

# Aspectos Basicos de la Absorción de Rayos X

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**INTRODUCCIÓN**

**DISPOSITIVO EXPERIMENTAL**

**PREPARACIÓN DE MUESTRAS**

**ANÁLISIS DE RESULTADOS**

**INTRODUCCIÓN**

**DISPOSITIVO EXPERIMENTAL**

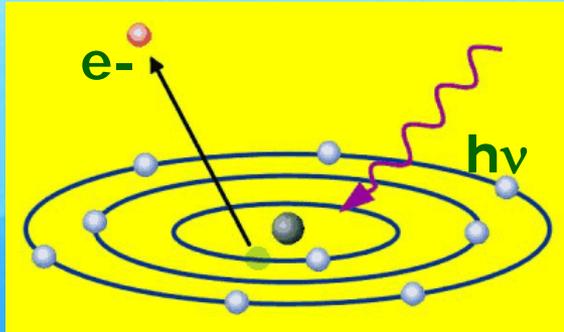
**PREPARACIÓN DE MUESTRAS**

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# INTRODUCCIÓN

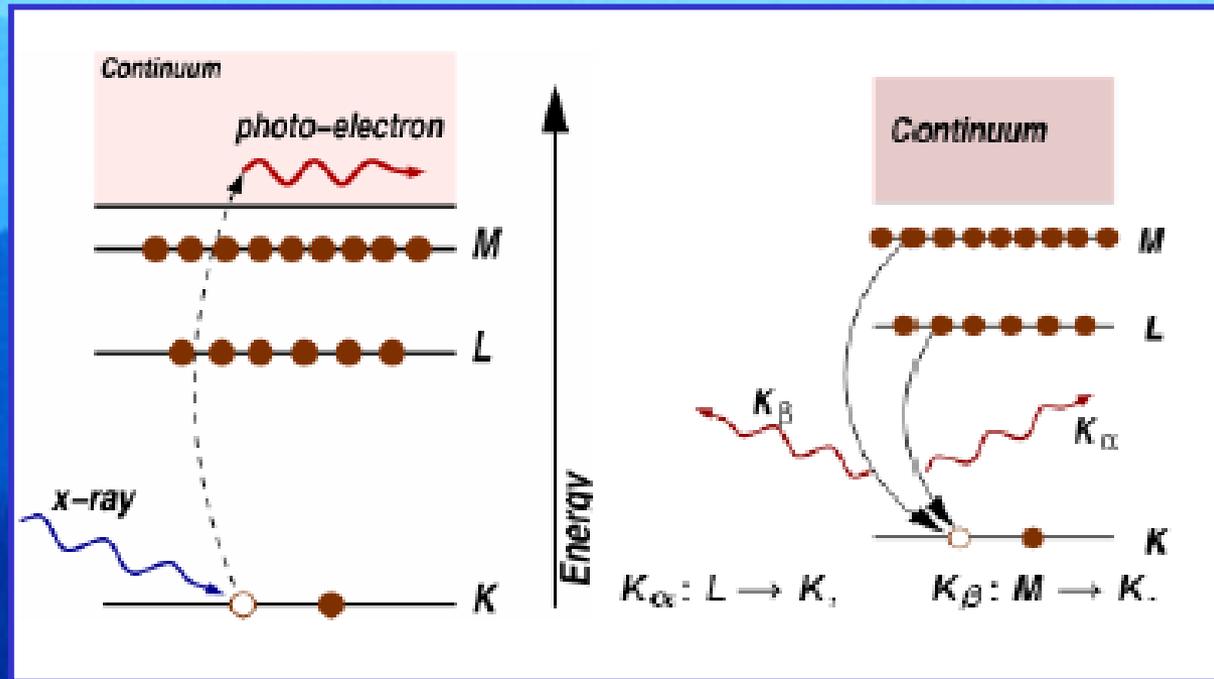
## INTERACCIÓN RAYOS X - MATERIAL

### Efecto Fotoeléctrico (Hertz)



### Excitación del átomo

### Relajación del átomo



Absorption edge	Core level
K	1s
L <sub>I</sub>	2s
L <sub>II</sub>	2p <sub>1/2</sub>
L <sub>III</sub>	2p <sub>3/2</sub>
M <sub>I</sub>	3s
M <sub>II</sub>	3p <sub>1/2</sub>
M <sub>III</sub>	3p <sub>3/2</sub>
M <sub>IV</sub>	3d <sub>3/2</sub>
M <sub>V</sub>	3d <sub>5/2</sub>

$$k^2 = \frac{2 m_e (E - E_0)}{\hbar^2} \sim 3.81 \Delta E$$

Mass of the electron

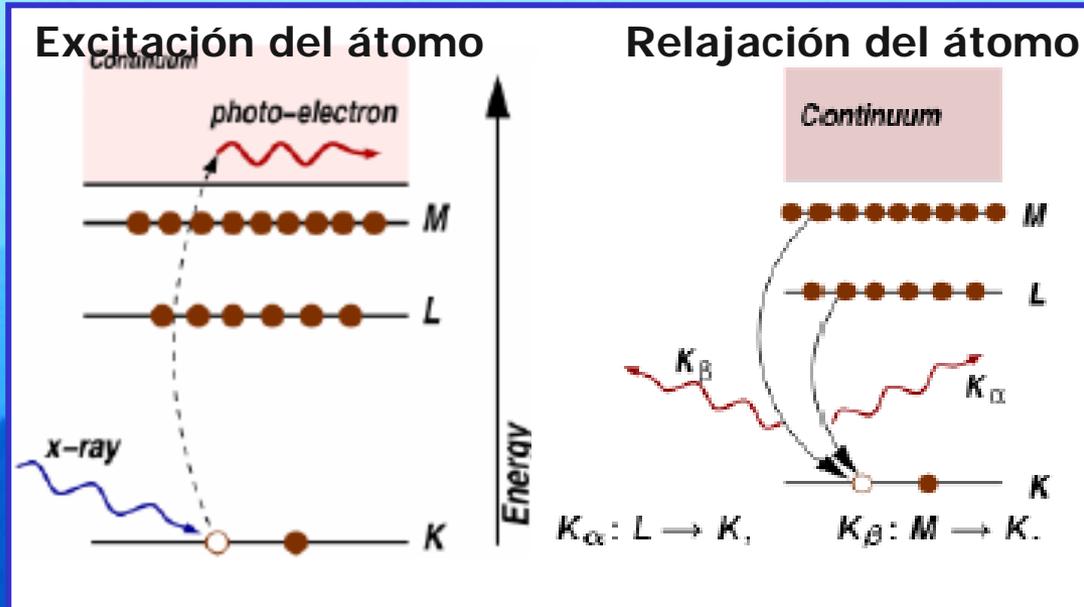
$\hbar$

Plank's constant

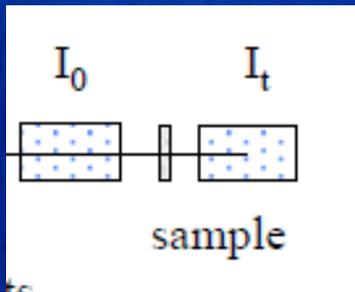
Fermi Energy

# INTRODUCCIÓN

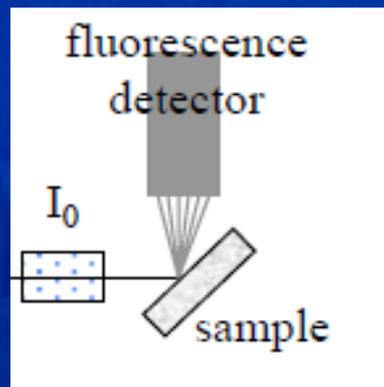
## Modos de medida de Absorción de rayos X:



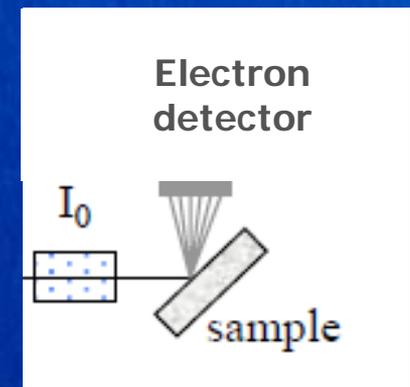
### TRANSMISIÓN



### FLUORESCENCIA



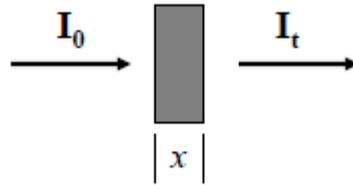
### "TOTAL ELECTRON YIELD"



# INTRODUCCIÓN

## Coeficiente de Absorción de rayos X:

La intensidad de los rayos X que pasan a través de un material de grosor  $x$  viene dada por:



## Ley de Beer:

$$I_t = I_0 e^{-\mu(E) \cdot x}$$

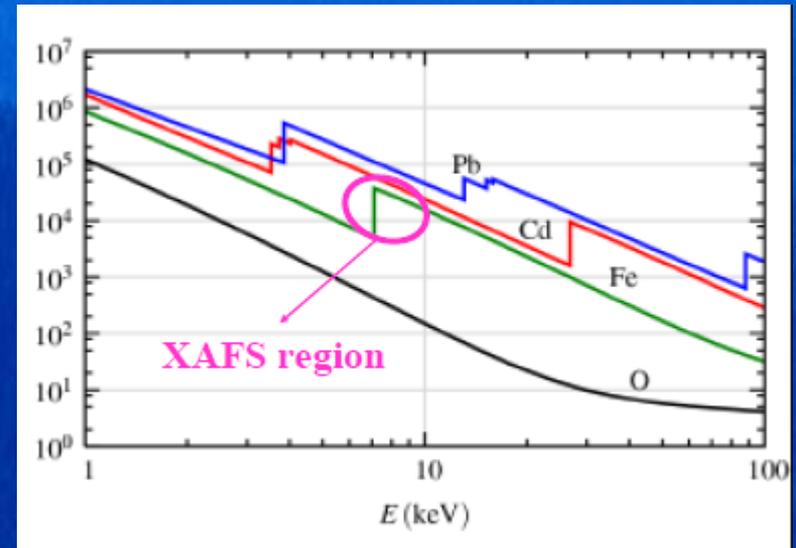
## Coeficiente de Absorción: $\mu(E)x$

Presenta saltos agudos característicos de los orbitales del átomo.

**Transmisión:**  $\mu(E)x = -\ln(I_t/I_0)$

**Fluorescencia:**  $\mu(E) \propto I_f/I_0$

**Total electron yield:**  $\mu(E) \propto I/I_0$



## ACRÓNIMOS

**EXAFS** – **E**xtended **X**-ray **A**bsorption **F**ine **S**tructure

**XAS** – **X**-ray **A**bsorption **S**pectroscopy

**XAFS** – **X**-ray **A**bsorption **F**ine **S**tructure

**XANES** - **X**-ray **A**bsorption **N**ear **E**dge **S**tructure

**NEXAFS**- **N**ear-**E**dge **X**-ray **A**bsorption **F**ine **S**tructure

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# EXAFS Measurement

- **Monochromatic x-rays:** need x-rays with small energy spread  $\Delta E \sim 1$  eV at 10 keV
- **Linear Detectors:** the XAFS signal is small ( $\chi(k) \sim 10^{-2}$  of total signal), so lots of photons needed and detectors that are linear in x-ray intensity
- **Well-aligned Beam:** the x-ray beam hitting the detectors should be the same as that hitting the sample
- **Homogeneous Sample:** uniform and of appropriate thickness, free of pinholes
- **Counting Statistics:** good  $\mu(E)$  data should have a noise level of  $\sim 10^{-3}$ , so need to collect at least  $\sim 10^6$  photons

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# DISPOSITIVO EXPERIMENTAL

## FUENTE DE RAYOS X: SINCROTRÓN



ESRF, Grenoble (Francia)



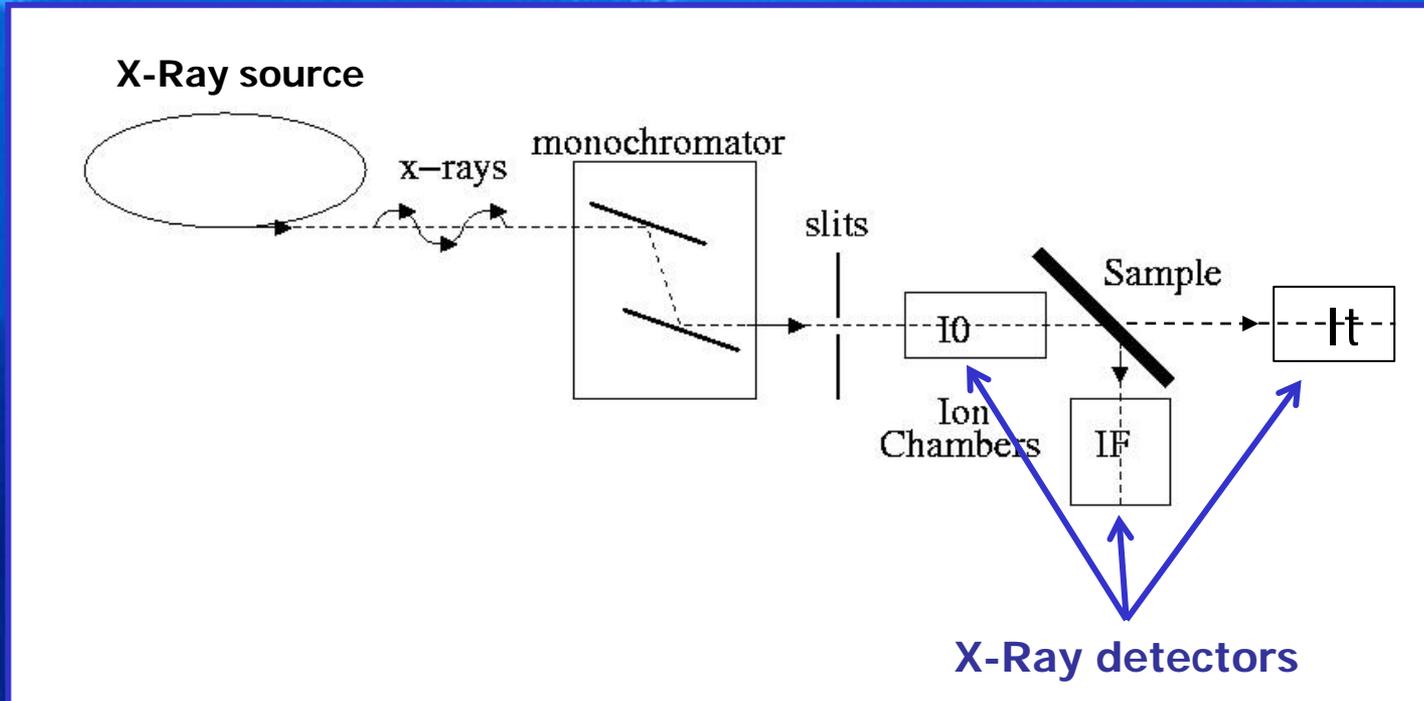
SLS, Villigen (Suiza)



