

ESTUDIO SISTEMÁTICO DE LAS ECUACIONES DE ESTADO EN LAS PEROVSKITAS KMF_3 $M=M_G, M_N, Fe, Co, Ni, Zn$

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Descripción general

- Motivaciones y Objetivos
- Metodología y detalles computacionales
- Resultados
 - ▣ Curvas E-V
 - ▣ Ecuaciones de Estado
 - ▣ Ecuaciones de Estado atómicas
- Conclusiones

Motivaciones y objetivos

□ Motivaciones

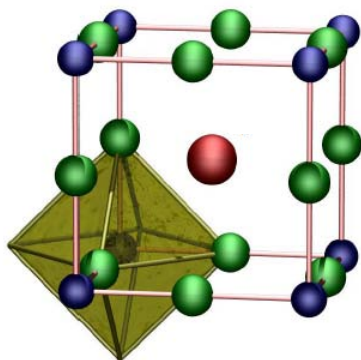
- ▣ Satisfacer intereses comunes con otros grupos MALTA
- ▣ Cumplir con los objetivos marcados en el proyecto

□ Objetivos

- ▣ Proporcionar EOS de iones en cristales
- ▣ Determinar parámetros estructurales (radios iónicos) utilizando criterios no ambiguos
- ▣ Interpretación resultados experimentales (perovskitas UCAN) y apoyo a modelos de ecuaciones de estado (spinodal UCM)

Metodología y Detalles Computacionales

□ Estructura cristalina



Grupo espacial: Pm-3m

$K^+ = (1/2, 1/2, 1/2)$

$M^{2+} \text{ (Mg, Mn, Fe, Co, Ni, Zn)} = (0, 0, 0)$

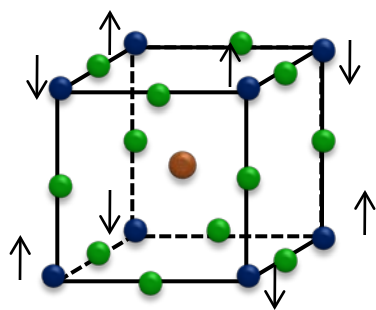
$F^- = (1/2, 0, 0)$

Indices de coordinación:

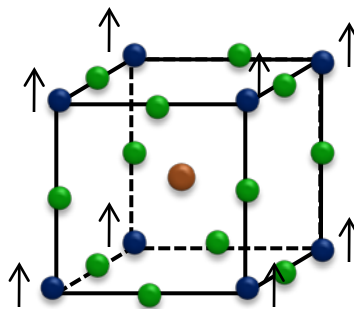
MF_6

KF_{12}

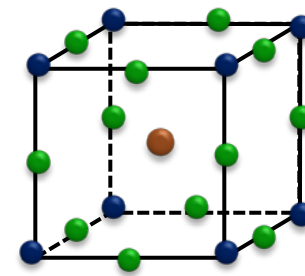
□ Ferro/antiferro/no magnético



Antiferromagnético



Ferromagnético



No magnético

Metodología y Detalles Computacionales

□ CRYSTAL06

- ▣ Estructura electrónica de sistemas periódicos: HF, DFT
- ▣ Funciones de Bloch: combinación lineal de orbitales atómicos
- ▣ Cálculos all-electron o valence only + pseudopotenciales

□ Gibbs: EOS (M.A. Blanco et al. Computer Physics Communications 158 (2004) 57)

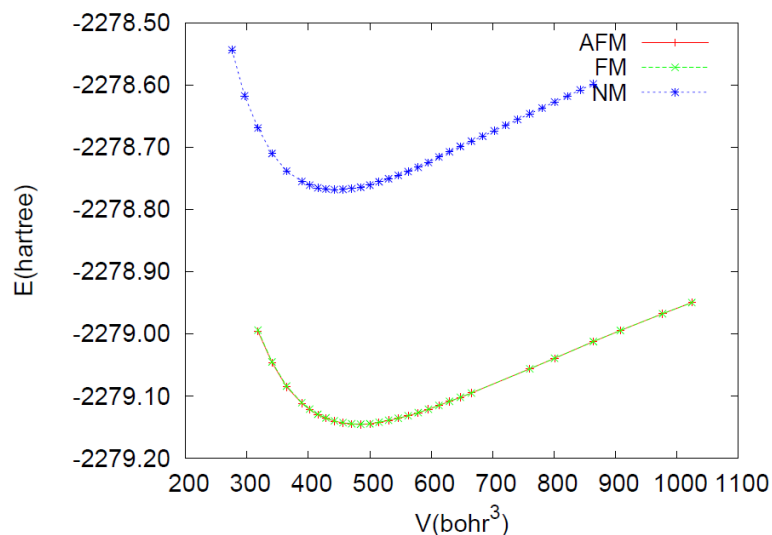
- ▣ Ecuaciones de estado analíticas (Vinet, Birch-Murnaghan, spinodal) y numéricas se obtienen a partir de una colección de puntos (E-V)
- ▣ Diversas propiedades termodinámicas se evalúan haciendo uso de la aproximación quasi-harmónica de Debye... and beyond

□ Critic (A. Otero de la Roza et al. Computer Physics Communications 180 (2009) 157)

- ▣ Analiza la topología de la densidad electrónica de sistemas cristalinos dentro del marco de la Teoría de Átomos en Moléculas
- ▣ Necesita las funciones de onda all electron del cristal
- ▣ Localiza puntos críticos de la densidad electrónica, determina cuencas atómicas e integra propiedades atómicas (V_i , q_i)

Resultados: E-V

Bases	F	K	Mg	Mn	Fe	Co	Ni	Zn
AOs	13	22	18	27	27	27	27	31



- La fase NM es notablemente superior en energía
- La fase AFM es siempre menor en energía que la FM
- ΔE crece con el tamaño del ion

La polarización de spin parece tener un importante efecto sobre el comportamiento bajo presión del cristal:

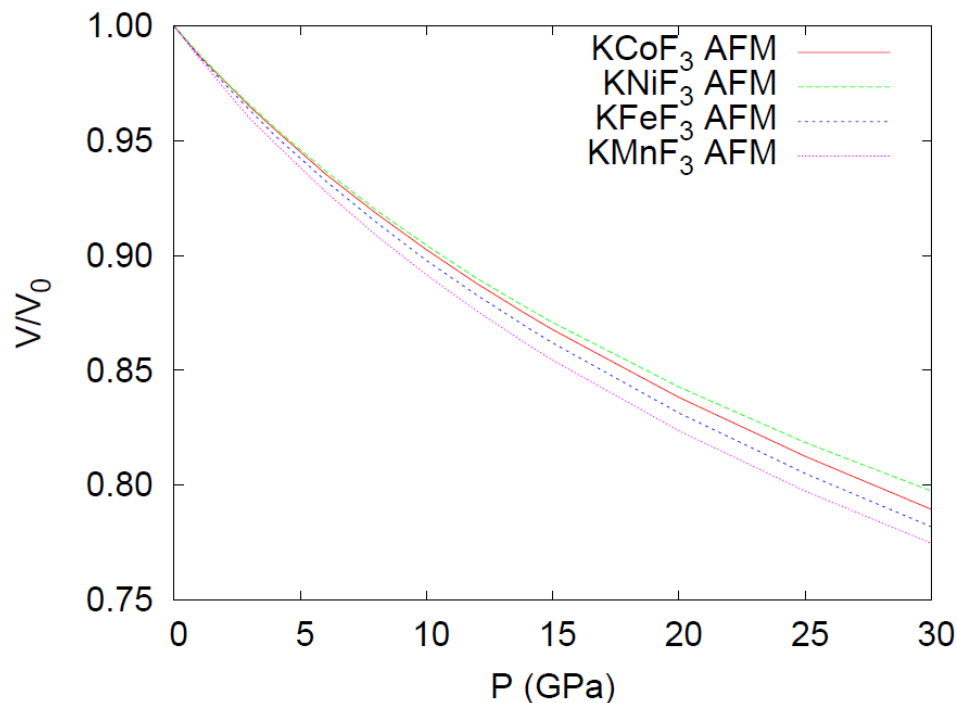
aumento de volumen hasta 14%

B_0 decrece hasta un 20%

	Antiferromagnético		No magnético	
	V (bohr³)	B_0 (GPa)	V (bohr³)	B_0 (GPa)
KMgF ₃	437.03	75.57		
KMnF ₃	524.56	67.25	450.95	81.38
KFeF ₃	500.01	76.92	451.24	76.81
KCoF ₃	479.34	79.08	445.71	82.24
KNiF ₃	461.67	80.47	438.40	90.34
KZnF ₃	467.56	76.87		

Resultados: EOS

	V (bohr ³)	B ₀ (GPa)	B ₀ '
KMgF ₃	437.03	75.57	4.72
	433.84 ^a	71.24 ^a / 77.01 ^c	
KMnF ₃	524.56	67.25	4.57
	496.41 ^b	65 ^b	
KFeF ₃	500.01	76.92	3.86
	471.94 ^a		
KCoF ₃	479.34	79.08	4.13
	453.84 ^b		
KNiF ₃	461.67	80.47	4.38
	435.3 ^b	85 ^b	
KZnF ₃	467.56	70.87	5.02
KZnF ₃	451.46 ^c	54.8 ^c	11 ^c



- razonable buen acuerdo con los datos experimentales
- B₀ aumenta con el número atómico para los metales de capa abierta

[a] G. Vaitheeswaran, et al. Phys. Rev. B 76 (2008) 014107

[b] P. Dovesi et al. Faraday Discuss., 106 (1997) 173

[c] F. Aguado et al. High Pressure Research, 28 (2008) 539

Resultados: Contribuciones atómicas

- ALM: división del cristal en N átomos con V_i

$$V = \sum_i V_i$$

- Compresibilidades locales

$$\kappa_i = -\frac{1}{V_i} \frac{dV_i}{dp}$$

$$B_i = -V_i \frac{dp}{dV_i}$$

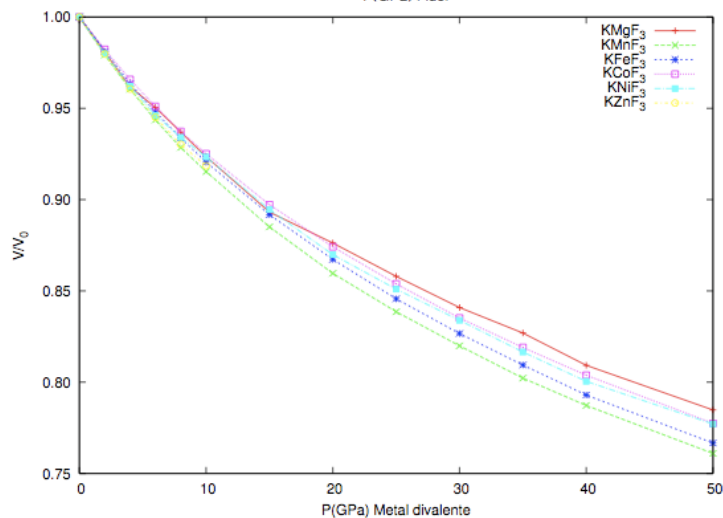
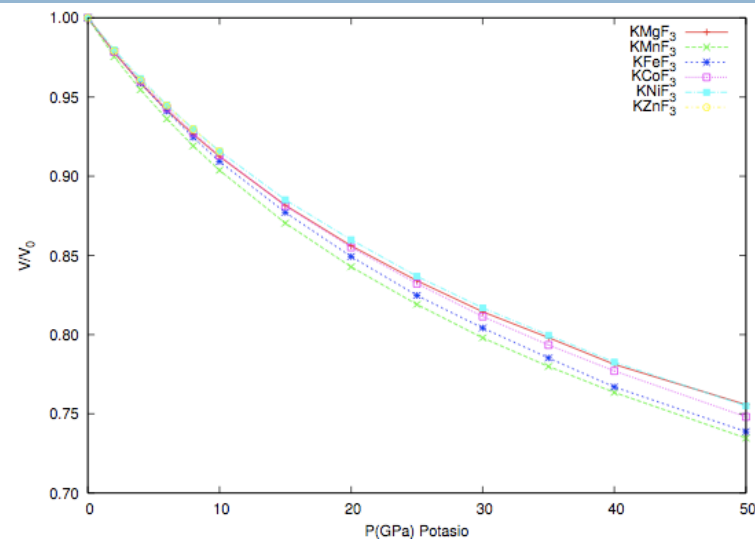
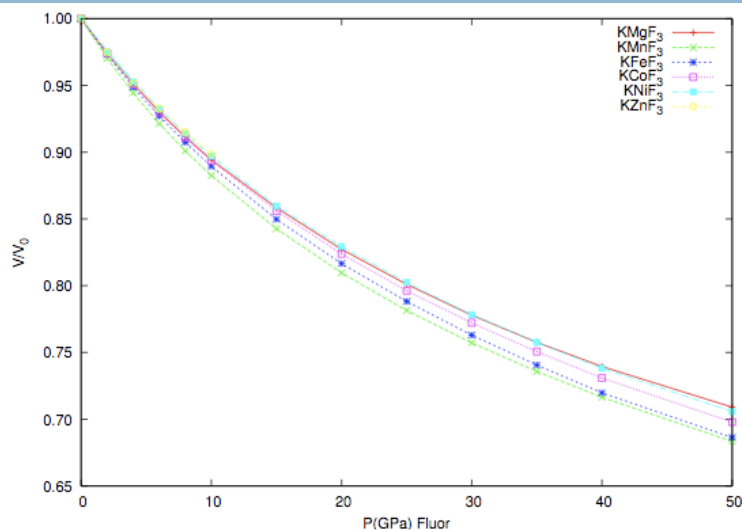
- Compresibilidad total

$$\kappa = \sum_i \frac{V_i}{V} \kappa_i$$

$$B = \sum_i B_i \frac{dV_i}{dV}$$

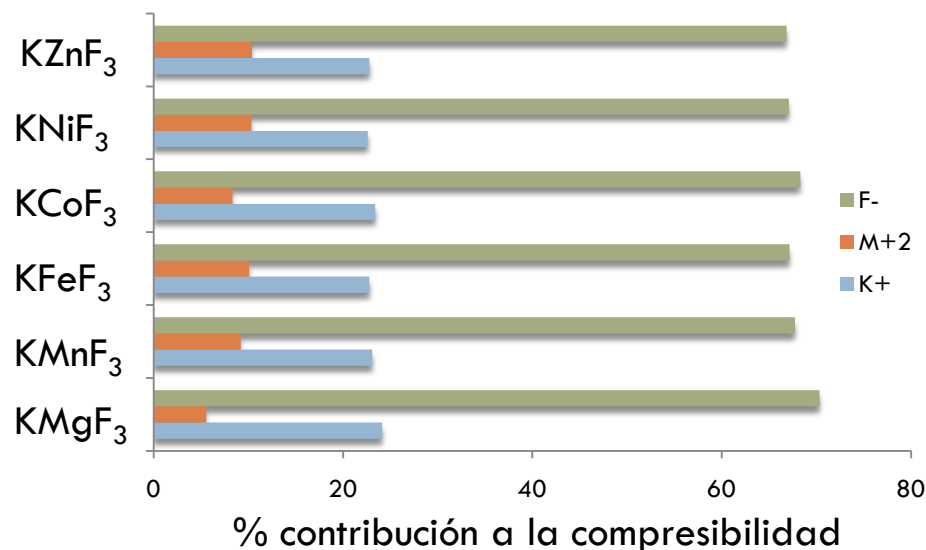
- Suma ponderada de las contribuciones atómicas
- Factor de ponderación es la ocupación fraccional y su primera derivada

Resultados: Contribuciones atómicas



	B_K	B'_K	B_M	B'_M	B_F	B'_F
KMgF ₃	85.05	5.45	95.90	6.77	71.28	4.27
KMnF ₃	76.53	5.07	88.80	5.45	62.17	4.10
KFeF ₃	87.23	4.28	98.56	5.03	69.40	3.57
KCoF ₃	88.42	4.78	105.3	5.22	72.24	3.78
KNiF ₃	93.00	4.75	94.06	6.19	74.75	3.89
KZnF ₃	89.00	5.74	90.25	5.93	72.32	4.91

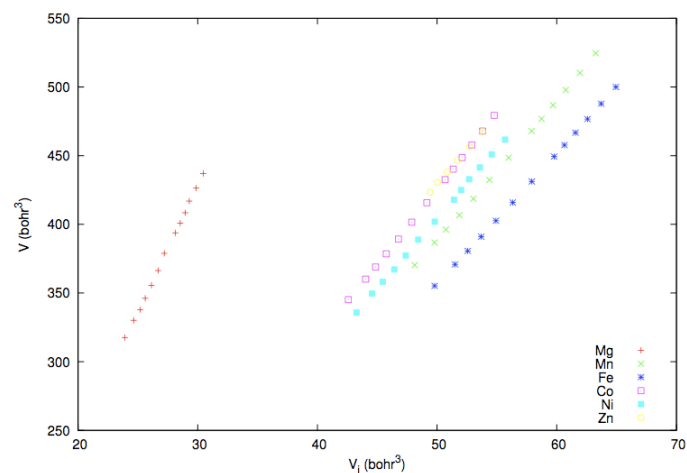
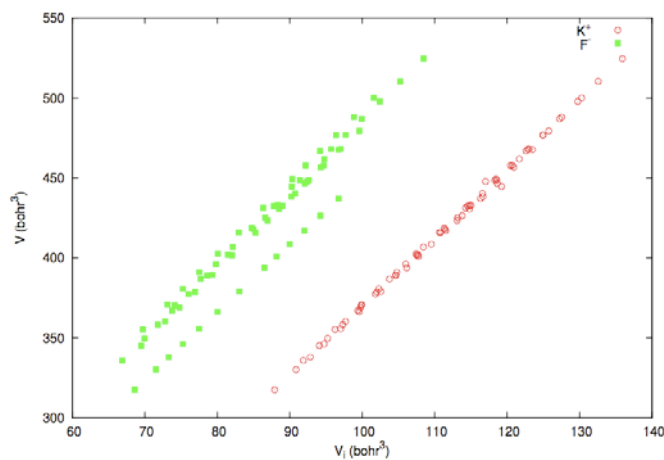
Resultados: EOS atómicas



Cuantificación de comportamiento esperado:

- Comportamiento familia de compuestos
- F es el mas compresible y el que mas contribuye
- Potasio (monovalente) actua casi como un anion
- Catión M (divalente) menos compresible

Transferibilidad de EOS atómicas



Rigorous treatment of first principles data for quasiharmonic thermodynamics of solids.

Alberto Otero de la Roza y Víctor Luaña

alberto@carbono.quimica.uniovi.es

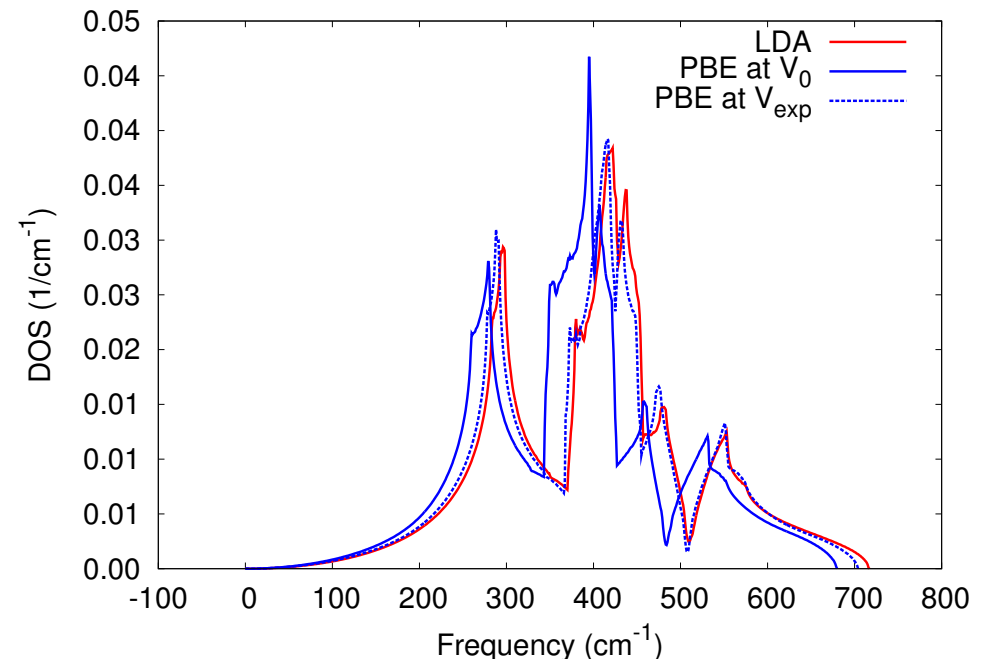
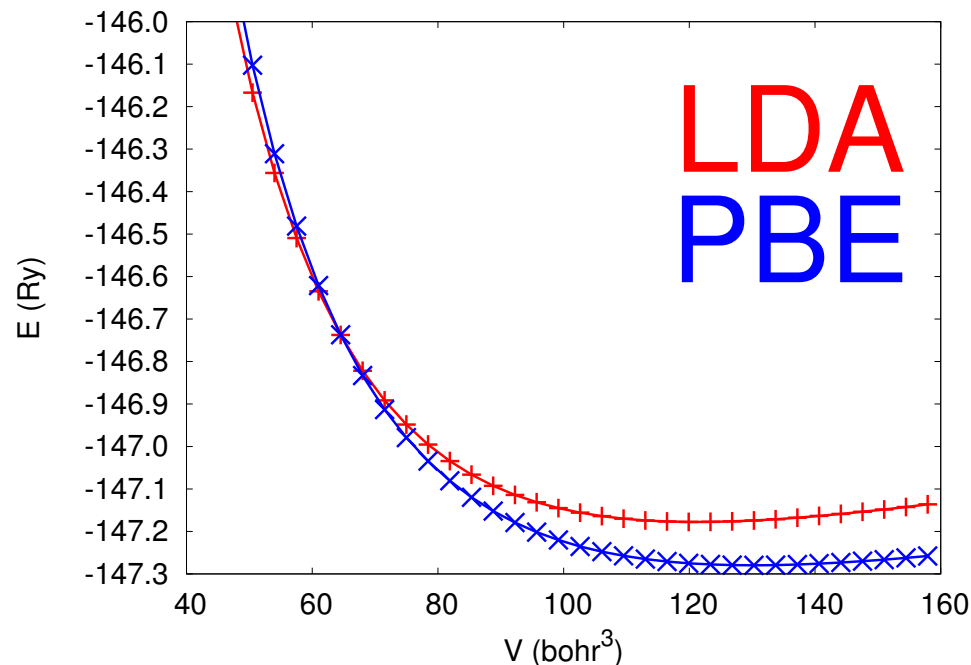
Departamento de Química Física y Analítica

Universidad de Oviedo, Spain

Workshop MALTA 2011, 23 al 26 de enero, Miraflores (Madrid)

Thermodynamic properties and EOS of MgO.

