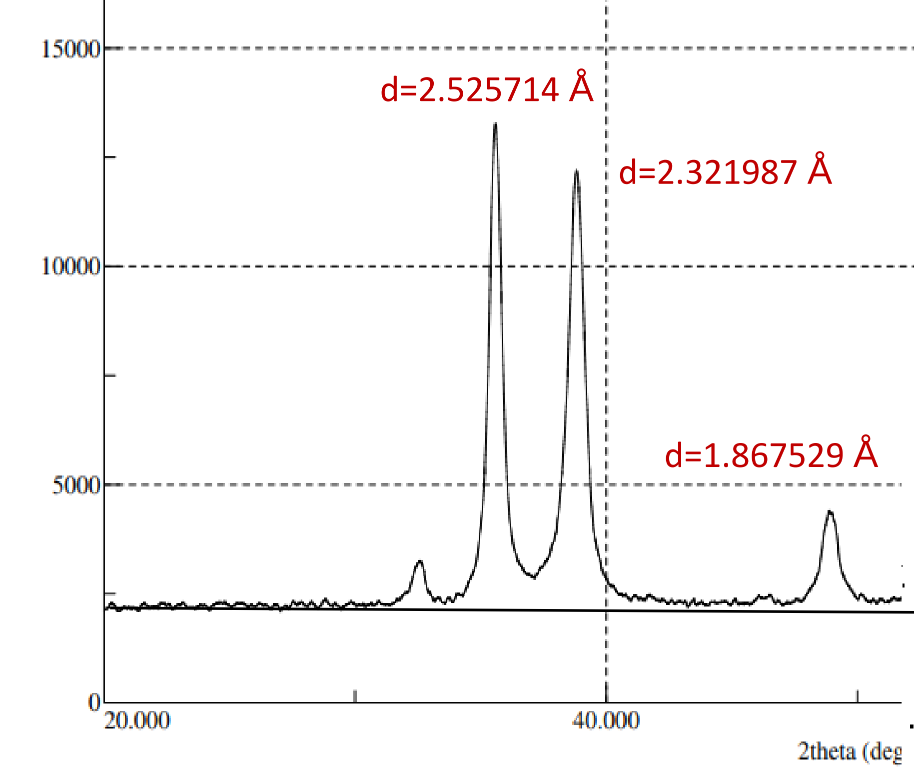


d Å	Int
2.421	100
2.218	75
2.121	75
2.020	50
1.922	25

d Å	Int.
2.422	100

Exemplo – catalisador de cobre
Example – copper catalyst

Tentativa de identificação   Atempt of identification



4-0836 MAJOR CORRECTION

d 4-0845	2.09	1.81	1.28	2.088	Cu
I/I_1 4-0836	100	46	20	100	COPPER (COPPER)

Cu (copper)

Rad. $CuK\alpha_1$ λ 1.5405 Filter Ni
Dia. Cut off Coll.
I/I_1 G. C. DIFFRACTOMETER d corr. abs.?
Ref. SWANSON AND TATGE, JC FEL. REPORTS, NBS (1949)

Sys. CUBIC S.G. O_h^5 - Fm3m
a_0 3.6150 b_0 c_0 A C
α β γ Z 4
Ref. IBID.

εα nωβ εγ Sign
2V D_x 8.936 mp Color
Ref. IBID.

JOHNSON AND MATTHEY-SPEC. SAMPLE, ANNEALED AT 700°C IN VACUUM.
AT 26°C
TO REPLACE 1-1241, 1-1242, 2-1225, 3-1005, 3-1015, 3-1018

