Introducción 1: Estructuras cristalinas

Prof. Martin Reich

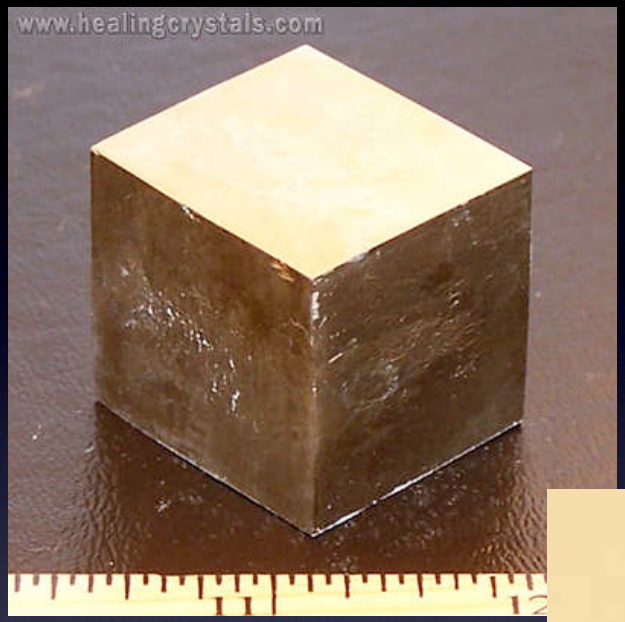
Temario

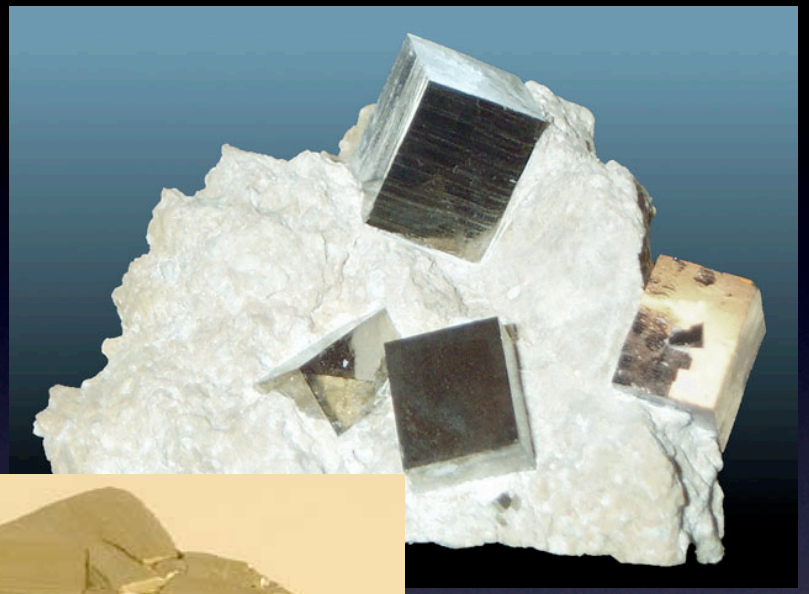
- Física/Química del Estado Sólido = Mineralogía
- Estructura = reticulo + simetría + átomos
- Retículo (lattice)
- Simetría rotacional (estática)= 32 grupos planos
- Simetría traslacional (dinámica)= 230 grupos espaciales
- Coordenadas atómicas: escalares y fraccionales

qué es un mineral?

- sólido cristalino natural
- composición definida (pero no fija)

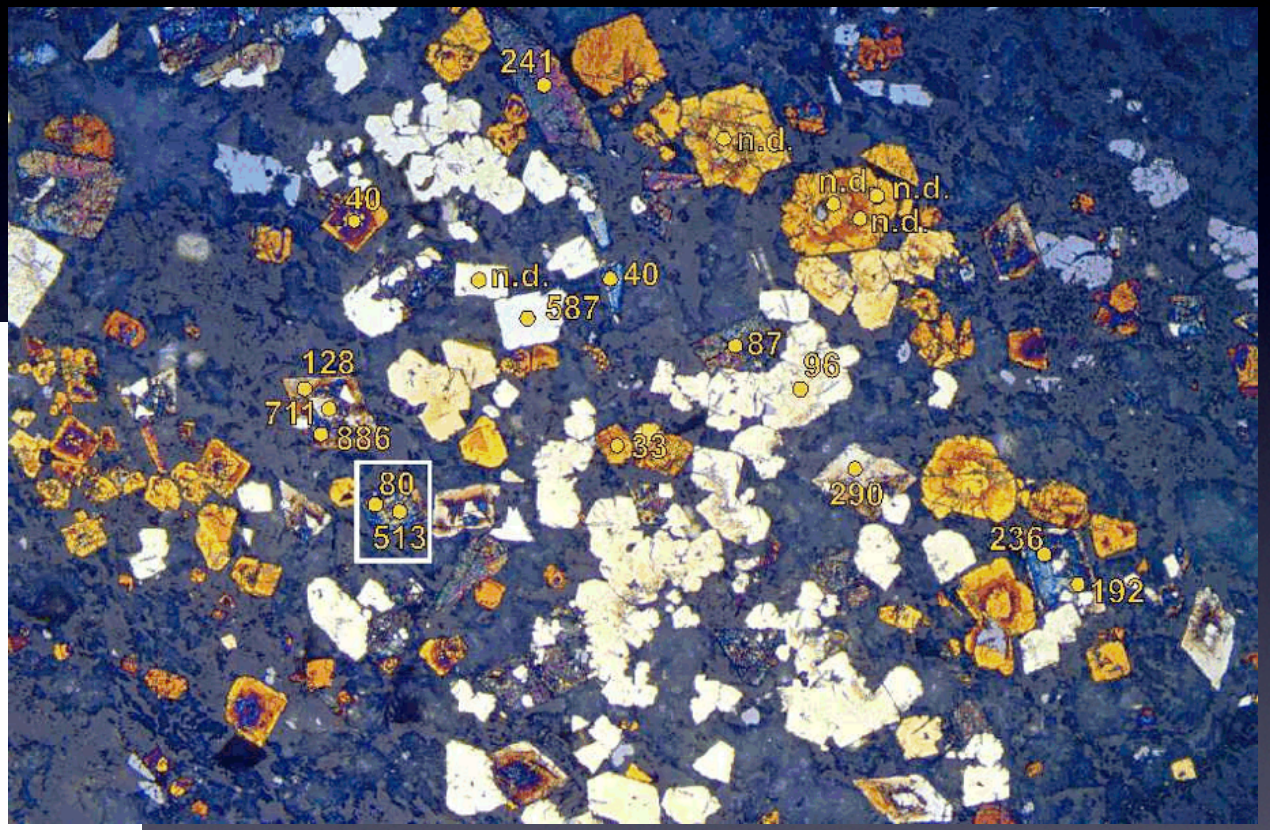
ESCALA MACROSCÓPICA (MUESTRA DE MANO)





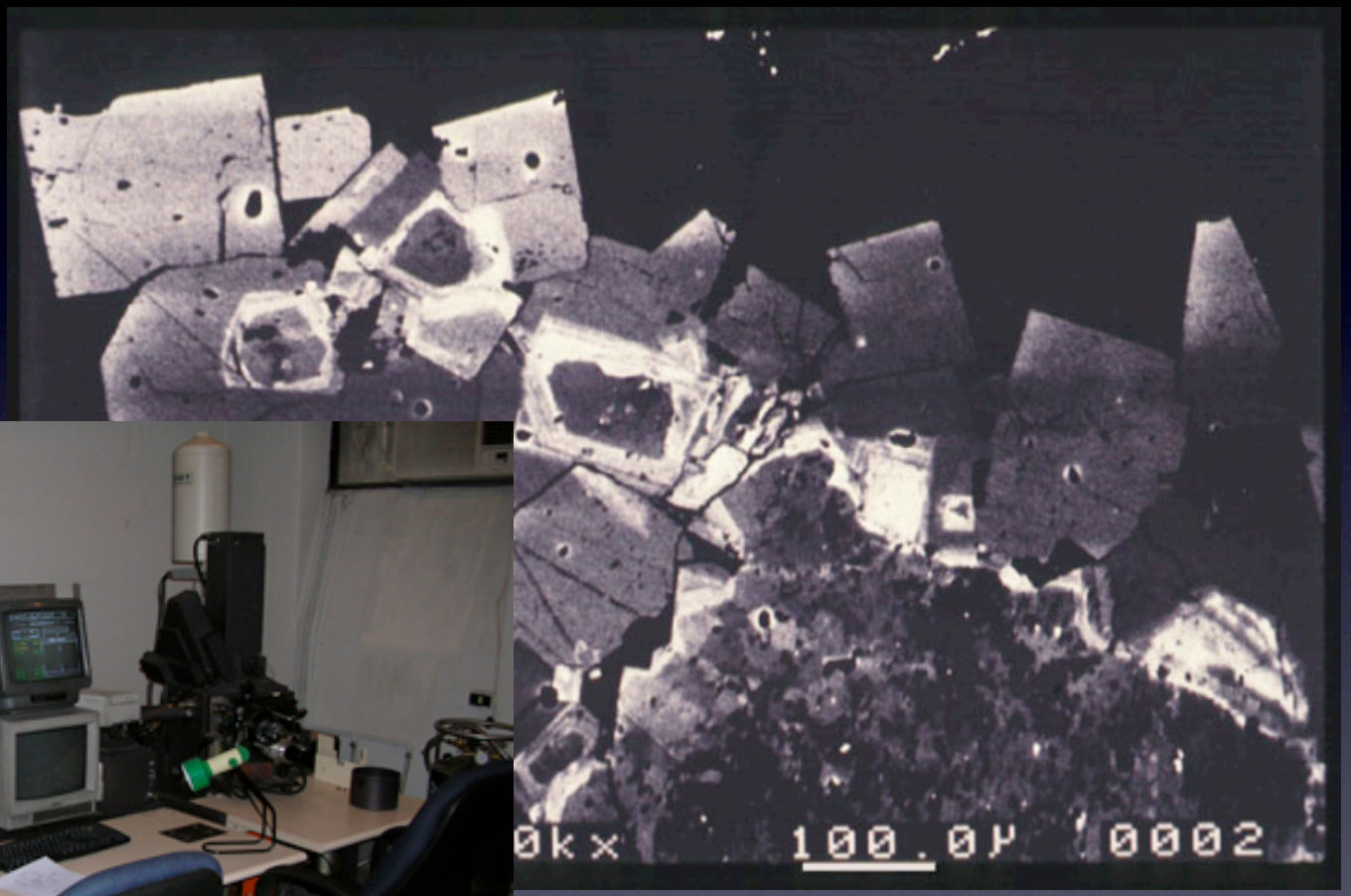
forma externa (cm-mm)

ESCALA MICROSCÓPICA (MICROSCOPIO ÓPTICO, LUZ REFLEJADA)