- MgO: component of the Earth's mantle—elastic properties at high p and T .
- Pressure scale. A very accurate $V(p, T)$ is needed.
- Starting point: DFT (PW, LDA and GGA) on a grid of volumes. With linear response theory, phonon DOS at every volume.
- Other examples: diamond, fcc Al.



Step 1: the equation of state.

- **Non-polynomial EOS.** Non-linear fit. For instance, AP2.

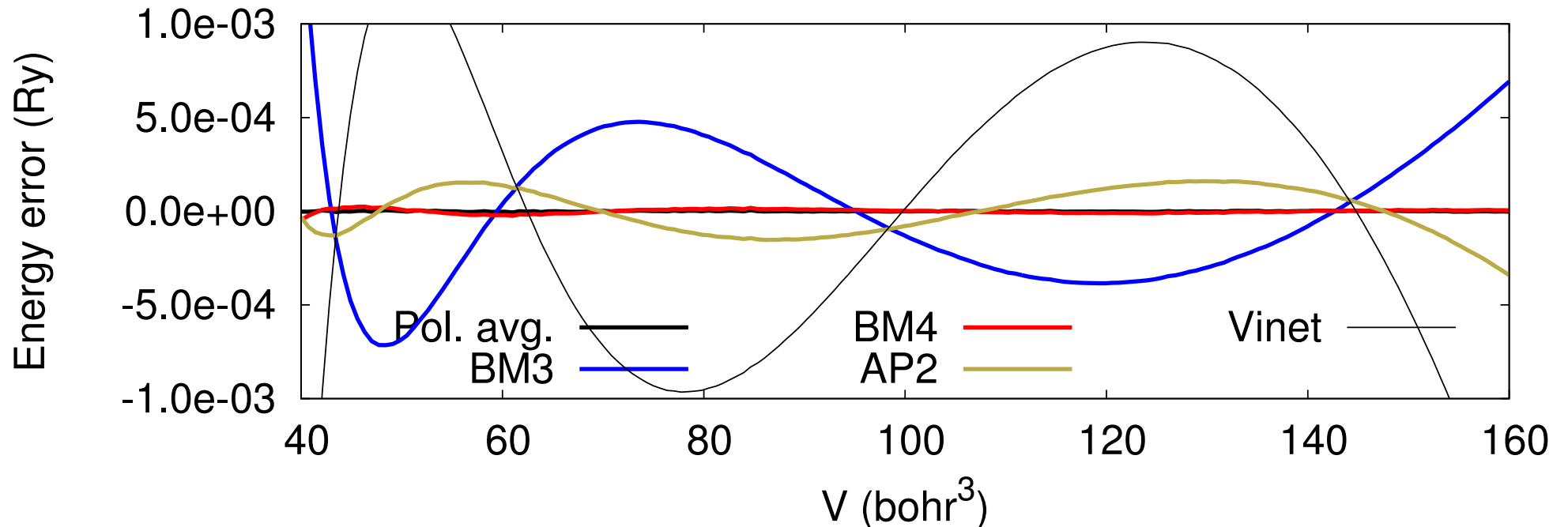
$$\begin{aligned}
 E &= E_0 + 9B_0 V_0 \left\{ [\Gamma(-2, c_0 \eta) - \Gamma(-2, c_0)] c_0^2 e^{c_0} \right. \\
 &\quad + [\Gamma(-1, c_0 \eta) - \Gamma(-1, c_0)] c_0 (c_2 - 1) e^{c_0} \\
 &\quad \left. - [\Gamma(0, c_0 \eta) - \Gamma(0, c_0)] 2c_2 e^{c_0} + \frac{c_2}{c_0} [e^{c_0(1-\eta)} - 1] \right\} \\
 p &= 3B_0 \frac{1-\eta}{\eta^5} e^{c_0(1-\eta)} [1 + c_2 \eta (1-\eta)],
 \end{aligned}$$

- **Polynomial EOS.** Taylor expansion of the strain energy, $E = \sum_{k=0}^n c_k f^k$. Impose conditions on the expression above. Polynomial fits. For instance, Eulerian strain (Birch-Murnaghan series). The BM4 is:

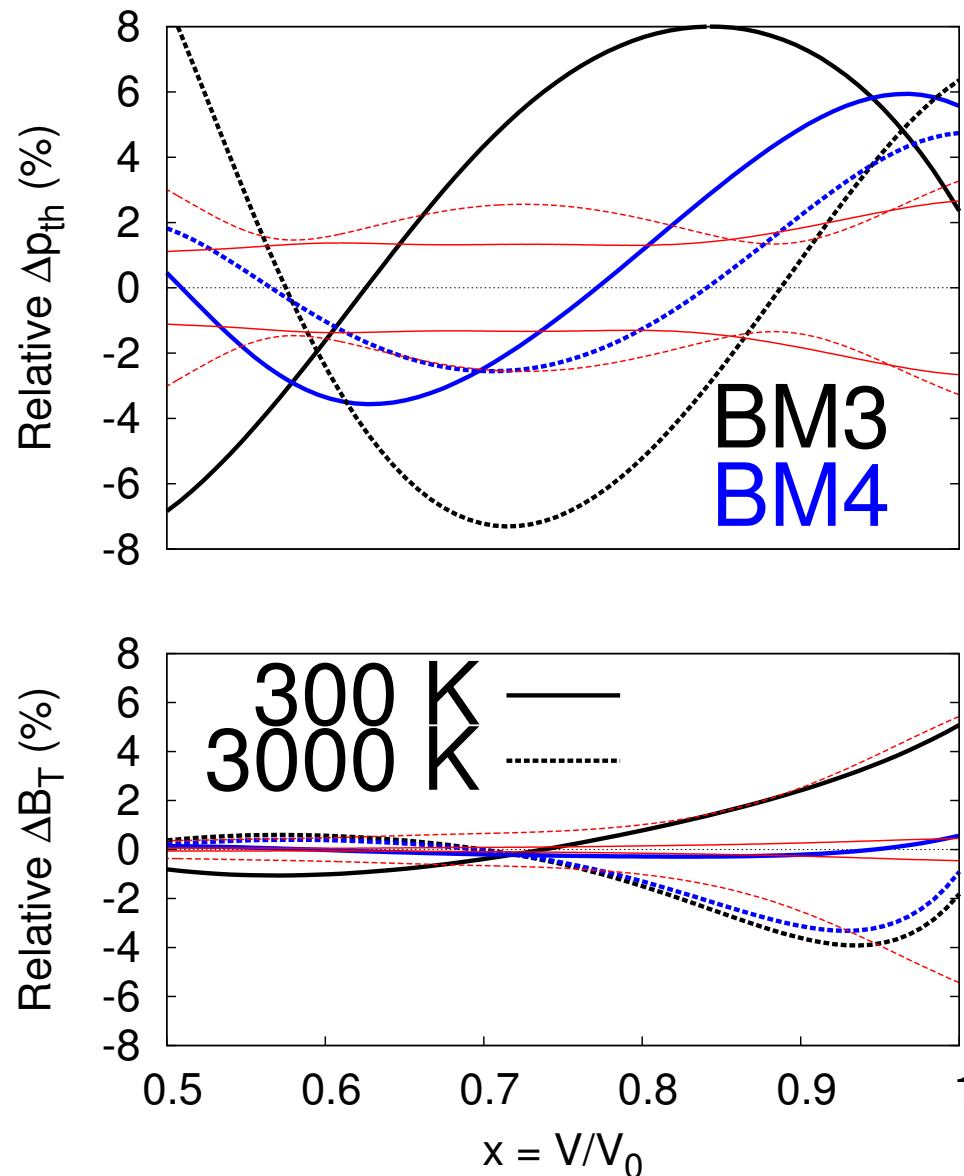
$$\begin{aligned}
 f &= \frac{1}{2} \left[(V_r/V)^{2/3} - 1 \right], \\
 E &= E_0 + \frac{3}{8} V_0 B_0 f^2 \{ (9H - 63B'_0 + 143) f^2 + 12(B'_0 - 4) f + 12 \}, \\
 p &= \frac{1}{2} B_0 (2f + 1)^{5/2} \{ (9H - 63B'_0 + 143) f^2 + 9(B'_0 - 4) f + 6 \},
 \end{aligned}$$

Step 1: the equation of state.

	E_0 (Ry)	V_0 (bohr ³)	B_0 (GPa)	B'_0	B''_0 (GPa ⁻¹)
BM3	-73.6401830	129.6757	158.70	3.9457	-0.0242
BM4	-73.6398599	130.0741	151.23	4.1001	-0.0279
Vinet	-73.6390622	130.7726	132.25	4.8306	-0.0584
AP2	-73.6397102	130.0648	147.98	4.3026	-0.0367
BM average	-73.6398334(69)	130.0792(50)	150.49(26)	4.1284(91)	-0.0266(22)



Step 1: the equation of state.

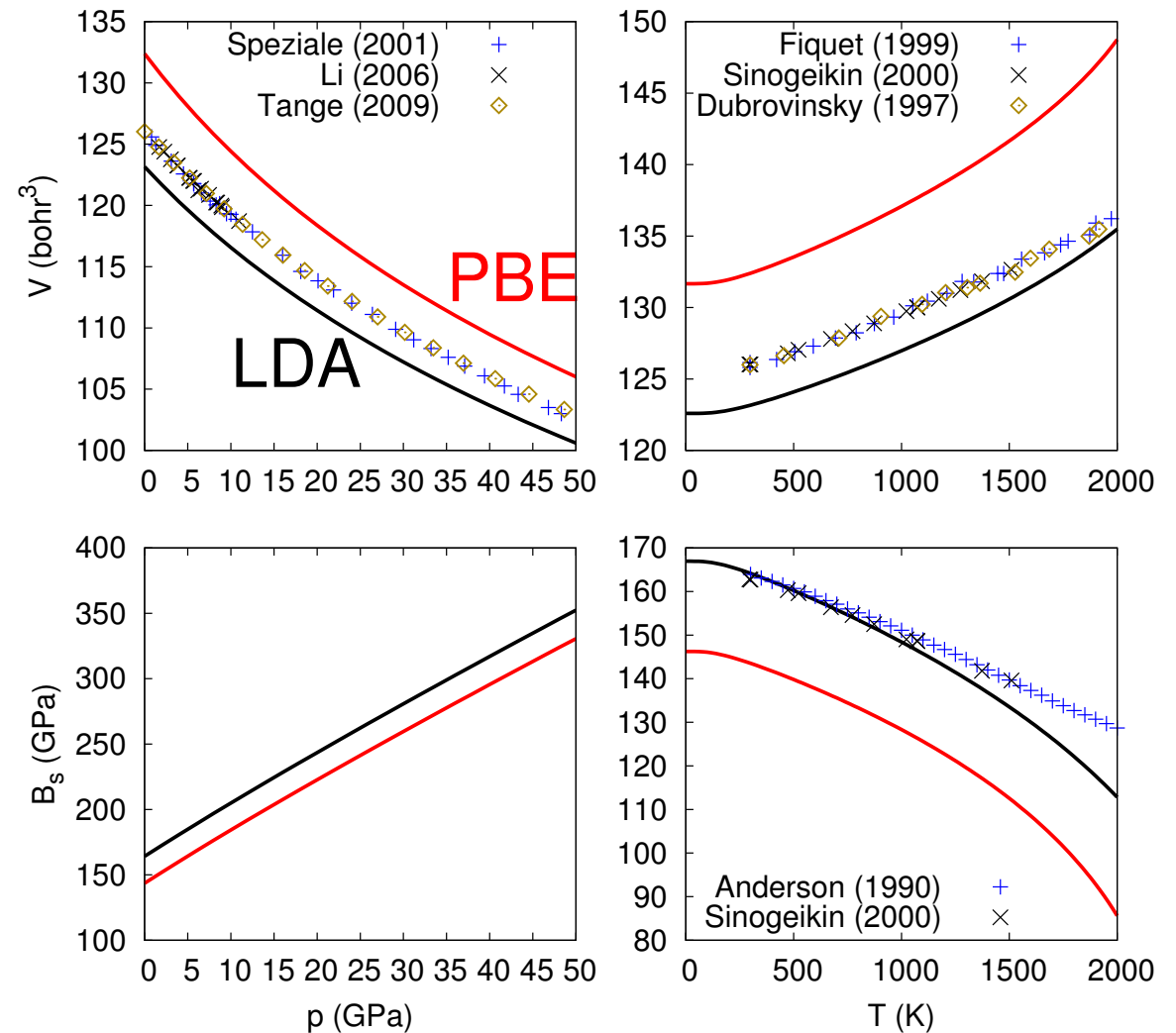


We propose a strain polynomial average to high degrees. Properties:

- Robust linear fit.
- Detection of noise and bad quality of data.
- Statistics with polynomials allow establishing an error bar for calculated properties.
- Good quality derivatives of the (free) energy. Can not extrapolate, but it is possible to generate V_0 , B_0 for lower order EOS.

Empirical energy corrections.

- The choice of exchange-correlation functional is the main source of uncertainty in DFT.
- LDA overbinds and PBE underbinds.
- No systematic ways of improving the results.



Empirical energy corrections.

The systematic deviations in the exchange-correlation functionals can be corrected by using one or two accurate experimental results: ambient conditions volume (V_{exp}^0) and bulk modulus (B_{exp}^0). The non-equilibrium Gibbs free energy:

$$G^*(\mathbf{x}, V; p, T) = E_{\text{sta}}(\mathbf{x}, V) + pV + F_{\text{vib}}^*(\mathbf{x}, V; T)$$

Static energy corrections using the observation: p/B_0 vs. V/V_0 transferable with V_0 and B_0 the static equilibrium volume and bulk modulus.

$$\frac{\tilde{E}'_{\text{sta}}(V)}{B_{\text{exp}}} = \frac{E'_{\text{sta}}\left(V \frac{V_0}{V_{\text{exp}}}\right)}{B_0} \quad ; \quad \tilde{E}_{\text{sta}}(V) = E_{\text{sta}}(V_0) + \frac{B_{\text{exp}} V_{\text{exp}}}{B_0 V_0} \left[E_{\text{sta}}\left(V \frac{V_0}{V_{\text{exp}}}\right) - E_{\text{sta}}(V_0) \right]$$

The experimental V_{exp} and B_{exp} extrapolated to *static* conditions are missing. To obtain them, impose:

$$-\frac{\partial \tilde{G}^*}{\partial V}(V; p, T) = 0 = \tilde{p}_{\text{sta}} - p + p_{\text{th}}$$

$$B_{\text{exp}}^0 = \left(V \frac{\partial^2 F^*}{\partial V^2} \right) (V_{\text{exp}}^0, T^0) = \frac{B_{\text{exp}}}{B_0} B_{\text{sta}}(fV_0) + B_T(V_{\text{exp}}^0, T^0) - B_{\text{sta}}(V_{\text{exp}}^0)$$

Empirical energy corrections.

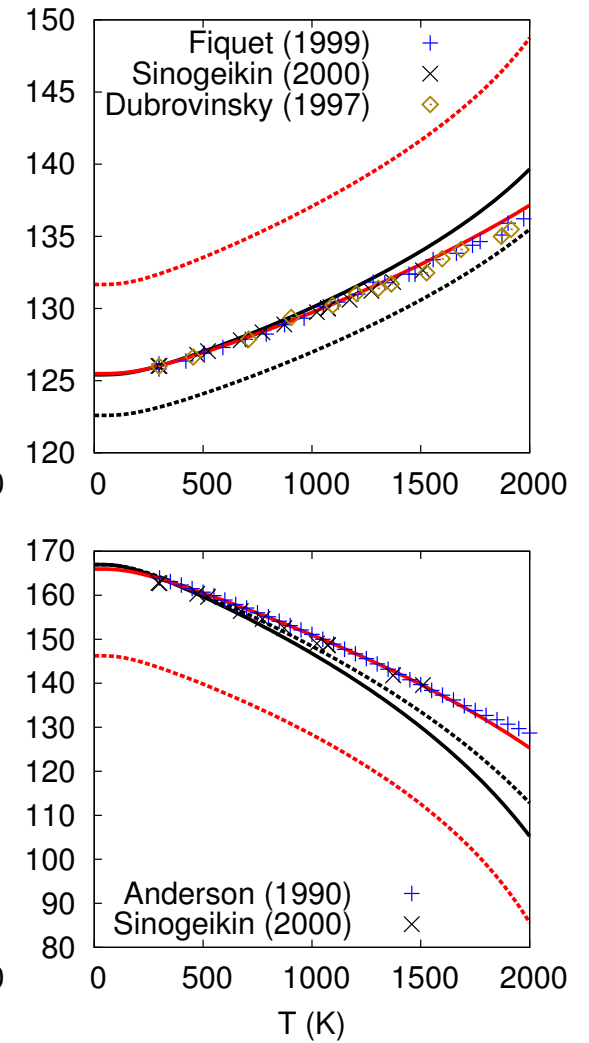
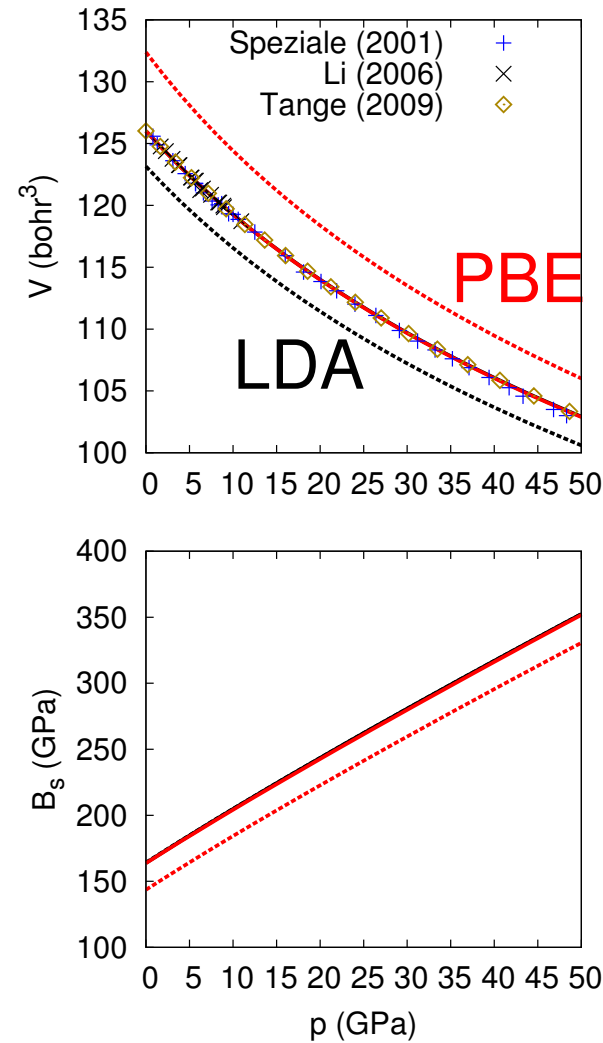
Definition of the static energy correction:

$$\frac{B_{\text{sta}}(fV_0)}{p_{\text{sta}}(fV_0)} =$$

$$= \frac{B_{\text{exp}}^0 - B_T(V_{\text{exp}}^0) + B_{\text{sta}}(V_{\text{exp}}^0)}{p_{\text{th}}(V_{\text{exp}}^0, T^0)}$$

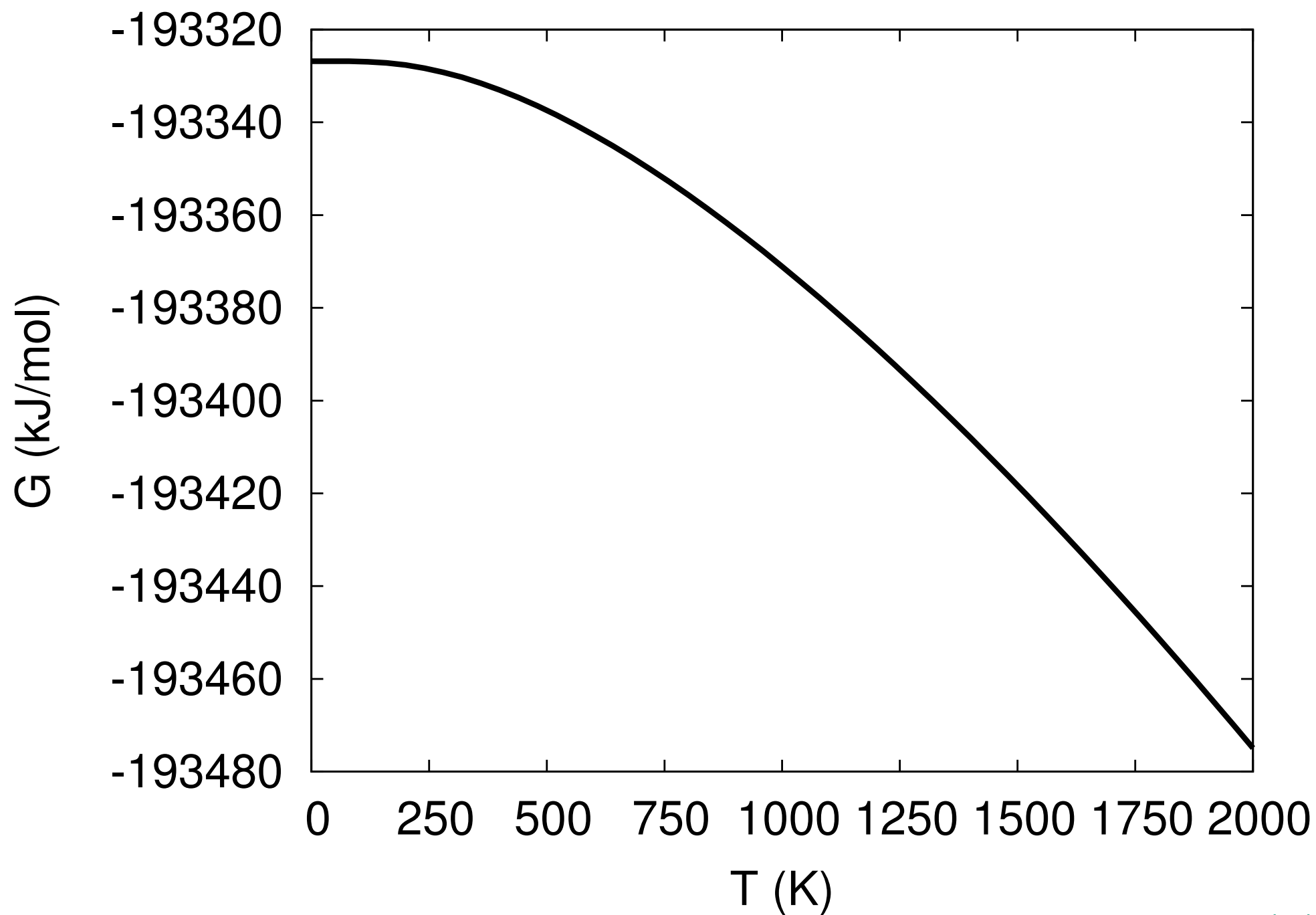
$$f = \frac{V_{\text{exp}}^0}{V_{\text{exp}}}$$