ALS, Berkeley (USA)



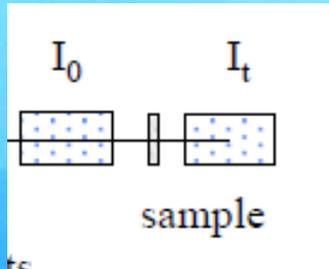
BESSY-II, Berlín (Alemania)



# DISPOSITIVO EXPERIMENTAL

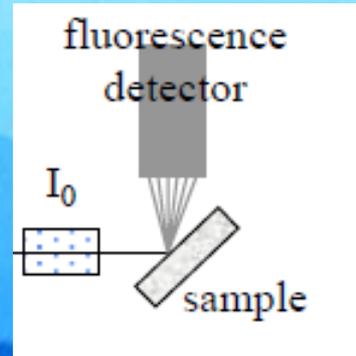
## DETECTORES DE RAYOS X

### TRANSMISIÓN



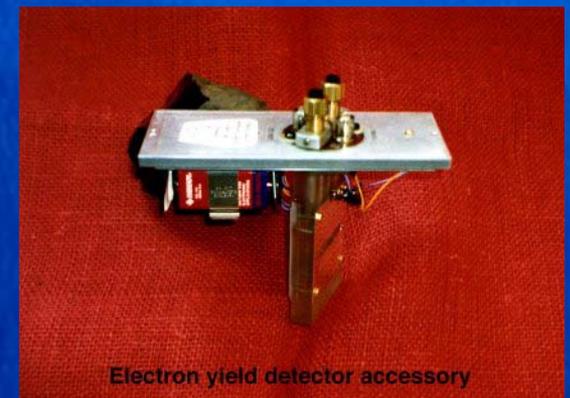
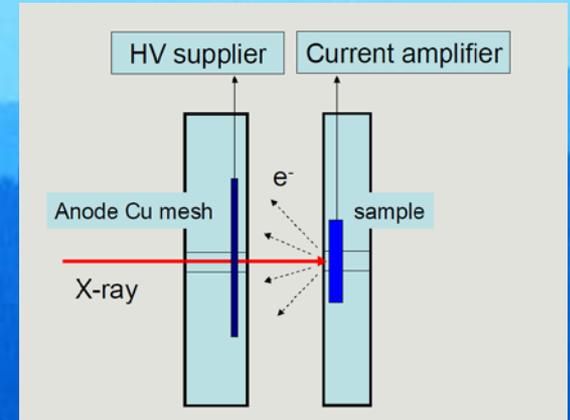
Cámaras de ionización

### FLUORESCENCIA



Detector de Fluorescencia

### "TOTAL ELECTRON YIELD"

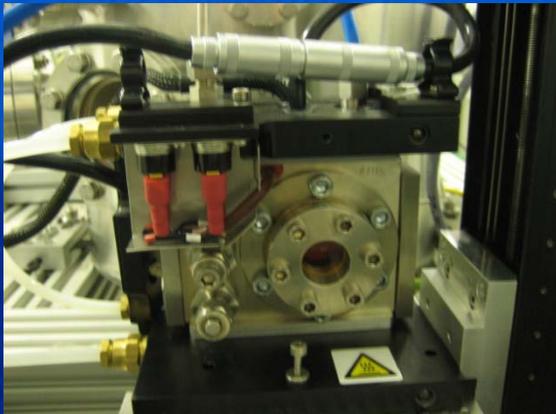
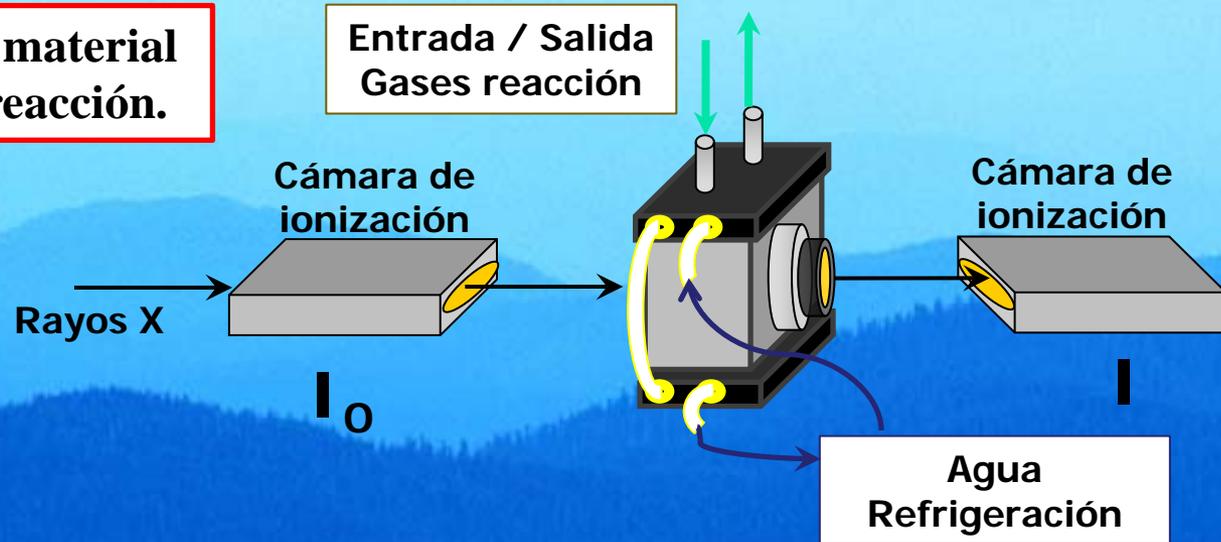


Electron yield detector accessory

# DISPOSITIVO EXPERIMENTAL

## XAS "in operando"

Permite estudiar el material en condiciones de reacción.



Celda Specac  
(T<sup>a</sup> hasta 800°C)



Portamuestras



Controladores de Flujo  
y sus electrónicas.  
Controladores de T<sup>a</sup>

**INTRODUCCIÓN**

**DISPOSITIVO EXPERIMENTAL**

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**La muestra debe presentar:**

## **Para Medidas en modo de Transmision:**

- Homogeneidad
- Grosor y cantidad adecuados ( $\mu \approx 2-3$ )
- Libre de agujeros
- Polvo sin aglomeraciones

## **Para Medidas en modo de Fluorescencia:**

- Muestras gruesas → diluidas
- Muestras delgadas → concentradas
- Homogeneidad no tan importante

# PREPARACIÓN DE MUESTRAS

## 1. Optimización de cantidad de muestra necesaria:

Software: Hephaestus (Ifeffit Package), Absorbix

**Moler bien** la muestra en polvo.

**Extender la muestra sobre cinta adhesiva:** capa lo más fina posible. La cinta adhesiva puede ser Kapton, Teflon, Mylar, or Scotch.

**Mezclar la cantidad deseada con un material de bajo Z.** Normalmente, se usa BN o carbón negro.

**Hacer pastilla.**

**Colocar muestra en soporte de medida.**

**INTRODUCCIÓN**

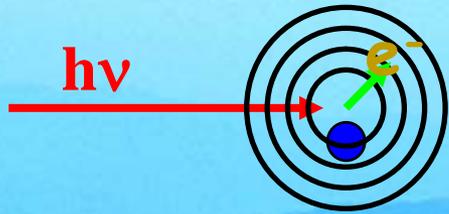
**DISPOSITIVO EXPERIMENTAL**

**PREPARACIÓN DE MUESTRAS**

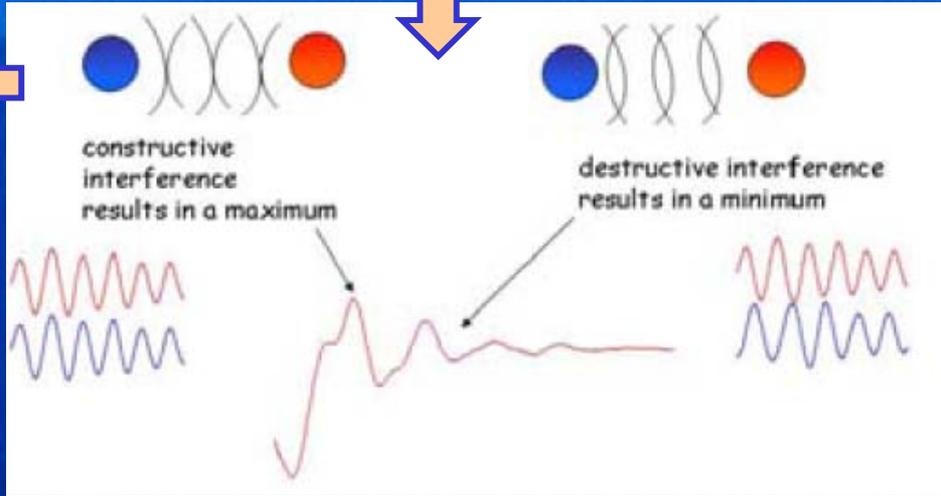
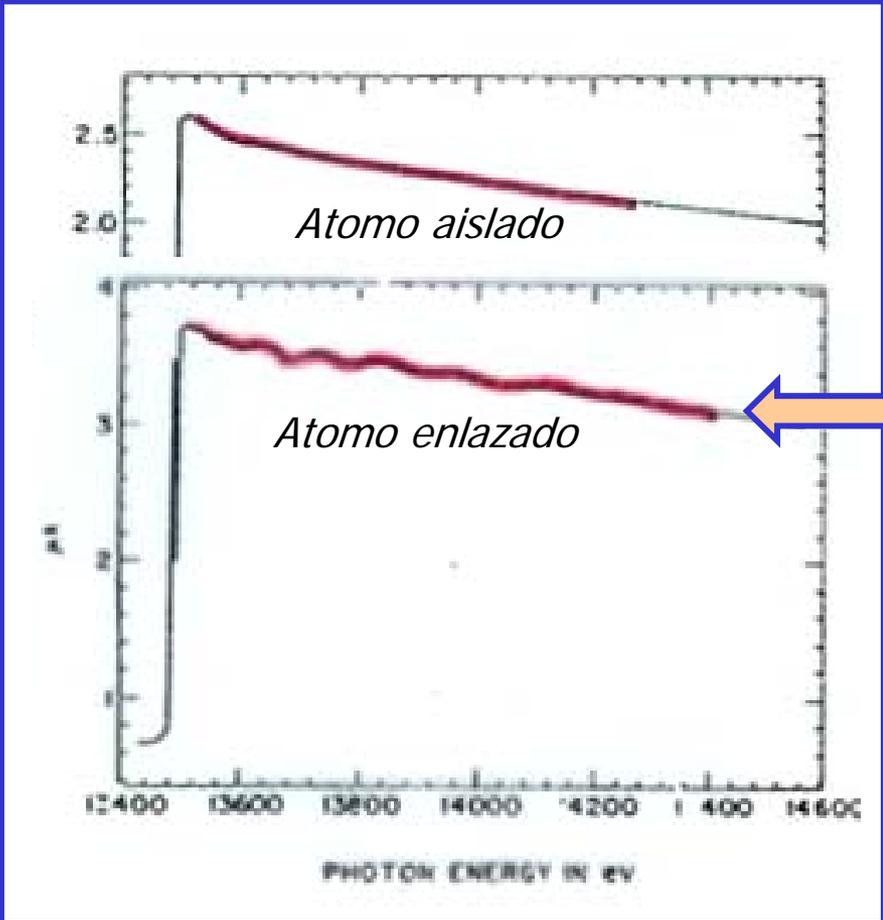
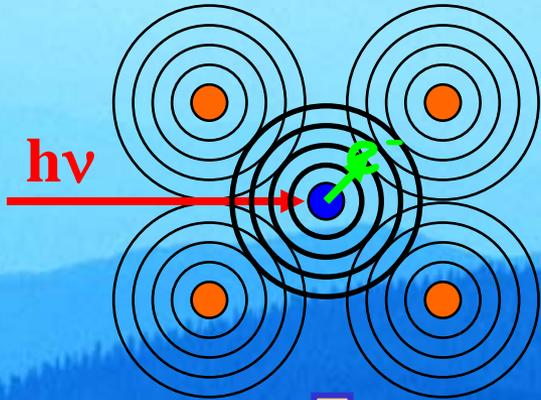
**ANÁLISIS DE RESULTADOS**