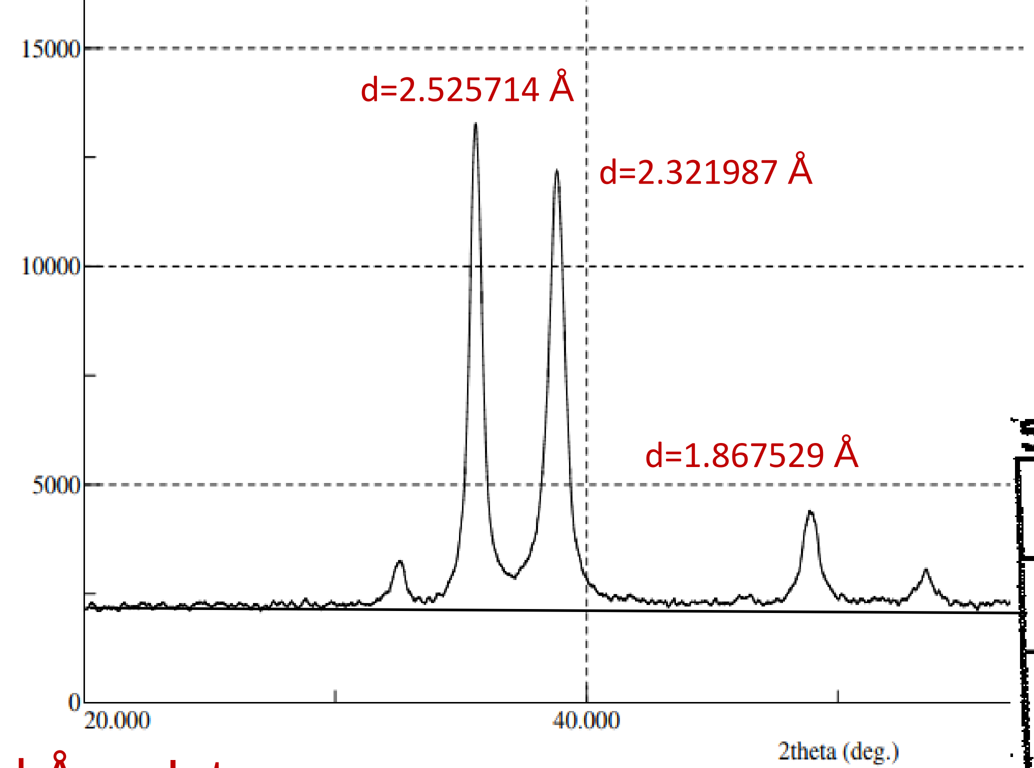
d Å	I/I_1	hkl
2.088	100	111
1.808	46	200
1.278	20	220
1.0900	17	311
1.0436	5	222
0.9038	3	400
.8293	9	331
.8083	8	420

d Å Int.
2.088 100

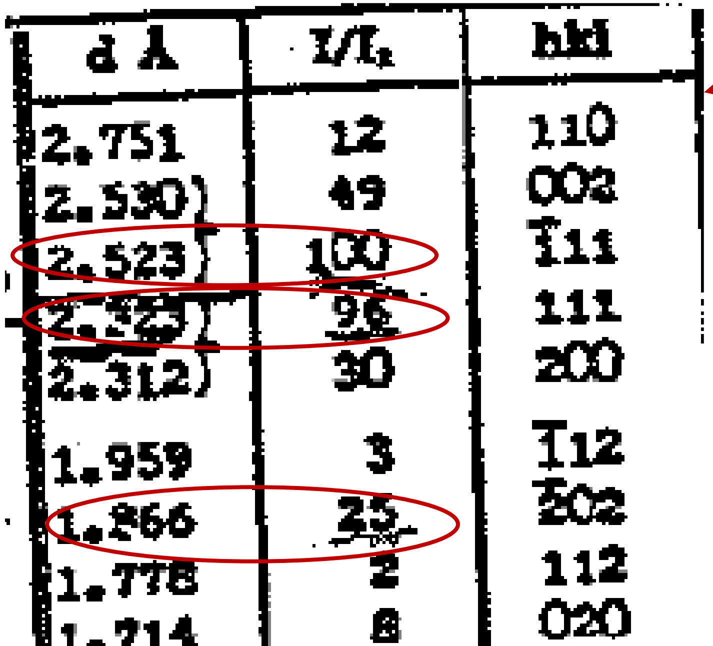
d Å	I/I_1	hkl
2.088	100	111
1.808	46	200
1.278	20	220
1.0900	17	311
1.0436	5	222