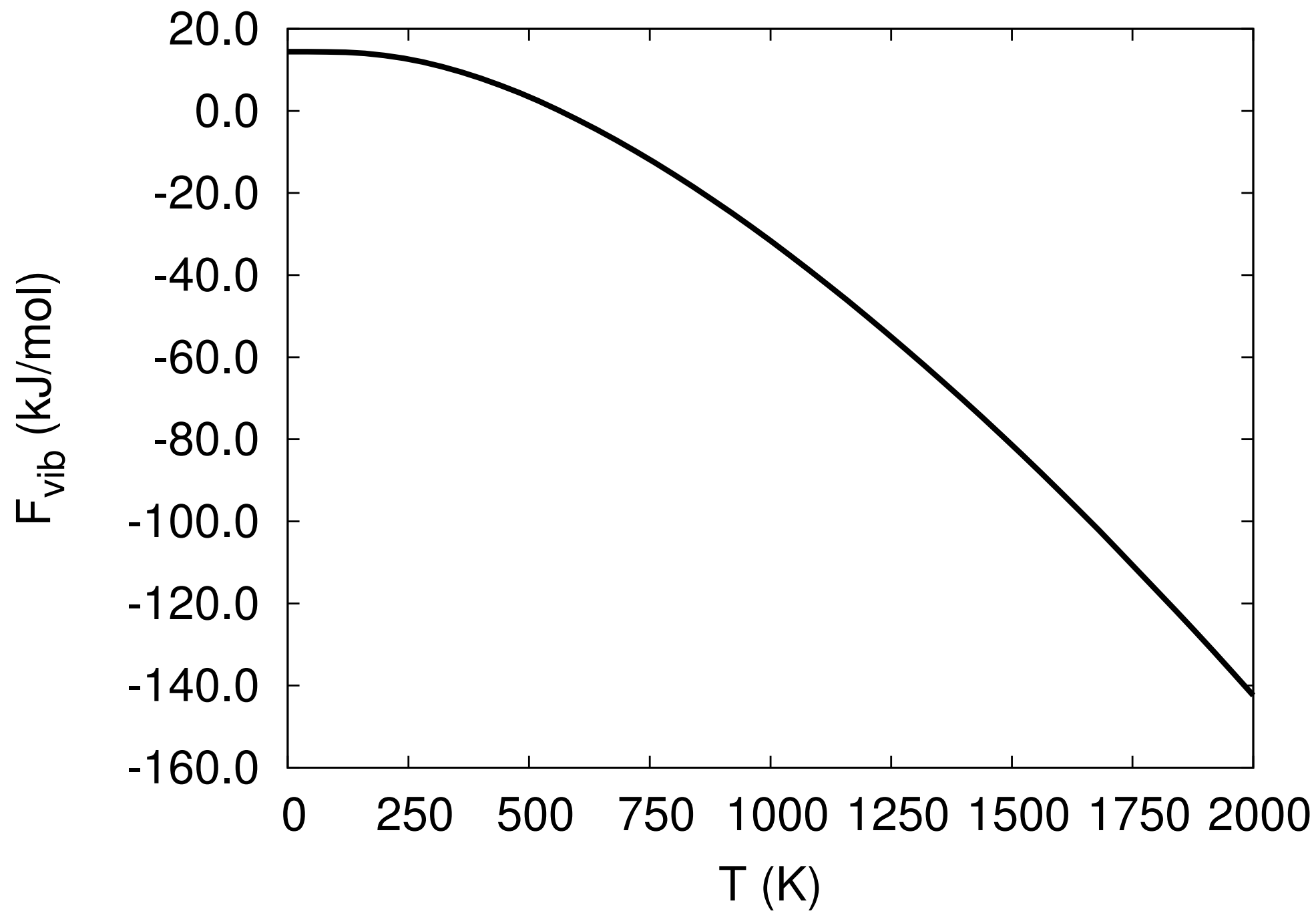
$$B_{\text{exp}} = -B_0 \frac{p_{\text{th}}(fV_0, T^0)}{p_{\text{sta}}(fV_0)}$$

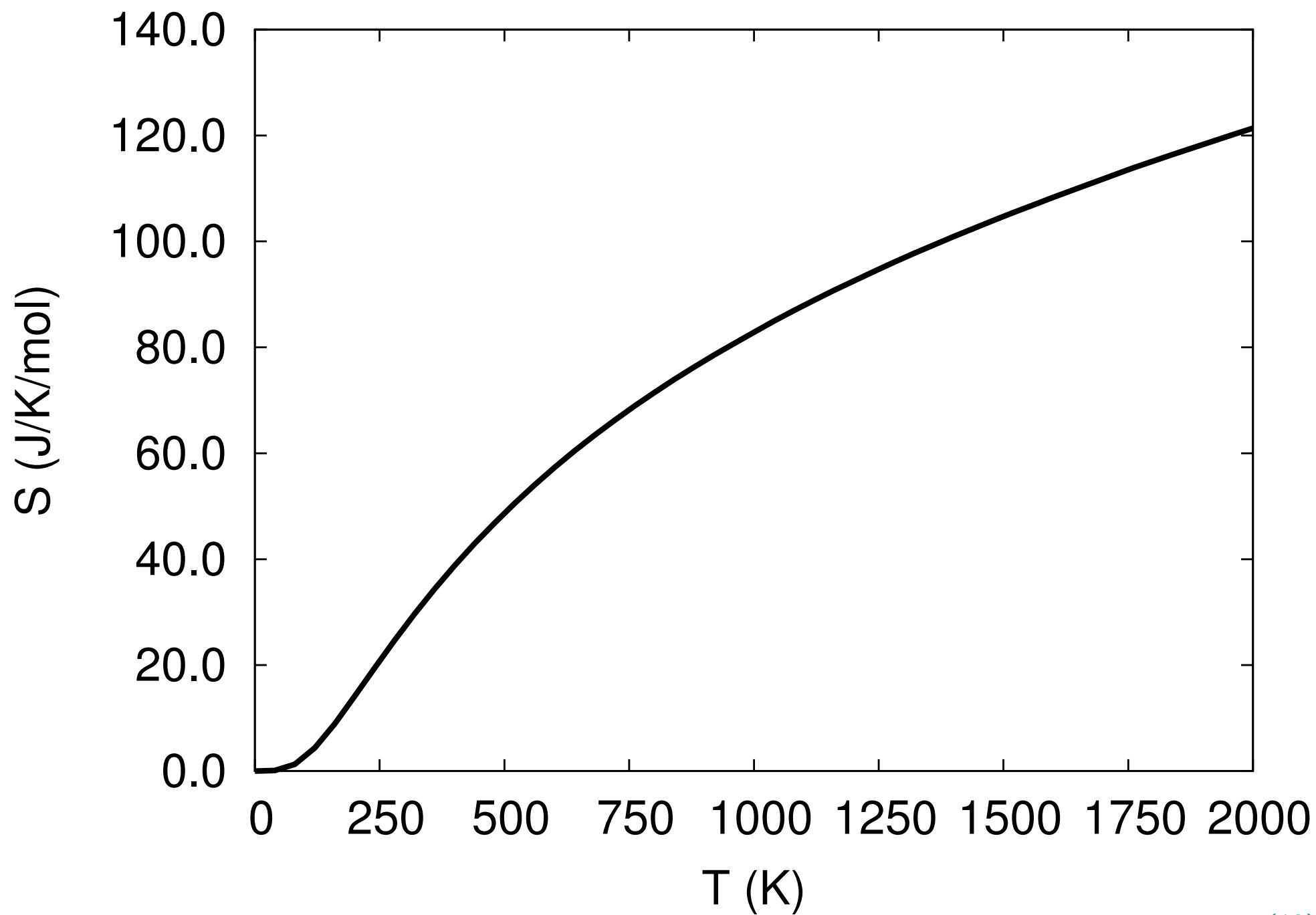


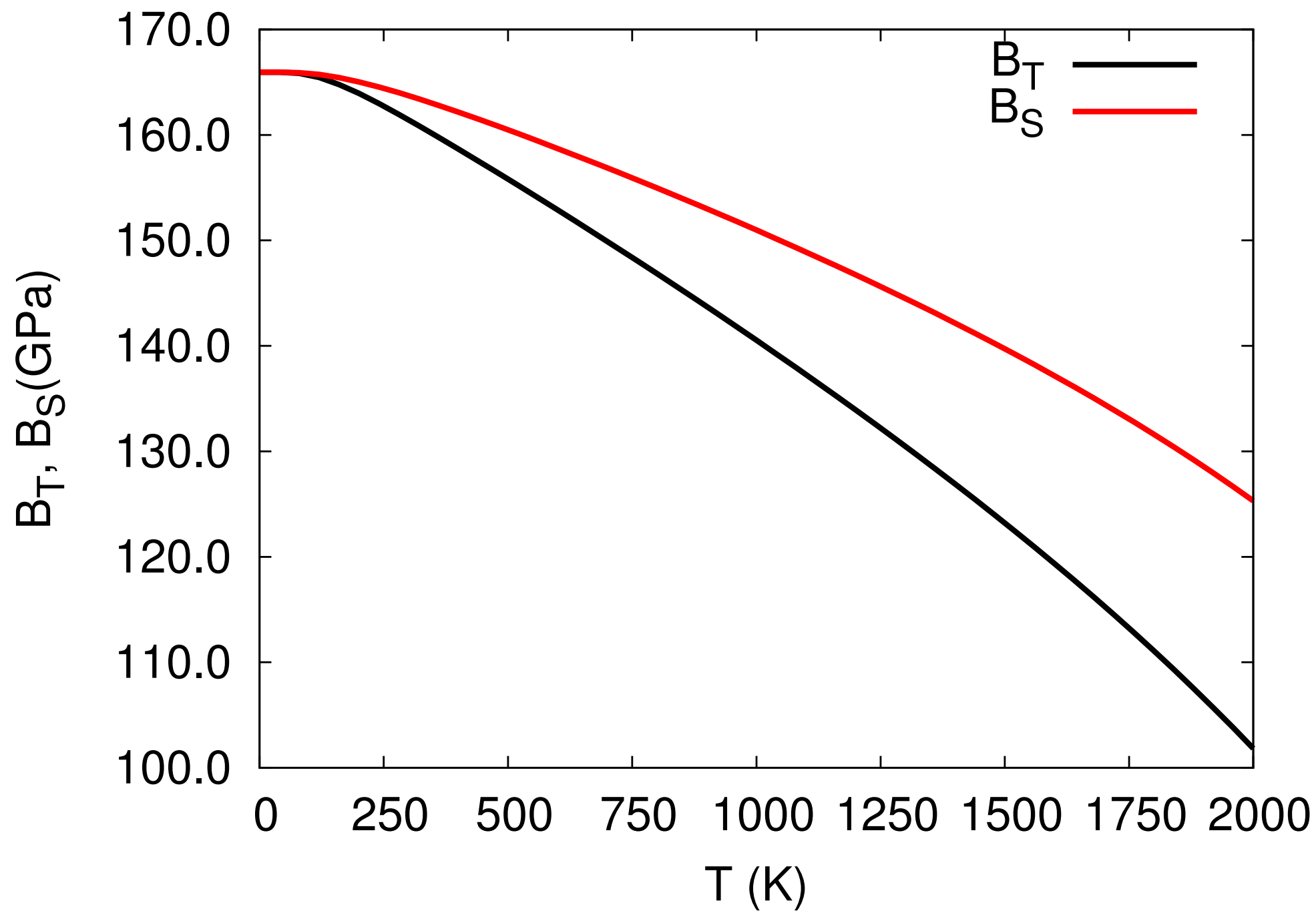
The gibbs2 code.

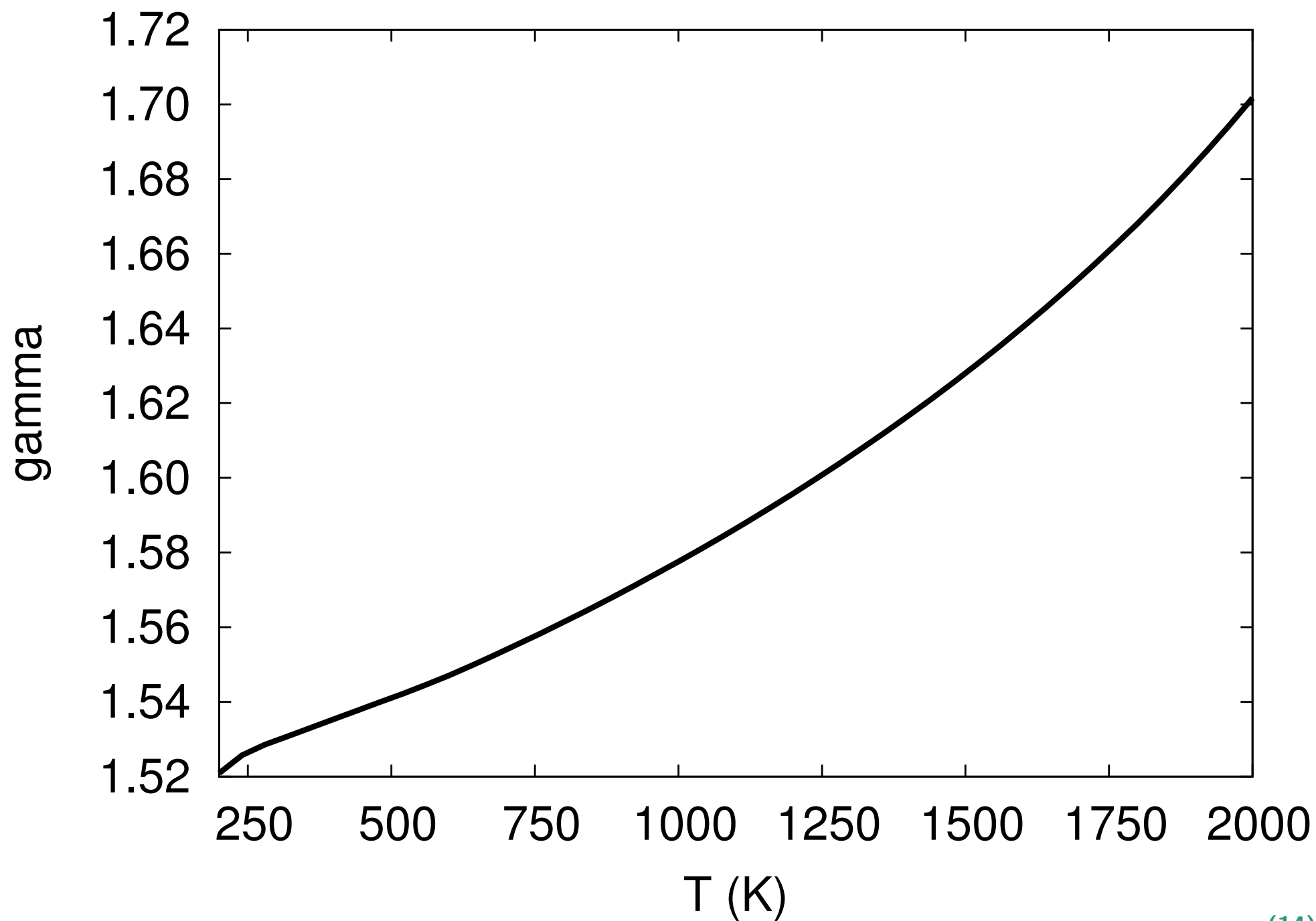
- Fortran code for the treatment of first principles data for thermodynamic calculations under the quasiharmonic approximation.
- Careful treatment of (free) energy fits. A good number of EOS are implemented, using linear and non-linear fits.
- Empirical energy corrections.
- Several temperature models, depending on how much information about the system is known.
- Soon to be published under open license.