# ANÁLISIS DE RESULTADOS

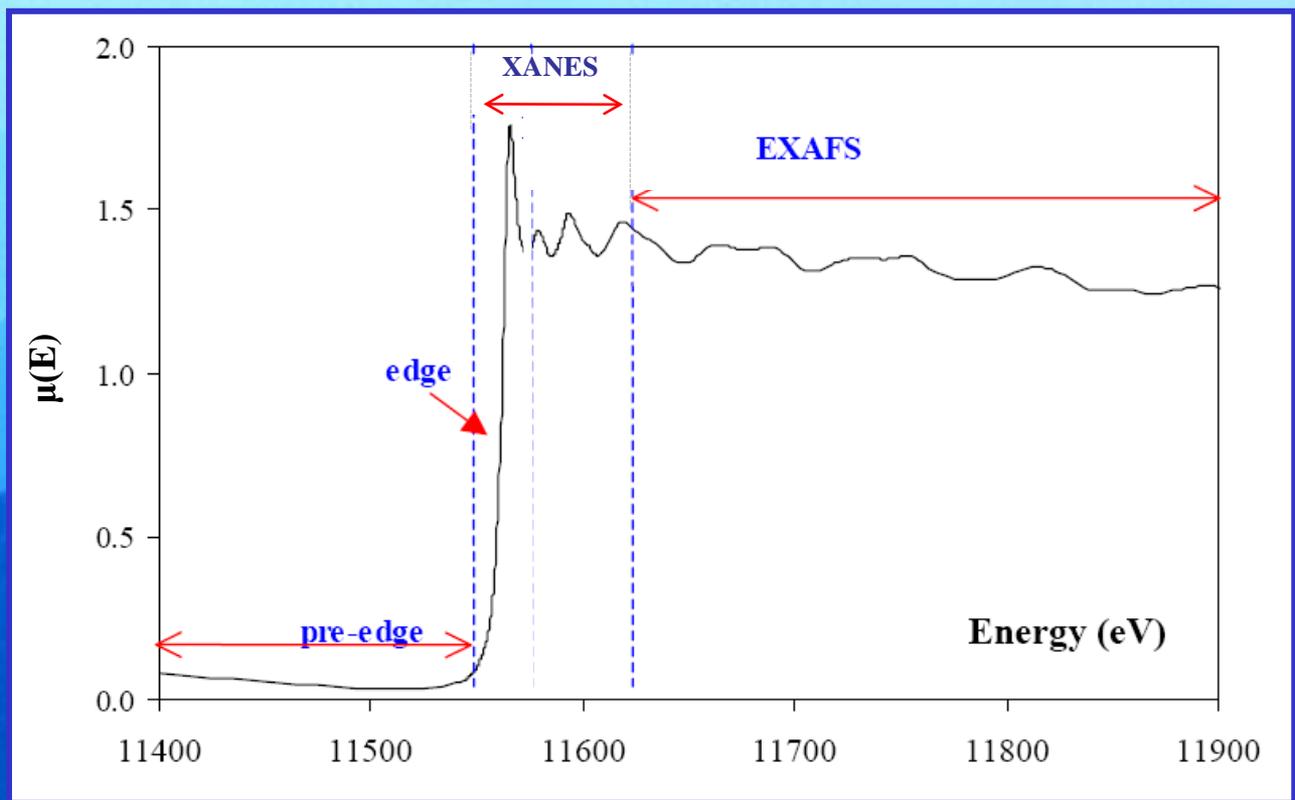
Atomo aislado



Atomo enlazado



# ANÁLISIS DE RESULTADOS



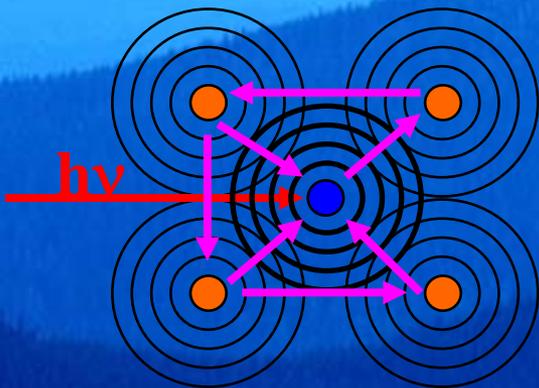
Region	Starting Energy (eV)	Ending Energy (eV)	Step Size (eV)
Pre-edge	-200	-20	5.0
XANES	-20	+30	0.5
EXAFS	+30	~900	$0.05 \text{ \AA}^{-1}$

# ANÁLISIS DE RESULTADOS

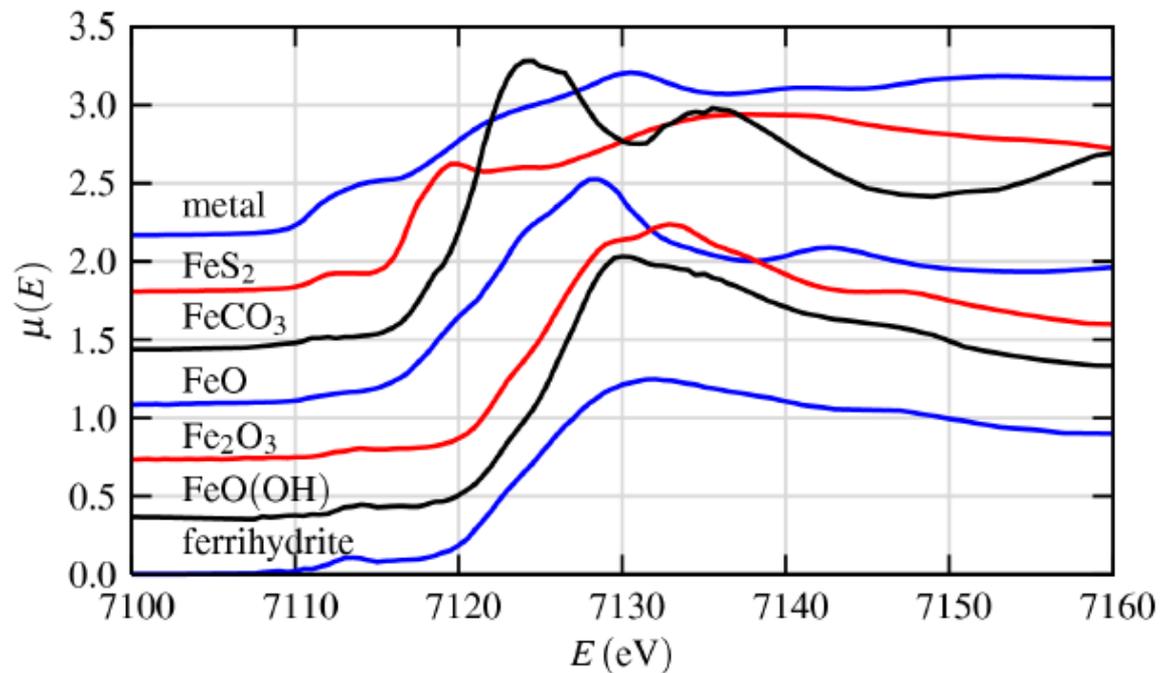
## ANÁLISIS ZONA XANES

**XANES (X-ray absorption near edge structure):**  
Información electrónica y estructural (cualitativa).  
“Huella dactilar”, Línea Blanca → Estado de oxidación

*Dispersión múltiple*



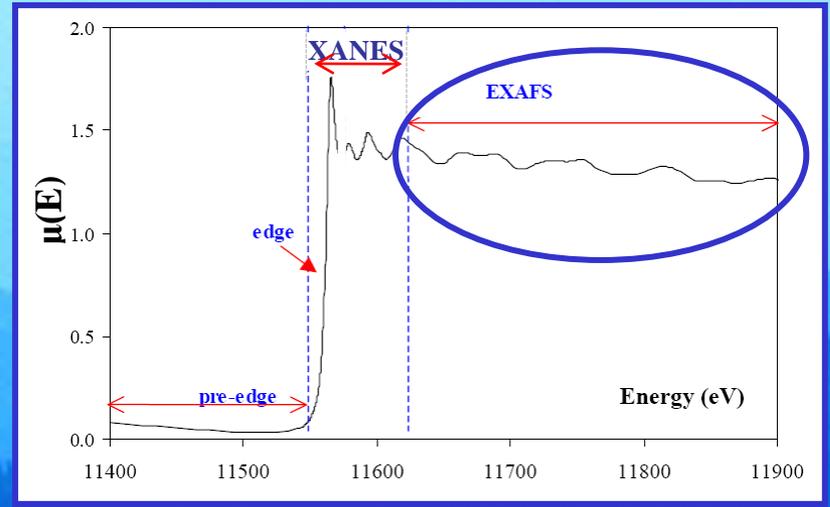
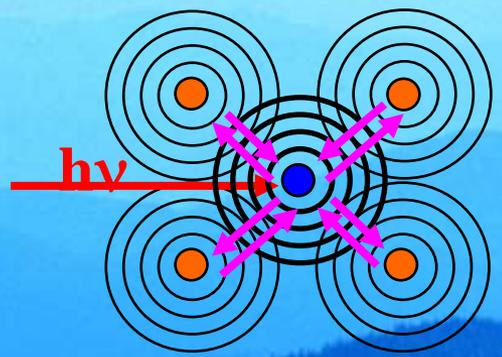
The Normalized XANES from several Fe compounds:



# ANÁLISIS DE RESULTADOS

## ANÁLISIS ZONA EXAFS

*Dispersión simple*



**Ecuación EXAFS**

**Función Amplitud de Retrodispersión**

**Factor D-W**

**Funciones Desplazamiento de Fase**

$$\chi(k) = -S_0^2 \sum_i N_i \frac{|f(\pi, k)|}{kR_i^2} e^{(-2\sigma_i^2 k^2)} e^{(-2R_i/\lambda(k))} \sin(2kR_i + 2\delta_1 + \varphi_i(\pi, k))$$

**Factor de reducción**

**Número de Coordinación**

**Recorrido Libre Medio**

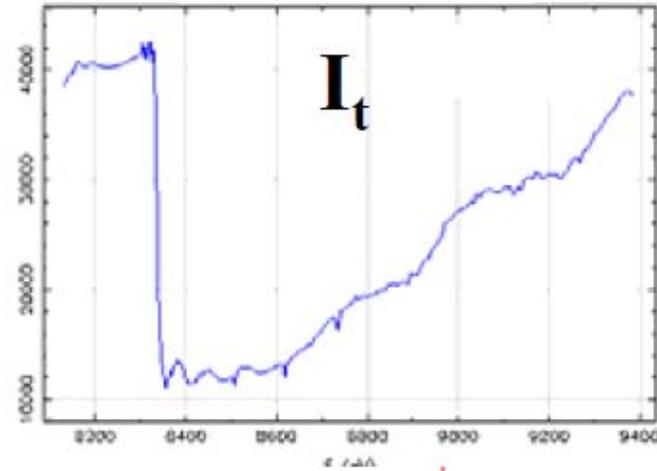
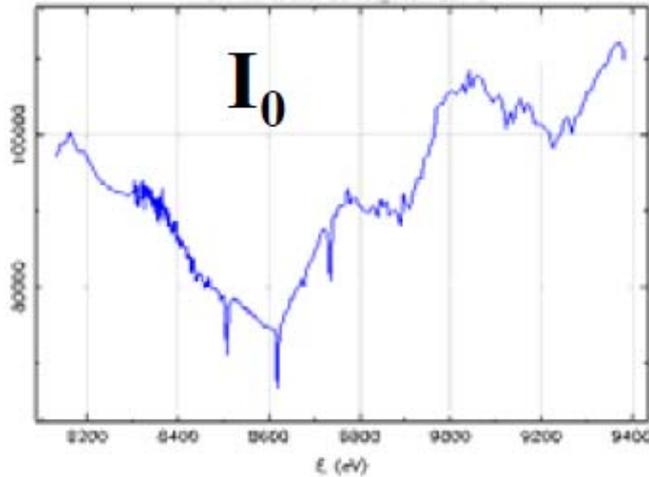
**Distancia Interatómica**



## Pasos a seguir:

- 1.- Convertir I medidas en  $\mu(E)$
- 2.- Sustracción del pre-edge
- 3.- Normalización de  $\mu(E)$ : de 0 a 1  $\rightarrow$  Análisis XANES
- 4.- Sustracción de Background zona post-edge
- 5.- Identificar  $E_0$  y convertir Energía a función de onda:  $E \rightarrow k$
- 6.- Dar peso a k y hacer Transformada de Fourier de k a R.