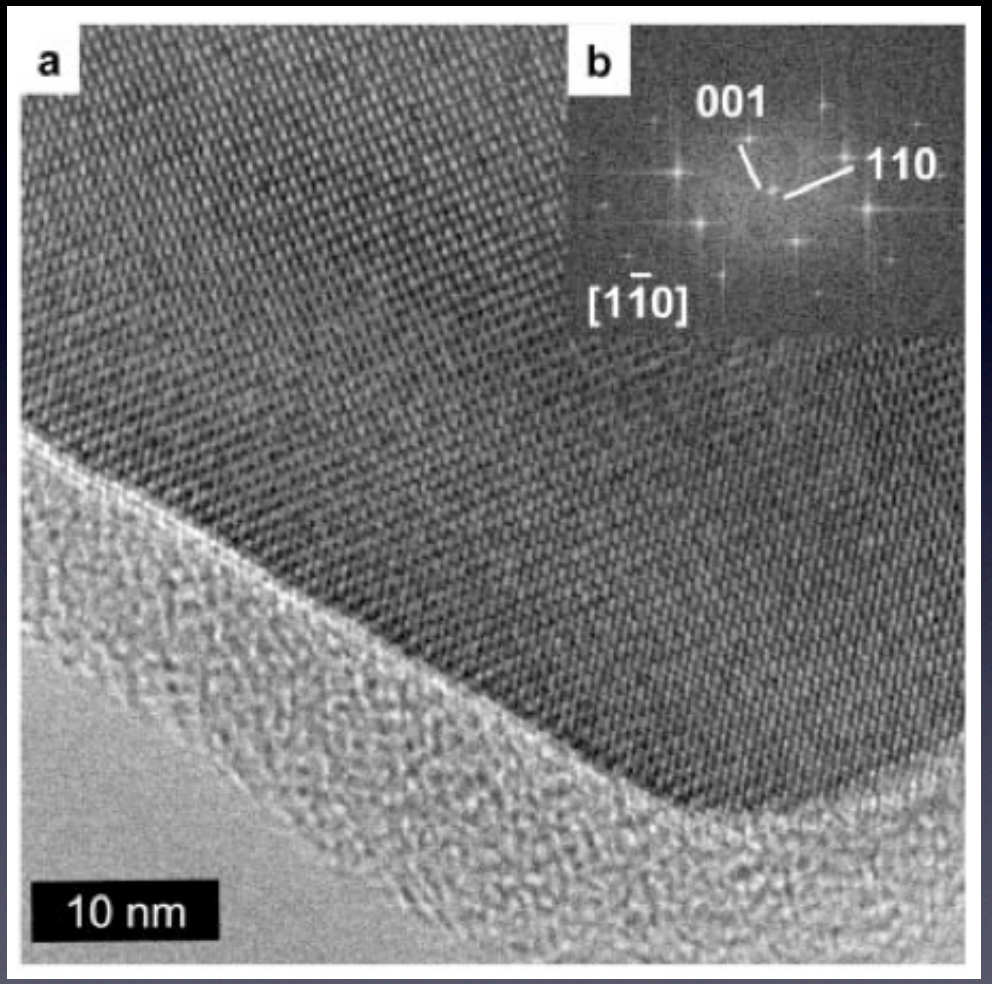
forma externa
(mm-µm)

ESCALA MICROSCÓPICA
(MICROSCOPIO ELECTRÓNICO DE BARRIDO, SEM)



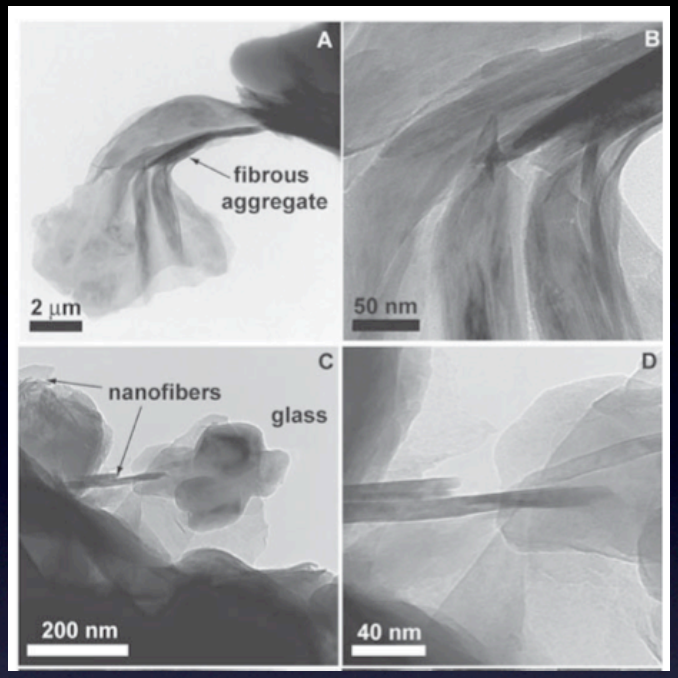
forma externa
(µm)

ESCALA NANOMÉTRICA
(MICROSCOPIO ELECTRÓNICO DE TRANSMISIÓN, TEM)



forma externa e interna (estructura) (µm-nm)

Nanofibras de Cristobalita en Ceniza Volcánica




nature Vol 459|28 May 2009

RESEARCH HIGHLIGHTS

Big volcano, tiny troubles

Geology **37**, 435–438 (2009)

Potentially dangerous silica nanofibres have been identified in airbourne ash spewed across southern South America by a Chilean volcano. Martin Reich and his colleagues at the University of Chile in Santiago used high-resolution transmission electron microscopy to image the one-dimensional crystalline silica nanostructures, called cristobalites. They were formed during the eruption of Patagonia's Chaitén Volcano, which began on 2 May 2008 and is ongoing.

The researchers propose that amorphous silica was reduced by carbon monoxide and then oxidized to become breathable crystalline nanostructures. The formation of these structures was enhanced by micrometre- to nanometre-sized silica glass fragments in the volcanic column.

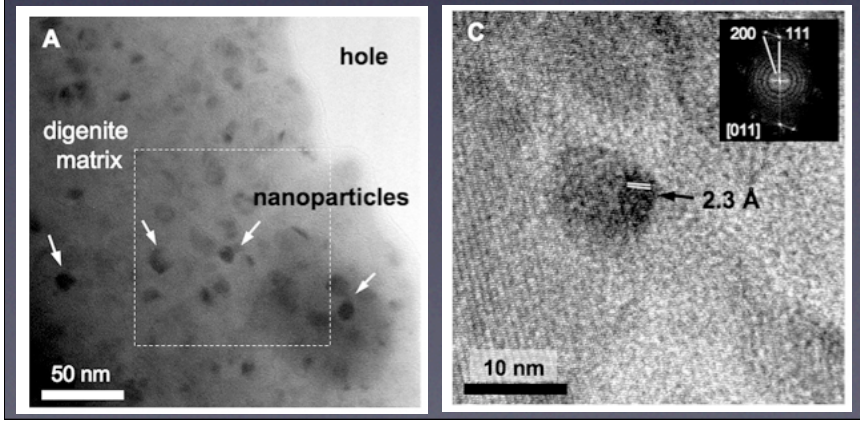
C. BROWN/EPA/CORBIS

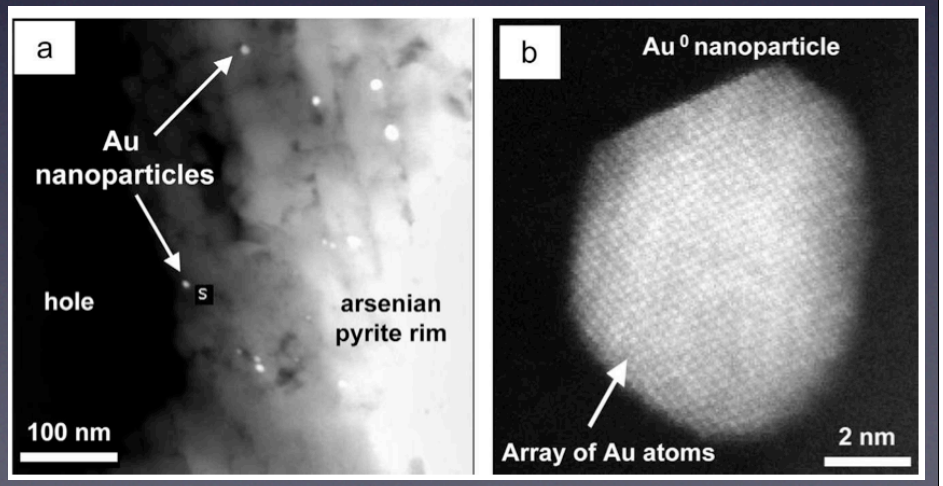
Reich et al., 2009 Nature

Reich et al., 2009 Geology

Nanopartículas de Oro y Plata en Pirita y CuS

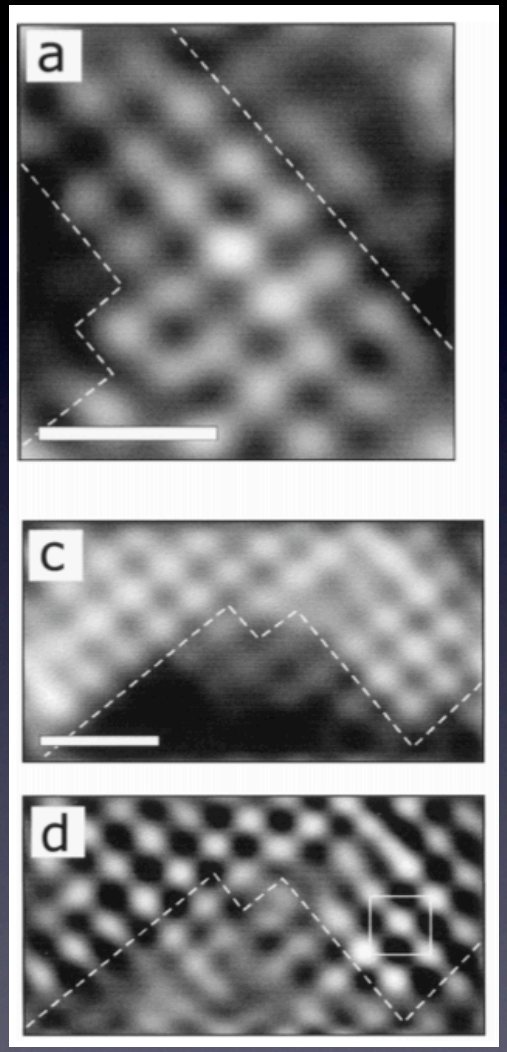
Reich et al., 2005 Geochimica Cosmochimica Acta

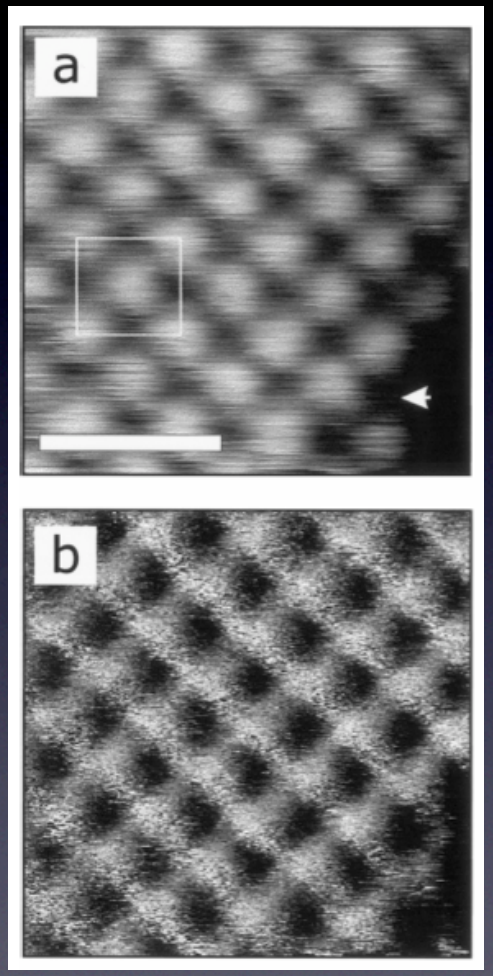




Reich et al., 2010 Geochimica Cosmochimica Acta

ESCALA ATÓMICA
(MICROSCOPIO DE EFECTO TÚNEL, STM)