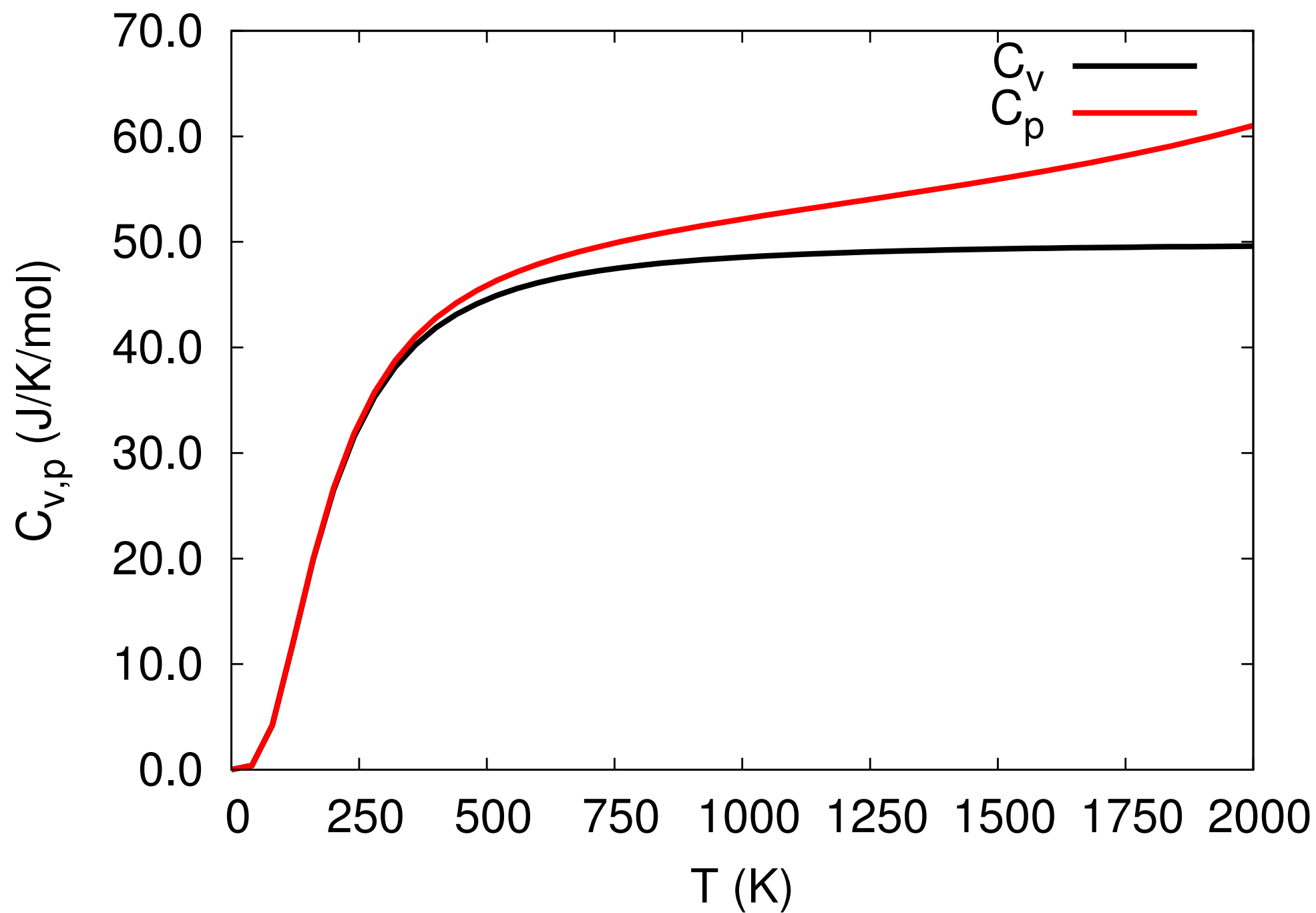


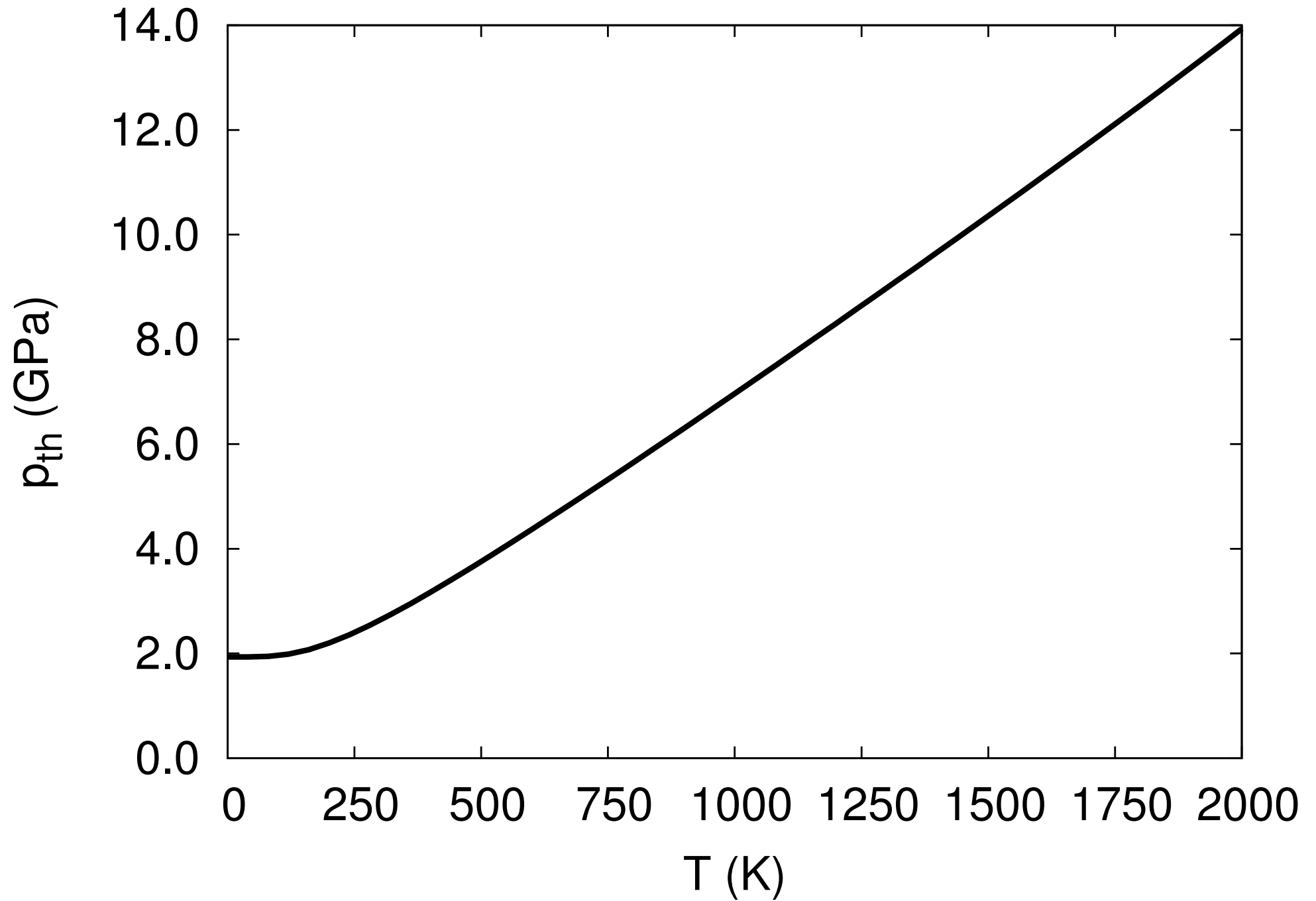


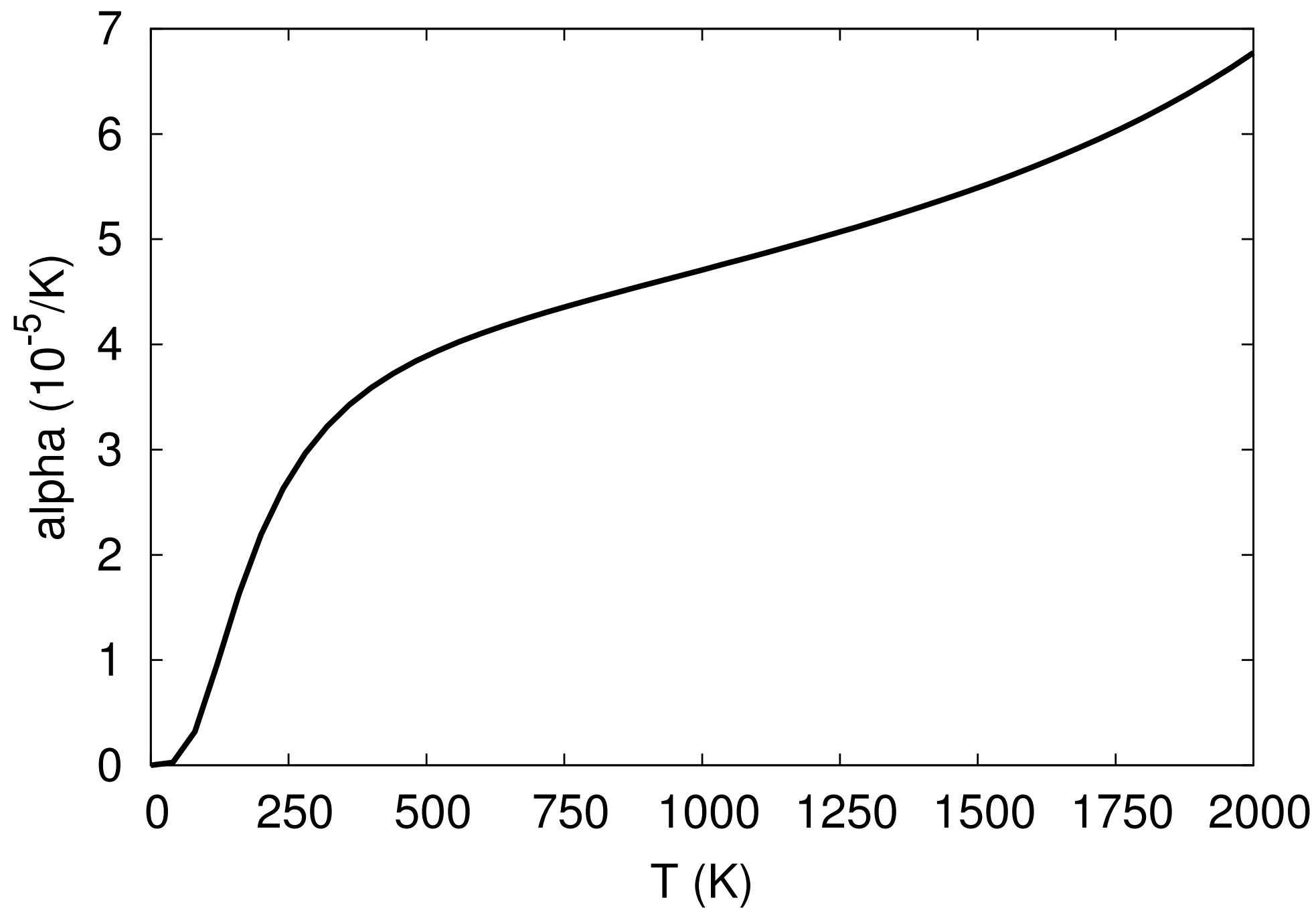












Conclusions.

Accurate and systematic treatment of first principles data for quasiharmonic thermodynamics of solids can be achieved by:

- Careful use of equations of state for interpolation and calculation of derivatives.
- Correction of DFT systematic deviations regarding the static energy.
- These techniques have been implemented in the GIBBS2 code.

Estudio de polimorfos de TiO_2

DFT+U

Ángel Morales García

Universidad Complutense de Madrid

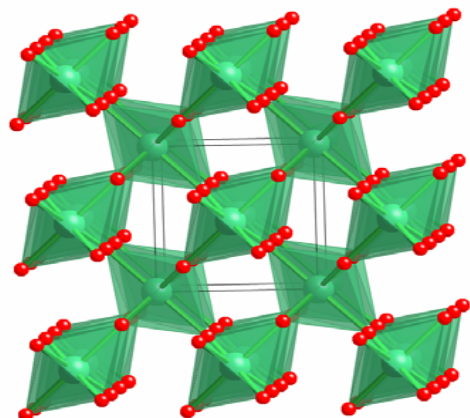


QUIMAPRES

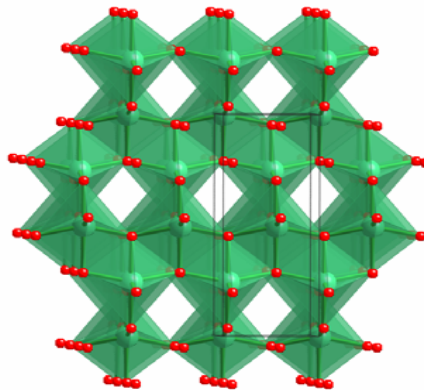
Miraflores de la Sierra (Madrid)
2011

MOTIVACIÓN

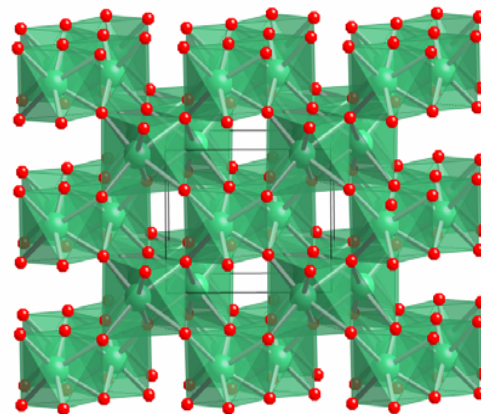
- Estudio computacional de compuestos oxifluorados de metales de transición ($M^{3+}OF$): propiedades eléctricas; electrodos baterías de litio; **TiOF**.
- Búsqueda de una referencia: TiO_2 (rutilo, anatasa y columbita). Metodología de cálculo GGA + U.



Rutilo



Anatasa



Columbita

Fase	G. Espacial	Z	Parámetros de celda (Å)	ρ (g/cm ³)
Rutilo	$P4_2/mnm$ (tetragonal)	2	$a = 4.59$; $c = 2.96$	4.13
Anatasa	$I4_1/amd$ (tetragonal)	4	$a = 3.79$; $c = 9.51$	3.79
Columbita	$Pbca$ (ortorómbico)	4	$a = 4.55$; $b = 5.46$; $c = 9.51$	4.33

J. Haines, and J. M. Leger,
Physica B **192**, 233 (1993).

OBJETIVOS

- Estudio de las propiedades estructurales, electrónicas, así como estabilidad relativa de fases en los tres polimorfos de TiO_2 (anatasa, rutilo y columbita) que permita llegar a una situación de compromiso en el valor de $U_{efectiva}$.
- Emplear la metodología de cálculo GGA + U en el estudio teórico del compuesto TiOF.

**TiOF; Ti^{3+}
(1e⁻ en orbital t_{2g})**



Metodología de cálculo: *Teoría del Funcional de la Densidad (DFT).*

Composición y estructura

Leyes básicas de la Física: Mecánica Cuántica

Energía Total, estructura cristalina y electrónica

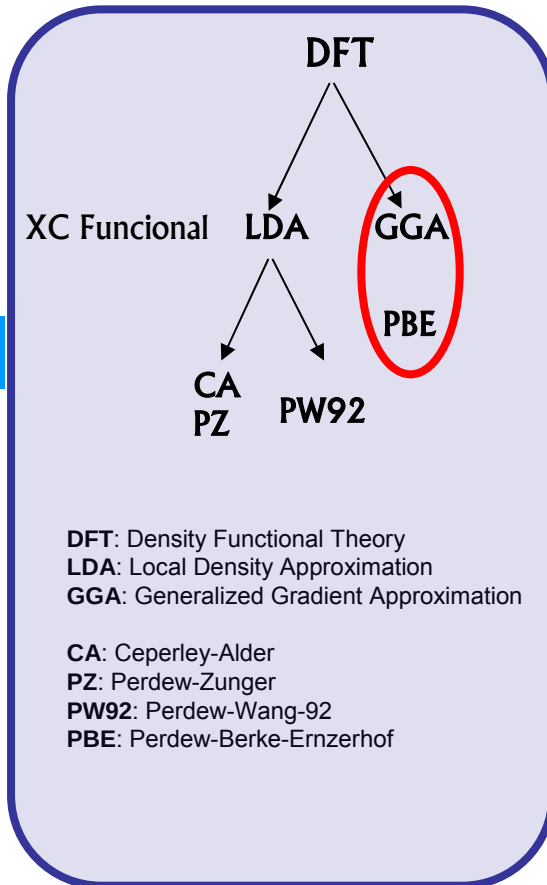
*Predecir y entender las
propiedades de los materiales*

Funcionales en DFT
Tratan el intercambio y la correlación

Generalized Gradient Approximation (GGA)

GGA+U

**U es el parámetro de Hubbard para el
tratamiento explícito de la correlación.**



DFT: resolución ec. Schrödinger

$$\hat{H}(\vec{r})\psi_k^n(\vec{r}) = \left\{ -\frac{\hbar^2}{2m_e} \nabla_{\vec{r}}^2 + \hat{V}_c + \hat{V}_{xc} \right\} \psi_k^n(\vec{r}) = \varepsilon_n(\vec{r}) \psi_k^n(\vec{r})$$

$$E_{xc} = F[\rho(r)] \quad V_{xc}[\rho] = \frac{\partial E_{xc}[\rho]}{\partial \rho}$$

El potencial de intercambio y correlación es desconocido: LDA, GGA,...

La calidad de los resultados DFT depende de cómo se defina el término V_{xc}

Limitación DFT: band gap $\longrightarrow$ DFT+U

Repulsión Culombica descrita hamiltoniano de Hubbard

¿GGA+U?

TiOF; Ti^{3+} (1e⁻ en orbital t_{2g})

Perebeinos y Vogt, PRB **69**, 115102 (2004)
estudian la transición Jahn-Teller en TiF_3 ,
empleando la metodología LDA+U

$$E_X^{GGA} = \int \rho(r)^{4/3} g(x) dr$$

$$g(x) = \alpha = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3}$$

$$E_C = E_C^{Op} + E_C^{\alpha\alpha} + E_C^{\beta\beta}$$

Parte no columbica

$$x = |\nabla \rho| \rho^{-4/3}$$

$$\longrightarrow E_X^{GGA} = E_X^{LDA}$$

$$H = \frac{U}{2} \sum_{m,m',s} n_{m,s} n_{m',-s} + \frac{(U-J)}{2} \sum_{m \neq m',s} n_{m,s} n_{m',s}$$

donde $n_{m,s}$ es el estado de ocupación de los electrones d con numero magnético m y spin s.

$$E_{GGA+U} = E_{GGA} + \frac{U-J}{2} \sum_s (n_{m,s} - n_{m,s}^2)$$

¿Valor del parámetro U?

Comparación con datos experimentales

Intervalo estudiado para U: 0 a 10 eV



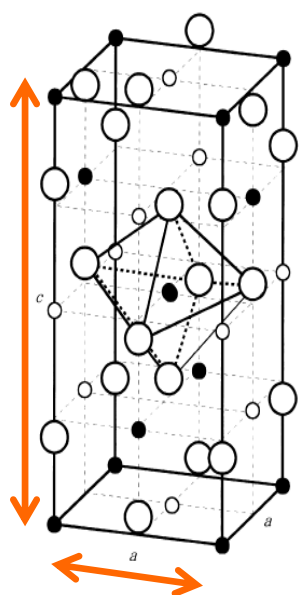
Resultados:

1. Análisis de la estructura cristalina
2. Análisis de la estructura electrónica
3. Estabilidad relativa de polimorfos
4. Curvas E - V. Ecuación de estado
5. Presión de transición

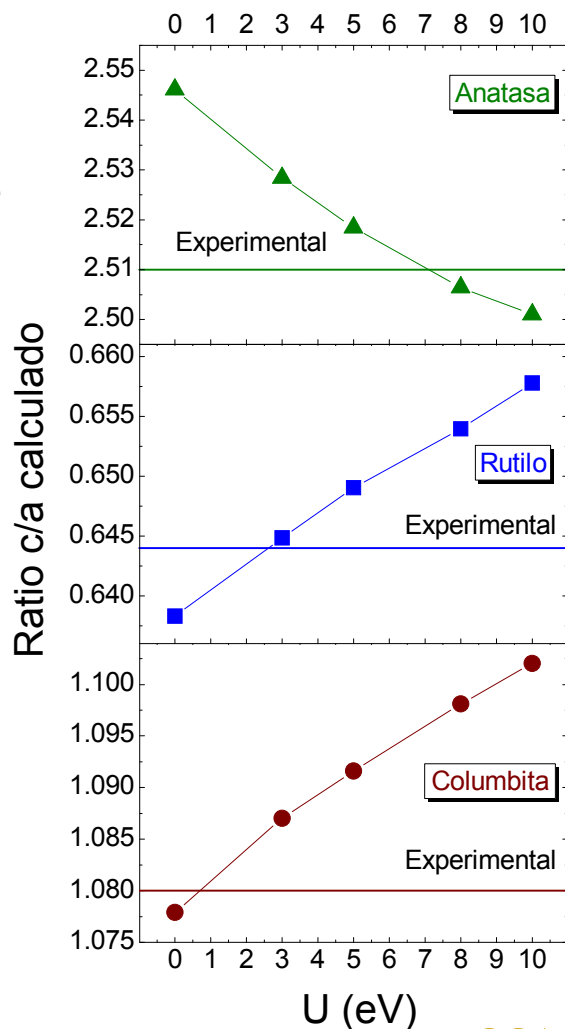


1. Análisis de la estructura cristalina.

Relación c/a en TiO_2



○ Oxígeno
● Titanio
Anatasa



GGA + U mejora los resultados de GGA

**Intervalo apropiado:
1 eV < U < 7 eV**

Polymorph	Method	U (eV)	a (Å)	b (Å)	c (Å)	(c/a)
ANATASA						
	GGA		3.807 (0.59)		9.693 (1.88)	2.545 (1.23)
	GGA+U	3	3.853 (1.81)		9.742 (2.39)	2.529 (0.60)
	GGA+U	5	3.881 (2.55)		9.774 (2.73)	2.518 (0.16)
	GGA+U	8	3.922 (3.63)		9.830 (3.32)	2.506 (-0.32)
	GGA+U	10	3.947 (4.29)		9.871 (3.75)	2.501 (-0.52)
	Experiment		3.7845		9.5143	2.514
RUTILO						
	GGA		4.650 (1.23)		2.968 (0.31)	0.638 (-0.93)
	GGA+U	3	4.671 (1.68)		3.012 (1.80)	0.645 (0.16)
	GGA+U	5	4.687 (2.03)		3.042 (2.82)	0.649 (0.78)
	GGA+U	8	4.709 (2.51)		3.081 (4.13)	0.654 (1.55)
	GGA+U	10	4.725 (2.86)		3.108 (5.05)	0.658 (2.17)
	Experiment		4.5937		2.9587	0.644
COLUMBITA						
	GGA		4.579 (0.84)	5.576 (1.51)	4.936 (0.61)	1.078 (-0.19)
	GGA+U	3	4.607 (1.45)	5.585 (1.67)	5.008 (2.08)	1.087 (0.65)
	GGA+U	5	4.629 (1.94)	5.603 (2.00)	5.053 (3.00)	1.092 (1.11)
	GGA+U	8	4.658 (2.58)	5.635 (2.59)	5.115 (4.26)	1.098 (1.67)
	GGA+U	10	4.674 (2.93)	5.664 (3.11)	5.151 (4.99)	1.102 (2.04)
	Experiment		4.541	5.493	4.906	1.080

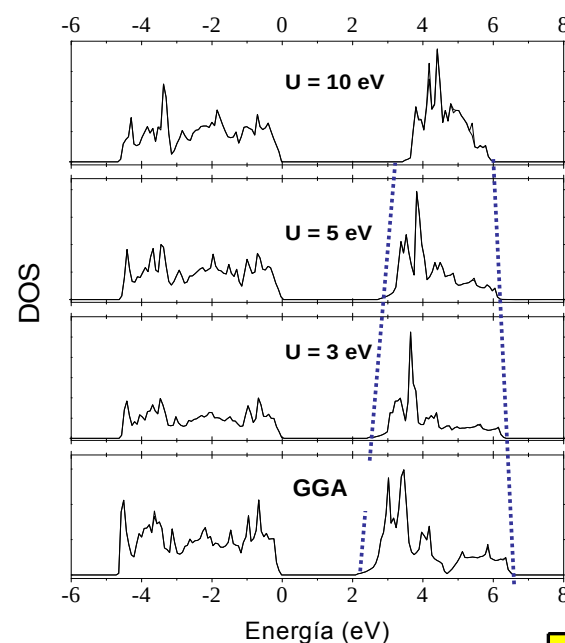
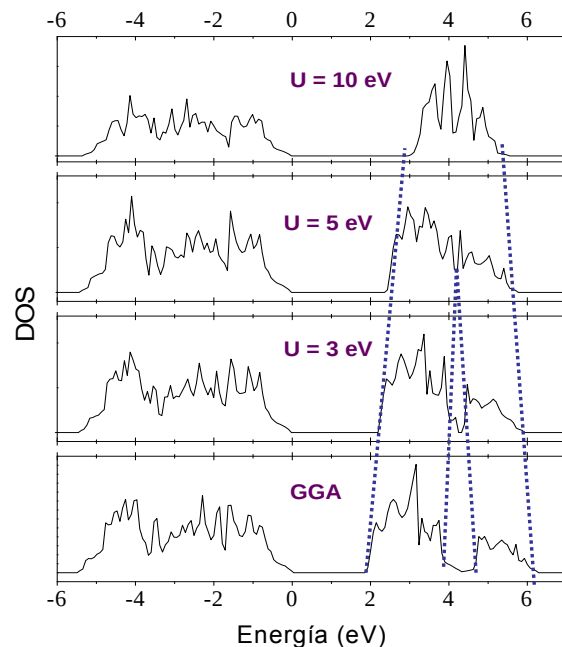
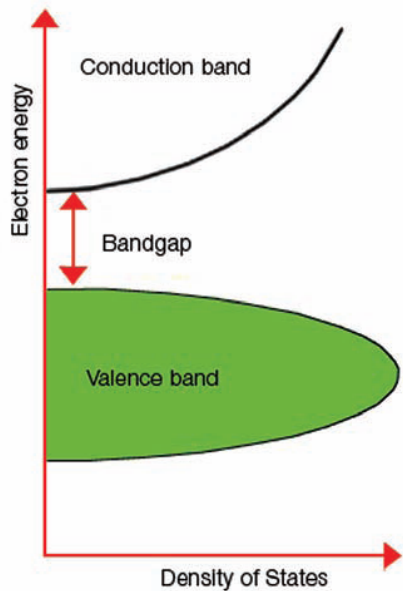


2. Análisis de la estructura electrónica.

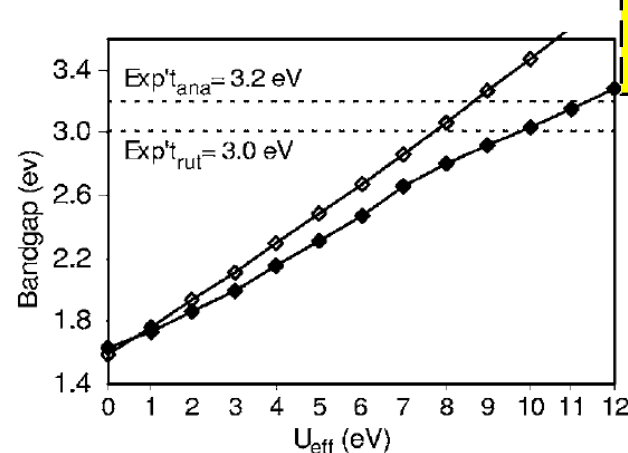
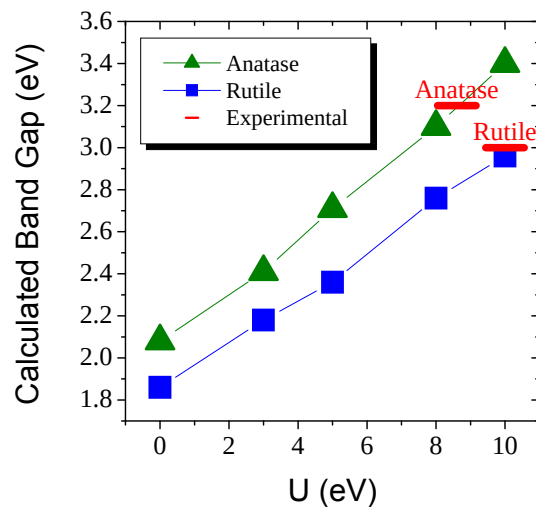
rutilo

anatasa

Densidad de estados (DOS) calculada en TiO_2



GGA + U mejora los resultados de GGA



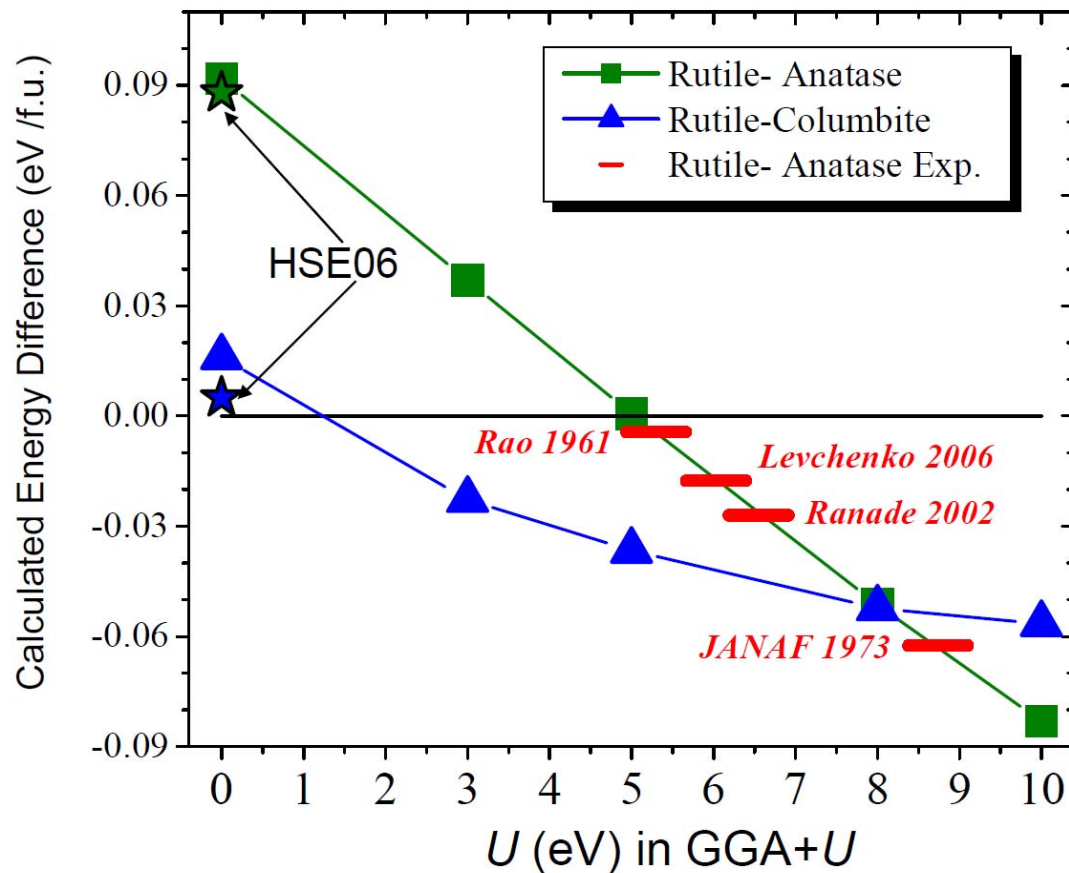
Intervalo apropiado:
 $3 \text{ eV} < U < 5 \text{ eV}$