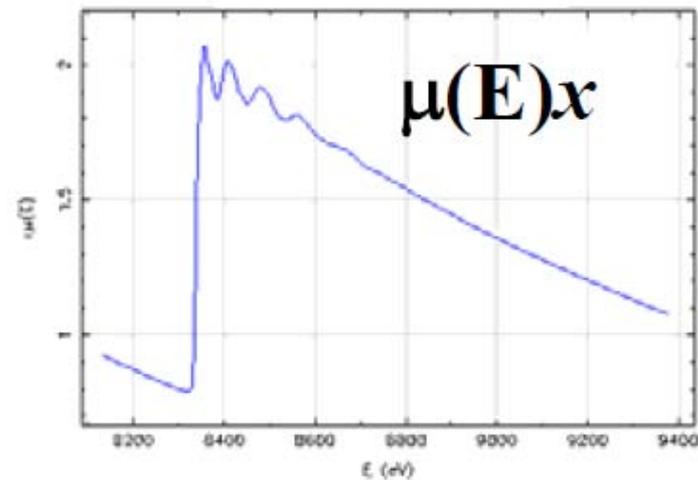
## 1.- Convertir I medidas en $\mu(E)$



**Transmisión:**  $\mu(E)x = -\ln(I_t/I_0)$

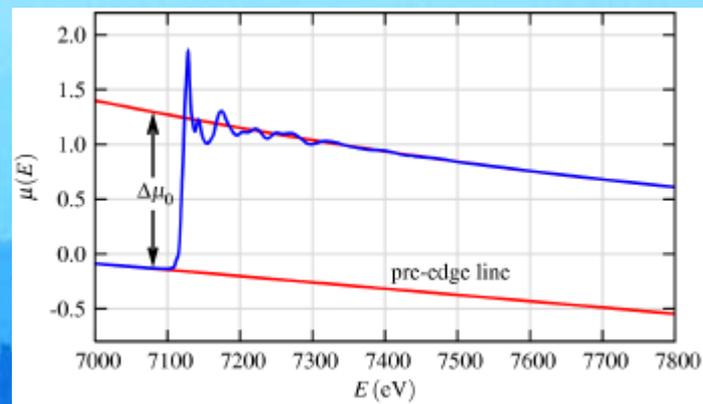
**Fluorescencia:**  $\mu(E) \propto I_f/I_0$

**Total electron yield:**  $\mu(E) \propto I/I_0$



## 2.- Sustracción del pre-edge

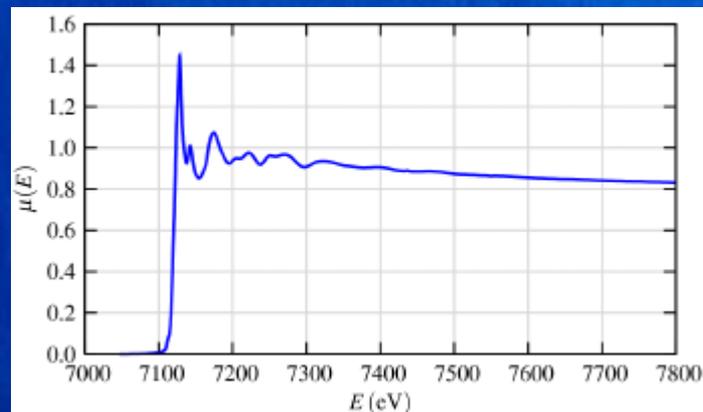
Esto elimina la absorción debida a otros "edges" en la muestra



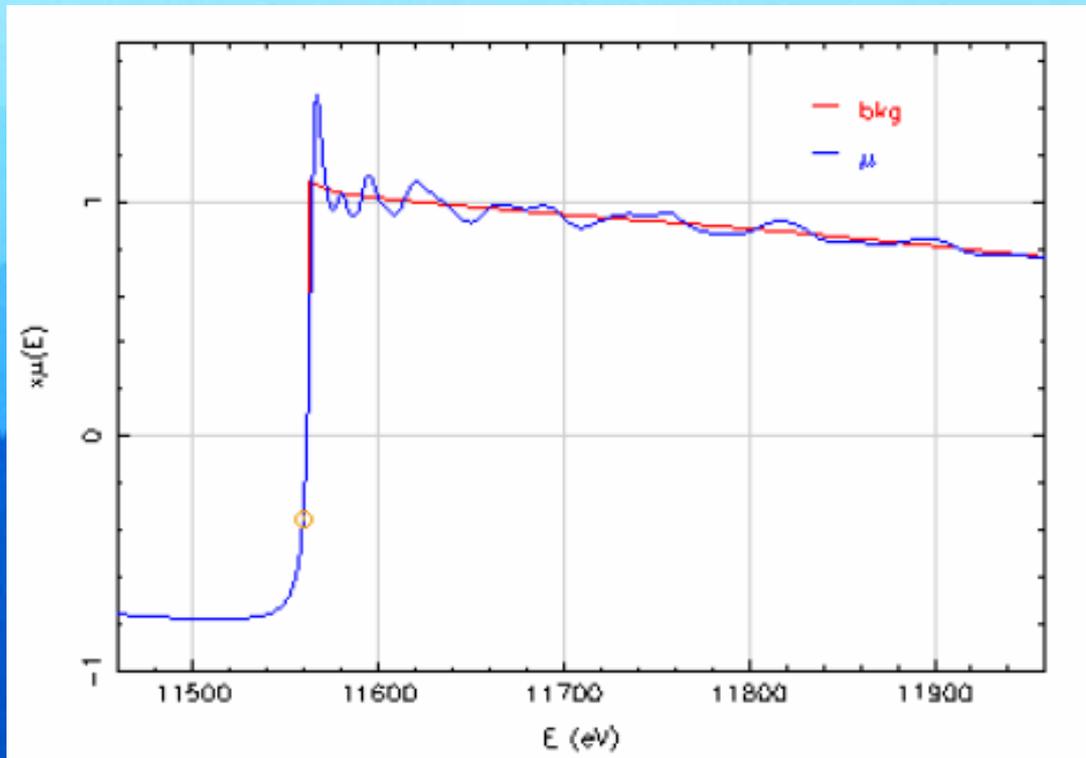
## 3.- Normalización de $\mu(E)$ : de 0 a 1 $\rightarrow$ Análisis XANES

$$\mu_{\text{Norm}}(E) = \mu(E) / \Delta\mu_0(E_0)$$

Ya se puede llevar a cabo el análisis XANES



## 4.- Sustracción de Background zona post-edge



Un buen background debe pasar por el "medio" de las oscilaciones y ser una función continua y suave. Se suelen utilizar funciones tipo "spline".

No debe ser ni muy "rígida" ni contener oscilaciones que formen parte de los datos.

# ANÁLISIS DE RESULTADOS

**Polynomial regression**

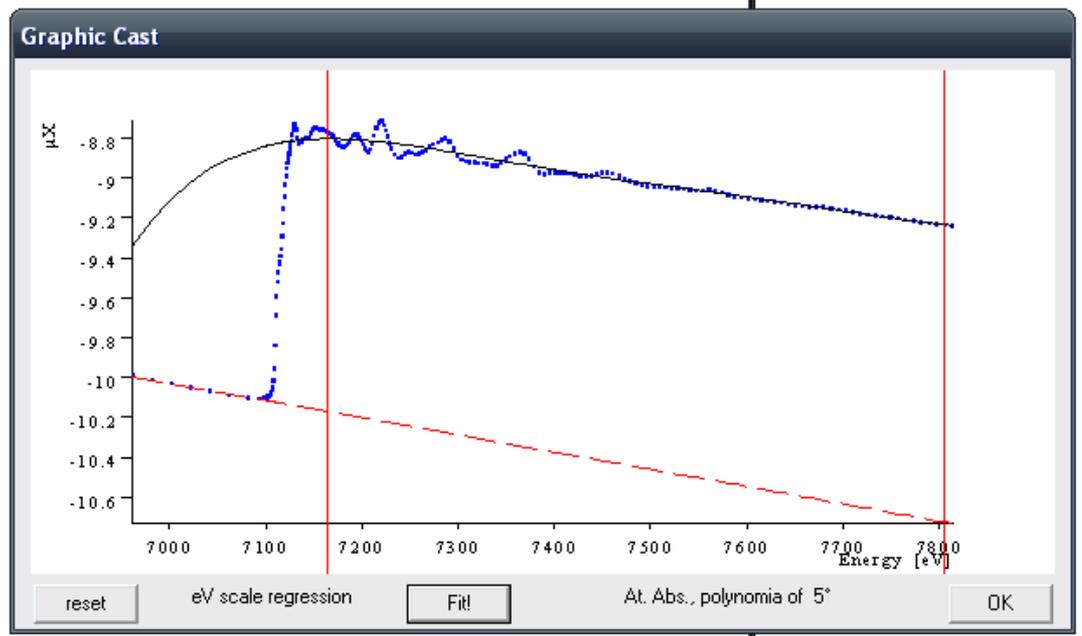
Polynomial order: 5

Polynomia vs. E-Eo (eV scale)  
 Polynomia vs. k (Å<sup>-1</sup> scale)

fit between:  
first point: 72  
last point: 204

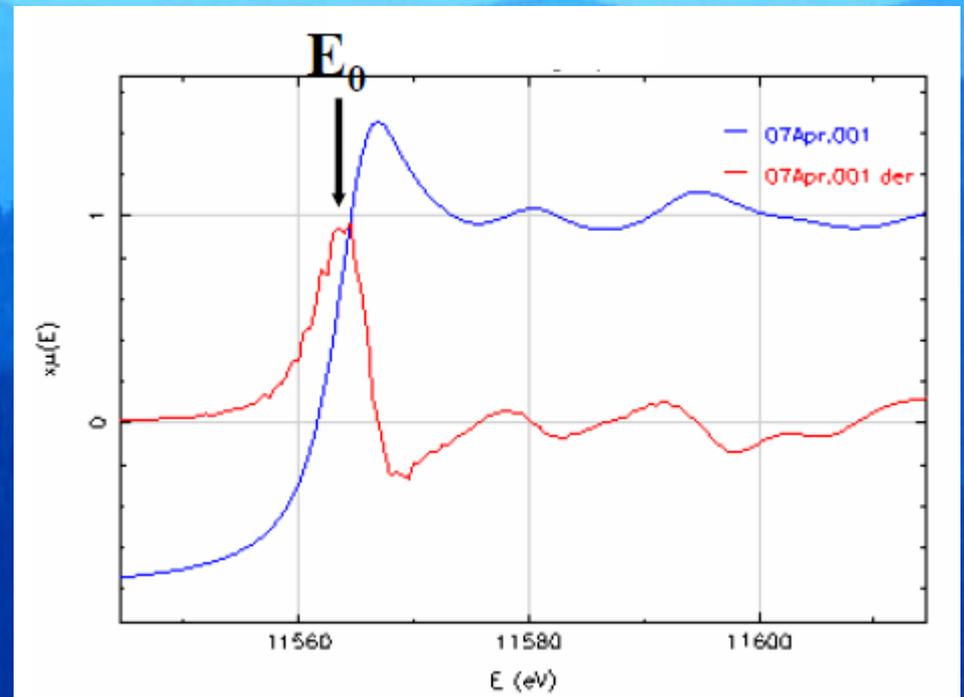
7223.00      7813.81

Buttons: Graphic cast, OK, Cancel



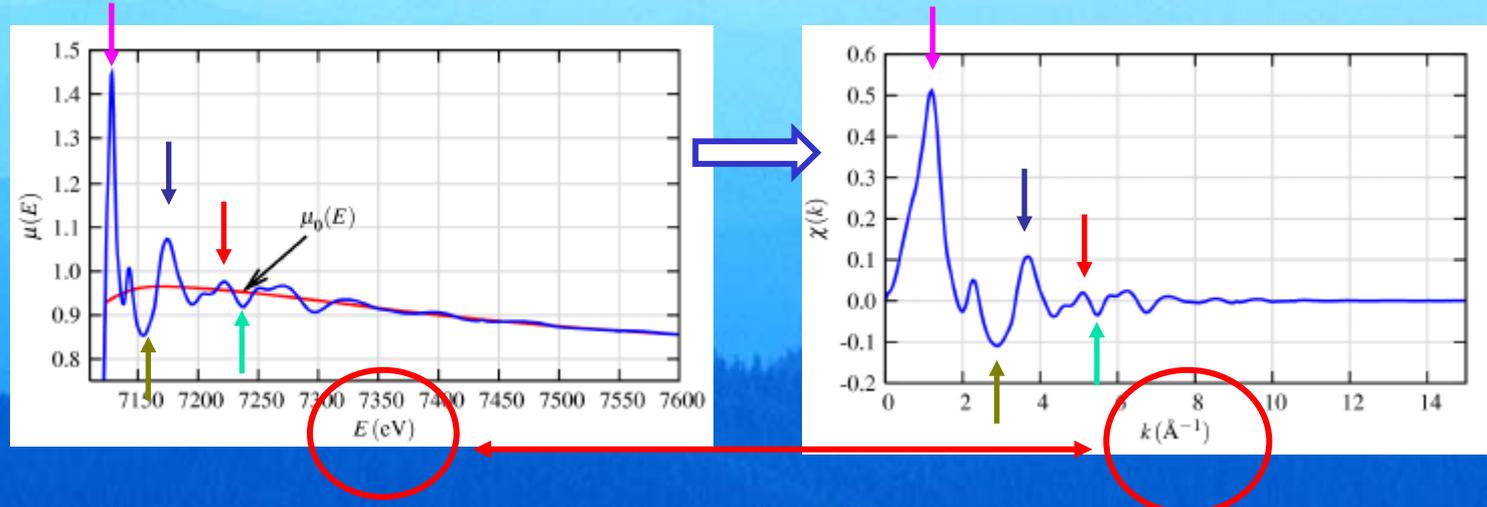
## 5.- Identificar $E_0$ y convertir Energía a función de onda: $E \rightarrow k$

Normalmente,  $E_0$  se toma como la energía en el **máximo de la derivada**.