Exemplo – catalisador de cobre
Example – copper catalyst

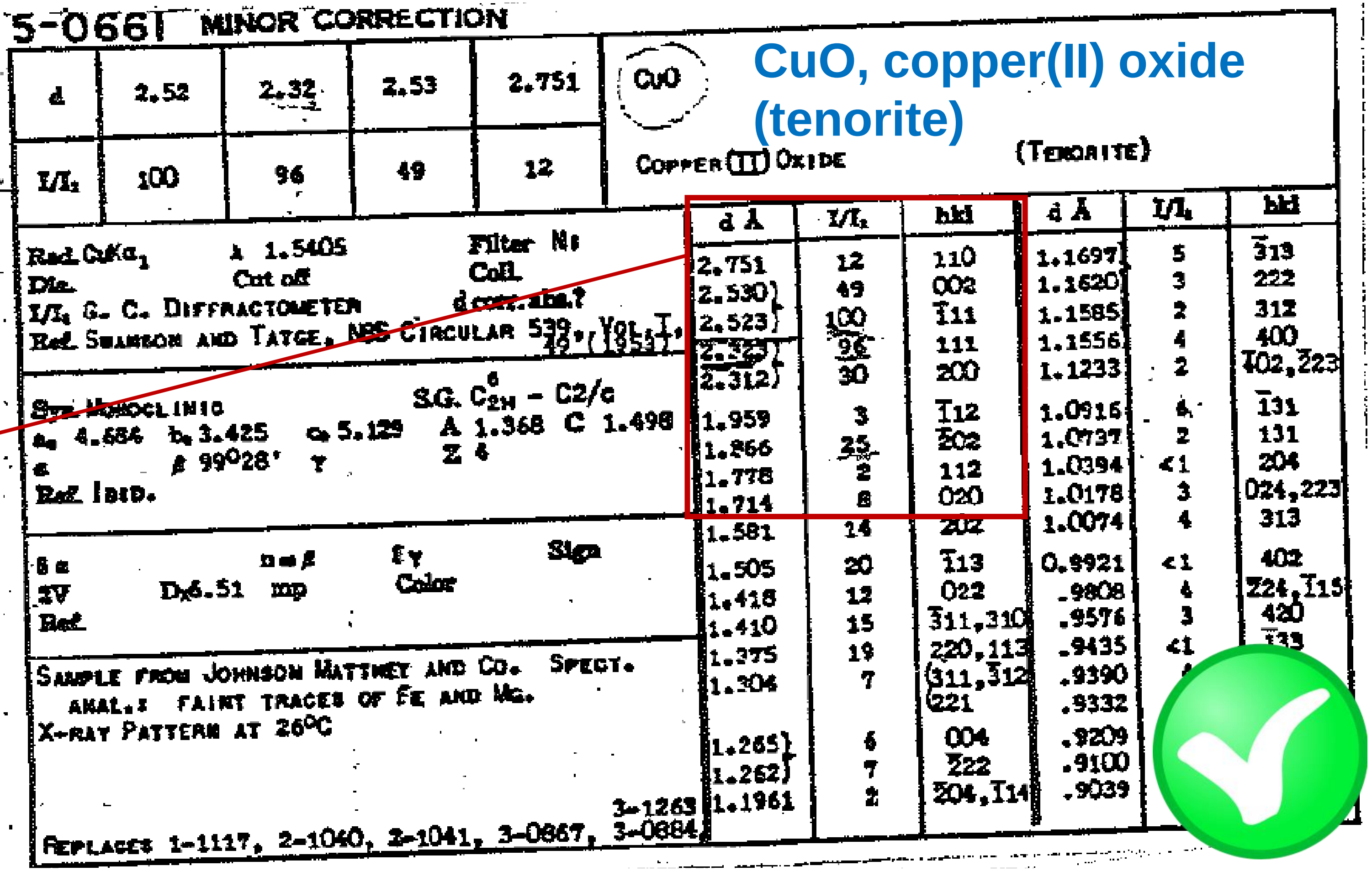
Tentativa de identificação   Atempt of identification



d Å	Int.
2.523	100
2.323	96
1.866	35



d Å	I/I1	hkl
2.751	12	110
2.530	49	002
2.523	100	$\bar{1}11$
2.323	96	111
2.312	30	200
1.959	3	$\bar{1}12$
1.866	25	$\bar{2}02$
1.778	2	112
1.714	8	020



CuO, copper(II) oxide (tenorite)

5-0661 MINOR CORRECTION

d	2.52	2.32	2.53	2.751	CuO
I/I1	100	96	49	12	Copper (II) Oxide (Tenorite)

Rad. $CuK\alpha_1$ λ 1.5405 Filter Ni
Dia. Cut off Coll.
I/I1 G. C. Diffractometer d corr. abs.?
Ref. Swanson and Tatge, NBS Circular 539, Vol. I, 49 (1953)

Sys. Monoclinic S.G. C^6_{2h} – C2/c
a_0 4.684 b_0 3.425 c_0 5.129 A 1.368 C 1.498
α β 99°28' γ Z 4
Ref. Ibid.