N. Aaron Deskins, and Michel Dupuis
PRB 75, 195212 (2007).

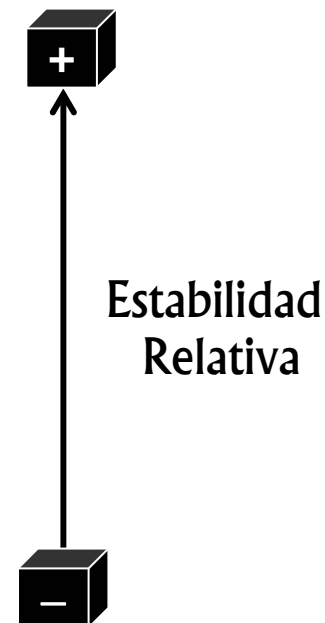


3. Estabilidad relativa de polimorfos.

Diferencia de energía total, $\Delta E = E_{\text{rutilo}} - E_{\text{polimorfo}}$



Si $\Delta E > 0$ el polimorfo es más estable que el rutilo-TiO₂



Orden en la estabilidad
T = 0 K

GGA	3	5	10
ANATASA	ANATASA	ANATASA	RUTILO
COLUMBITA	RUTILO	RUTILO	COLUMBITA
RUTILO	COLUMBITA	COLUMBITA	ANATASA

Intervalo apropiado:
 $5 \text{ eV} < U < 8 \text{ eV}$



4. Curvas E-V. Ecuación de estado.

Energía-Volumen calculada

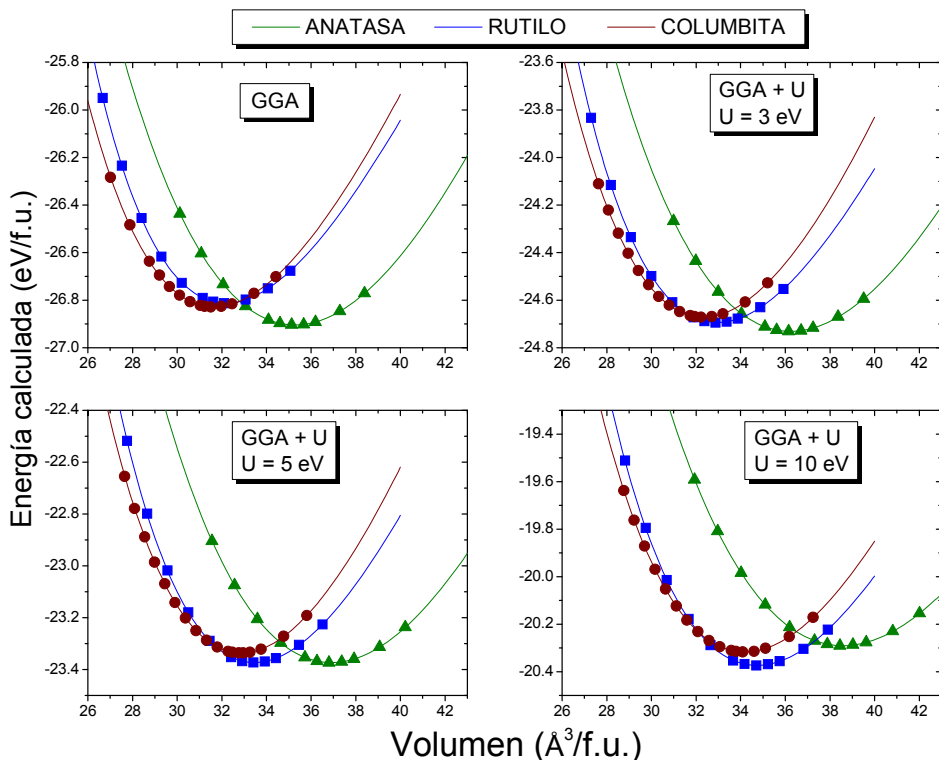
Ajustes a la ecuación de estado de Birch-Murnaghan

$$E(V) = E_0 + \frac{9B_0V_0}{16} \left[B_0' \left(x^{2/3} - 1 \right)^3 + \left(x^{2/3} - 1 \right)^2 \left(6 - 4x^{2/3} \right) \right]$$



B_0, B_0', V_0, E_0

$$B_T = -V \left(\frac{\partial p}{\partial V} \right)_T \quad B_0 = B_T (P = 0)$$



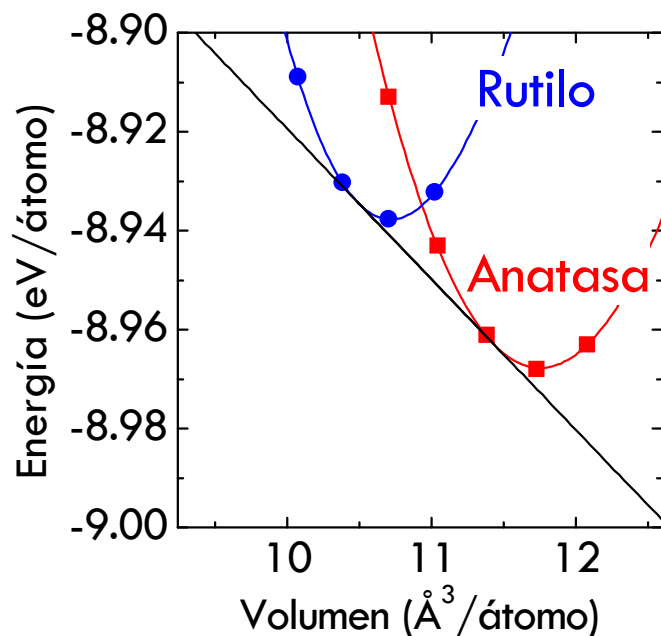
Intervalo apropiado: $3 \text{ eV} < U < 5 \text{ eV}$

Polimorfo	Método	U (eV)	V_0 (Å³/f.u.)	B_0 (GPa)	B_0'
ANATASA	GGA		35.272	169.9	2.27
	GGA+U	3	36.239	164.9	2.53
	GGA+U	5	36.902	162.3	2.61
	GGA+U	10	38.572	157.6	2.67
	Exp ^(a)		34.06	179±2	4.5
RUTILO	GGA		32.186	200.4	4.98
	GGA+U	3	32.946	199.5	4.77
	GGA+U	5	33.458	198.7	4.62
	GGA+U	10	34.740	195.3	4.40
	Exp ^(b)		31.22	211±7	6.76
COLUMBITA	GGA		31.651	195.9	4.22
	GGA+U	3	32.334	206.8	3.62
	GGA+U	5	32.866	202.3	3.69
	GGA+U	10	34.179	193.9	3.75
	Exp ^(a)		30.59	258±8	4.1

^(a)T. Arlt et al. PRB **61**, 14414 (2000). ^(b)D. G. Isaak et al. Phys. Chem. Miner. **26**, 31 (1998).

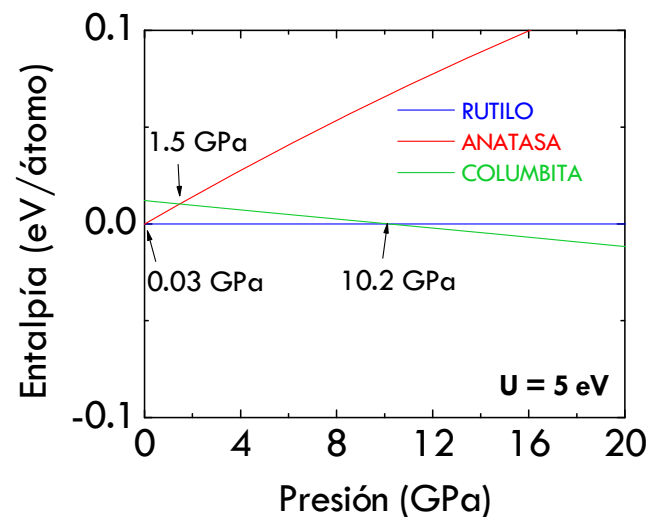


5. Presión de transición.



a $T = 0 \text{ K}$
 $G = H = E + P \cdot V$
 Energía Gibbs: G
 Entalpía: H

$H_1 = H_2$
 a la presión de
 transición



GGA + U		Presión de transición calculada en GPa	
U / eV	Anatasa → Columbita	Rutilo → Columbita	Anatasa → Rutilo
0	3.3	--	4.8
3	2.5	6.1	1.8
5	1.5	10.1	0.03
10	--	16	--
Presión experimental	2.6 – 7 GPa	10 GPa	

Intervalo apropiado:
 $3 \text{ eV} < U < 7 \text{ eV}$



Conclusiones.

La metodología GGA+U mejora los resultados obtenidos GGA por lo que se puede considerar apropiada para estudiar los diversos polimorfos del TiO_2 .

Análisis de la estructura cristalina.

Análisis de la estructura electrónica.

Análisis de la estabilidad.

Energía-Volumen. Ecuación de Estado.

Análisis de las presiones de transición.

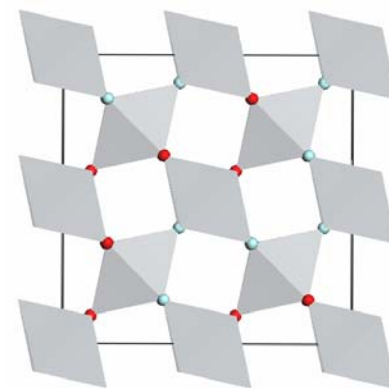
Valor del mismo orden que el encontrado para otros óxidos de metales de transición

Intervalo apropiado para U:

$$3 \text{ eV} < U < 8 \text{ eV}$$

$$U_{\text{efec}} \sim 5 \text{ eV}$$

Empleo en el estudio del sistema TiOF



Materiales	MnO	FeO	CoO	NiO
U (a)	4.7	4.8	5.1	5.2
(b)	6.9	6.8	7.8	8.0
(c)	3.6	4.6	5.0	5.1
(d)		4.3		4.6

- (a) Jiang et al. PRB **82**, 045108 (2010).
- (b) Anisimov et al. PRB **44**, 943 (1991).
- (c) Pickett et al. PRB **58**, 1201 (1998).
- (d) Cococcioni et al. PRB **71**, 035105 (2005).



GRACIAS POR SU ATENCIÓN

Ángel Morales García

Universidad Complutense de Madrid

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Mercedes Taravillo Corralo

M^a Elena Arroyo de Dompablo

Valentín García Baonza



QUIMAPRES

Miraflores de la Sierra (Madrid)
2011

Persepolis

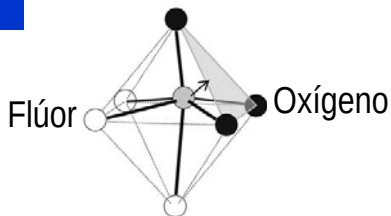


Polimorfos estudiados en TiOF

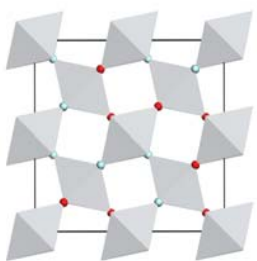
Metodología: *GGA* + *U* ($U = 5$ eV)

Rutilo-TiOF

Ya ha sido sintetizado

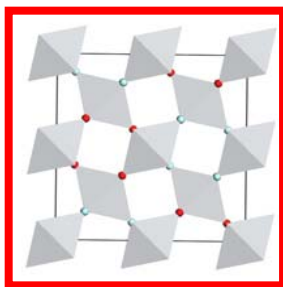


● Oxígeno ● Flúor



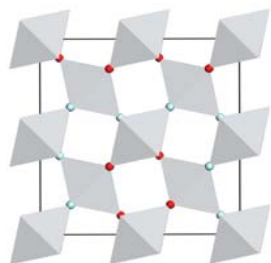
$$E_{\text{GGA}} = 0.02 \text{ eV}$$

$$E_{\text{GGA}+U} = 0.07 \text{ eV}$$



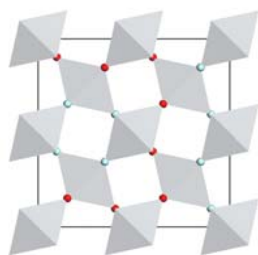
$$E_{\text{GGA}} = 0 \text{ eV}$$

$$E_{\text{GGA}+U} = 0 \text{ eV}$$



$$E_{\text{GGA}} = 0.58 \text{ eV}$$

$$E_{\text{GGA}+U} = 0.94 \text{ eV}$$



$$E_{\text{GGA}} = 0.58 \text{ eV}$$

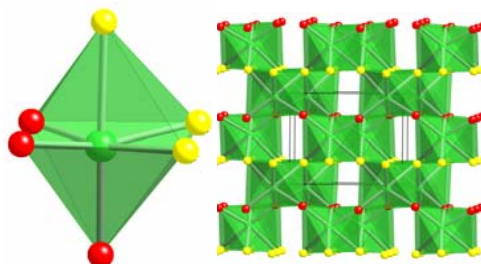
$$E_{\text{GGA}+U} = 0.94 \text{ eV}$$

Columbita-TiOF

Polimorfo todavía no descrito

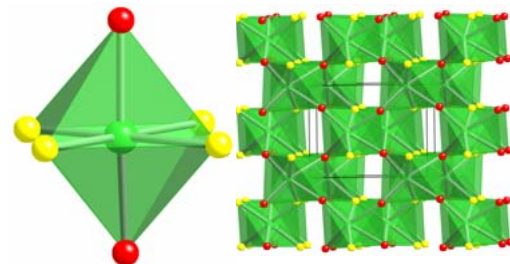
● Oxígeno

● Flúor



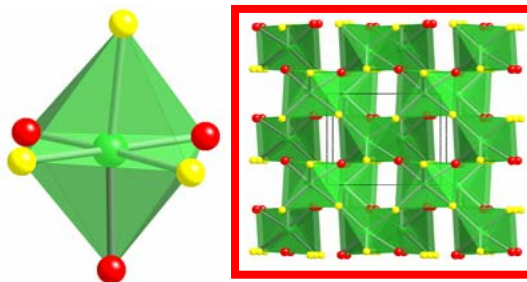
$$E_{\text{GGA}} = 0.4 \text{ eV}$$

$$E_{\text{GGA}+U} = 0.2 \text{ eV}$$



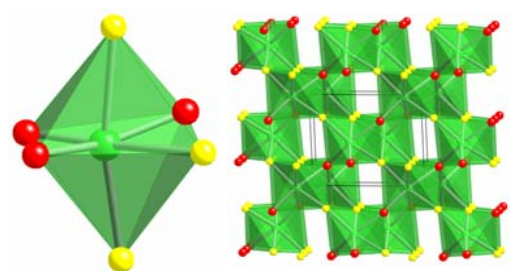
$$E_{\text{GGA}} = 1.9 \text{ eV}$$

$$E_{\text{GGA}+U} = 0.7 \text{ eV}$$



$$E_{\text{GGA}} = 0 \text{ eV}$$

$$E_{\text{GGA}+U} = 0 \text{ eV}$$



$$E_{\text{GGA}} = 0.7 \text{ eV}$$

$$E_{\text{GGA}+U} = 0.2 \text{ eV}$$



Estudios previos

Experimental

Material de partida
Tamaño de partícula

Transición	P _r . GPa	Material de partida	Referencia
Anatasa - Columbita	2.6	Policristalino	Ohsaka et al. 1979
	~7	Policristalino	Haines et al. 1993
	4.5-7	Monocristal	Lagarec et al. 1995
	4.5	Monocristal	Arlt et al. 2000
	5	Policristalino	Hearne et al. 2004
Rutilo - Columbita	10		Arashi 1992

Anatasa

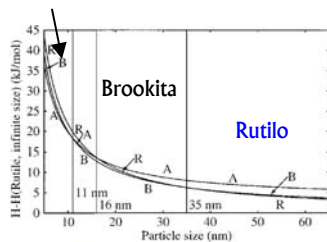
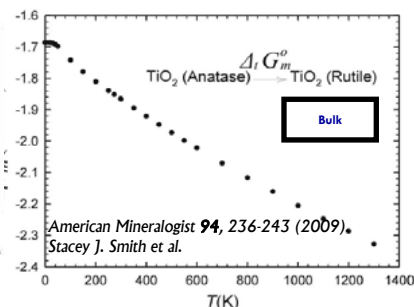


Figure 4. Variation of enthalpies of anatase, brookite, and rutile with particle size.

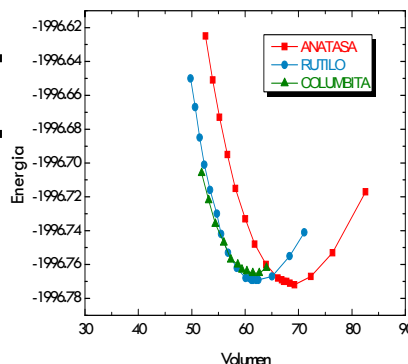
Hengzhong Zhang* and Jillian F. Banfield.
J. Phys. Chem. B, Vol. 104, No. 15, 2000



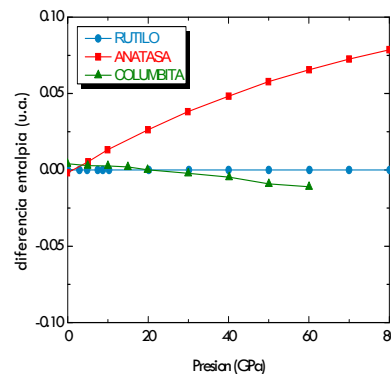
American Mineralogist 94, 236-243 (2009).
Stacey J. Smith et al.

Bulk la fase rutilo es más estable que la anatasa
nanopartícula la fase anatasa es más estable.

Teoría



Muscat et al. PRB 65, 224112 (2000). LCAO-HF



Método	$\Delta E = E_{\text{rutilo}} - E_{\text{anatasa}}$
LCAO	TVAE
LDA	-0.32
GGA	5.46
PW	$E_{\text{cut}} = 340 \text{ eV}$
LDA	3.31
GGA	7.17

	LDA-PP	GGA-PP	GGA-PBE	GGA-PBE U = 3 eV	GGA-PBE U = 5 eV	Experimental (**)
ANATASA						
V (Å ³)	33.66	35.34	35.16	36.27	36.92	34.173
(V _{cal} -V _{exp})/V _{exp} (%)	-1.5	3.4	2.9	6.1	8.0	
E (eV/átomo)	-9.821	-8.955	-8.968	-8.238	-7.791	
RUTILO						
V (Å ³)	30.60	32.25	30.90	32.96	33.46	31.20
(V _{cal} -V _{exp})/V _{exp} (%)	-1.9	3.4	-1.0	5.6	7.2	
E (eV/átomo)	-9.813	-8.928	-8.937	-8.230	-7.790	
COLUMBITA						
V (Å ³)	30.03	31.62	31.53	32.62	32.87	30.594
(V _{cal} -V _{exp})/V _{exp} (%)	-1.8	3.4	3.1	6.6	7.4	
E (eV/átomo)	-9.82	-8.931	-8.942	-8.22	-7.768	

(**)L. Gerward, and J. S. Olsen, Jj. Appl. Crystallogr. 30, 259 (1997).