# ANÁLISIS DE RESULTADOS

5.- Identificar  $E_0$  y convertir Energía a función de onda:  $E \rightarrow k$



$$k^2 = \frac{2 m_e (E - E_0)}{\hbar^2} \sim 3.81 \Delta E$$

Mass of the electron (points to  $m_e$ )  
 Fermi Energy (points to  $E_0$ )  
 Plank's constant (points to  $\hbar$ )

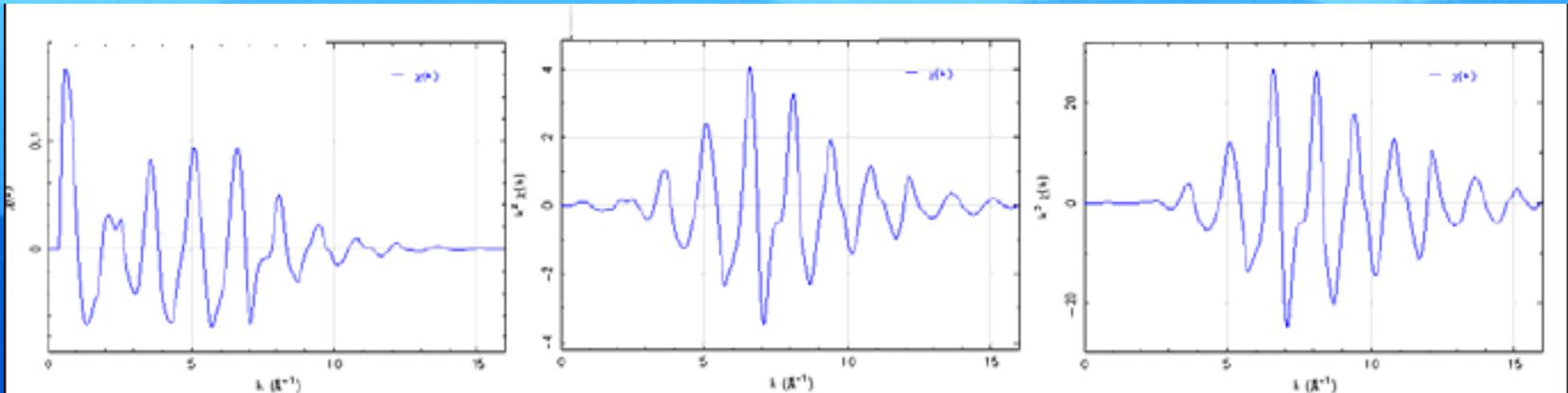
E (eV)	k ( $\text{\AA}^{-1}$ )
10	1.6
20	2.3
30	2.8
40	3.2
50	3.6
75	4.4
100	5.1
150	6.3
200	7.2
250	8.1
500	11.5
750	14.0
1000	16.2

## 6.- Dar peso a $k$ y hacer Transformada de Fourier de $k$ a $R$ .

$k$

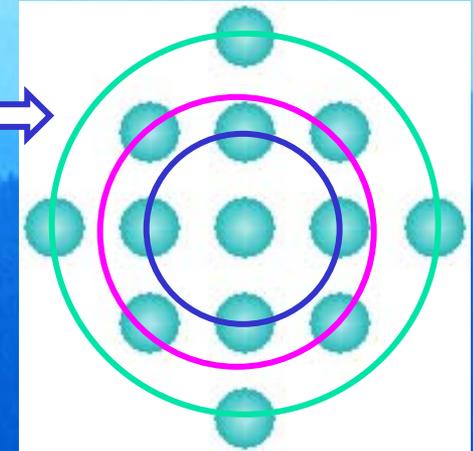
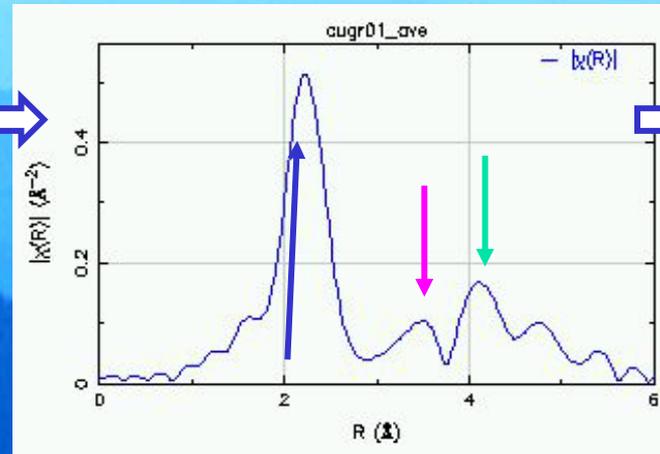
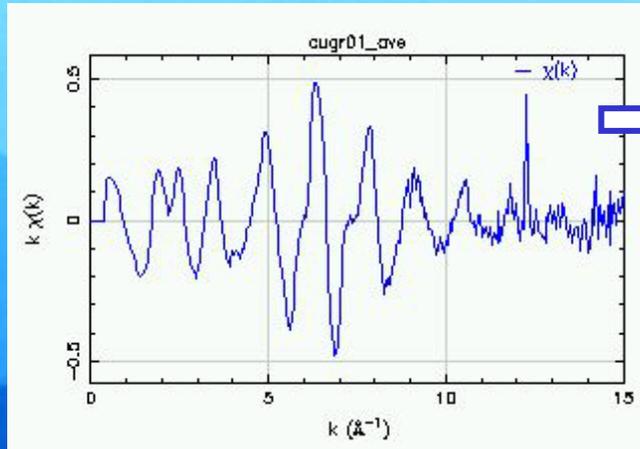
$k^2$

$k^3$



Al aumentar el peso de  $k$  se enfatizan las oscilaciones más lejanas  $\rightarrow$  ¡¡¡Cuidado con ruido!!!

## 6.- Dar peso a $k$ y hacer Transformada de Fourier de $k$ a $R$ .



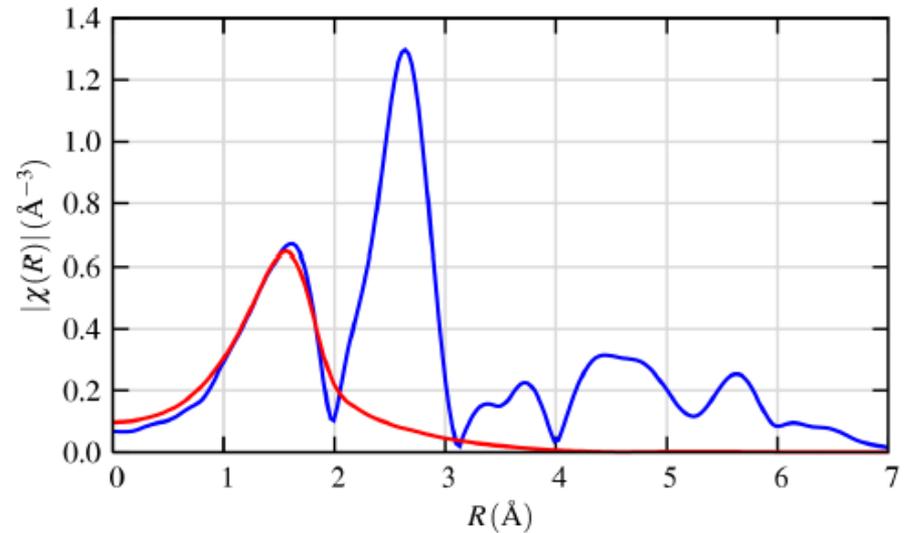
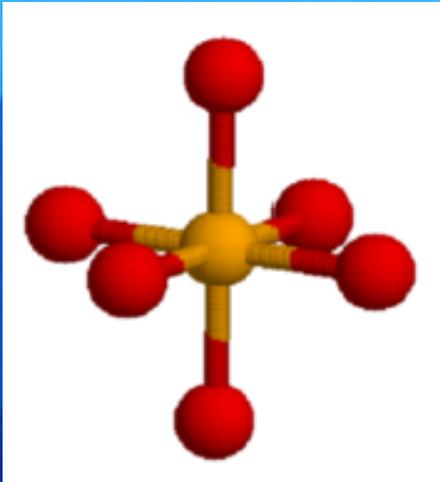
### ■ Similar a una función de distribución radial

- Distancia
- Numero de vecinos
- Tipo de vecinos
- Desorden Estructural

# ANÁLISIS DE RESULTADOS

## AJUSTE (MODELADO)

Utilización de Software específico:  
IFEFFIT Package: **Artemis**



Fit results:

$$N = 5.8 \pm 1.8$$

$$R = 2.10 \pm 0.02 \text{\AA}$$

$$\Delta E_0 = -3.1 \pm 2.5 \text{ eV}$$

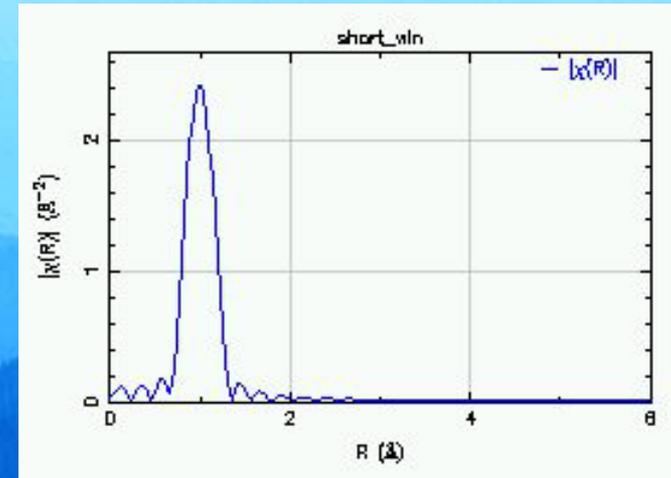
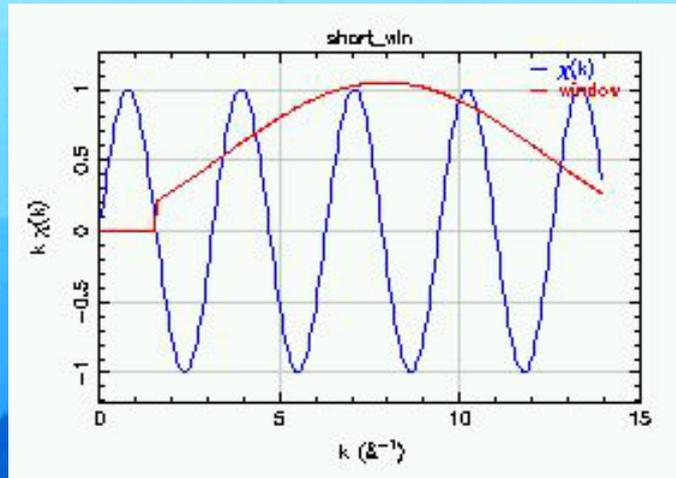
$$\sigma^2 = 0.015 \pm 0.005 \text{ \AA}^2.$$

## **Software de Tratamiento de datos EXAFS:**

**<http://www.esrf.fr/computing/scientific/exafs/>**

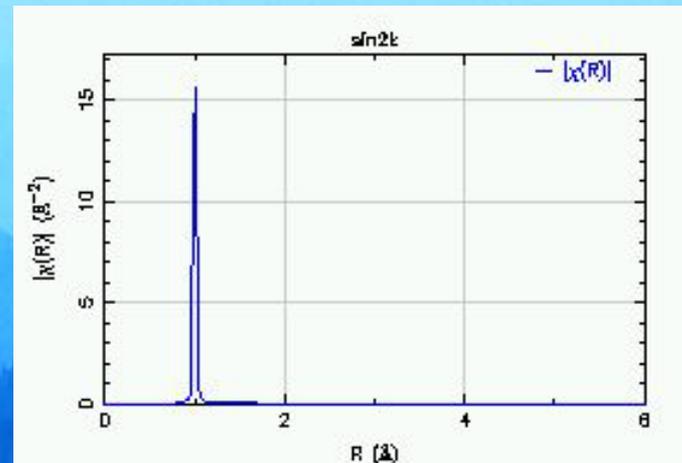
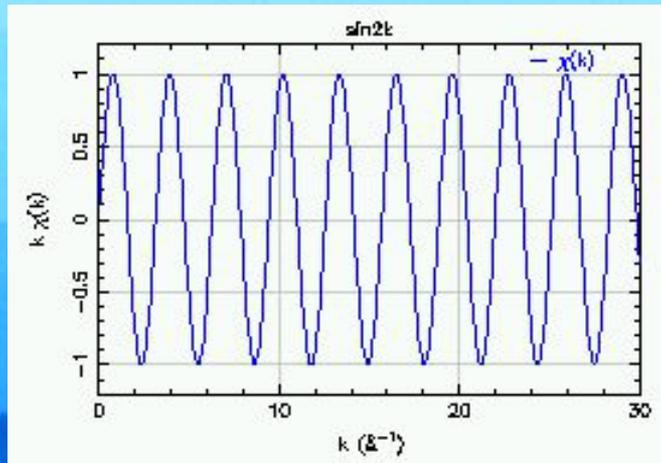
**[http://cars9.uchicago.edu/IXS-cgi/XAFS Programs](http://cars9.uchicago.edu/IXS-cgi/XAFS%20Programs)**

# La transformada de Fourier



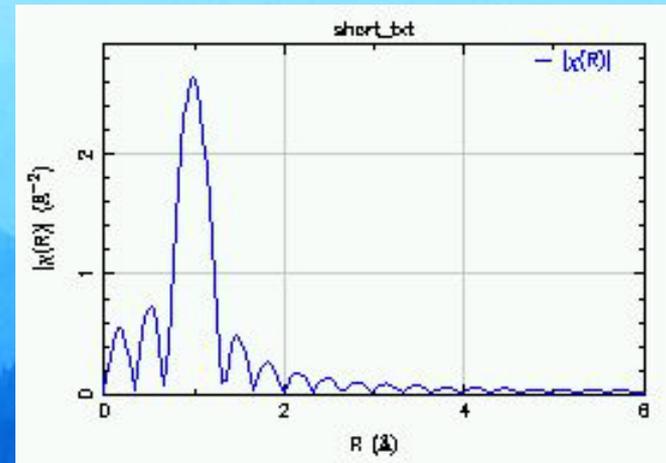
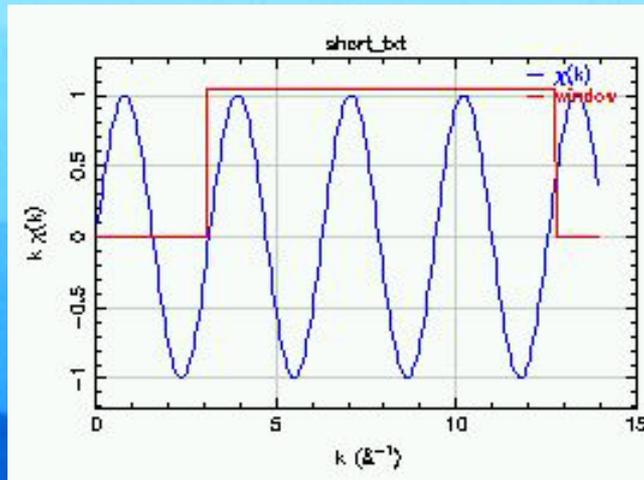
- La FT de una oscilación sinusoidal da lugar a un pico en el espacio R (La posición está relacionada con la frecuencia de oscilación)