εα nωβ εγ Sign
2V Dx 6.51 mp Color
Ref

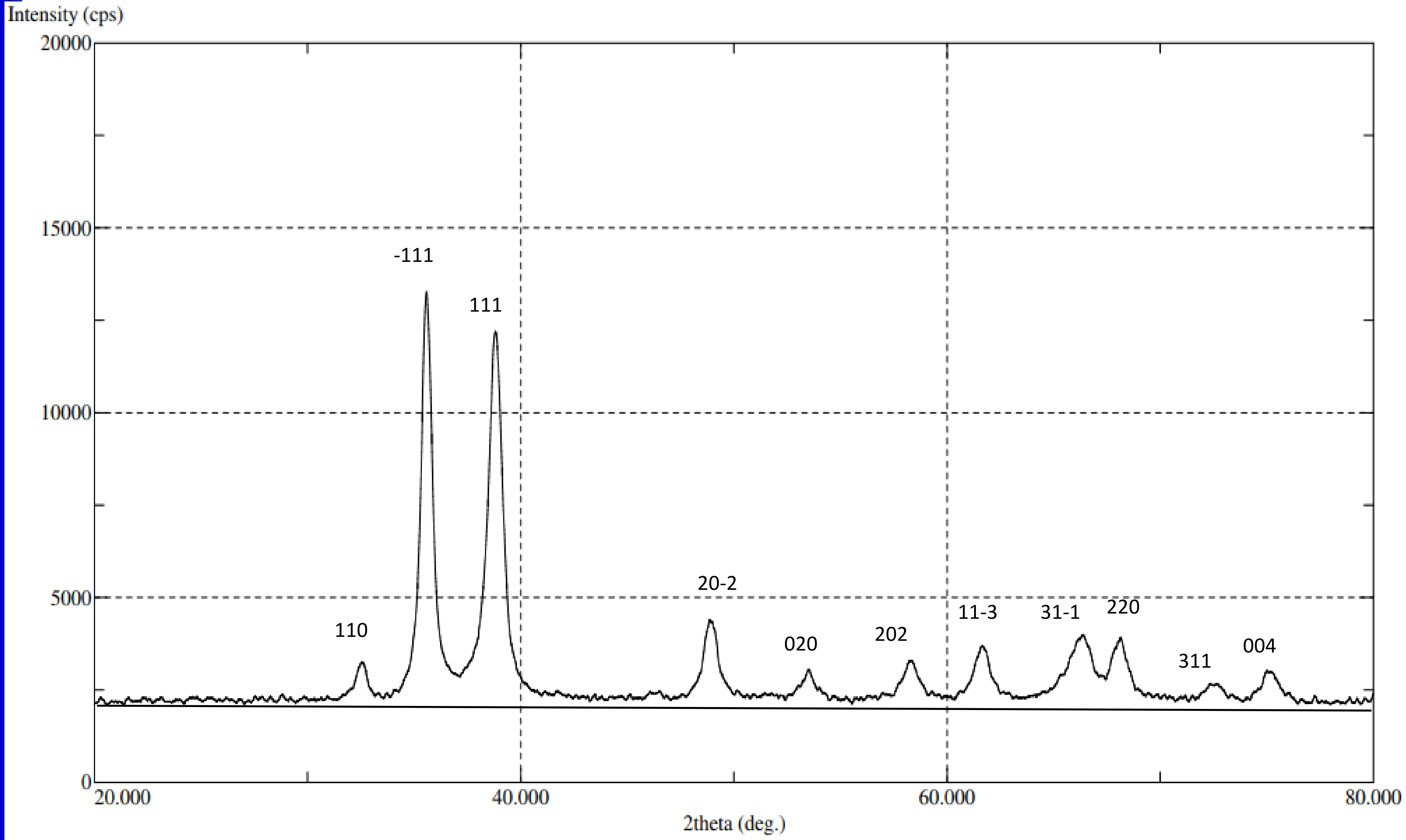
Sample from Johnson Matthey and Co. Spect. Anal.: faint traces of Fe and Mg.
X-ray pattern at 26°C

Replaces 1-1117, 2-1040, 2-1041, 3-0867, 3-1263 3-0884

d Å	I/I1	hkl	d Å	I/I1	hkl
2.751	12	110	1.1697	5	$\bar{3}13$
2.530	49	002	1.1620	3	222
2.523	100	$\bar{1}11$	1.1585	2	312
2.323	96	111	1.1556	4	400
2.312	30	200	1.1233	2	$\bar{4}02,\bar{2}23$
1.959	3	$\bar{1}12$	1.0916	6	$\bar{1}31$
1.866	25	$\bar{2}02$	1.0737	2	131
1.778	2	112	1.0394	<1	204
1.714	8	020	1.0178	3	024,223
1.581	14	202	1.0074	4	313
1.505	20	$\bar{1}13$	0.9921	<1	402
1.418	12	022	.9808	4	$\bar{2}24,\bar{1}15$
1.410	15	$\bar{3}11$,310	.9576	3	420
1.375	19	220,113	.9435	<1	$\bar{1}33$
1.304	7	($\bar{3}11$,312 $\bar{2}21$	.9390		
			.9332		
1.265	6	004	.9209		
1.262	7	$\bar{2}22$	.9100		
1.1961	2	$\bar{2}04,\bar{1}14$	.9039		

CuO (óxido de cobre (II), tenorite) CuO (copper oxide (II), tenorite)

Identificação dos índices de Miller dos picos / Identification of Miller indices of peaks