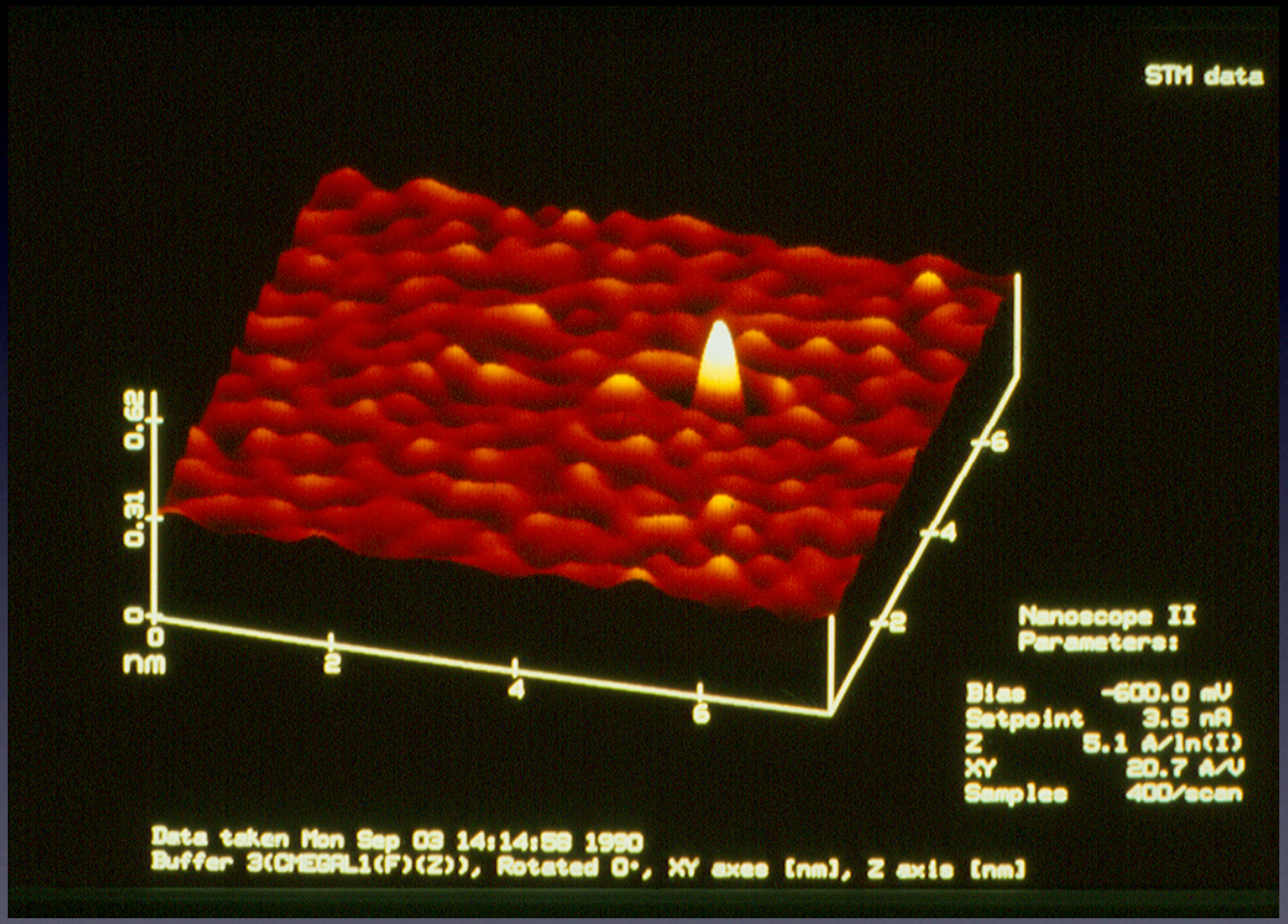




STM

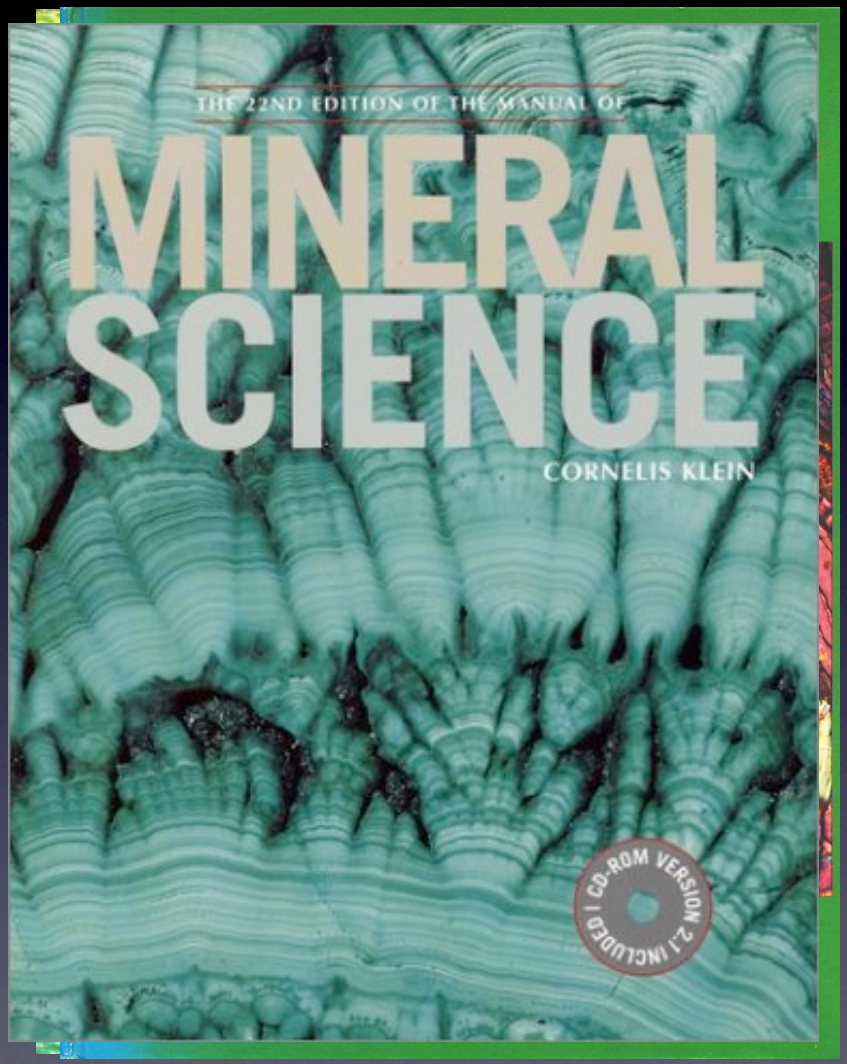
forma interna o estructura (nm-Å)

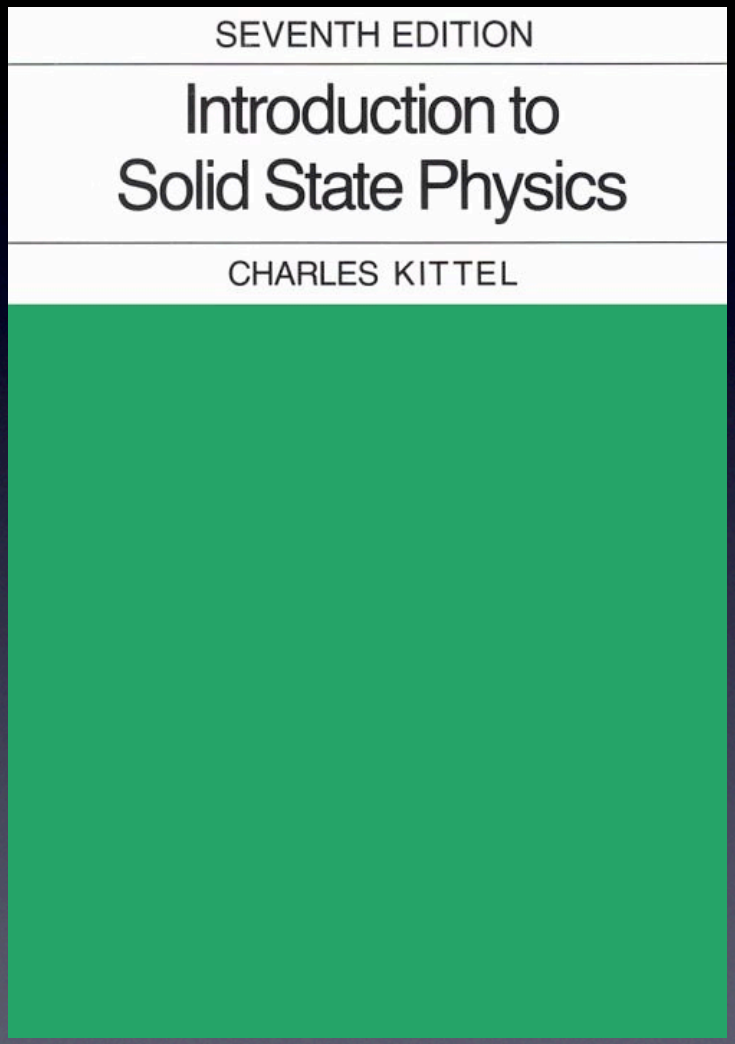
ESCALA ATÓMICA
(MICROSCOPIO DE EFECTO TÚNEL, STM)



átomo de Au en superficie de FeS

Mineralogía = Física y Química del Estado Sólido





http://folk.uio.no/dragos/Solid/FYS230-Exercises.html

intuitivamente, qué es una estructura cristalina (EC)?

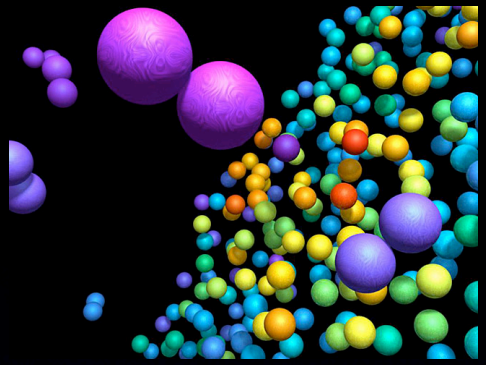
EC = A + R + S

A = átomos
R = retículo (lattice)
S = simetría

un mineral es una "sociedad" altamente ordenada y que obecede a reglas bien definidas

EC = A + R + S ??