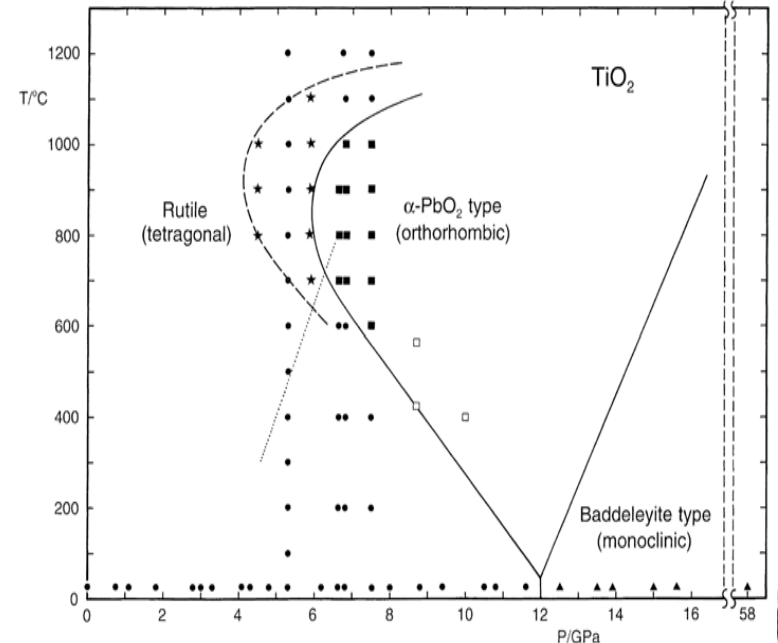
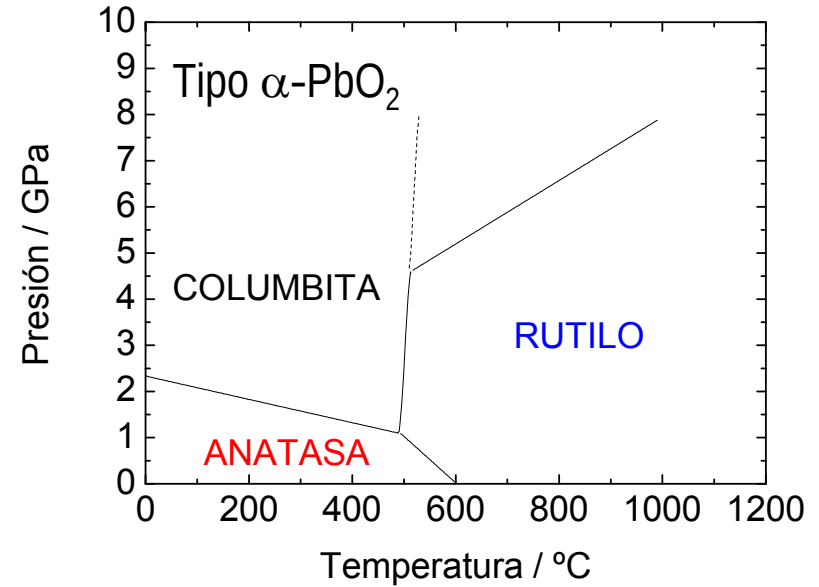
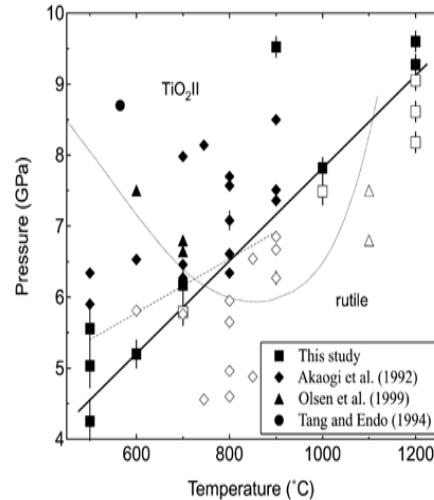
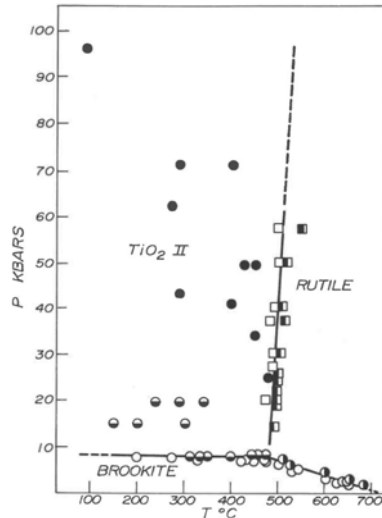
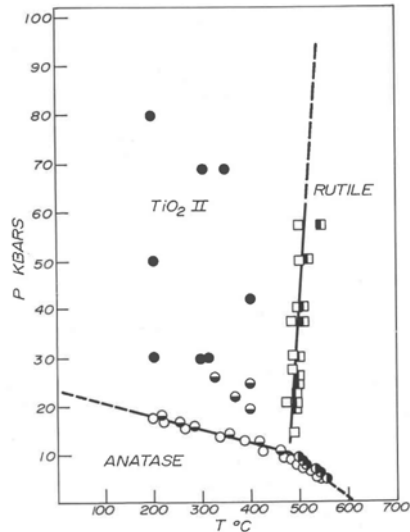


Diagrama de Fases del TiO_2

THE AMERICAN MINERALOGIST, VOL. 53, NOVEMBER-DECEMBER, 1968

PRESSURE-TEMPERATURE STUDIES OF ANATASE, BROOKITE, RUTILE AND TiO_2 -II

FRANK DACHILLE, P. Y. SIMONS¹ AND RUSTUM ROY,



VASP-Relajación de la estructura

ISIF-tag

ISIF = 0|1|2|3|4|5|6

ISIF controls whether the stress tensor is calculated. The calculation of the stress tensor is relatively time-consuming, and therefore by default switched off for ab initio MD's. Forces are always calculated.

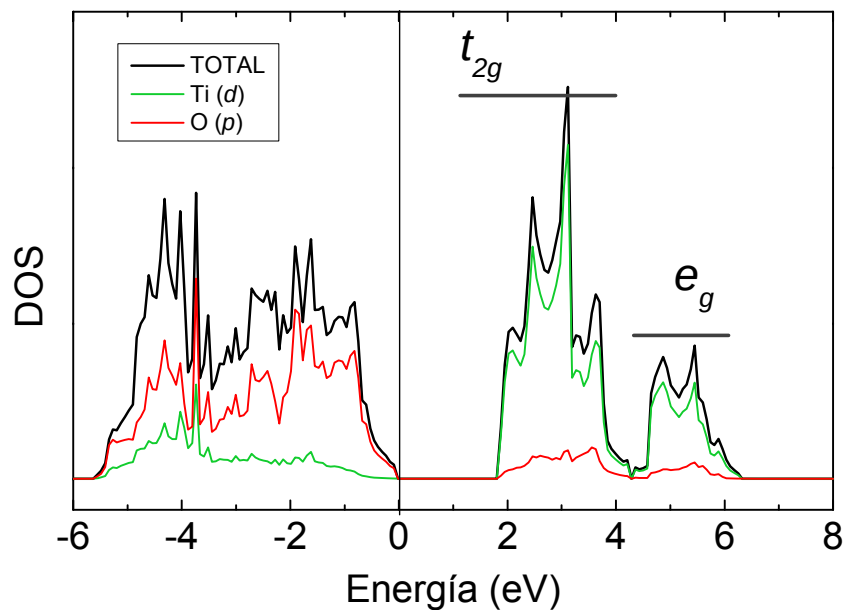
In addition ISIF determines which degrees of freedom (ions, cell volume, cell shape) are allowed to change. The following table shows the meaning of ISIF. At the moment cell changes are only supported for relaxations and not for molecular dynamics simulations.

ISIF	calculate force	calculate stress tensor	relax ions	change cell shape	change cell volume
0	yes	no	yes	no	no
1	yes	trace only *	yes	no	no
2	yes	yes	yes	no	no
3	yes	yes	yes	yes	yes
4	yes	yes	yes	yes	no
5	yes	yes	no	yes	no
6	yes	yes	no	yes	yes
7	yes	yes	no	no	yes

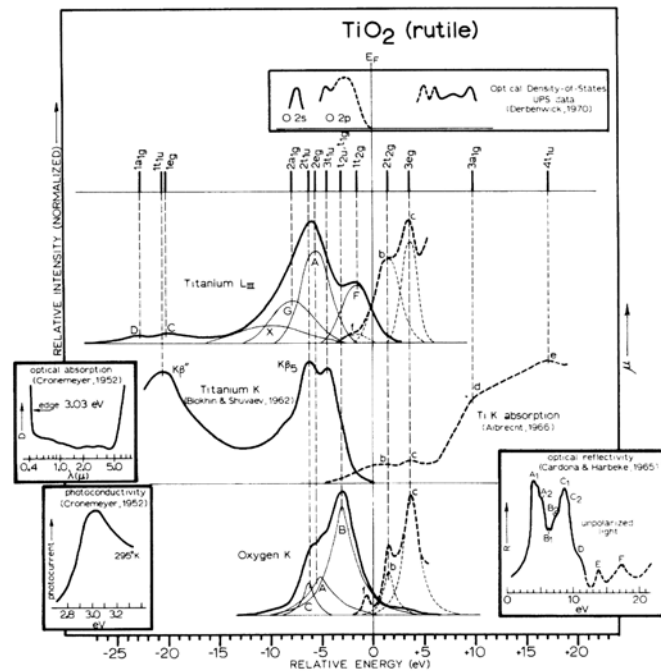


Análisis de la estructura electrónica

Densidad de estados del rutilo-TiO₂



Densidad de estados obtenida con VASP
TiO₂-rutilo
DFT: GGA PAW-PBE



D. W. Fisher, *Phys. Rev. B* **5**, 4219 (1972)



Ajuste de las curvas E-V a la ec. de Murnaghan

U (eV)	Polimorfo	B_0 (GPa)	B_0'	V_0 (Å ³)
EXP	ANATASA	179 ± 2	4.5	34.06
	RUTILO	211 ± 7	6.76	31.22
	COLUMBITA	258 ± 8	4.1 ± 3	30.59
0	ANATASA	170.6	2.14	35.258
	RUTILO	212.6	4.14	32.151
	COLUMBITA	205.4	3.53	31.624
3	ANATASA	169.6	1.95	36.223
	RUTILO	202.9	4.30	32.941
	COLUMBITA	215.5	2.89	32.313
5	ANATASA	163.8	2.30	36.902
	RUTILO	198.8	4.47	33.453
	COLUMBITA	206.3	3.27	32.855
10	ANATASA	163.2	2.00	38.542
	RUTILO	200.7	3.90	34.730
	COLUMBITA	197.6	3.35	34.168



Otros polimorfos de alta presión del TiO_2

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NATURE | VOL 410 | 5 APRIL 2001 | www.nature.com

Materials science

The hardest known oxide

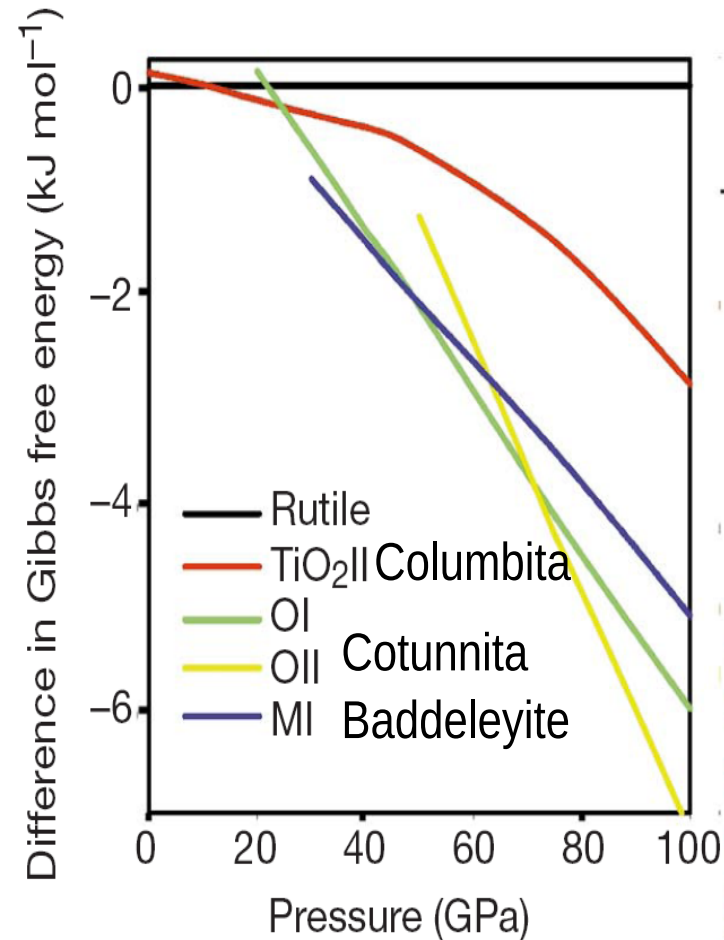
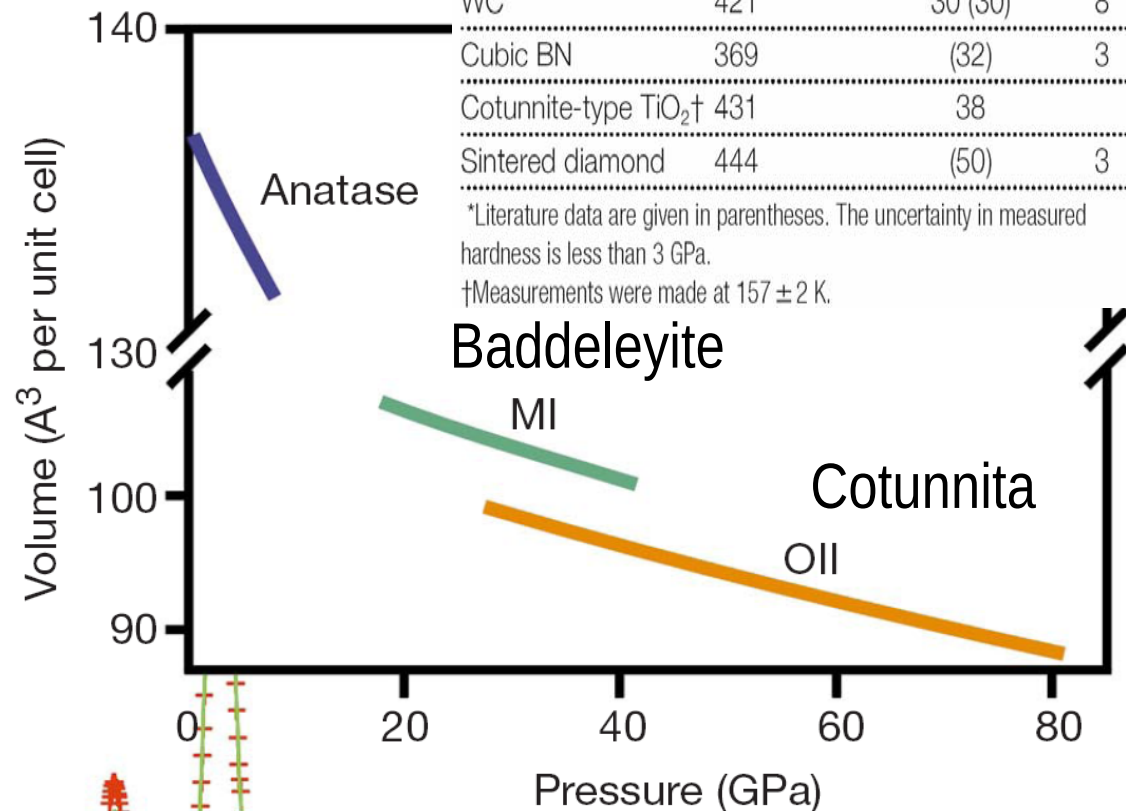


Table 1 Hardness of polycrystalline materials

Material	Bulk modulus (GPa)	Hardness* (GPa)	Ref.
B_4C	200	30 (30)	3
SiC	248	29 (29)	3
Al_2O_3	252	20 (19)	7
SiO_2 , stishovite	291	32 (33)	7
WC	421	30 (30)	8
Cubic BN	369	(32)	3
Cotunnite-type TiO_2 †	431	38	
Sintered diamond	444	(50)	3

*Literature data are given in parentheses. The uncertainty in measured hardness is less than 3 GPa.

†Measurements were made at 157 ± 2 K.



ECUACIÓN DE ESTADO DEL TiO_2

TABLE IV. Experimental bulk moduli of the TiO_2 polymorphs.

Polymorph	B_0 (GPa)	B'_0	ρ_0 (g/cm ³)	$\rho_0/\rho_{0,\text{rutile}}$
Anatase	179(2)	4.5(10)	3.8941(2)	0.9166(1)
Rutile ^a	211(10)	6.5(7)	4.2485(2)	1.0000
α - PbO_2 type	258(8)	4.1(3)	4.336(12)	1.021(1)
Baddeleyite type	290(10)	4.0 ^b	4.728(15) ^c	1.113(1)

^aData from Gerward and Olsen (Ref. 11).

^bAssumed value.

^cExtrapolated value.

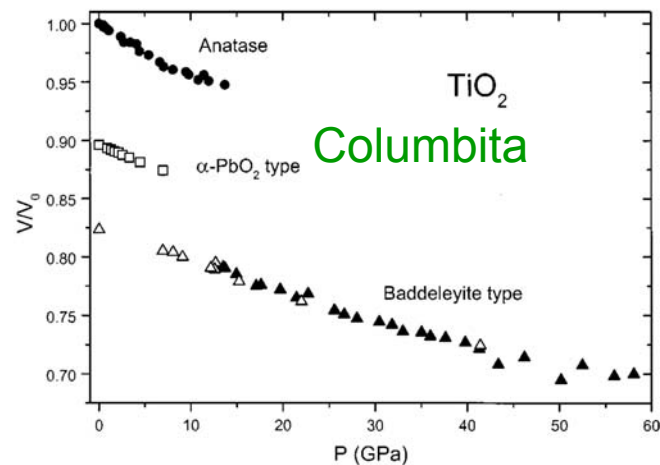
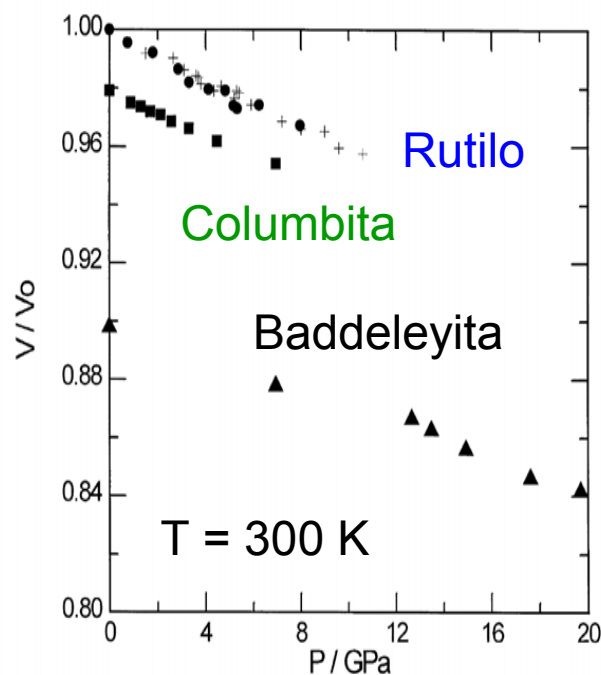


FIG. 3. Experimental pressure-volume data for the polycrystalline TiO_2 polymorphs investigated in the present work. The notation is the same as in Fig. 2. The unit-cell volumes have been normalized by dividing with $V_{0,\text{anatase}}$.

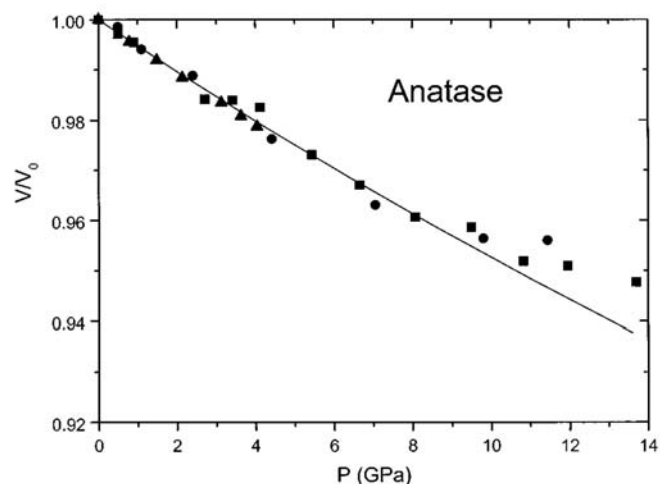


FIG. 4. Relative volume of anatase TiO_2 . Circles and squares denote two experimental runs with polycrystalline anatase, triangles denote single-crystal data, and the solid curve is the result of the theoretical calculation using the *ab initio* perturbed ion model.

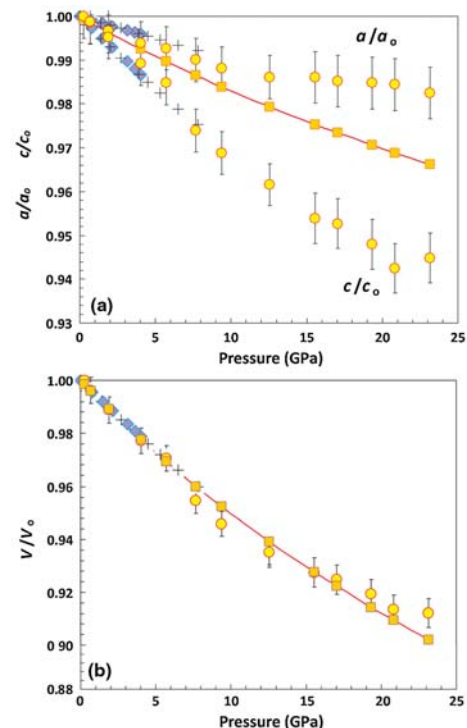


FIG. 3 (color online). The pressure-dependent variations of the relative unit cell constants. (a) a/a_0 for Au (squares) and a/a_0 and c/c_0 for anatase (diamonds: single crystal data from Ref. [18]; plus: microparticle data from Ref. [23]; and circles: 6-nm anatase of this study). (b) V/V_0 versus pressure for Au and anatase. Symbols as in (a). A clear break in the pressure evolution of the nc-anatase unit cell constants is discernible at 10–12 GPa.