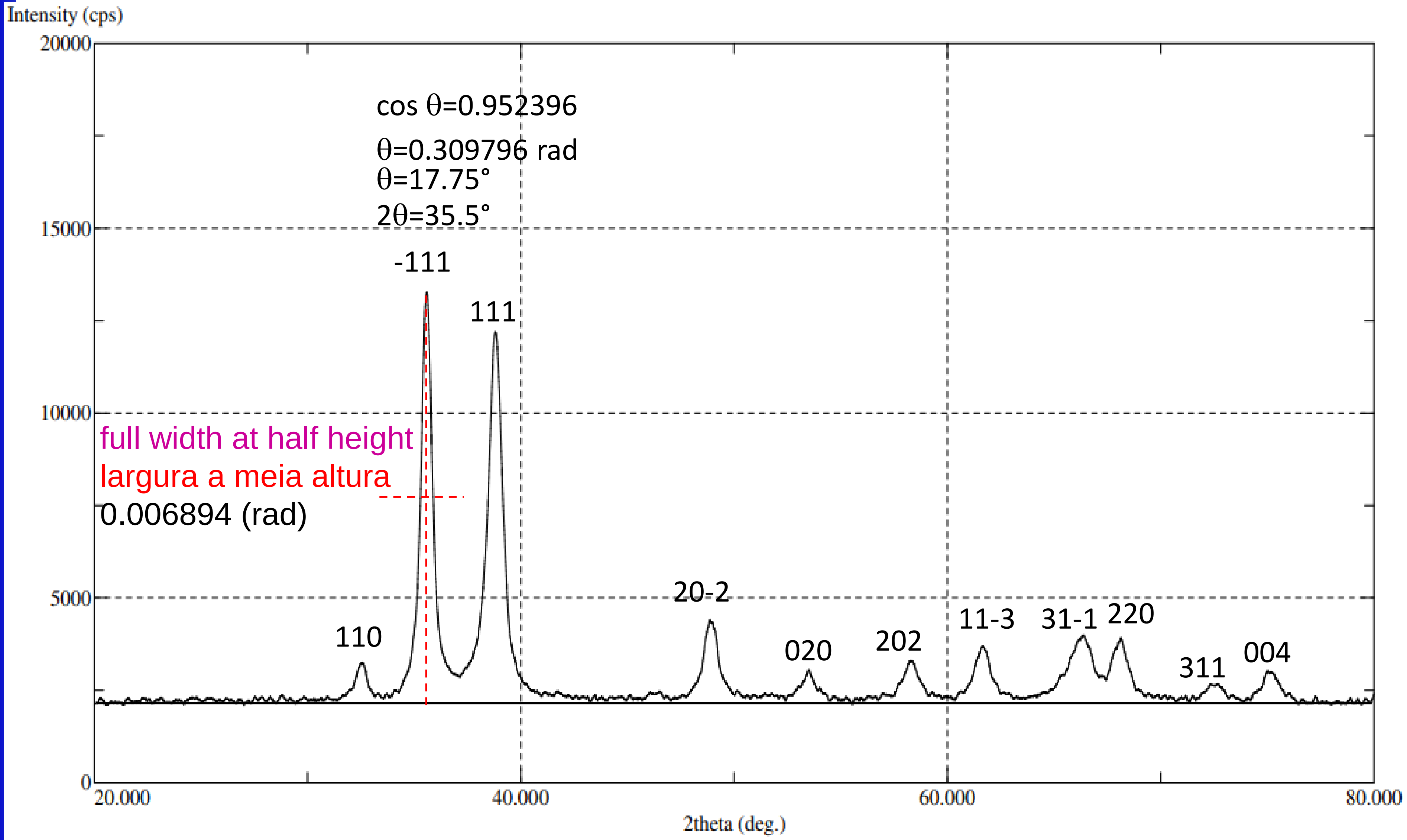
OXIDE (TENORITE)

I/I_1	hkl	d Å	I/I_1	hkl
12	110	1.1697	5	$\bar{3}13$
49	002	1.1620	3	222
100	$\bar{1}11$	1.1585	2	312
96	111	1.1556	4	400
30	200	1.1233	2	$\bar{4}02,\bar{2}23$
3	$\bar{1}12$	1.0916	4	$\bar{1}31$
25	$\bar{2}02$	1.0737	2	131
2	112	1.0394	<1	204
8	020	1.0178	3	024,223
14	202	1.0074	4	313
20	$\bar{1}13$	0.9921	<1	402
12	022	.9808	4	$\bar{2}24,\bar{1}15$
15	$\bar{3}11$,310	.9576	3	420
19	220,113	.9435	<1	$\bar{1}33$
7	311,$\bar{3}12$	.9390	4	$\bar{4}22$
	221	.9332	2	$\bar{4}04$
6	004	.9209	2	115,$\bar{3}31$
7	$\bar{2}22$	.9100	2	133
2	$\bar{2}04$,$\bar{1}14$	.9039	1	$\bar{5}11$

CuO (óxido de cobre (II), tenorite) CuO (copper oxide (II), tenorite)

Cálculo do diâmetro das cristalites (usando o pico mais intenso)

Calculation of the diameter of crystallites (using the most intense peak)



$$dp = \frac{\beta \lambda}{b \cos\theta}$$

$\beta = 1$

$\lambda = 1.54$ Å

$\theta = 0.309796$ rad

$\cos\theta = 0.952396$

$b = 0.006894$ rad

dp = 234.55 Å

dp = 23.45 nm

Exemplo – catalisador de cobalto   Example – cobalt catalyst

De acordo com os seguintes dados de difração de Raios X obtidos para um catalisador com 1% de Cobalto suportado em carvão ativado.