ATOMOS/
MOLECULAS

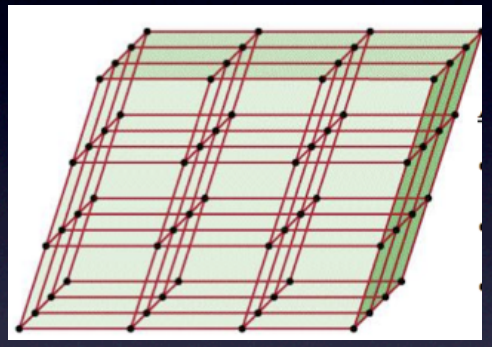


identidad del sistema

"quienes somos"

+

RED CRISTALINA

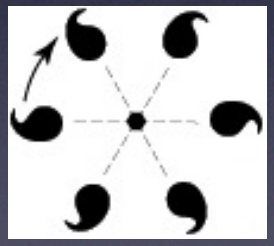


sistema de coordenadas

"donde nos paramos"

+

OPERACIONES
DE SIMETRÍA



instrucciones

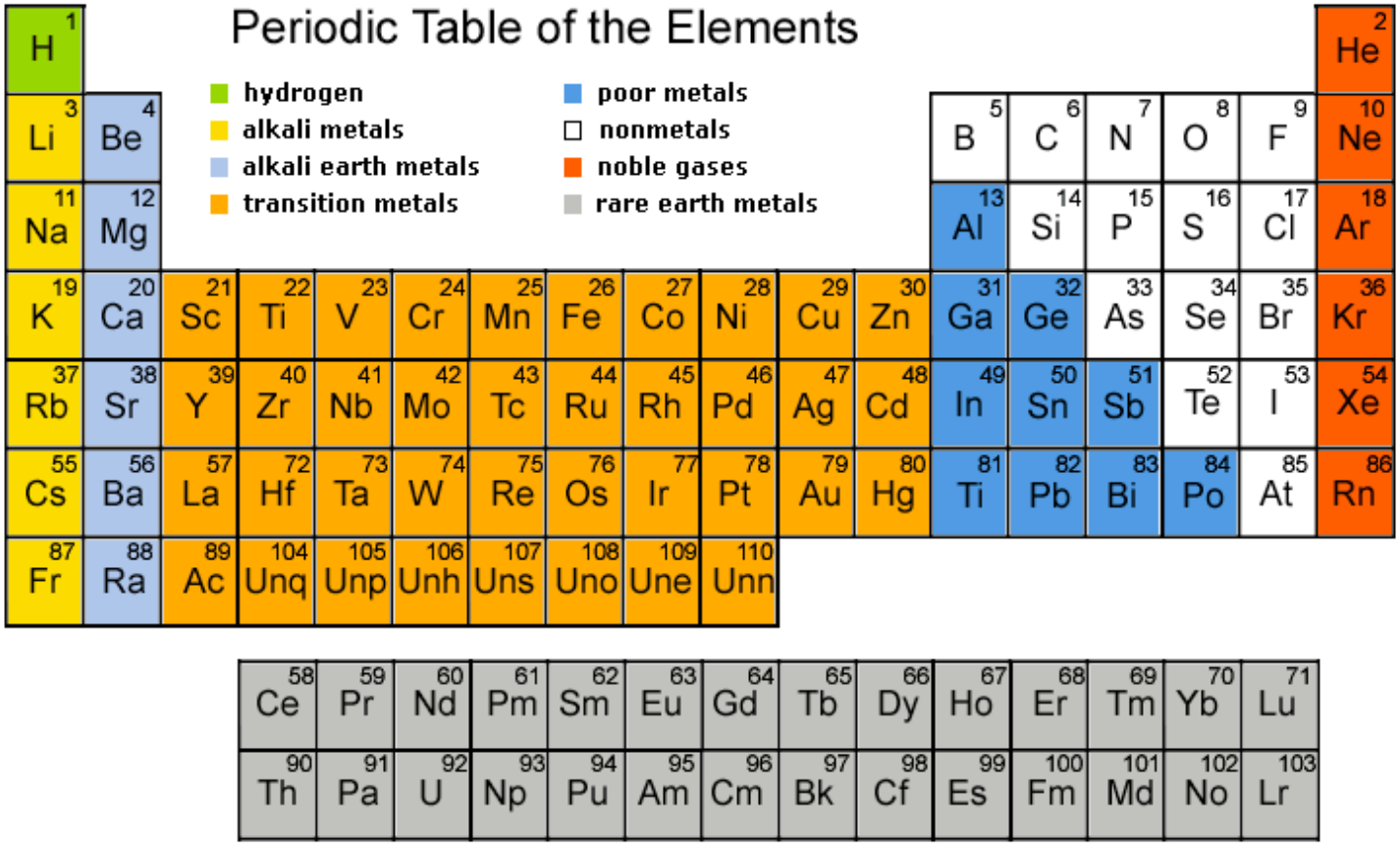
"como nos relacionamos"

=

ESTRUCTURA CRISTALINA
(MINERAL)

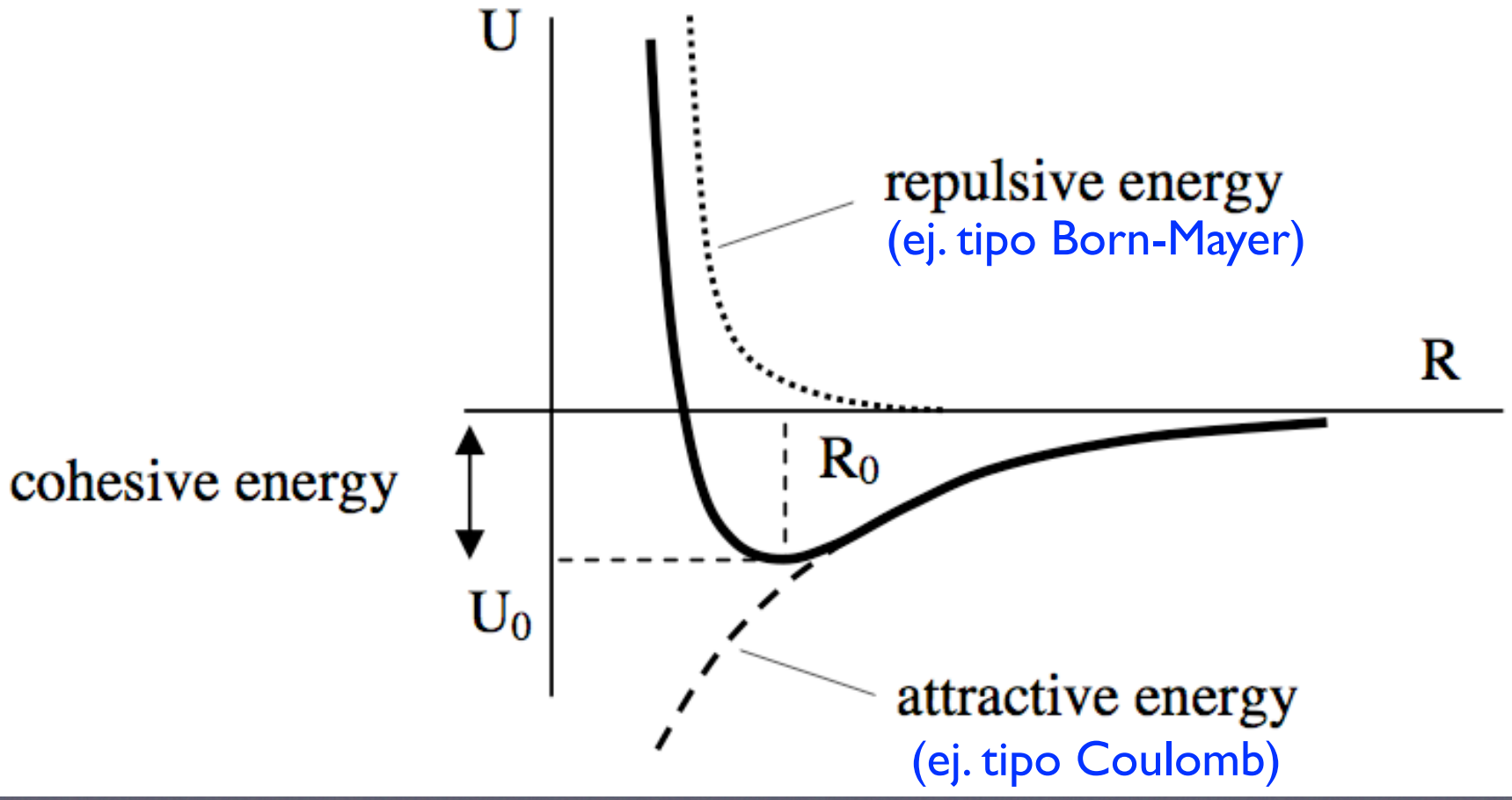
"sociedad"

1. Átomos


Periodic Table of the Elements
hydrogen
alkali metals
alkali earth metals
transition metals
poor metals
nonmetals
noble gases
rare earth metals
H 1
He 2
Li 3
Be 4
B 5
C 6
N 7
O 8
F 9
Ne 10
Na 11
Mg 12
Al 13
Si 14
P 15
S 16
Cl 17
Ar 18
K 19
Ca 20
Sc 21
Ti 22
V 23
Cr 24
Mn 25
Fe 26
Co 27
Ni 28
Cu 29
Zn 30
Ga 31
Ge 32
As 33
Se 34
Br 35
Kr 36
Rb 37
Sr 38
Y 39
Zr 40
Nb 41
Mo 42
Tc 43
Ru 44
Rh 45
Pd 46
Ag 47
Cd 48
In 49
Sn 50
Sb 51
Te 52
I 53
Xe 54
Cs 55
Ba 56
La 57
Hf 72
Ta 73
W 74
Re 75
Os 76
Ir 77
Pt 78
Au 79
Hg 80
Ti 81
Pb 82
Bi 83
Po 84
At 85
Rn 86
Fr 87
Ra 88
Ac 89
Unq 104
Unp 105
Unh 106
Uns 107
Uno 108
Une 109
Unn 110
Ce 58
Pr 59
Nd 60
Pm 61
Sm 62
Eu 63
Gd 64
Tb 65
Dy 66
Ho 67
Er 68
Tm 69
Yb 70
Lu 71
Th 90
Pa 91
U 92
Np 93
Pu 94
Am 95
Cm 96
Bk 97
Cf 98
Es 99
Fm 100
Md 101
No 102
Lr 103

Binding potential

$$V_{ij}(r_{ij}) = V_{repulsive}(r_{ij}) + b_{ijk} V_{attractive}(r_{ij})$$



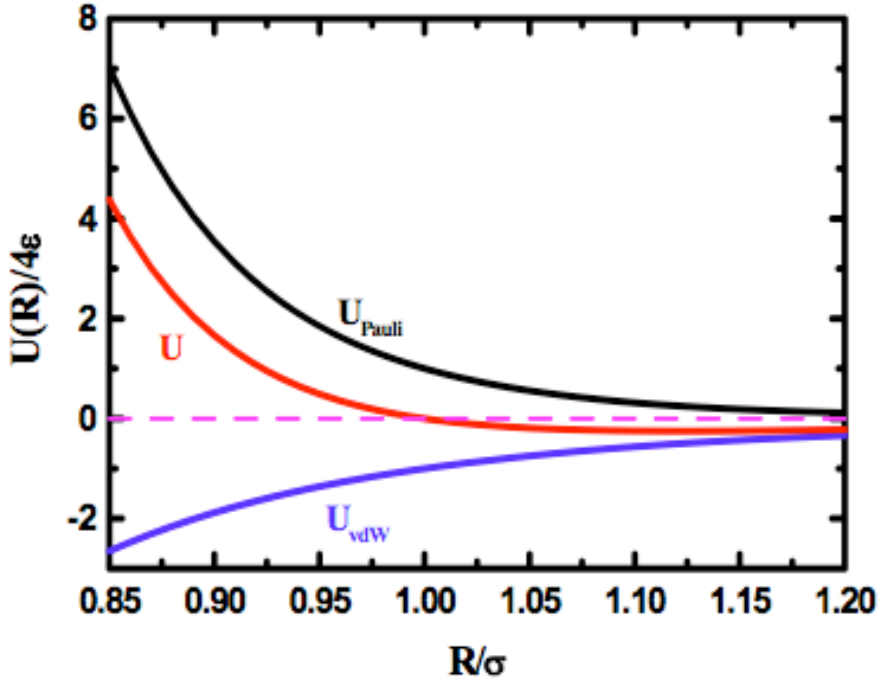
Potencial de Lennard-Jones

Empirical formula for such repulsive potential: $\Delta U = \frac{B}{R^{12}} > 0$

The total potential for inert gas system

$$U(R) = U_{Pauli}(R) + U_{vdW}(R)$$
$$= \frac{B}{R^{12}} - \frac{A}{R^{6}}$$
$$= 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

the Lennard-Jones potential



where empirical parameters $A=4\varepsilon\sigma^6$ and $B=4\varepsilon\sigma^{12}$ are determined from independent measurements made in the gas phase.

Values of ε[energy] and σ[length] are shown in Table 4 in Kittel.

En minerales...