# La transformada de Fourier



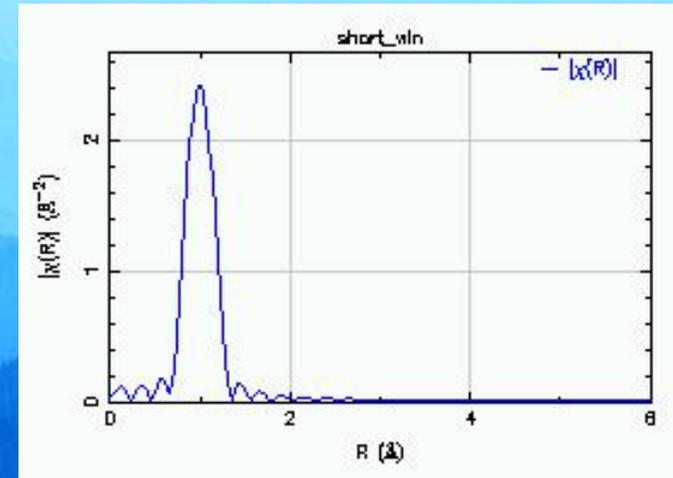
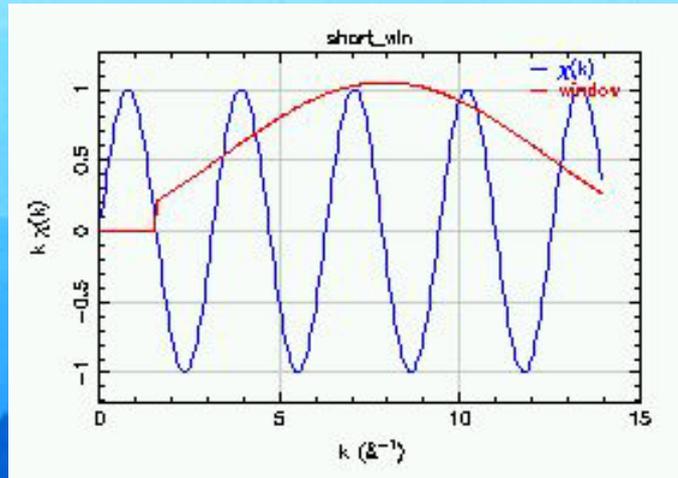
**FT de una onda sinusoidal  
infinita es una función  
delta**

# La transformada de Fourier



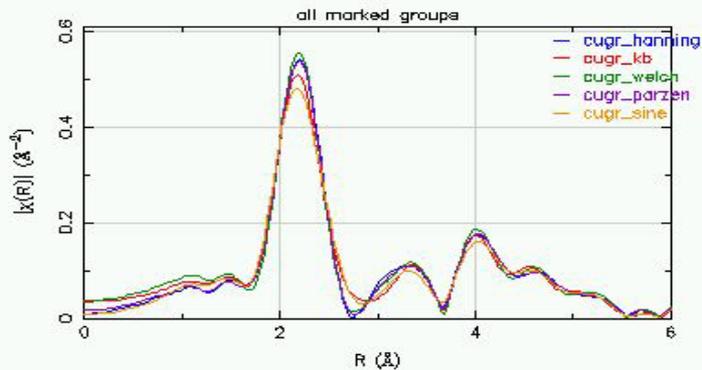
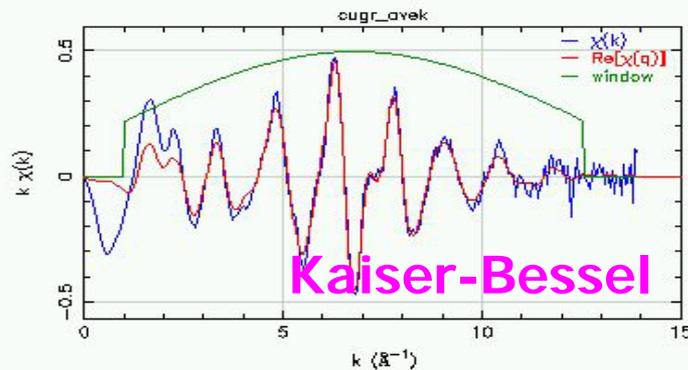
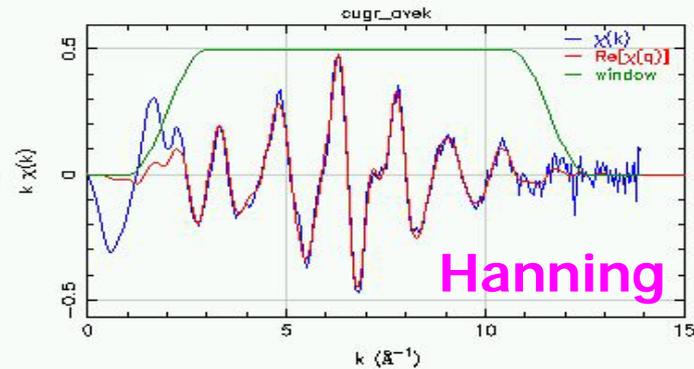
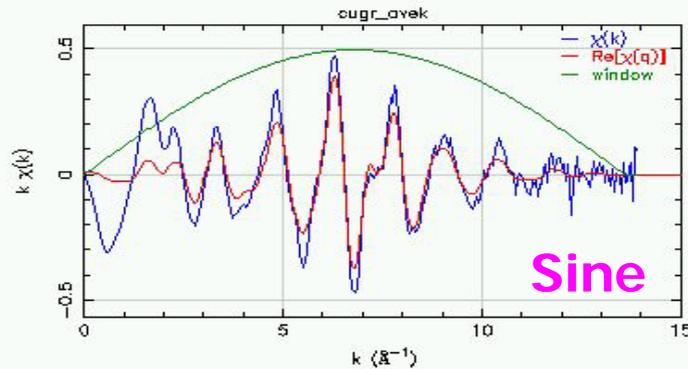
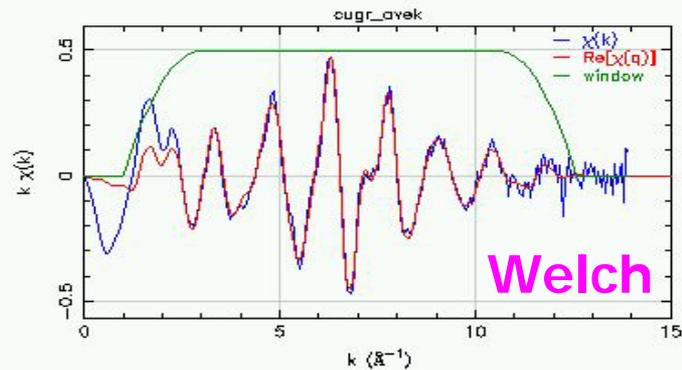
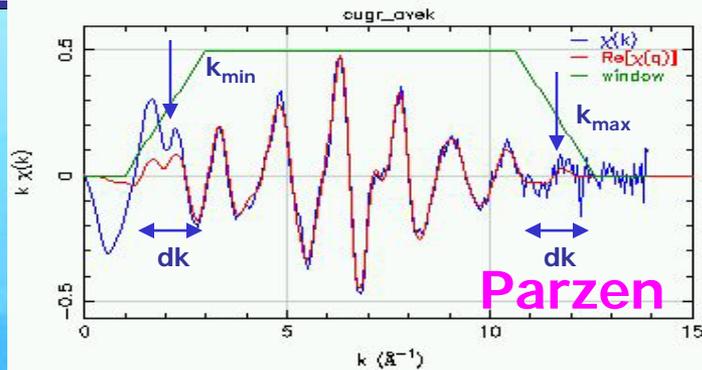
- FT de una onda sinusoidal truncada es un pico (distorsionado)

# La transformada de Fourier

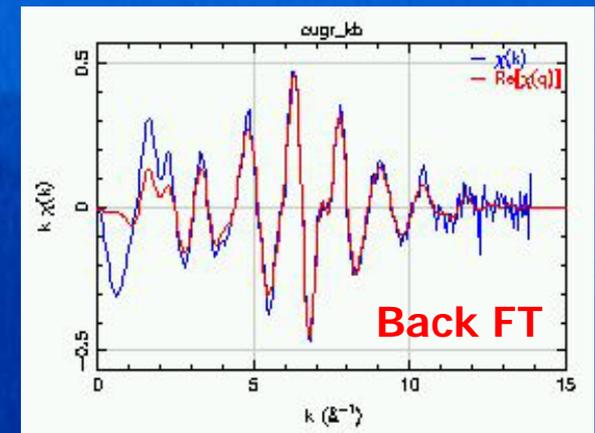
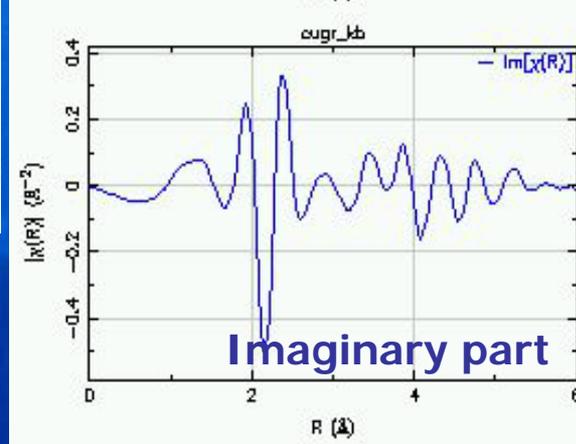
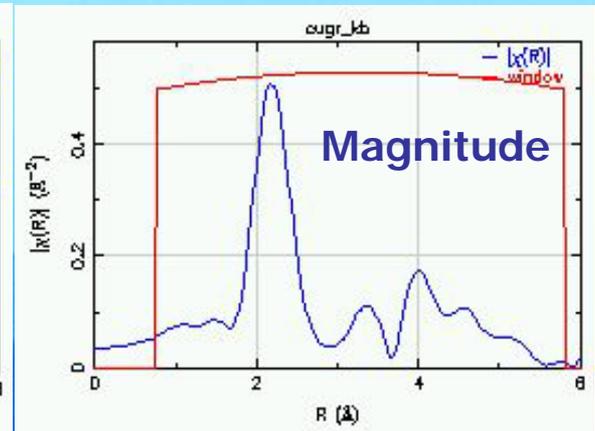
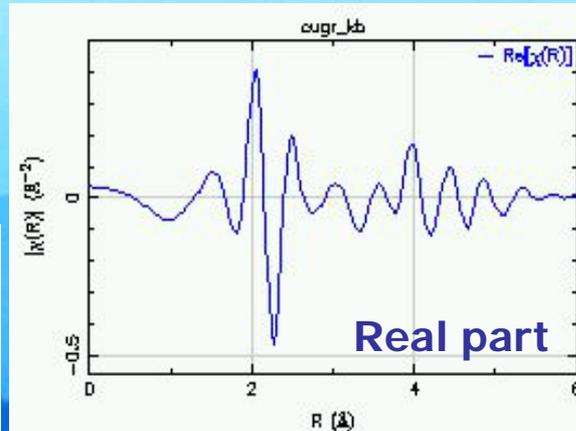
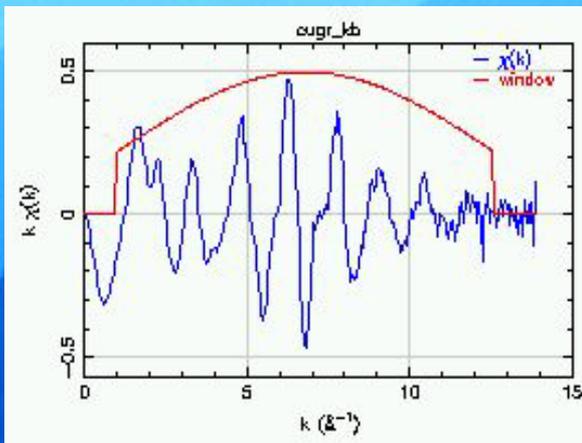


- Si se multiplica la onda sinusoidal por una función "ventana" que incrementa gradualmente la amplitud, la transformada resultante es más suave.