According to the following X-ray diffraction data obtained for a catalyst with 1% Cobalt supported on activated carbon.

a) Identifique as fases presentes no suporte / Identify the phases present in the support.

b) Determine o tamanho das partículas do metal, a área metálica e a dispersão metálica. Considere a largura a meia altura do pico mais intenso do metal, igual a 10° (2θ)

Determine the size of the metal particles, the metal area, and the metal dispersion. Consider the width at half height of the metal's most intense peak, equal to 10° (2θ)

2θ	I/I_0	hkl	d
36,48	75	111	
42,38	100	200	
44,14	100	111	
51,59	40	200	
61,50	50	220	
73,65	20	311	
76,08	30	220	
92,09	30	311	
98,08	10	222	

c) Como procederia para obter a área metálica usando outras técnicas de caracterização? Justifique.

How would you proceed to obtain the metallic area using other characterization techniques? Justify.

$n_s = 1.51 \times 10^{19}$ atoms/m^2

$\rho = 8.9$ g/cm^3

M = 58.9 g/mol

$\lambda = 1.54$ Å

a) Identifique as fases presentes no suporte. Identify the phases present in the support.

2θ	I/I_0	hkl	d
36,48	75	111	2.46
42,38	100	200	2.13
44,14	100	111	2.05
51,59	40	200	1.77
61,50	50	220	1.51
73,65	20	311	1.28
76,08	30	220	1.25
92,09	30	311	1.07
98,08	10	222	1.02

$n\lambda = 2d\,\mathrm{sen}\theta \Leftrightarrow d = 0.77/\mathrm{sen}\theta$ (θ, rad)

9-402

d	2.13	2.46	1.51	2.46	CoO
I/I_1	100	75	50	75	Cobalt (II) Oxide

Rad. $CoK\alpha_1$ λ 1.7889 Filter Fe Dia.
Cut off I/I_1 Diffractometer
Ref. Nat. Bur. Standards Circ. 539 9 (1959)

Sys. Cubic S.G. O_H^5 – Fm3m
a_0 4.260 b_0 c_0 A C
α β γ Z 4 Dx 6.437
Ref. Ibid.

d Å	I/I_1	hkl
2.460	75	111
2.130	100	200
1.5062	50	220
1.2846	20	311
1.2298	15	222
1.0651	9	400
0.9775	13	331

1.77	1.07	2	(Co) 4F
40	30	100	Cobalt (cubic)

λ 1.7889 Filter Fe Dia.
I/I_1 Diffractometer
Stds. Mono. 25, Sec.4 (1965)

S.G. Fm3m (No. 225)
c_0 A C
γ Z 4 Dx 8.788
n ω β ε γ Sign
mp Color dark grey

d Å	I/I_1	hkl
2.0467	100	111
1.7723	40	200
1.2532	25	220
1.0688	30	311
1.0233	12	222

100	100	90	Cobaltic Oxide

λ 0.709 Filter
Cut off Coll.
d corr. abs.?
and Strada, Gazz. chim. ital., 58 431 (1928)

onal (Shomo. ?) S.G. D_{3d}^6 $R\bar{3}c$
b_0 c_0 5.75 A C 1.24
β γ Z 2
n ω β ε γ
D mp Color Black

d Å	I/I_1
3.21	90
2.87	100
2.33	100
1.78	100
1.63	90
1.57	50
1.39	90

Co c.f.c. (>450°C)

d(Å)	I/I_0	2θ $CuK\alpha_1$
2,05	100	44,141
1,77	40	51,594
1,25	30	76,082
1,07	30	92,091
1,02	10	98,082
0,8874		120,454
0,8444		142,428
0,7937		152,076
0,7246		

b) Determine o tamanho das partículas do metal, a área metálica e a dispersão metálica. Considere a largura a meia altura do pico mais intenso do metal, igual a 10° (2θ)

Determine the size of the metal particles, the metal area, and the metal dispersion. Consider the width at half height of the metal's most intense peak, equal to 10° (2θ)

2θ	I/I_0	hkl	d	
36,48	75	111	2.46	CoO
42,38	100	200	2.13	CoO
44,14	100	111	2.05	Co ⇐
51,59	40	200	1.77	Co
61,50	50	220	1.51	CoO
73,65	20	311	1.28	CoO
76,08	30	220	1.25	Co
92,09	30	311	1.07	Co
98,08	10	222	1.02	Co

O **metal** é o Co (CoO é um óxido)

The **metal** is Co (CoO is an oxide)

O **pico mais intenso** do Co é o que tem $I/I_0 = 100$, ou seja 2θ = 44.14°, logo θ = 22.07° = 0.3852 rad.