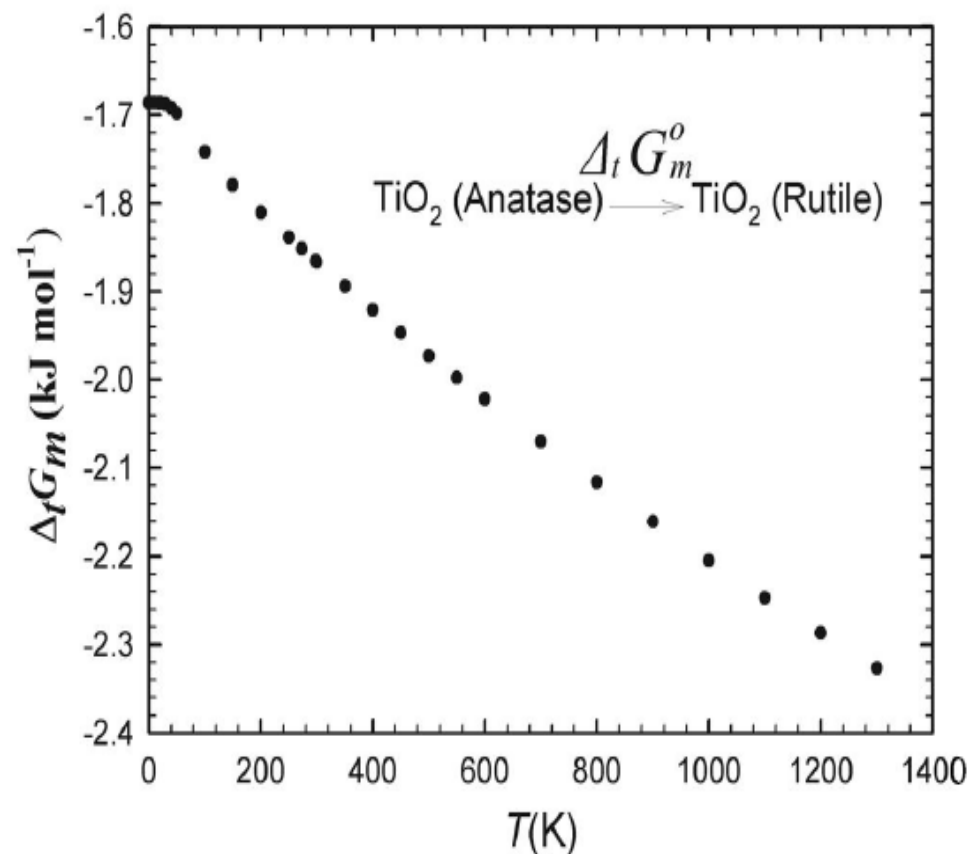


Análisis de la estabilidad Anatasa-Rutilo

American Mineralogist, Volume 94, pages 236–243, 2009

Heat capacities and thermodynamic functions of TiO₂ anatase and rutile: Analysis of phase stability

STACEY J. SMITH,¹ REBECCA STEVENS,¹ SHENGFENG LIU,¹ GUANGSHE LI,²
ALEXANDRA NAVROTSKY,³ JULIANA BOERIO-GOATES,¹ AND BRIAN F. WOODFIELD^{1,*}



Diferencia de energía $E_{\text{anatasa}} - E_{\text{rutilo}}$ (kJ/mol)	
$GGA + U$	
U / eV	Anatasa → Rutilo
0	-8.71
3	-3.97
5	-0.32
10	7.99



E vs tamaño de partícula del TiO₂

Hengzhong Zhang* and Jillian F. Banfield. *J. Phys. Chem. B*, Vol. 104, No. 15, 2000

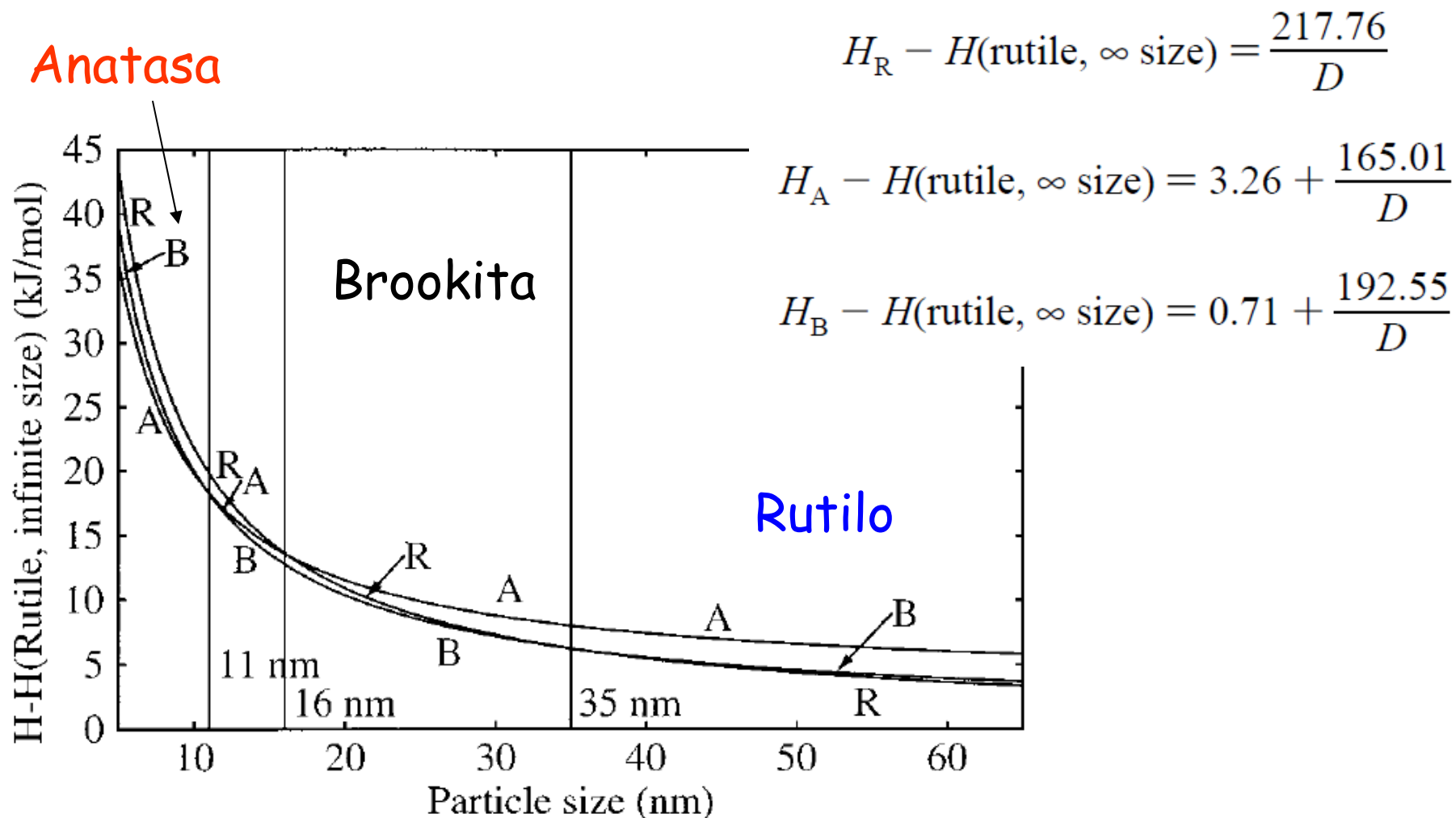


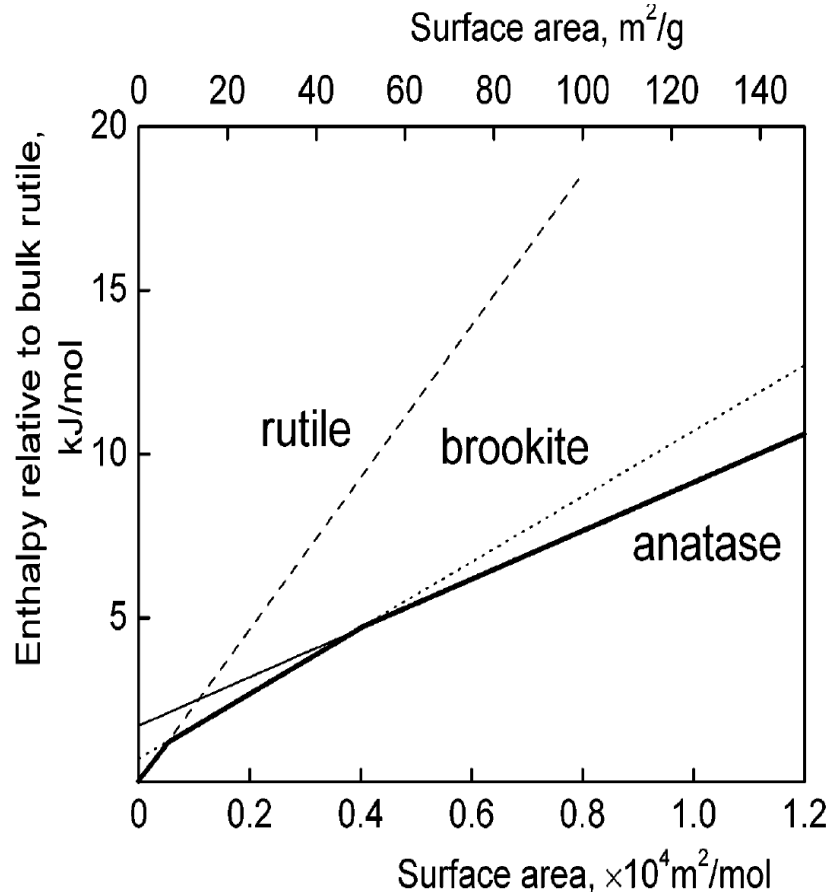
Figure 4. Variation of enthalpies of anatase, brookite, and rutile with particle size.



E vs tamaño de partícula del TiO_2

Chem. Mater. **2006**, *18*, 6324–6332

TiO_2 Stability Landscape: Polymorphism, Surface Energy, and Bound Water Energetics



La fase **rutilo** es energéticamente estable a temperatura ambiente para áreas superficiales menores de $7 \text{ m}^2/\text{g}$.

La fase **anatasa** es estable para áreas superficiales $50 \text{ m}^2/\text{g}$.

La región de estabilidad de la fase **brookita** está entre $7\text{-}50 \text{ m}^2/\text{g}$.

Anatasa es la nanofase estable del TiO_2 debido a su baja energía superficial.

Energía superficial (rutilo) = $2.22 \pm 0.07 \text{ J/m}^2$

Energía superficial (anatasa) = $0.74 \pm 0.07 \text{ J/m}^2$

La energía superficial de la anatasa es casi de un 66% más alta que el rutilo.



En la naturaleza ..



**An Ultradense Polymorph of Rutile with
Seven-Coordinated Titanium from the Ries Crater**
Ahmed El Goresy, *et al.*
Science 293, 1467 (2001);
DOI: 10.1126/science.1062342

American Mineralogist, Volume 90, pages 1458–1461, 2005

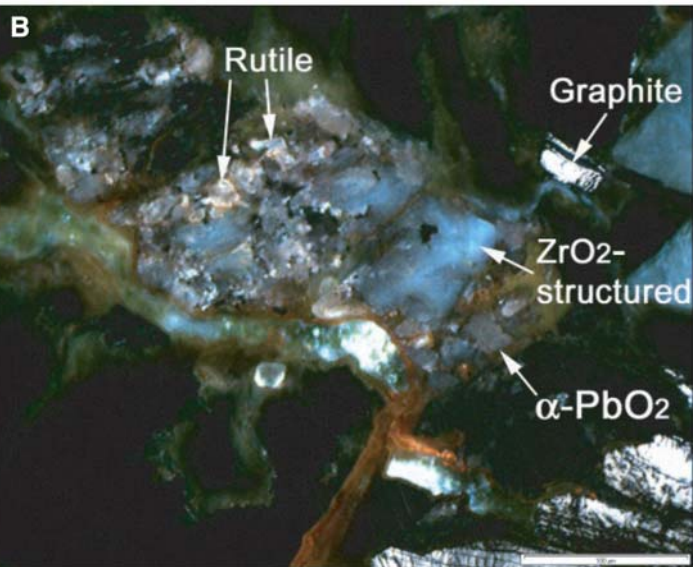
LETTER

α -PbO₂-type nanophase of TiO₂ from coesite-bearing eclogite in the Dabie Mountains, China

XIULING WU,^{1,2} DAWEI MENG,^{1,2,*} AND YUJING HAN¹

Explicación para tener la fase columbita en una muestra natural:

- Formación en el interior de la Tierra a muy alta presión.
- Formación debido a un impacto de meteorito.



Variación de B_0 con tamaño de partícula

PRL **96**, 035509 (2006)

PHYSICAL REVIEW LETTERS

week ending
27 JANUARY 2006

Ultrastability and Enhanced Stiffness of ~ 6 nm TiO_2 Nanoanatase and Eventual Pressure-Induced Disorder on the Nanometer Scale

V. Pischedda, G. R. Hearne, A. M. Dawe, and J. E. Lowther

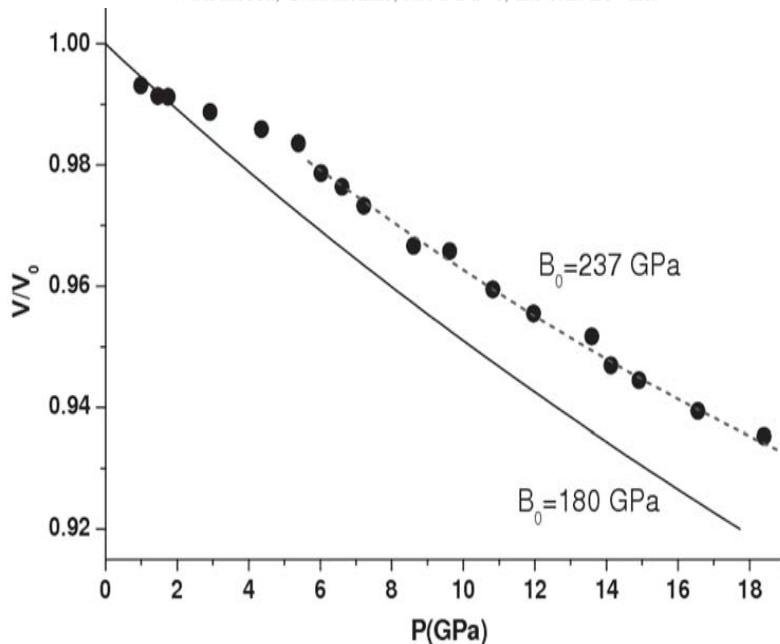


FIG. 5. Relative volume of 6 nm nanoanatase TiO_2 as a function of pressure. The dashed line through the data points is to guide the eye. The lower curve is the extrapolated EOS of bulk anatase with $B_0 = 180$ GPa and $B'_0 = 4$.

A 300 K nanoanatasa de tamaño nanométrico (6 nm) ultrafinos ultrafinos retiene su integridad estructural hasta 18 GPa. Hay un progresivo desorden estructural a un estado altamente distorsionado a $P > 18$ GPa. Las señales de orden a corto alcance persiste bien más allá de 18 GPa en los de Rayos-X y de Raman. Simulaciones de dinámica molecular sugieren que el desorden se inició en la capa superficial de un nanograno con la cristalinidad retenida en el core. Un Módulo de compresión $B_0 = 237$ GPa para la nanoanatasa (un 30% más alto que el valor del bulk) se deriva de los datos presión-volumen.



Size-Dependent Pressure-Induced Amorphization in Nanoscale TiO_2

Varghese Swamy,^{1,*} Alexei Kuznetsov,² Leonid S. Dubrovinsky,² Paul F. McMillan,^{3,†} Vitali B. Prakapenka,⁴ Guoyin Shen,⁴ and Barry C. Muddle¹

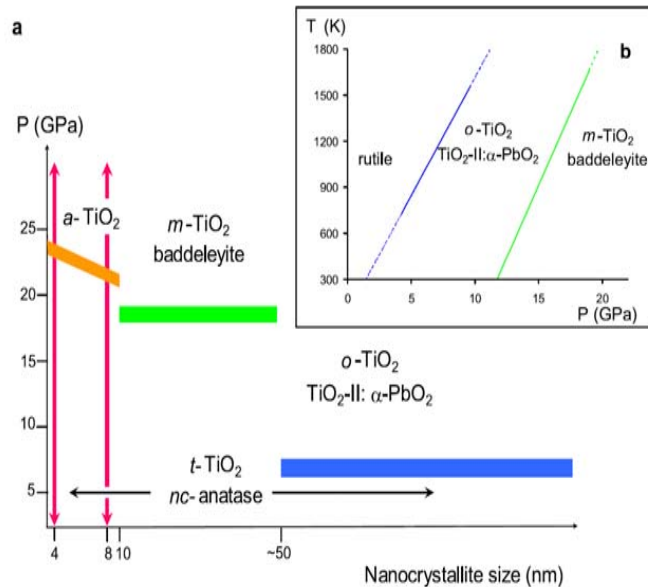


FIG. 1 (color online). (a) Size-dependent pressure stability of nc - t - TiO_2 (modified after Ref. [7]). The average transition pressures of the three phase transition regimes are shown. Nanocrystals of size <10 nm undergo PIA and remain amorphous (a - TiO_2) upon further compression and decompression. Approximately 12–50 nm crystallites transform to m - TiO_2 upon compression, which then transforms to o - TiO_2 on decompression. Coarser crystallites transform directly to o - TiO_2 . The compression-decompression paths of the two samples of this study are indicated. (b) Known stable P - T relations [9,19–21] in the bulk TiO_2 system.

Unusual Compression Behavior of Anatase TiO_2 Nanocrystals

Varghese Swamy,^{1,*} Alexei Y. Kuznetsov,² Leonid S. Dubrovinsky,³ Alexander Kurnosov,³ and Vitali B. Prakapenka⁴

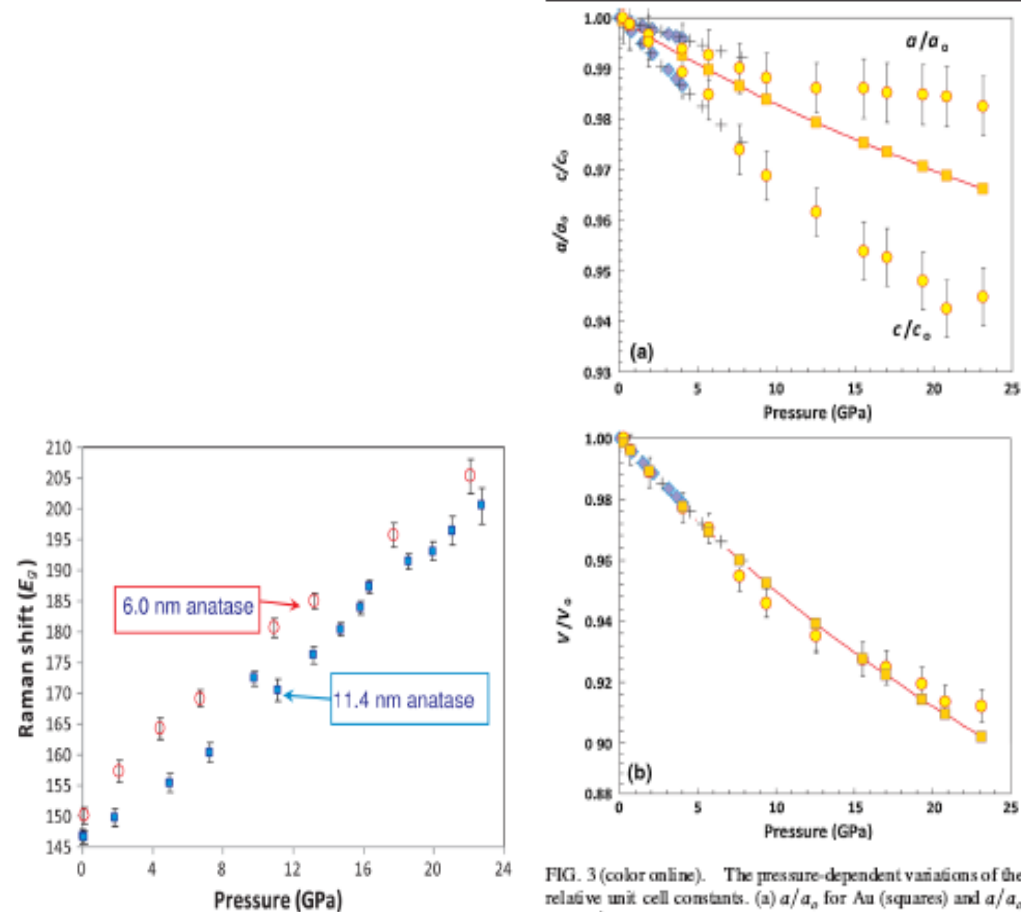


FIG. 5 (color online). The pressure shifts of the most intense E_g Raman band measured for the two nanocrystalline samples. Subtle breaks are seen at 10–12 and 14–16 GPa, more clear for the 11 nm anatase.

FIG. 3 (color online). The pressure-dependent variations of the relative unit cell constants. (a) a/a_0 for Au (squares) and a/a_0 and c/c_0 for anatase (diamonds: single crystal data from Ref. [18]; plus: microparticle data from Ref. [23]; and circles: 6-nm anatase of this study). (b) V/V_0 versus pressure for Au and anatase. Symbols as in (a). A clear break in the pressure evolution of the nc -anatase unit cell constants is discernible at 10–12 GPa.

Efecto temperatura.