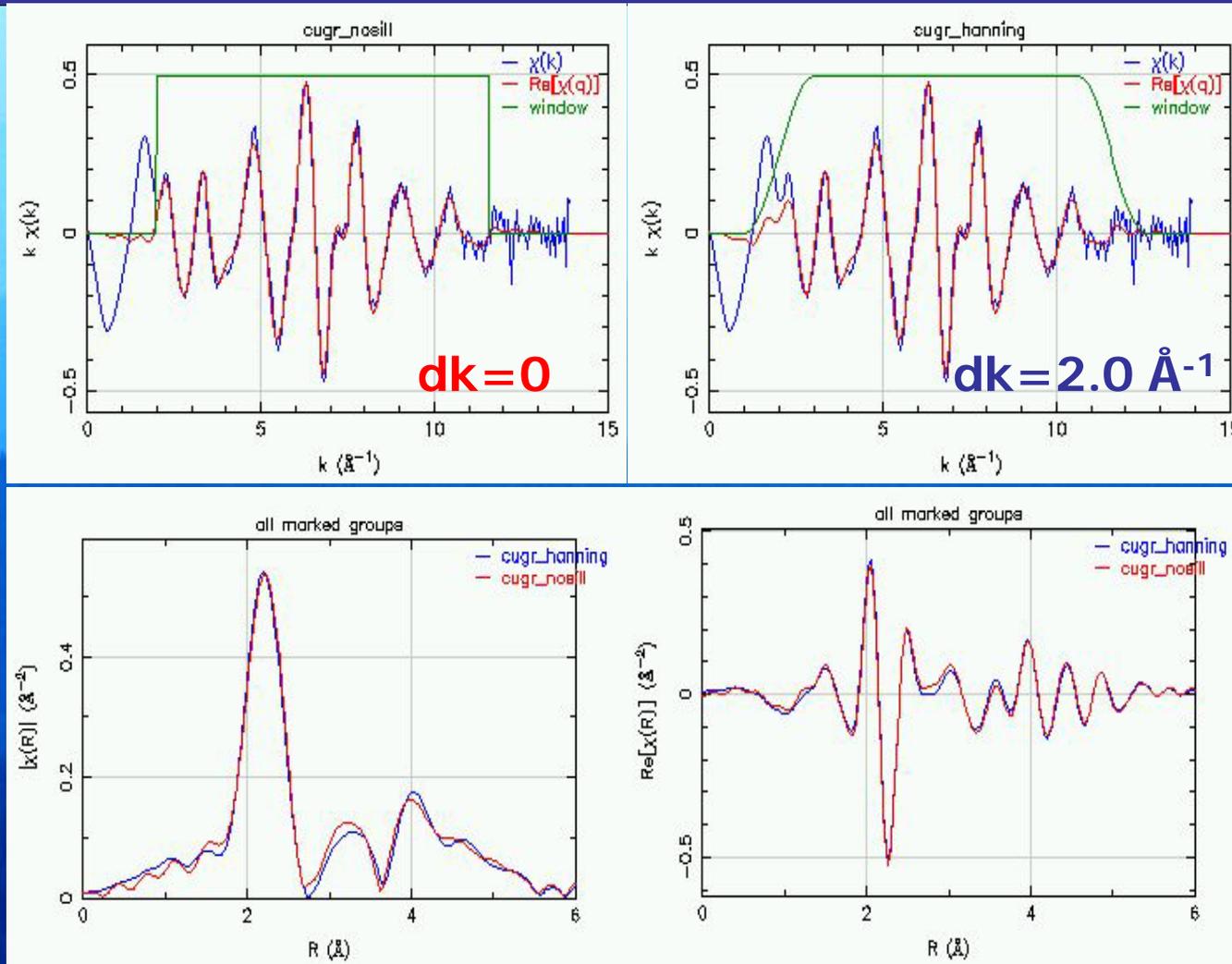
# Fourier Transform Windows



# Fourier Transform parts

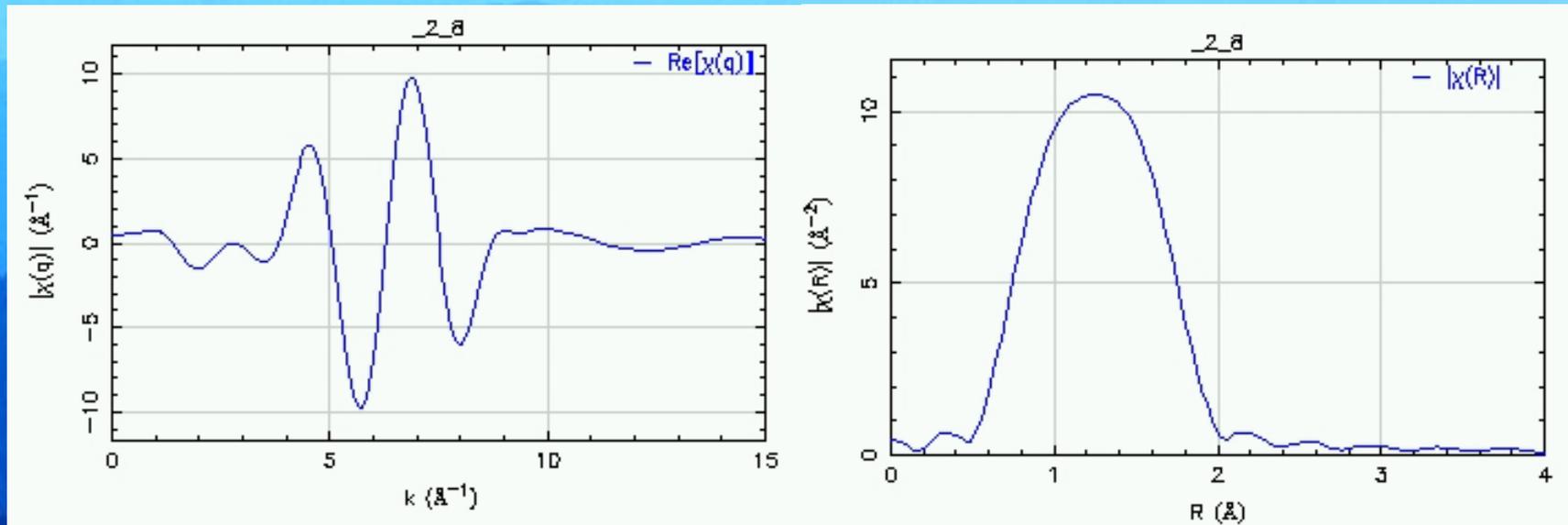


# Fourier Transform window sill



# Rango de transformación: efecto en la transformada

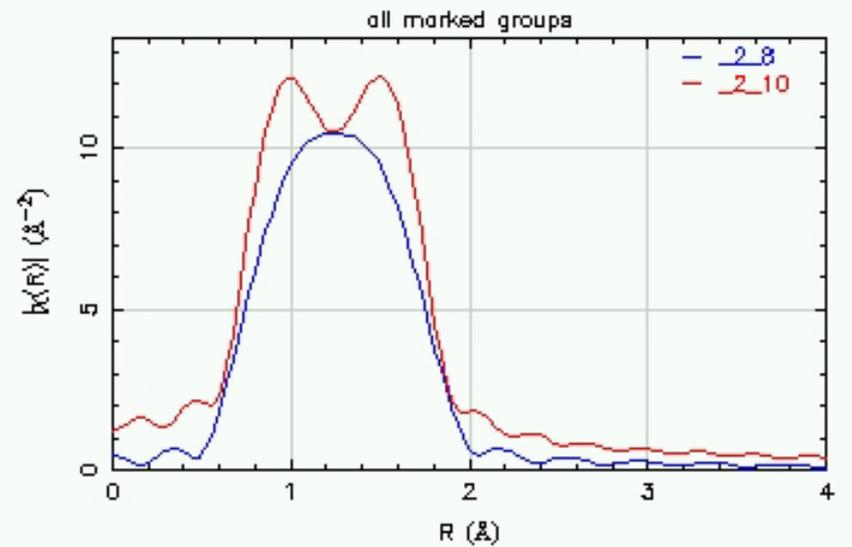
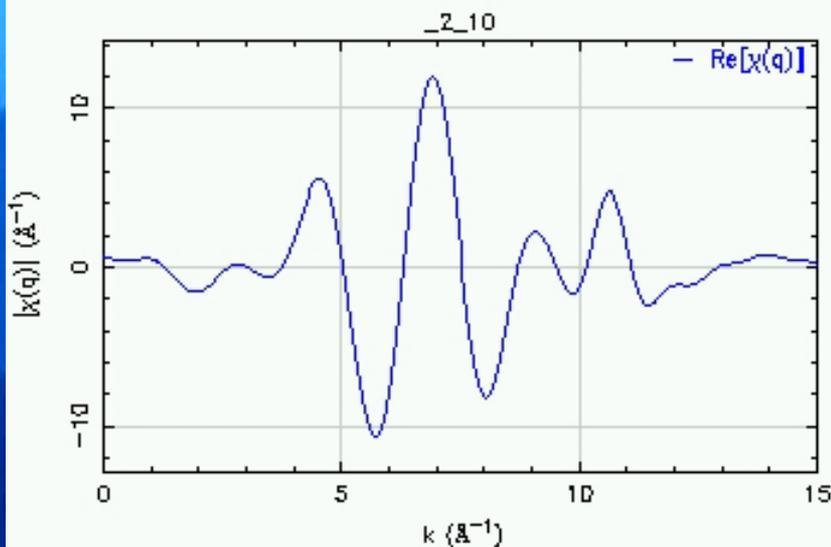
$$\text{FT k-range} = 2-8 \text{ \AA}^{-1}$$



- La cantidad de información en los dato depende el rango de R y K

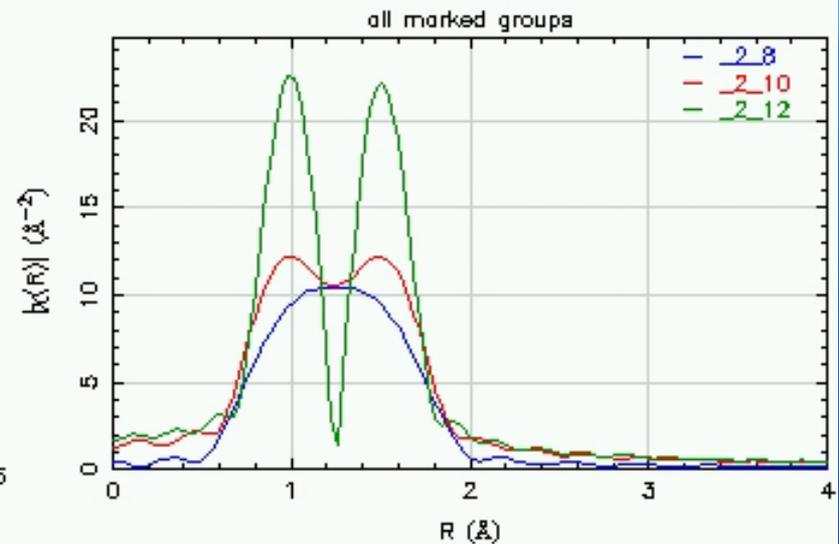
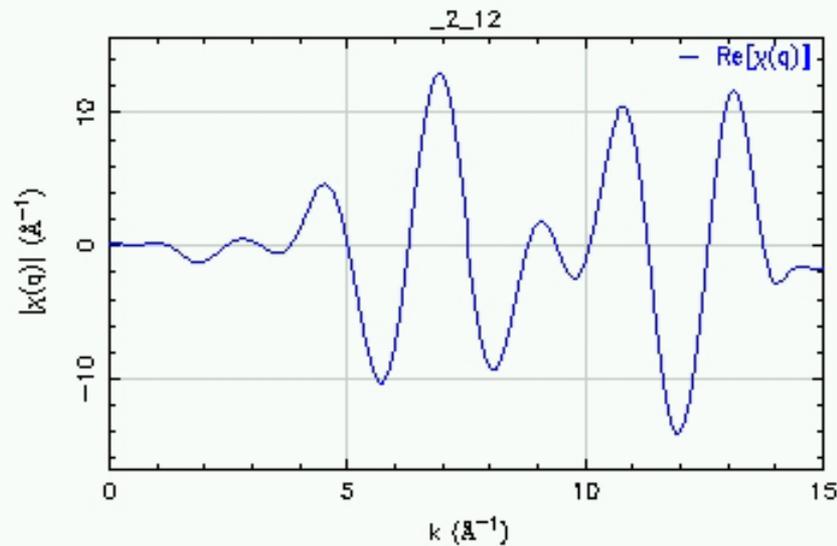
# Rango de transformación: efecto en la transformada

FT k-range = **2-10** Å<sup>-1</sup>



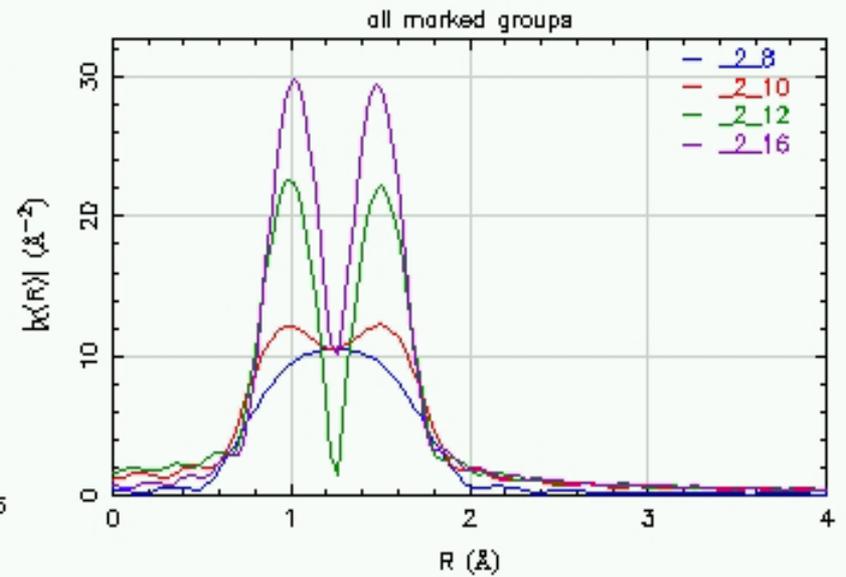
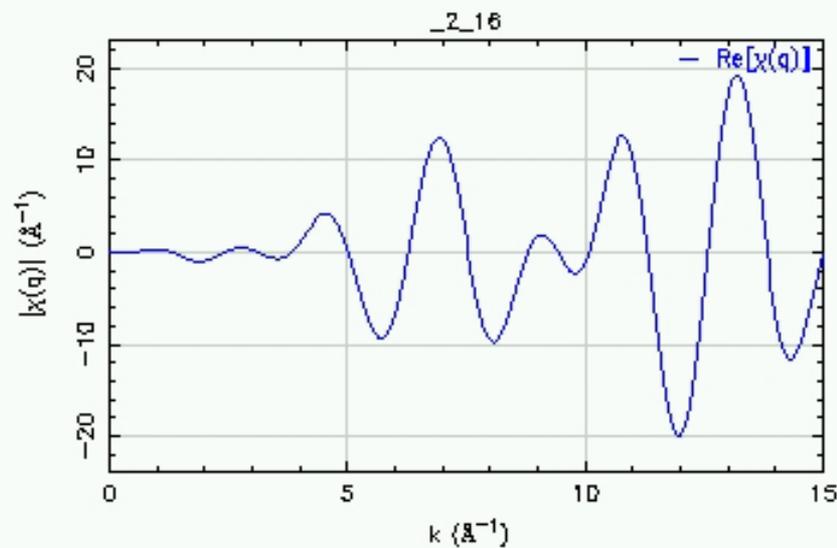
# Rango de transformación: efecto en la transformada