The **most intense peak** of Co is the one that has $I/I_0 = 100$, that has 2θ = 44.14°, thus θ = 22.07° = 0.3852 rad.

π rad ----- 180º

x ---------22.07º

$x = \pi \times 22.07/180 = 0.3852$ rad

π rad ----- 180º

x --------- 5º

$x = \pi \times 5/180 = 0.0873$ rad

Dados/Data

$n_s = 1.51\times10^{19}$ atoms m^{-2}

$\rho = 8.9$ g cm^{-3}

M = 58.9 $gmol^{-1}$

λ = 1.54 Å

$\beta = 1$

y = 1% Co = 0.01

N = 6.023 $\times10^{23}$ atoms mol^{-1}

A **largura a meia altura** (b) é 10° (2θ), ou seja 5° (θ) = 0.0873 rad.

The **full width at half maximum** is 10° (2θ), that is 5° (θ) = 0.0873 rad.

Logo:
Thus:

$$dp = \frac{\beta\ \lambda}{b \cos\theta} = 1\times1.54 /[0.0873\times\cos(0.3852)] = 19.04 \text{ Å}$$

$$dp = \frac{\beta\ \lambda}{b\ \cos\theta} = 1.54\ /[0.0873 \times \cos(0.3852)] = 19.04\ Å$$

Dados / Data

$n_s = 1.51\times10^{19}$ atoms m^{-2}

$\rho = 8.9$ g cm^{-3}

$M = 58.9$ $gmol^{-1}$

$\lambda = 1.54$ Å

$\beta = 1$

$y = 1\%$ Co $= 0.01$

$N = 6.023 \times10^{23}$ atoms mol^{-1}

Para calcular a **área metálica S_M**:

To calculate the **metal área S_M**:

$$dp = \frac{\beta\ \lambda}{b\ \cos\theta} = \frac{6\ y}{\rho\ S_M}$$

$$S_M = (6\times0.01)/(8.9\times10^6 gm^{-3}\times19.04\times10^{-10}m) = 3.53\ m^2/g$$

Para calcular a **dispersão metálica**:

To calculate the **metal dispersion**:

$$D_M = \frac{S_M\ n_s}{N\ y\ /\ M}$$

$$D_M = \frac{3.53\ \cancel{m^2}\cancel{g^{-1}}\times1.51\times10^{19}\ \cancel{atoms}\ \cancel{m^{-2}}}{6.023\times10^{23}\ \cancel{atoms}\ \cancel{mol^{-1}}\times0.01/58.9\ \cancel{g}\cancel{mol^{-1}}} = 0.52 = 52\%$$

c) Como procederia para obter a área metálica usando outras técnicas de caracterização? Justifique.

How would you proceed to obtain the metallic area using other characterization techniques? Justify.

Microscopia eletrónica de transmissão para calcular o diâmetro das cristalites. **Quimissorção** para calcular dispersão e área metálica.

Transmission electron microscopy to calculate the diameter of crystallites. **Chemisorption** to calculate dispersion and metal area.

Exemplo – catalisador de níquel   Example – nickel catalyst

Tentativa de identificação
Atempt of identification

d, Å	I/I_0	hkl	
2.41	91	111	NiO
2.09	100	200	NiO
2.03	100	111	Ni
1.76	42	200	Ni
1.47	57	220	NiO
1.24	21	220	Ni
0.93	21	420	NiO

d 4-0854	2.034	1.762	1.246	2.034	Ni
I/I_1 4-0850	100	42	21	100	NICKEL

Rad. Cu λ 1.5405 Filter Ni
Dia. Cut off Coll.
I/I_1 d corr. abs.?
Ref. Swanson and Tatge, JC Fel. Reports, NBS 1951

S.G. O_H^5 - Fm3m

d Å	I/I_1	hkl
2.034	100	111
1.762	42	200
1.246	21	220
1.0624	20	311
1.0172	7	222
0.8810	4	400
.8084	14	331
.7880	15	420

2.410	1.476	2.410	NiO
91	57	91	Nickel Oxide Bunsenite

λ 1.5405 Filter Ni
Cut off Coll.
d corr. abs.?
...and Tatge, JC Fel. Reports, NBS 1950