Potenciales de enlace en el circón (ZrSiO4)

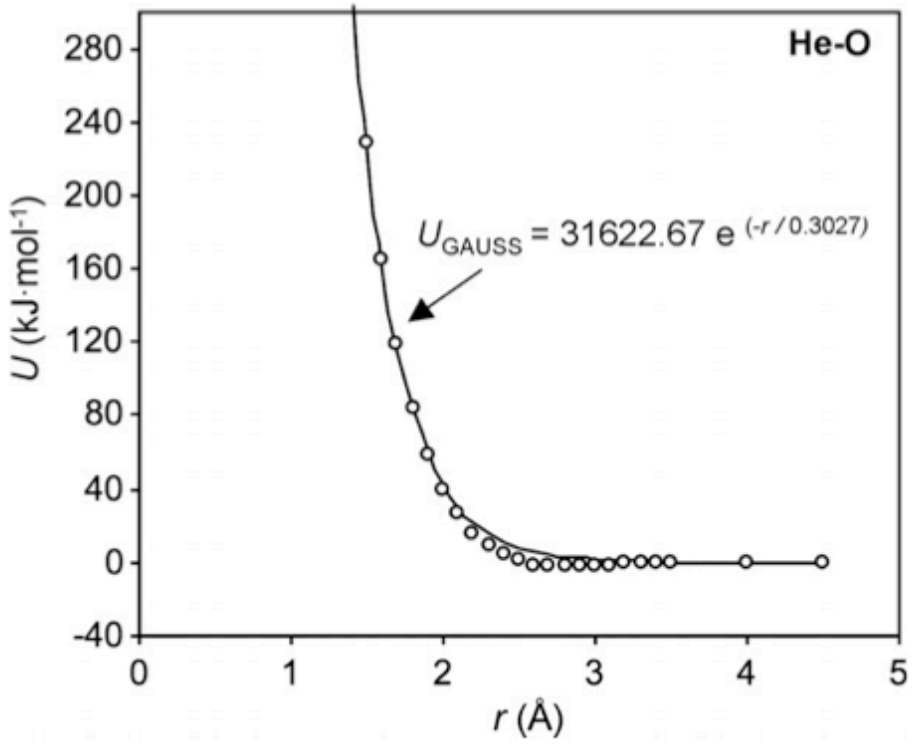


Fig. 2. He–O pair interaction calculated from quantum-mechanics using GAUSSIAN (open circles). Data was fitted to a Born-Mayer potential (solid line).

$$U_{GULP} = \sum_{i,j} \left(-\frac{|q_i q_j|}{4\pi\varepsilon_0 r_{ij}} + A_{ij} \exp\left[\frac{-r_{ij}}{\rho_0}\right] \right)$$

Coulomb Born-Mayer

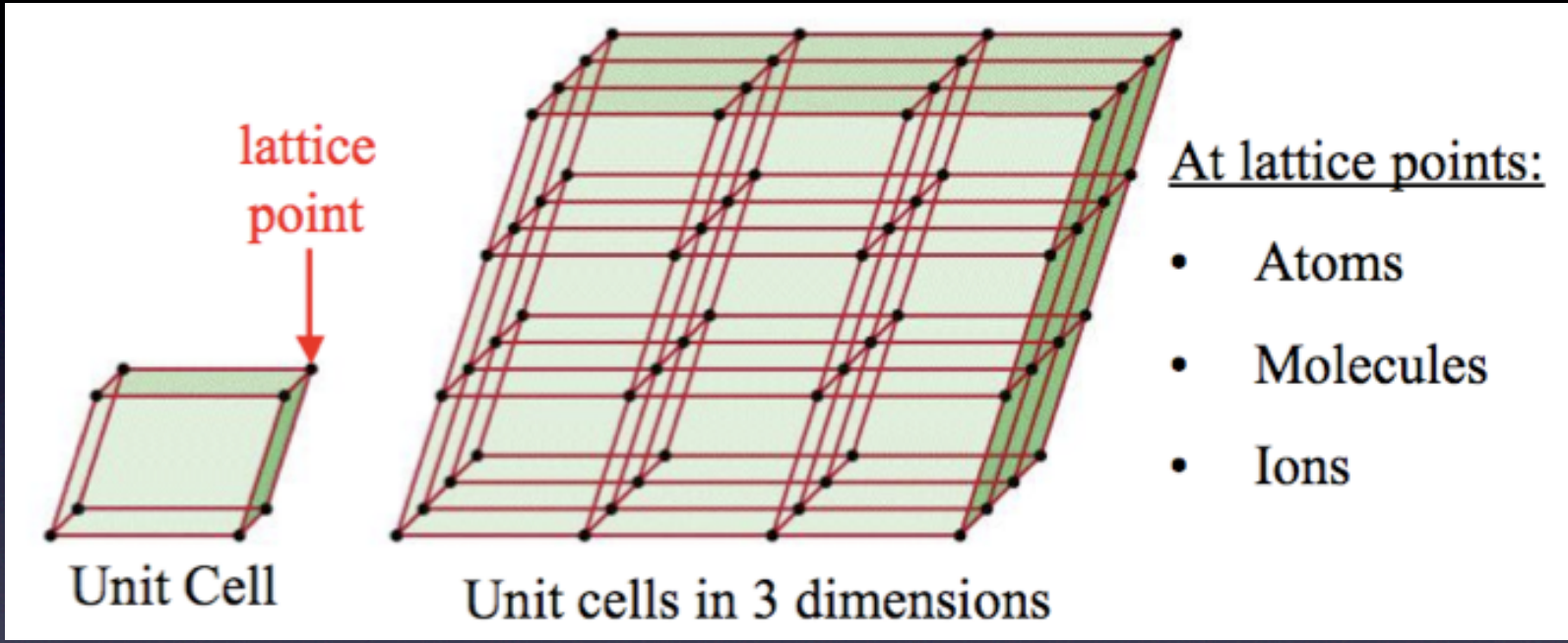
Table 1
Born-Mayer pair-potential parameters used for geometry optimization of zircon (taken from Devanathan et al., 2004)

Pair interaction	A_{ij} (kJ mol^{-1})	ρ_0 (Å)	Charges
Zr–O	5225.31	0.305004	Zr: + 3.8
Si–O	3389.91	0.227225	Si: + 2.0
O–O	4662.15	0.306820	O: −1.45
He–Zr	154515.12	0.240800	Zr: + 4.0
He–Si	164975.12	0.189100	Si: + 4.0
He–O	31622.67	0.302700	O: −2.0

Helium interactions calculated from first-principles using GAUSSIAN.

Reich et al., 2007 Geochimica Cosmochimica Acta

2. Retículo (lattice)



es una construcción VIRTUAL, un marco de referencia o "sistema de coordenadas" definido por el observador

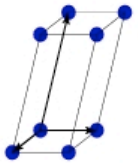
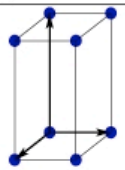
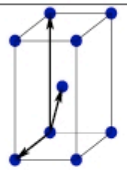
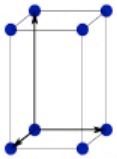
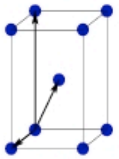
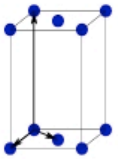
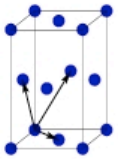
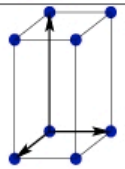
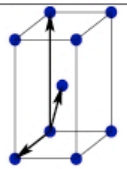
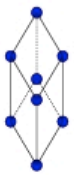
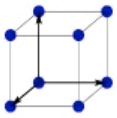
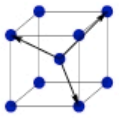
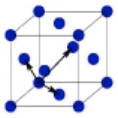
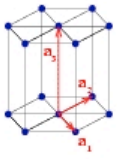
Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

Table 1.1: Bravais lattices in three-dimensions.

14
Retículos de Bravais
(tridimensionales)

definen la geometría
del marco de referencia

Coordenadas cristalográficas (de los átomos en el retículo)

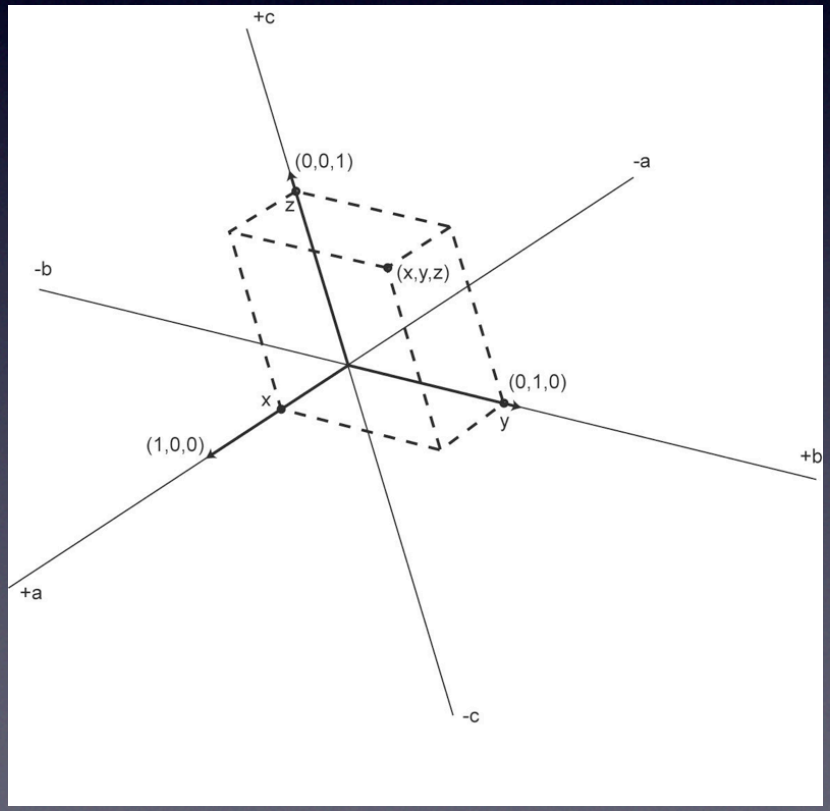
coordenadas atómicas (cartesianas)

coord. "reales", determinadas mediante difracción de rayos X

coordenadas fraccionales

coordenadas "unitarias" reducidas a la unidad en cada eje

www.minsocam.org



xFe = 2.3 Å
yFe = 1.5 Å
zFe = 0.9 Å

celda cub = 5 Å

más usadas porqué?

x'Fe = 2.3/5 = 0.46
y'Fe = 1.5/5 = 0.3
z'Fe = 0.9/5 = 0.18

celda cub = 1

transformación de coordenadas cartesianas (Xc) a fraccionales (Xf) mediante la matriz de transformación N

$$\overline{X}_f = \overline{\overline{N}}\,\overline{X}_c$$

$$\overline{\overline{N}} = \begin{bmatrix} 1/a & \left(\frac{-\cos\gamma}{a\cdot\sin\gamma}\right) & \left(\frac{\cos\alpha\cdot\cos\gamma-\cos\beta}{a\cdot\sin\gamma\cdot f}\right) \\ 0 & \left(\frac{1}{b\cdot\sin\gamma}\right) & \left(\frac{\cos\beta\cdot\cos\gamma-\cos\alpha}{b\cdot\sin\gamma\cdot f}\right) \\ 0 & 0 & \left(\frac{\sin\gamma}{c\cdot f}\right) \end{bmatrix}$$

$$f = \left(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cdot\cos\alpha\cdot\cos\beta\cdot\cos\gamma\right)^{1/2}$$