FT k-range = **2-12** Å<sup>-1</sup>

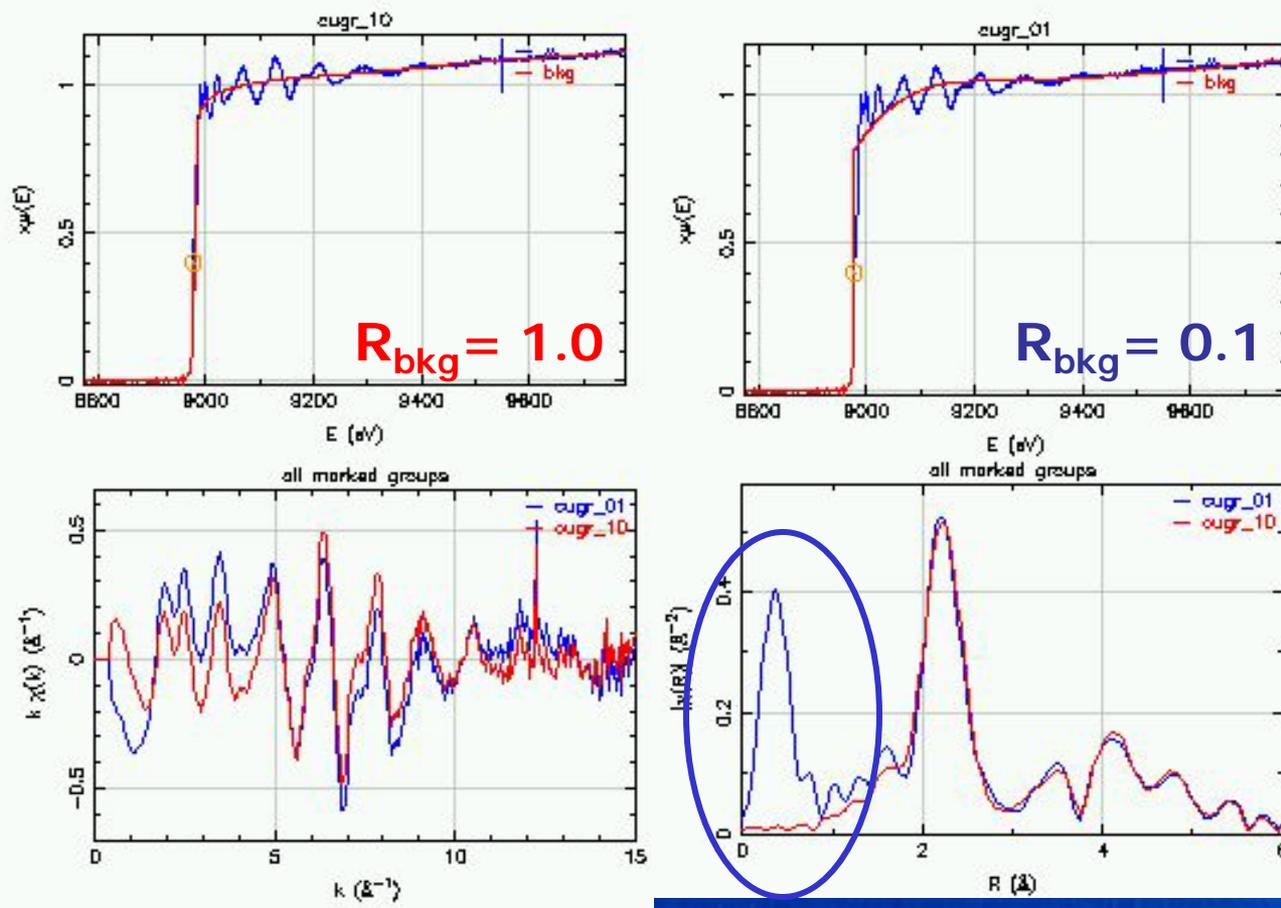


# Rango de transformación: efecto en la transformada

FT k-range = **2-16** Å<sup>-1</sup>

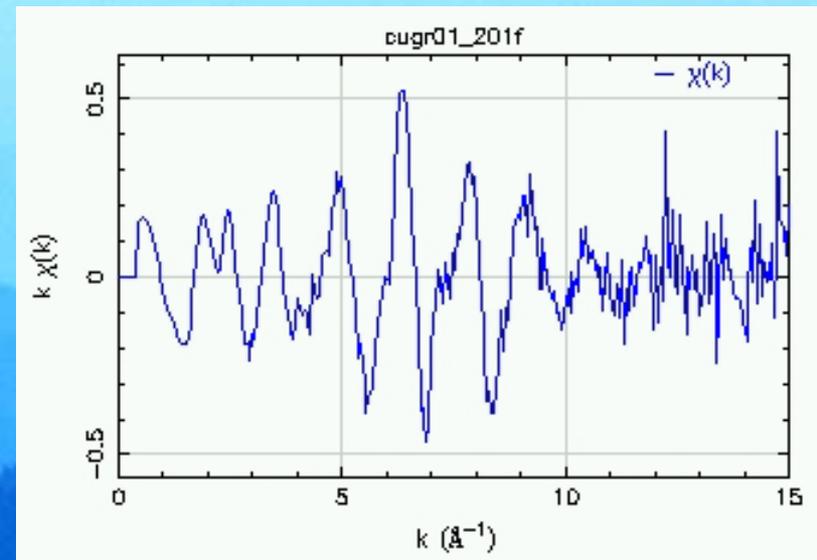
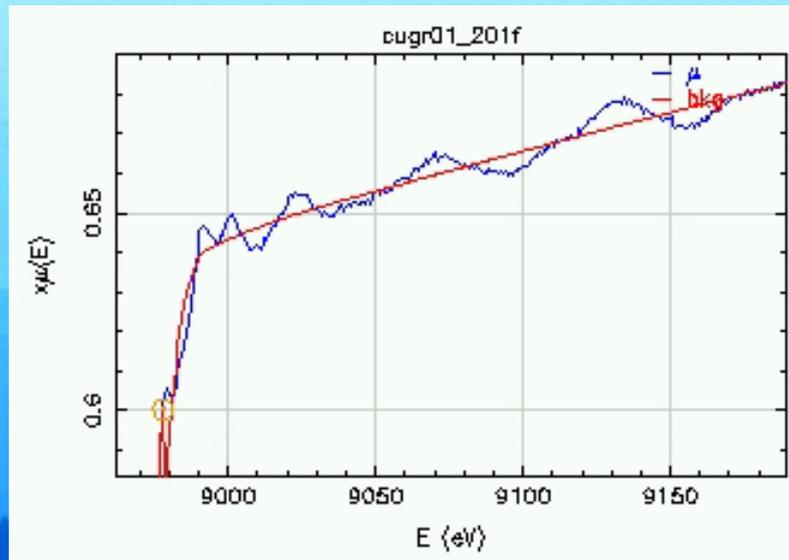


# FT y el background



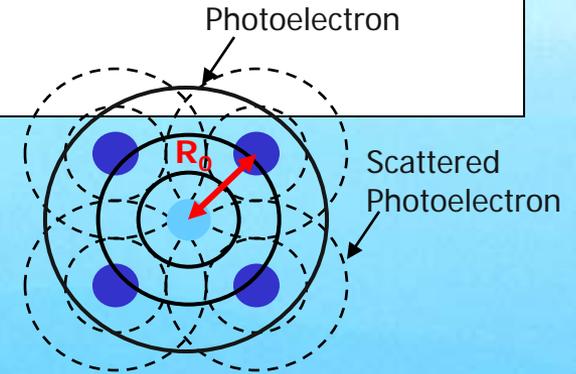
- Las oscilaciones de alta (y baja) frecuencia pueden dar lugar a picos falsos en la FT

# Resumen del Background



- Un buen background debe eliminar las oscilaciones de baja frecuencia (alta longitud de onda) de  $\chi(k)$ .
- Estas oscilaciones de baja frecuencia suelen aparecer por debajo de  $\frac{1}{2}$  del primer pico real en FT
- Se debe restringir el background para que no contenga oscilaciones que forman parte de los datos.

# The EXAFS Equation



$$\chi(k) = \sum_i \chi_i(k)$$

with

$$\chi_i(k) = \text{Im} \left( \frac{N_i S_0^2 F_i(k)}{k R_i^2} \exp(i(2kR_i + \phi_i(k))) \exp(-2\sigma_i^2 k^2) \exp(-2R_i/\lambda(k)) \right)$$

$$R_i = R_0 + \Delta R$$

$$k^2 = 2 m_0 (E - E_0) / \hbar$$

Theoretically calculated values

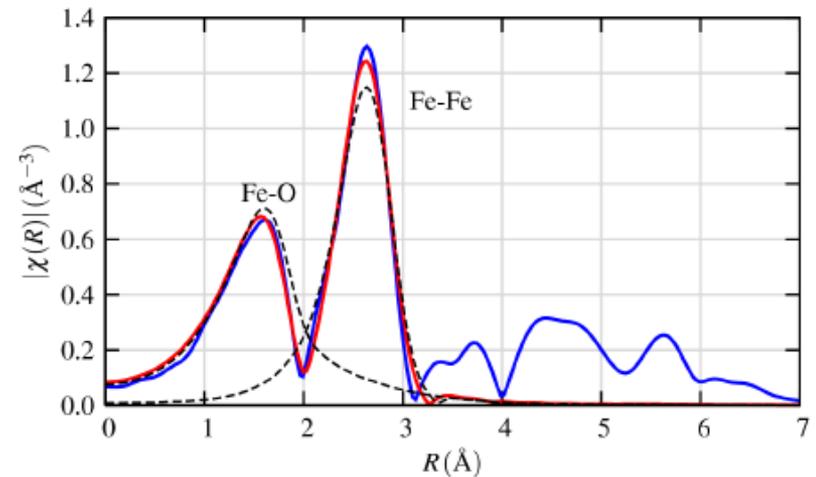
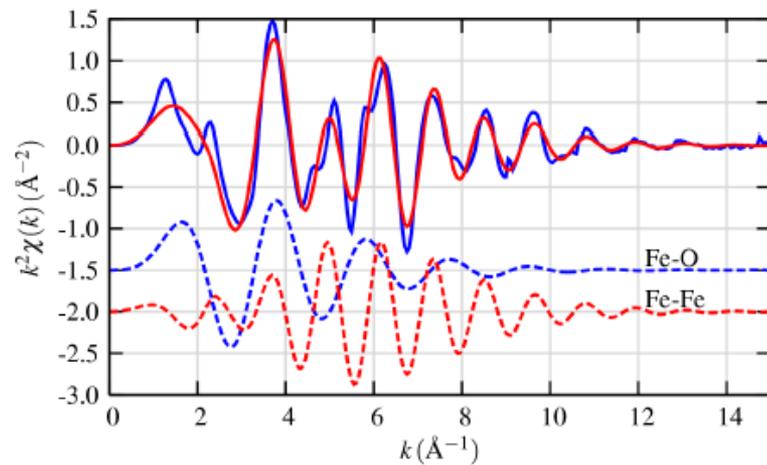
- $F_i(k)$  effective scattering amplitude
- $\phi_i(k)$  effective scattering phase shift
- $\lambda(k)$  mean free path
- $R_0$  initial path length

Parameters often determined from a fit to data

- $N_i$  degeneracy of path
- $S_0^2$  passive electron reduction factor
- $\sigma_i^2$  mean squared displacement
- $E_0$  energy shift
- $\Delta R$  change in half-path length

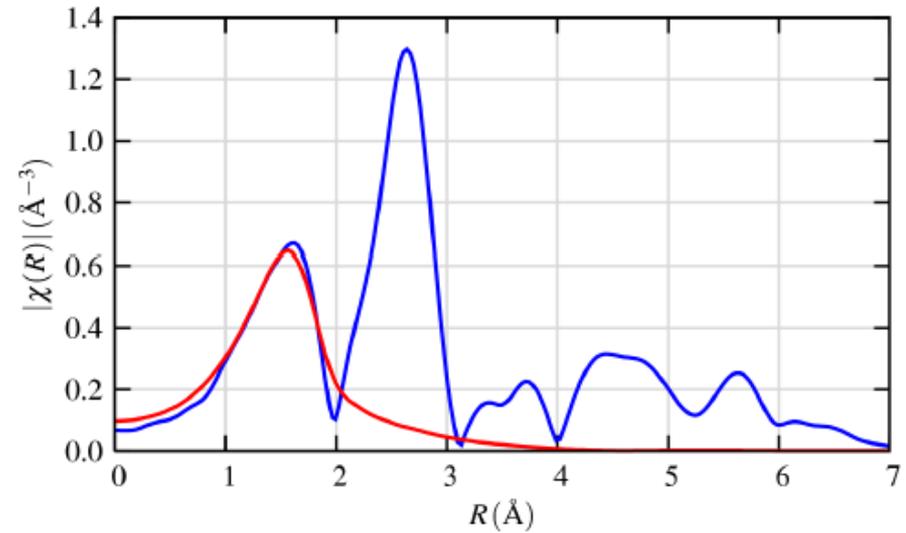
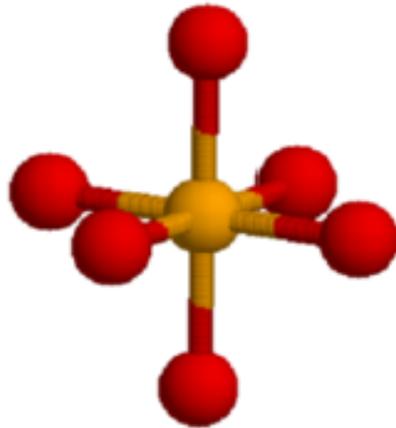
# Ajuste (modelado)

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2 \sigma_j^2}}{k R_j^2} \sin[2k R_j + \delta_j(k)]$$



Shell	N	R ( $\text{\AA}$ )	$\sigma^2$ ( $\text{\AA}^2$ )	$\Delta E_0$ (eV)
Fe-O	6.0(1.0)	2.10(.02)	0.015(.003)	-2.1(0.8)
Fe-Fe	11.7(1.3)	3.05(.02)	0.014(.002)	-2.1(0.8)

# Ajuste (modelado)



## Fit results:

$$N = 5.8 \pm 1.8$$

$$R = 2.10 \pm 0.02 \text{ \AA}$$

$$\Delta E_0 = -3.1 \pm 2.5 \text{ eV}$$

$$\sigma^2 = 0.015 \pm 0.005 \text{ \AA}^2.$$