S.G. O_H^5 - Fm3m

n ω β 2.73 ε γ (Li) Sign
806 mp Color

d Å	I/I_1	hkl
2.410	91	111
2.088	100	200
1.476	57	220
1.259	16	311
1.206	13	222
1.0441	8	400
0.9582	7	331
.9338	21	420
.8527	17	422
.8040	7	511

2.02	1.77	3.23	$(Ni_2O_3)H$
100	100	20	Nickel(III) Oxide

Filter Dia.
I/I_1
...and Goswami, J. Phys. Chem. 65 2105 (1961)
S.G. a 5.61 c 1.22

d Å	I/I_1	hkl
3.23	20	101
2.80	100	002
2.30	80	110
2.02	100	200
1.77	100	112
1.62	100	202
1.40	40	004
1.11	40	311

Determine o tamanho das partículas do metal, a área metálica e a dispersão metálica, considerando 1%Ni. Considere a largura a meia altura do pico mais intenso do metal 8° (2θ).

Determine the metal particle size, metal area, and metal dispersion by considering 1%Ni. Consider the full width at half height of the most intense peak of the metal to be equal to 8° (2θ).

	d, Å	I/I_0	hkl	sen θ	θ, rad
NiO	2.41	91	111	0.3195	0.3252
NiO	2.09	100	200	0.3684	0.3773
Ni	2.03	100	111	0.3793	0.3891
Ni	1.76	42	200	0.4375	0.4528
NiO	1.47	57	220	0.5238	0.5513
Ni	1.24	21	220	0.6210	0.6700
Ni	0.93	21	420	0.8280	0.9755

⇐ **mais intenso**
most intense

$$n\,\lambda = 2\,d\,\text{sen}\theta$$

$d=(1.54\ \text{sen}\theta)/2 = 0.77 / \text{sen}\ \theta$ (θ in rad)

$\text{sen}\ \theta = 0.77/d \Rightarrow \theta = \text{arc sen}\ (0.77/d)$

O **metal** é o Ni (NiO é um óxido)
The **metal** is Ni (NiO is an oxide)

O **pico mais intenso** do Ni é a $I/I_0 = 100$, ou seja d=2.03 Å.
The **most intense peak** of Ni is at $I/I_0=100$, that is, d=2.03 Å.

A **largura a meia altura** (b) é 8° (2θ), ou seja 4° (θ) = 0.06981 rad.
The **full width at half maximum** is 8° (2θ), ou seja 4° (θ) = 0.06981 rad.

Dados/Data:

$n_s = 1.2\times10^{19}$ atoms m^{-2}
$\rho = 8.9$ g cm^{-3} ; M = 58.7 $gmol^{-1}$
$\lambda = 1.54$ Å; $\beta = 1$
y = 1% Ni = 0.01
N = 6.023×10^{23} atoms mol^{-1}

O **diâmetro das cristalites** fica:
The **crystallite diameters** is:

$$dp = \frac{\beta\ \lambda}{b\ \cos\theta} = 1\times1.54 /[0.06981\times\overbrace{\cos(0.3891)}^{0.9252}] = 23.84\ \text{Å}$$

Dados/Data:

$n_s = 1.2\times10^{19}$ átomos m^{-2}

$\rho = 8.9\ g\ cm^{-3}$; $M = 58.7\ gmol^{-1}$

$\lambda\ = 1.54$ Å; $\beta = 1$

$y = 1\%$ Ni $= 0.01$

$N = 6.023\times10^{23}$ átomos mol^{-1}

$$dp = \frac{\beta\ \lambda}{b\ \cos\theta} = 1.54\ /[0.06981 \times \cos(0.3891)] = 23.84\ \text{Å}$$

Para calcular a **área metálica S_M**:

To calculate the **metal área S_M**:

$$dp = \frac{\beta\ \lambda}{b\ \cos\theta} = \frac{6\ y}{\rho\ S_M}$$

logo

thus

$$S_M = (6\times0.01)/(8.9\times10^{6}gm^{-3}\times23.84\times10^{-10}m) = 2.83\ m^2/g$$

Outra maneira de determinar cos θ seria:

Another way to determine cos θ would be:

$$(\text{sen}\ \theta)^2 + (\cos\ \theta)^2 = 1$$

$$\cos\ \theta = \sqrt{1-(\text{sen}\ \theta)^2} = \sqrt{1-0.3793^2} = 0.9252$$

Para calcular a **dispersão metálica**:

To calculate the **metal dispersion**:

$$D_M = \frac{S_M\ n_s}{N\ y\ /\ M} = \frac{2.83\ \cancel{m^2}\cancel{g^{-1}}\times1.2\times10^{19}\ \cancel{\text{átomos}}\ \cancel{m^{-2}}}{6.023\times10^{23}\cancel{\text{átomos}}\ \cancel{mol^{-1}}\times0.01/58.7\ \cancel{g}\cancel{mol^{-1}}} = 0.331 = 33.1\%$$