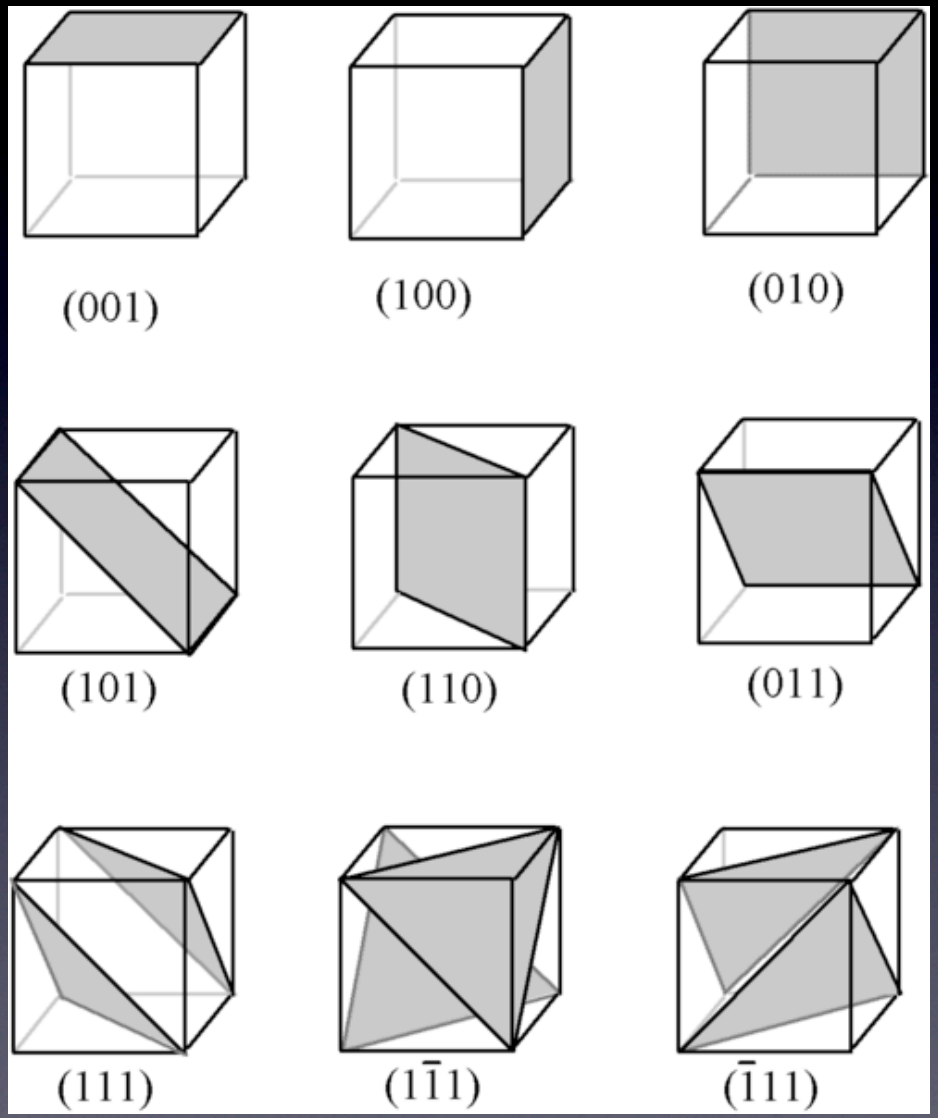
transformacion de coordenadas fraccionales (Xf) a cartesianas (Xc) mediante la matriz de transformación M

$$\overline{X_c} = \overline{\overline{M}}\,\overline{X_f}$$

$$\overline{\overline{M}} = \begin{bmatrix} a & b\cdot\cos\gamma & c\cdot\cos\beta \\ 0 & b\cdot\sin\gamma & \left(\dfrac{c(\cos\alpha-\cos\beta)}{\sin\gamma}\right) \\ 0 & 0 & \left(\dfrac{c\cdot f}{\sin\gamma}\right) \end{bmatrix}$$

$$f = \left(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cdot\cos\alpha\cdot\cos\beta\cdot\cos\gamma\right)^{1/2}$$

Indices de Miller y espacio recíproco



notación hkl

h = 1/a
k = 1/b
l = 1/c

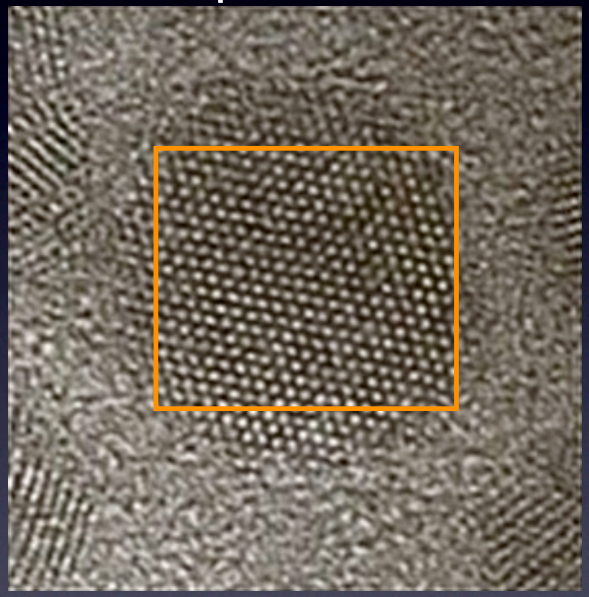
"recíprocos"

( ) ?
[ ] ?
{ } ?

De dónde vienen los índices de Miller?

El espacio real (estructura, a,b,c) se relaciona con el espacio recíproco (hkl) mediante la transformada de Fourier

espacio real

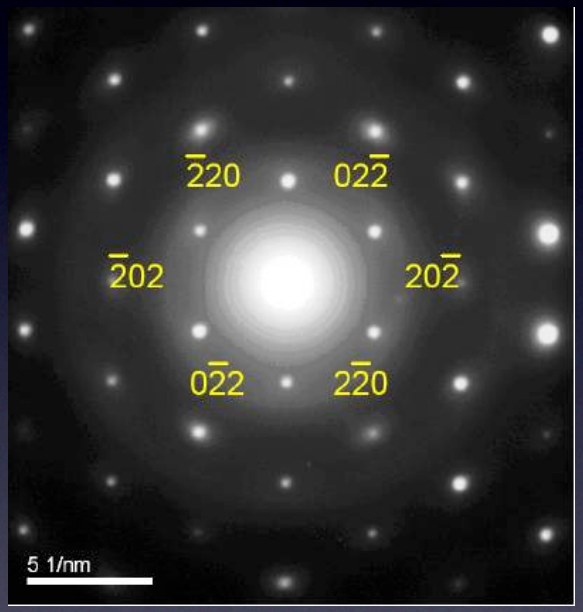


a(Å)

b(Å)

transformada de Fourier

espacio recíproco



$$\rho(xyz) = \frac{1}{V}\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}F(hkl)e^{(-2\pi i(hx+ky+lz)}$$

densidad electrónica

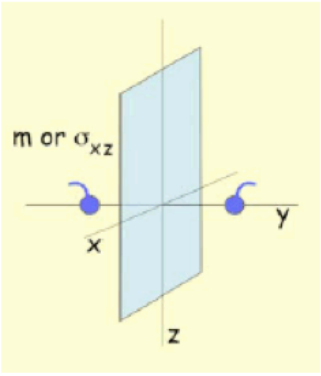
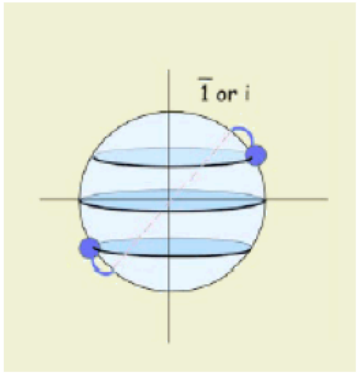
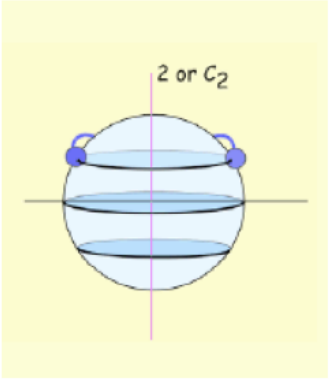
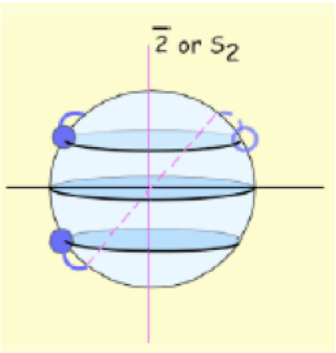
cada punto (intensidad) representa un set de planos cristalográficos

$n\lambda=2d\sin\theta$

3. Simetría

Rotacional (Sin traslación)

operación

Reflección	Inversión	Rotación	Rotoinversión
			
Plano especular	Centro de simetría	Eje de rotación	Eje de roto-inversión

elemento

14 retículos de Bravais

+

4 operaciones de simetría rotacional

=

32 grupos puntuales ("point groups")

Table 3. Crystallographic Point Groups

System	Essential Symmetry	Point Groups
Triclinic	none	1, $\bar{1}$
Monoclinic	2 or m	2, m, **2/*m***
Orthorhombic	222 or $mm2$[1]	222, $mm2$, ***mmm***
Tetragonal	4 or $\bar{4}$	4, 422, $\bar{4}$, **4/*m***, 4mm, $\bar{4}2m$, **4/*mmm***
Trigonal	3 or $\bar{3}$	3, $\bar{3}$, 32^2, $3m^2$, $\bar{3}m^2$
Hexagonal	6 or $\bar{6}$	6, 622, $\bar{6}$, **6/*m***, 6mm, $\bar{6}2m$, **6/*mmm***
Cubic	23	23, **2/*m*$\bar{3}$**, 432, $\bar{4}3m$, **4/*m*$\bar{3}$2/*m* = *m*$\bar{3}$*m***

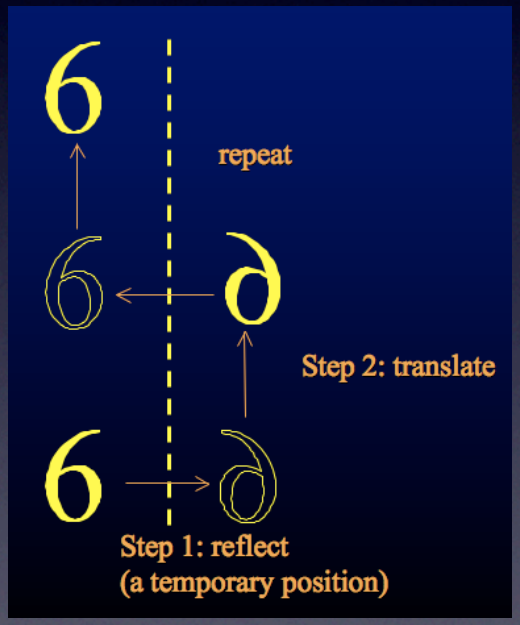
[1] The symbol $mm2$ also represents the point groups $2mm$ and $m2m$.

[2] These point groups represent sets of groups, e.g., 32 represents 321 and 312

Simetría traslacional

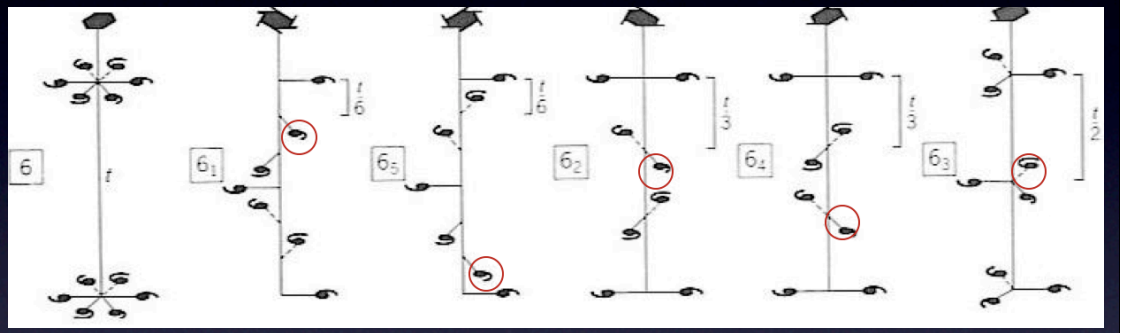
glide (reflección + traslación)

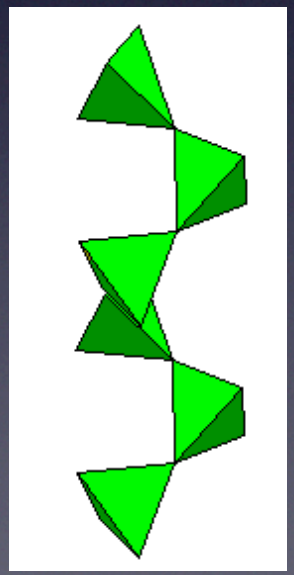
operación: reflección con traslación

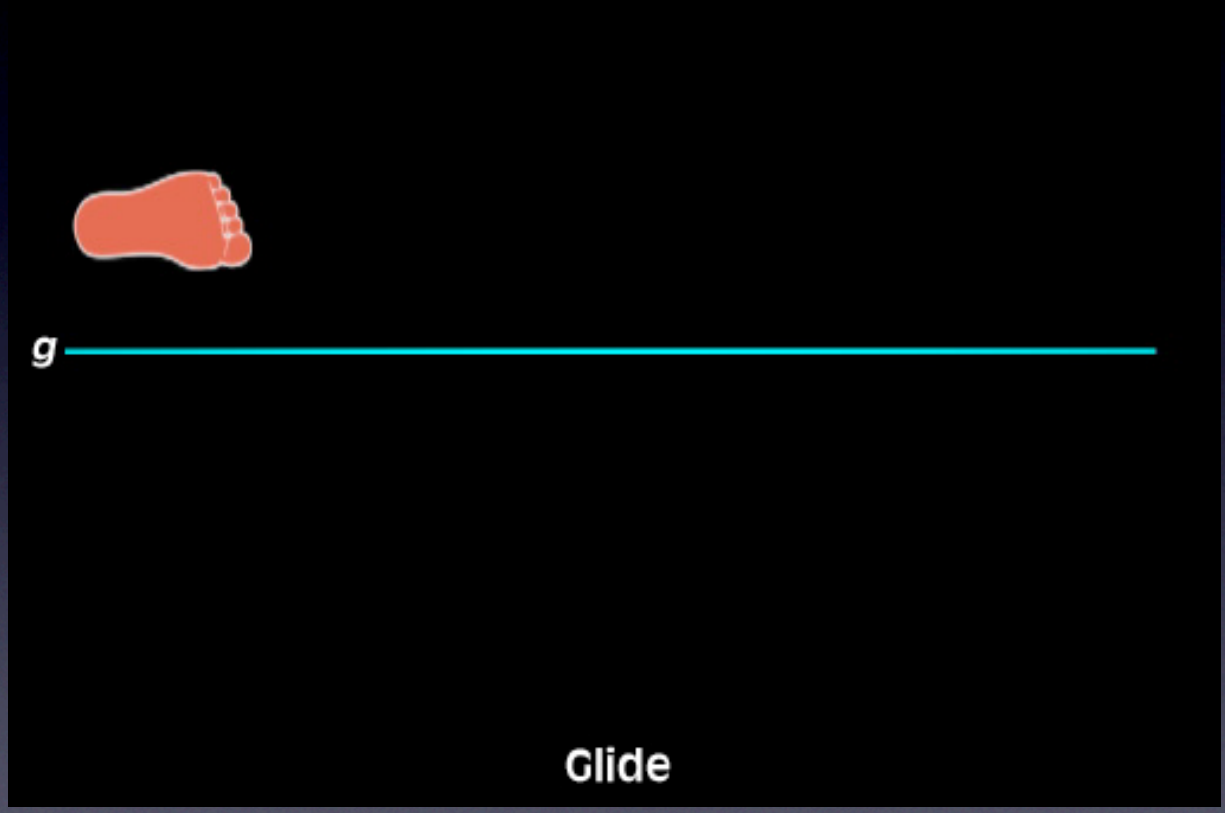


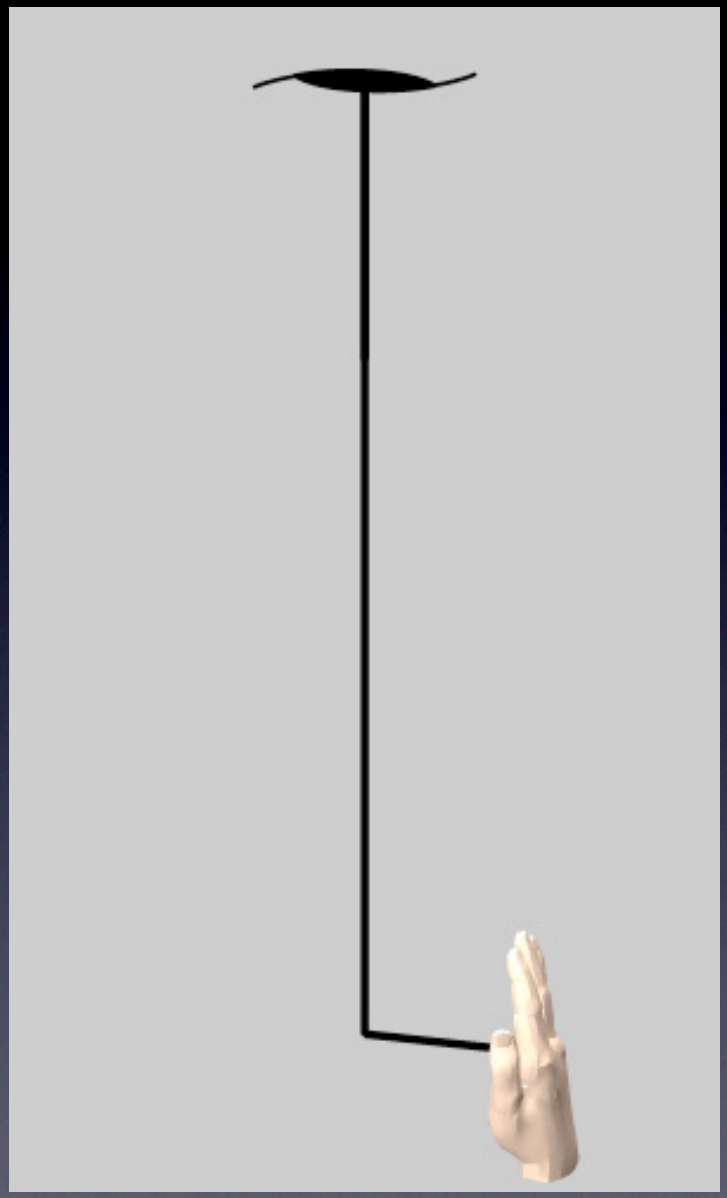
elemento: plano de deslizamiento ("glide plane")

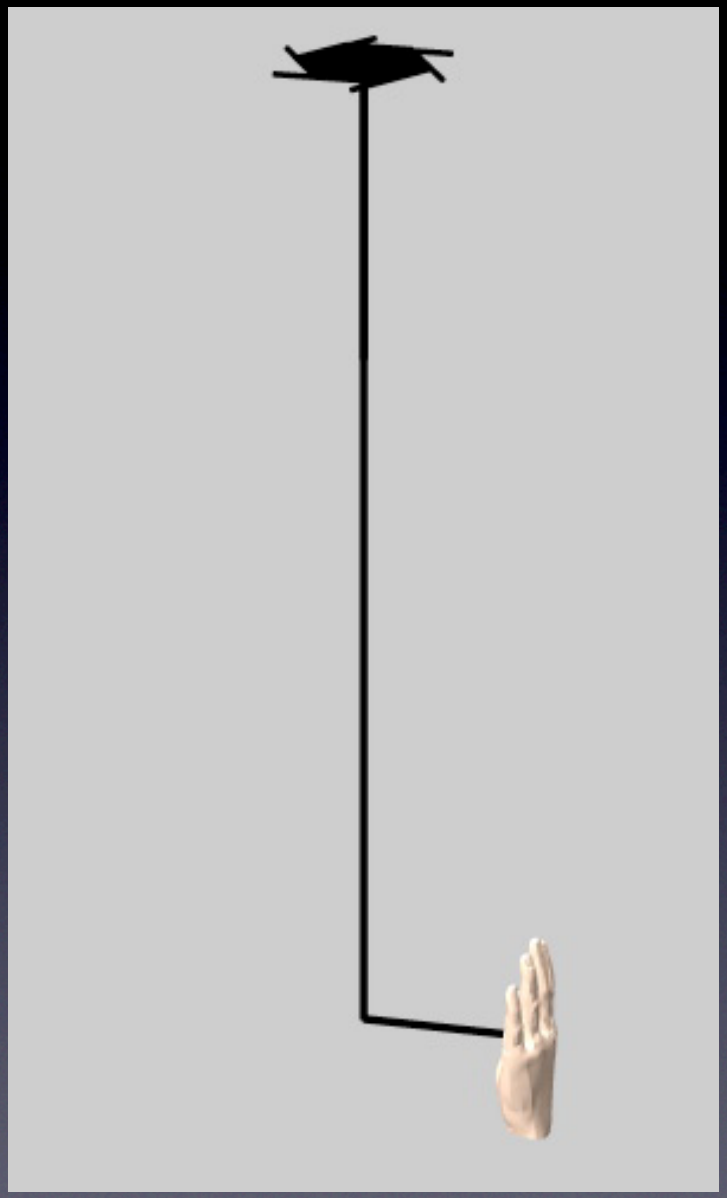
eje de tuerca (rotación + traslación)






g
Glide





14 retículos de Bravais

+

operaciones de simetría rotacional

+

operaciones de simetría traslacional

=

230 grupos espaciales (”space groups”)

230 grupos espaciales

monoclinic	2/*m*	*P*2, *P*2$_1$, *C*2, *Pm*, *Pc*, *Cm*, *Cc*, ***P*2/*m***, ***P*2$_1$/*m***, ***C*2/*m***, ***P*2/*c***, ***P*2$_1$/*c***, ***C*2/*c***
orthorhombic	*mmm*	*P*222, *P*222$_1$, *P*2$_1$2$_1$2, *P*2$_1$2$_1$2$_1$, *C*222$_1$, *C*222, *F*222, *I*222, *I*2$_1$2$_1$2$_1$, *Pmm*2, *Pmc*2$_1$, *Pcc*2, *Pma*2, *Pca*2$_1$, *Pnc*2, *Pmn*2$_1$, *Pba*2, *Pna*2$_1$, *Pnn*2, *Cmm*2, *Cmc*2$_1$, *Ccc*2, *Amm*2, *Aem*2, *Ama*2, *Aea*2, *Fmm*2, *Fdd*2, *Imm*2, *Iba*2, *Ima*2, ***Pmmm***, ***Pnnn***, ***Pccm***, ***Pban***, ***Pmma***, ***Pnna***, ***Pmna***, ***Pcca***, ***Pbam***, ***Pccn***, ***Pbcm***, ***Pnnm***, ***Pmmn***, ***Pbcn***, ***Pbca***, ***Pnma***, ***Cmcm***, ***Cmce***, ***Cmmm***, ***Cccm***, ***Cmme***, ***Ccce***, ***Fmmm***, ***Fddd***, ***Immm***, ***Ibam***, ***Ibca***, ***Imma***
tetragonal	4/*m*	*P*4, *P*4$_1$, *P*4$_2$, *P*4$_3$, *I*4, *I*4$_1$, *P*$\bar{4}$, *I*$\bar{4}$, ***P*4/*m***, ***P*4$_2$/*m***, ***P*4/*n***, ***P*4$_2$/*n***, ***I*4/*m***, ***I*4$_1$/*a***
tetragonal	4/*mmm*	*P*422, *P*42$_1$2, *P*4$_1$22, *P*4$_1$2$_1$2, *P*4$_2$22, *P*4$_2$2$_1$2, *P*4$_3$22, *P*4$_3$2$_1$2, *I*422, *I*4$_1$22, *P*4*mm*, *P*4*bm*, *P*4$_2$*cm*, *P*4$_2$*nm*, *P*4*cc*, *P*4*nc*, *P*4$_2$*mc*, *P*4$_2$*bc*, *I*4*mm*, *I*4*cm*, *I*4$_1$*md*, *I*4$_1$*cd*, *P*$\bar{4}$2*m*, *P*$\bar{4}$2*c*, *P*$\bar{4}$2$_1$*m*, *P*$\bar{4}$2$_1$*c*, *P*$\bar{4}$*m*2, *P*$\bar{4}$*c*2, *P*$\bar{4}$*b*2, *P*$\bar{4}$*n*2, *I*$\bar{4}$*m*2, *I*$\bar{4}$*c*2, *I*$\bar{4}$2*m*, *I*$\bar{4}$2*d*, ***P*4/*mmm***, ***P*4/*mcc***, ***P*4/*nbm***, ***P*4/*nnc***, ***P*4/*mbm***, ***P*4/*mnc***, ***P*4/*nmm***, ***P*4/*mcc***, ***P*4$_2$/*mmc***, ***P*4$_2$/*mcm***, ***P*4$_2$/*nbc***, ***P*4$_2$/*nnm***, ***P*4$_2$/*mbc***, ***P*4$_2$/*mnm***, ***P*4$_2$/*nmc***, ***P*4$_2$/*ncm***, ***I*4/*mmm***, ***I*4/*mcm***, ***I*4/*amd***, ***I*4/$_1$*acd***
trigonal	$\bar{3}$	*P*3, *P*3$_1$, *P*3$_2$, *R*3, ***P*$\bar{3}$**, ***R*$\bar{3}$**,
trigonal	$\bar{3}m$	*P*312, *P*321, *P*3$_1$12, *P*3$_1$21, *P*3$_2$12, *P*3$_2$21, *R*32, *P*3*m*1, *P*31*m*, *P*3*c*1, *P*31*c*, *R*3*m*, *R*3*c*, ***P*$\bar{3}$1*m***, ***P*$\bar{3}$1*c***, ***P*$\bar{3}$*m*1**, ***P*$\bar{3}$*c*1**, ***R*$\bar{3}$*m***, ***R*$\bar{3}$*c***
hexgonal	6/*m*	*P*6, *P*6$_1$, *P*6$_5$, *P*6$_2$, *P*6$_4$, *P*6$_3$, *P*$\bar{6}$, ***P*6/*m***, ***P*6$_3$/*m***
hexagonal	6/*mmm*	*P*622, *P*6$_1$22, *P*6$_5$22, *P*6$_2$22, *P*6$_4$22, *P*6$_3$22, *P*6*mm*, *P*6*cc*, *P*6$_3$*cm*, *P*6$_3$*mc*, *P*$\bar{6}$*m*2, *P*$\bar{6}$*c*2, *P*$\bar{6}$2*m*, *P*$\bar{6}$2*c*, ***P*6/*mmm***, ***P*6/*mcc***, ***P*6$_3$/*mcm***, ***P*6$_3$/*mmc***
cubic	*m*3	*P*23, *F*23, *I*23, *P*2$_1$3, *I*2$_1$3, ***Pm*$\bar{3}$**, ***Pn*$\bar{3}$**, ***Fm*$\bar{3}$**, ***Fd*$\bar{3}$**, ***Im*$\bar{3}$**, ***Pa*$\bar{3}$**, ***Ia*$\bar{3}$**
cubic	*m*3*m*	*P*432, *P*4$_2$32, *F*432, *F*4$_1$32, *I*432, *P*4$_3$32, *P*4$_1$32, *I*4$_1$32, *P*$\bar{4}$3*m*, *F*$\bar{4}$3*m*, *I*$\bar{4}$3*m*, *P*$\bar{4}$3*n*, *F*$\bar{4}$3*c*, *I*$\bar{4}$3*d*, ***P*m$\bar{3}$*m***, ***P*n$\bar{3}$*n***, ***P*m$\bar{3}$*n***, ***P*n$\bar{3}$*m***, ***F*m$\bar{3}$*m***, ***F*m$\bar{3}$*c***, ***F*d$\bar{3}$*m***, ***F*d$\bar{3}$*c***, ***I*m$\bar{3}$*m***, ***I*a$\bar{3}$*d***

Grupos espaciales

simetría estática
+ retículo

32 grupos
puntuales

simetría estática + dinámica
+ retículo

230 grupos
espaciales

algunas sociedades expresan muy bien sus caras,
con un evidente orden (forma) externo

... otras no expresan su orden interno al manifestarse

La forma externa (o desarrollo de caras cristalinas) depende de 2 factores:

- factor intrínseco: resultado de la estructura cristalina

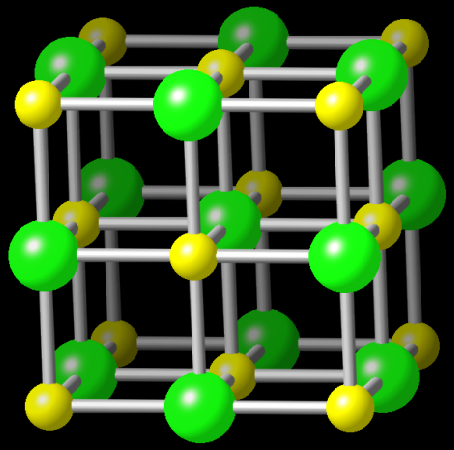
"cadenas de enlace periódicas" (periodic bond chains)

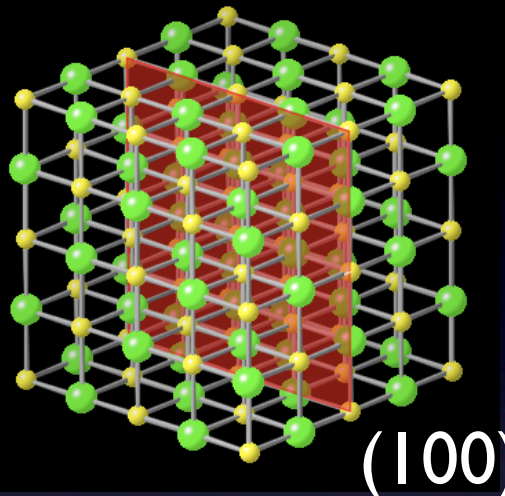
- factor extrínseco: resultado de las condiciones de formación

cristalización rápida/lenta, con espacio/sin espacio, etc

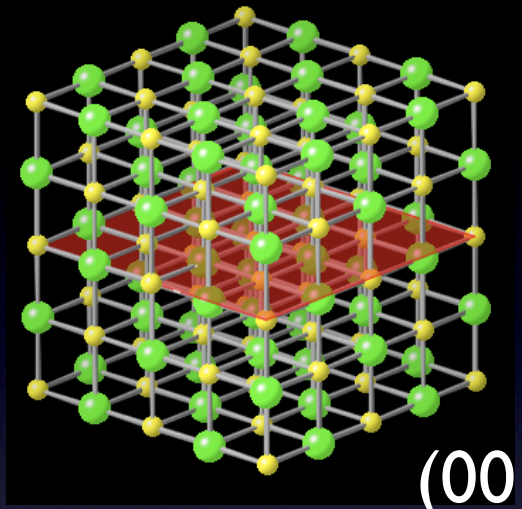
Cadenas de enlace periódicos (+-+-+-)

celda unitaria NaCl

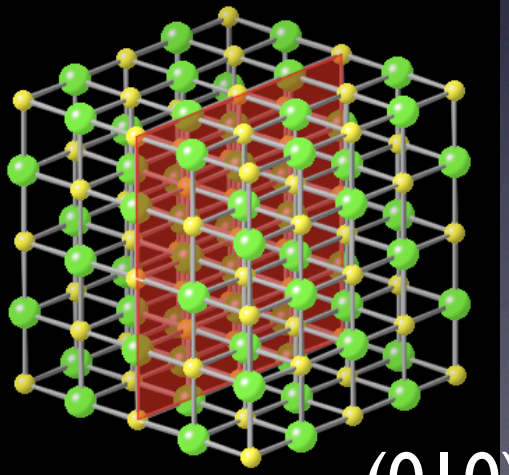




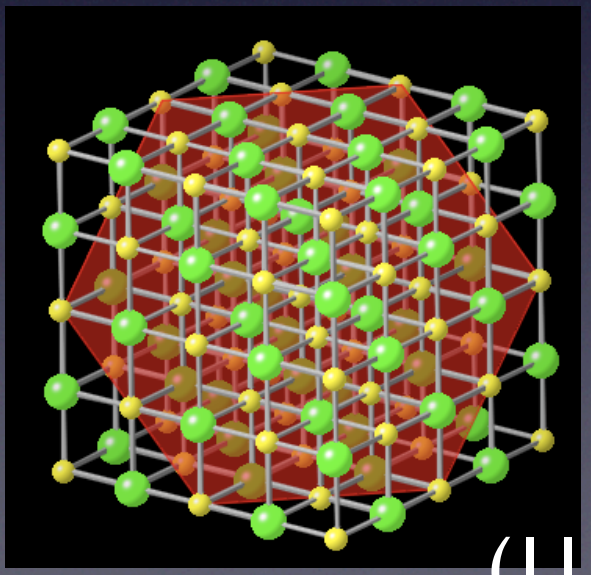
(100)



(001)



(010)

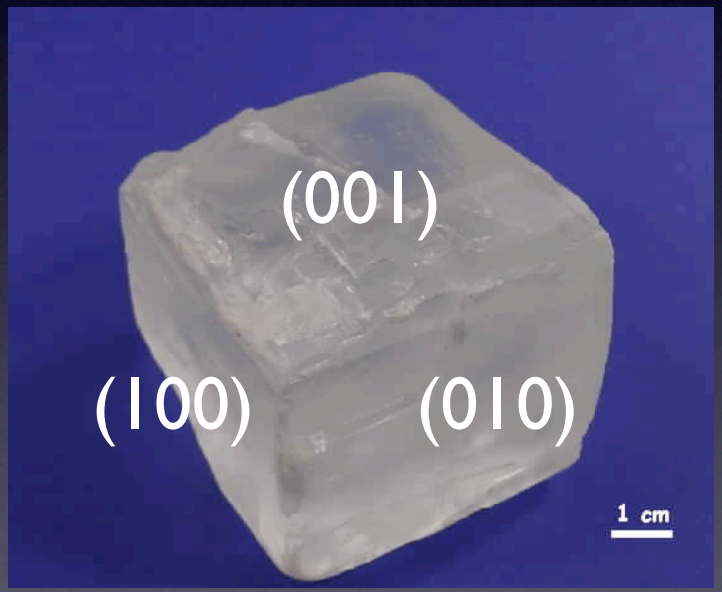


(111)

qué caras son más estables?

Cadenas de enlace periódicos

Las caras más estables (por ende que tienen la posibilidad de desarrollarse) son aquellas que NO poseen momento dieléctrico (es decir, eléctricamente neutras)



caras que poseen alternancia periodica de Na+ y Cl-

Próxima clase: Jueves 3 Noviembre

Radiación electromagnética, óptica, microscopía

Lectura 2 (enlaces), Lectura 2a (electromag.)