PHYSICAL REVIEW B 81, 134108 (2010)

Polarizable interatomic force field for TiO_2 parametrized using density functional theory

X. J. Han,^{1,2} L. Bergqvist,^{1,3} P. H. Dederichs,¹ H. Müller-Krumbhaar,¹ J. K. Christie,^{4,5} S. Scandolo,^{5,6} and P. Tangney^{7,*}

¹IFF-Theory III, Forschungszentrum Jülich, D-52425 Jülich, Germany

²School of Materials Science and Engineering, Shanghai Jiao Tong University, 200240 Shanghai, People's Republic of China

³Department of Physics and Material Science, Uppsala University, P.O. Box 530, SE-751 21 Uppsala, Sweden

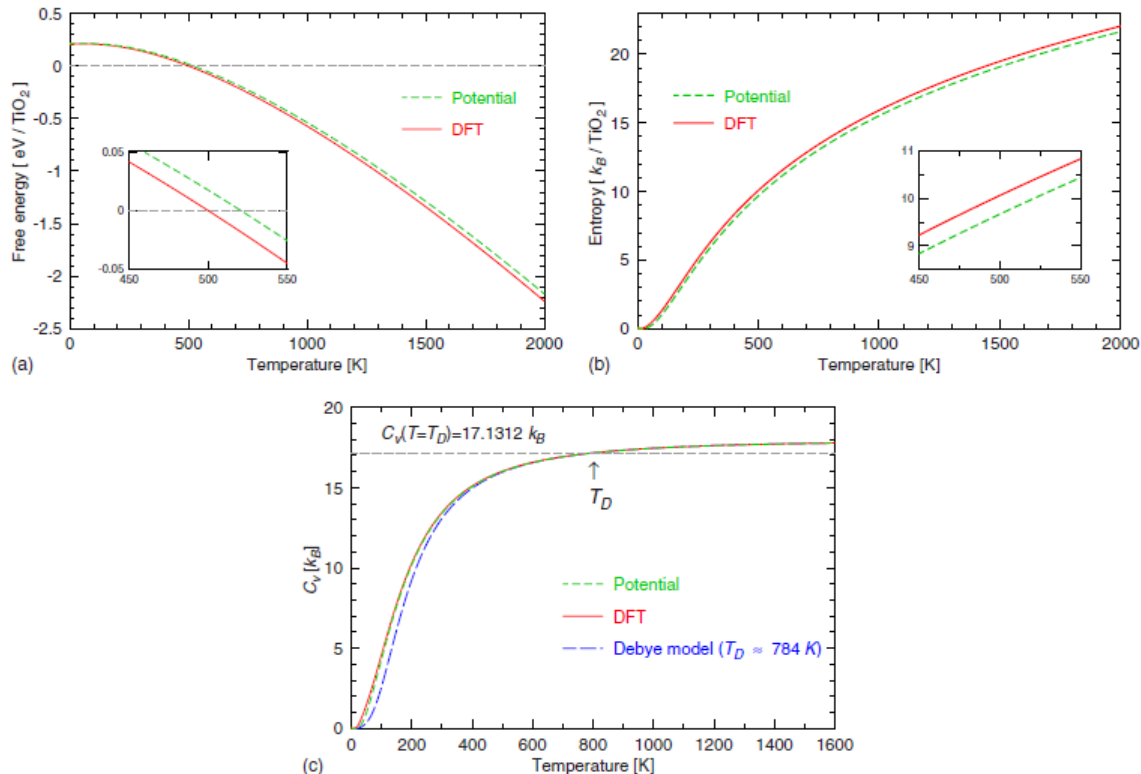
⁴Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

⁵The Abdus Salam International Centre for Theoretical Physics (ICTP), Strada Costiera 11, I-34014 Trieste, Italy

⁶INFN/DEMOCRITOS National Simulation Center, Via Beirut 2-4, I-34014 Trieste, Italy

⁷Department of Physics and Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom

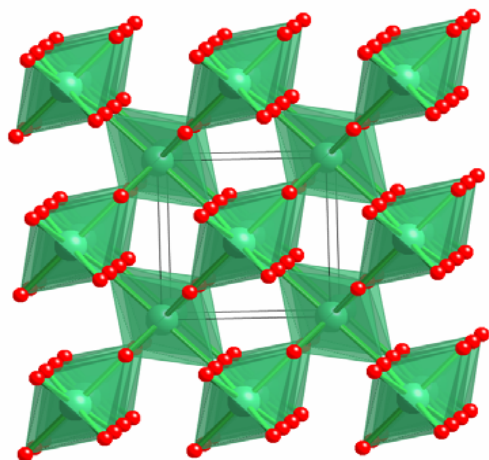
(Received 27 November 2009; revised manuscript received 25 March 2010; published 20 April 2010)



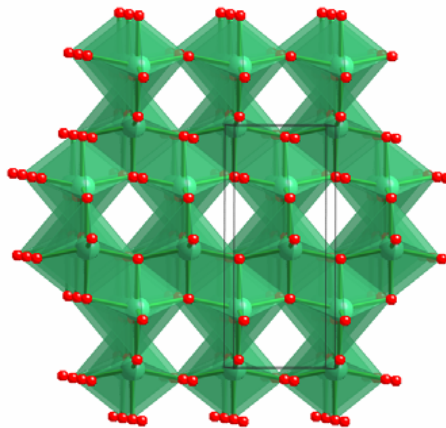
Thermodynamic properties of rutile TiO_2 derived from phonon properties: a free energy F ; b entropy S ; and specific heat C_v under constant volume



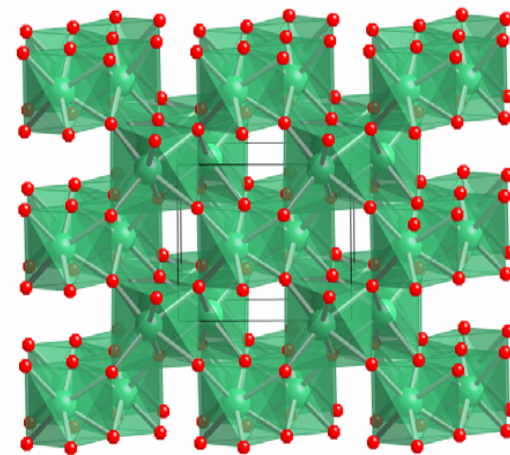
Polimorfos TiO_2



Rutilo



Anatasa

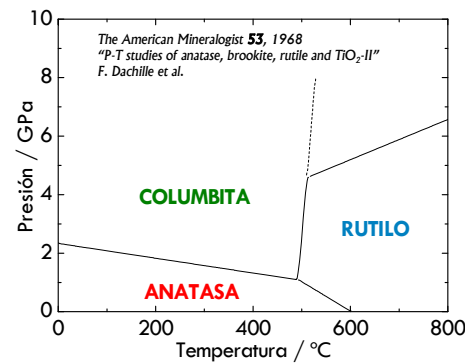


Columbita

● Oxígeno

● Titanio

Fase	G. Espacial	Z	Parámetros de celda (Å) / ρ (g/cm ³)
Rutilo	$P4_2/mnm$ (tetragonal)	2	$a=4.59$; $c=2.96$ / 4.13
Anatasa	$I4_1/amd$ (tetragonal)	4	$a=3.79$; $c=9.51$ / 3.79
Columbita	$Pbca$ (ortorómbico)	4	$a=4.55$; $b=5.46$; $c=9.51$ / 4.33



J. Haines, and J. M. Leger, *Physica B* **192**, 233 (1993).

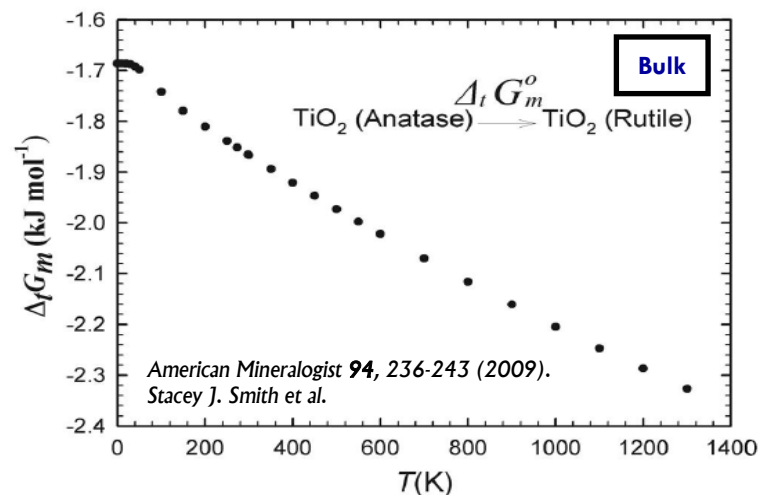


Estudios previos

Experimentalmente debemos tener en cuenta:

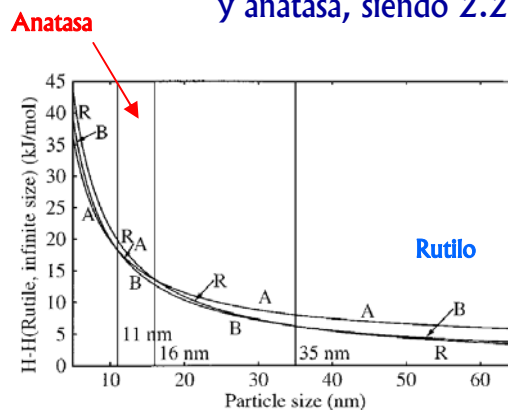
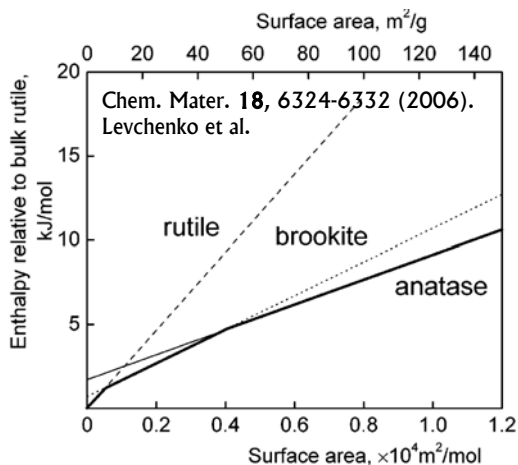
- monocristal o policristalino,
- Tamaño de partícula

Transición	P _{tr.} GPa	Material de partida	Referencia
Anatasa - Columbita	2.6	Policristalino	Ohsaka et al. 1979
	~7	Policristalino	Haines et al. 1993
	4.5-7	Monocristal	Lagarec et al. 1995
	4.5	Monocristal	Arlt et al. 2000
	5	Policristalino	Hearne et al. 2004
Rutilo - Columbita	10		Arashi 1992



La diferencia en energía libre entre anatasa y rutilo es muy pequeña, 2.3 KJ/mol o menor en un amplio rango de temperatura.

Levchenko et al. (2006) determinan la energía de superficie del rutilo y anatasa, siendo 2.22 ± 0.07 J/m² y 0.74 ± 0.07 J/m².



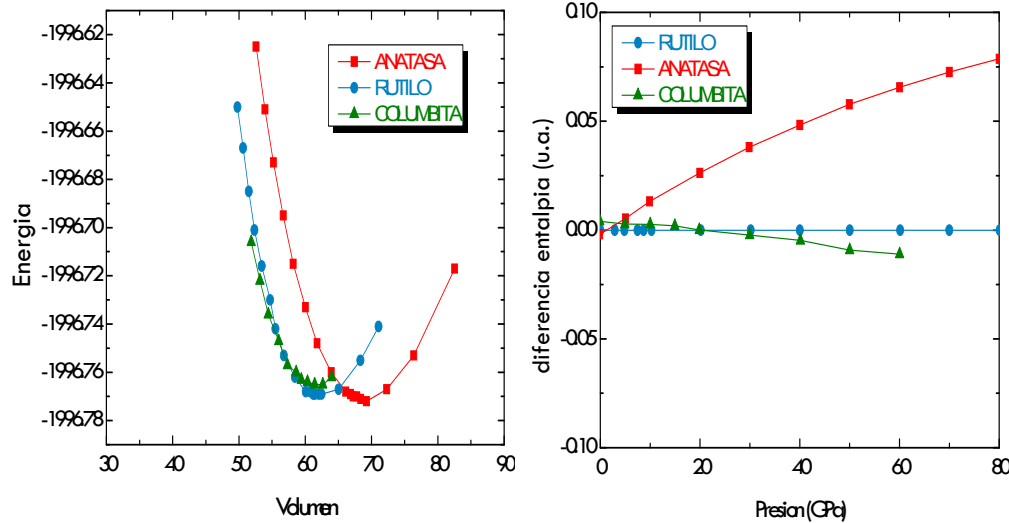
Bulk la fase rutilo es más estable que la anatasa nanopartícula la fase anatasa es más estable.

J. Phys. Chem. B **104**, 15 (2000).
Zhang et al.



Punto de vista **teórico**

Muscat et al. PRB **65**, 224112 (2000). LCAO-HF



Método	$\Delta E = E_{\text{rutilo}} - E_{\text{anatasa}}$
LCAO	TVAE
LDA	-0.32
GGA	5.46
PW	$E_{\text{cut}} = 340$ eV
LDA	3.31
GGA	7.17

MOTIVACIÓN

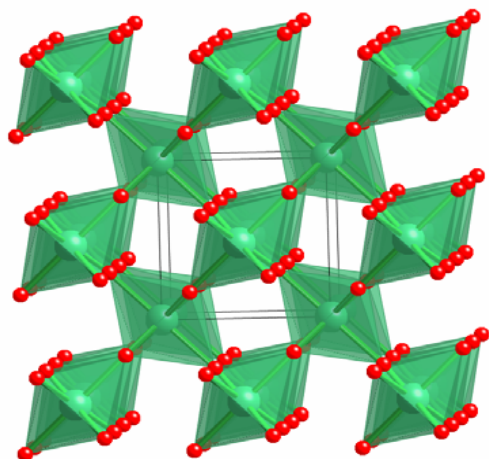
- La mayoría de los cálculos computacionales predicen que la fase estable a $T=0$ K es la fase **anatasa**.
- El TiO_2 es un semiconductor de **band gap** amplio (~ 3 eV) cuyo valor no es reproducido, en general, por los cálculos computacionales.



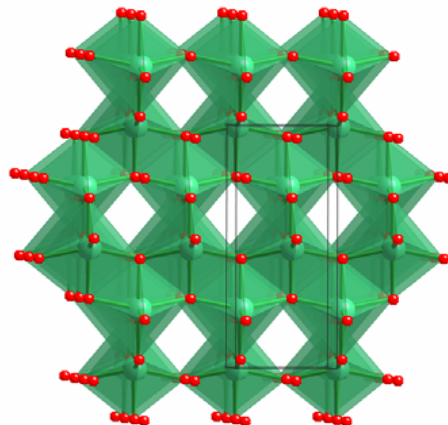
DFT+U



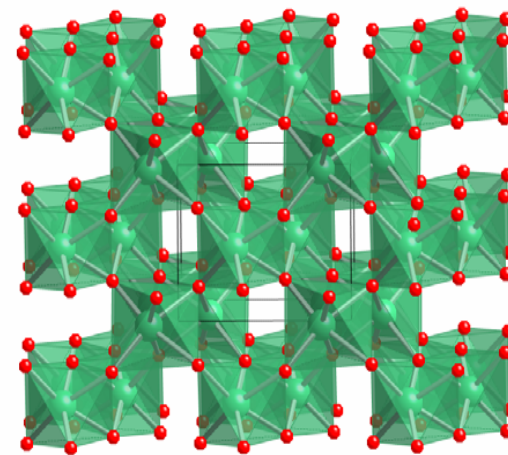
Polimorfos TiO₂



Rutilo



Anatasa



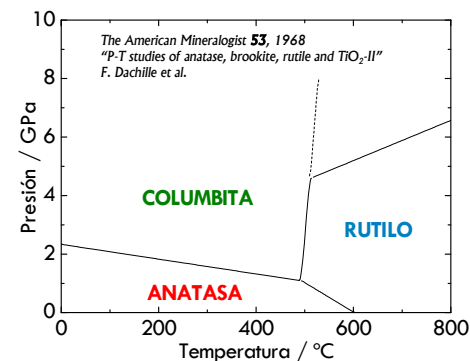
Columbita

● Oxígeno

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J. Haines, and J. M. Leger, *Physica B* **192**, 233 (1993).



MOTIVACIÓN

- La mayoría de los cálculos computacionales predicen que la fase estable a $T = 0$ K es la fase **anatasa**.
- El TiO₂ es un semiconductor de **band gap** amplio (~ 3 eV) cuyo valor no es reproducido, en general, por los cálculos computacionales.



Jahn-Teller transition in TiF_3 investigated using density-functional theory

Vasili Perebeinos* and Tom Vogt

Department of Physics, Brookhaven National Laboratory, Upton, New York 11973-5000, USA

(Received 28 April 2003; revised manuscript received 9 September 2003; published 8 March 2004)

We use first-principles density-functional theory to calculate the electronic and magnetic properties of TiF_3 using the full-potential-linearized augmented-plane-wave method. The local density approximation (LDA) predicts a fully saturated ferromagnetic metal and finds degenerate energy minima for high- and low-symmetry structures. The experimentally observed Jahn-Teller phase transition at $T_c = 370$ K cannot be driven by the electron-phonon interaction alone, which is usually described accurately by the LDA. Electron correlations beyond the LDA are essential to lift the degeneracy of the singly occupied Ti t_{2g} orbital. Although the on-site Coulomb correlations are important, the direction of the t_{2g} -level splitting is determined by dipole-dipole interactions. The LDA+U functional predicts an antiferromagnetic insulator with an orbitally ordered ground state. The input parameters $U = 8.1$ eV and $J = 0.9$ eV for the Ti $3d$ orbital were found by varying the total charge on the TiF_6^{2-} ion using the molecular NRLMOL code. We estimate the Heisenberg exchange constant for spin 1/2 on a cubic lattice to be approximately 24 K. The symmetry lowering energy in LDA+U is about 900 K per TiF_3 formula unit.

DOI: 10.1103/PhysRevB.69.115102

PACS number(s): 71.15.Mb, 62.20.-x, 71.30.+h, 64.60.-i



Electron transport via polaron hopping in bulk TiO₂: A density functional theory characterization

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Chemical Sciences Division, Pacific Northwest National Laboratory, Battelle Boulevard, K1-83, Richland, Washington 99354, USA

(Received 20 October 2006; revised manuscript received 22 March 2007; published 22 May 2007)

This work focuses on the intrinsic electron transport in stoichiometric TiO₂. Electron hopping is described by a polaron model, whereby a negative polaron is localized at a Ti³⁺ site and hops to an adjacent Ti⁴⁺ site. Polaron hopping is described via Marcus theory formulated for polaronic systems and quasiequivalent to the Emin-Holstein-Austin-Mott theory. We obtain the relevant parameters in the theory (namely, the activation energy ΔG^* , the reorganization energy λ , and the electronic coupling matrix elements V_{AB}) for selected crystallographic directions in rutile and anatase, using periodic density functional theory (DFT)+ U and Hartree-Fock cluster calculations. The DFT+ U method was required to correct the well-known electron self-interaction error in DFT for the calculation of polaronic wave functions. Our results give nonadiabatic activation energies of similar magnitude in rutile and anatase, all near ~ 0.3 eV. The electronic coupling matrix element V_{AB} was determined to be largest for polaron hopping parallel to the c direction in rutile and indicative of adiabatic transfer (thermal hopping mechanism) with a value of 0.20 eV, while the other directions investigated in both rutile and anatase gave V_{AB} values of about one order of magnitude smaller and indicative of diabatic transfer (tunneling mechanism) in anatase.

DOI: 10.1103/PhysRevB.75.195212

PACS number(s): 71.38.Ht, 72.20.Ec, 71.20.Nr, 72.80.Ga

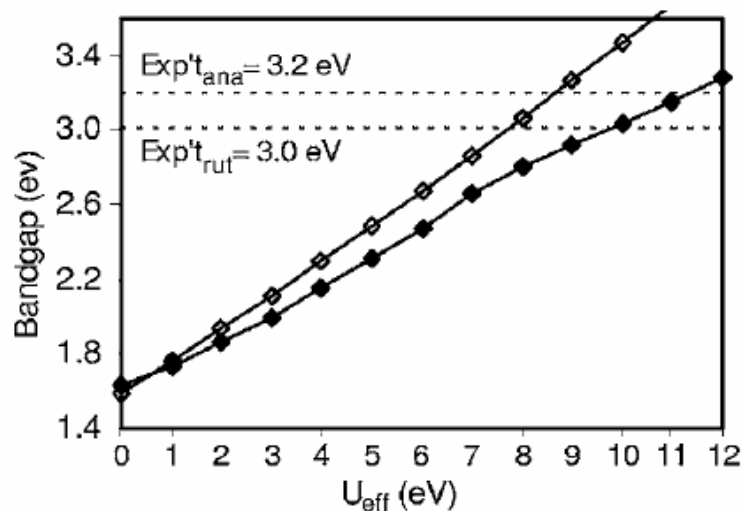


FIG. 5. Band gap versus U_{eff} . Closed diamonds represent results for rutile, while open diamonds represent results for anatase.

III. COMPUTATIONAL METHODOLOGY

Spin-polarized density functional theory (DFT) with a plane-wave basis set, as implemented in the Vienna *ab initio* software package (VASP),^{38–41} allowed the accurate modeling of polarons in bulk TiO₂. We described the core electrons using the projector augmented-wave method.⁴² Two valence electron schemes for Ti were considered: $4s^2 3d^2$ (large core) and $3p^6 4s^2 3d^2$ (small core). Preliminary calculations determined that the former (large core) scheme was insufficient for obtaining the correct band gap, but tests showed that this scheme did give similar polaron transfer rates to the small core model. Nonetheless, we used the $3p^6 4s^2 3d^2$ scheme for our calculations to ensure proper description of valence electrons. The oxygen atoms had valence configurations of $2s^2 2p^4$. The exchange-correlation functional for this work was the functional of Perdew *et al.*^{43,44}

It is important to ensure convergence of simulation parameters. We therefore tested our k -point meshes ($2 \times 2 \times 2$ for rutile and $2 \times 2 \times 1$ for anatase) and cutoff energies and found them to be sufficiently converged. We also used Gaussian smearing to describe the electronic occupation. The cells that we considered were the rutile ($3 \times 3 \times 3$) and anatase ($3 \times 3 \times 2$) supercells. These cells have 162 and 216 atoms, respectively, and are shown in Fig. 3. Our calculations gave lattice parameters of 4.65 and 2.97 Å for rutile and 3.81 and 9.73 Å for anatase, all in good agreement with experiment.⁴⁵ This leads to simulation box lengths of 14.01 Å and 8.91 Å for the rutile cell and 11.46 Å and 19.42 Å for the anatase cell. We also tested a $(4 \times 4 \times 4)$ rutile cell and found little effect on the results (for example, Ti-O distance, E_{act} , etc.).



Polimorfo	Método	U (eV)	V_0 (Å ³ /f.u.)	B_0 (GPa)	B_0'
ANATASA	GGA		35.272	169.9	2.27
	GGA+U	3	36.239	164.9	2.53
	GGA+U	5	36.902	162.3	2.61
	GGA+U	10	38.572	157.6	2.67
	Exp		34.06	179±2	4.5
RUTILO	GGA		32.186	200.4	4.98
	GGA+U	3	32.946	199.5	4.77
	GGA+U	5	33.458	198.7	4.62
	GGA+U	10	34.740	195.3	4.40
	Exp		31.22	211±7	6.76
COLUMBITA	GGA		31.651	195.9	4.22
	GGA+U	3	32.334	206.8	3.62
	GGA+U	5	32.866	202.3	3.69
	GGA+U	10	34.179	193.9	3.75
	Exp		30.59	258±8	4.1



Estudio de la transición de fase del CuWO_4 bajo presión mediante SXRD

VNIVERSITAT
DE VALÈNCIA

JOHANN WOLFGANG GOETHE
UNIVERSITÄT
FRANKFURT AM MAIN



Javier Ruiz Fuertes

Daniel Errandonea

Alfredo Segura

Julio Pellicer Porres

Alexandra Friedrich

Wolfgang Morgenroth

Eiken Haussühl

Zhao-Jie Zhu

Chao-Yang Tu

Comparación de la estructura del CuWO_4 con las wolframitas normales

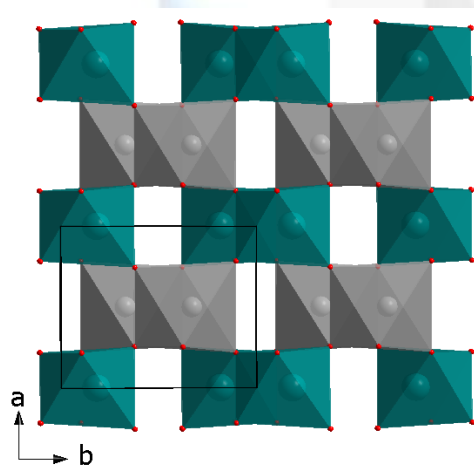
Resultados anteriores: Absorción óptica, PXRD y espectroscopia Raman

Difracción de Rayos X con monocristal bajo presión: SXRD

Resultados

Conclusiones

Familia wolframitas: AWO_4 con $A = \text{Mg, Mn, Fe, Co, Ni, Zn y Cd}$



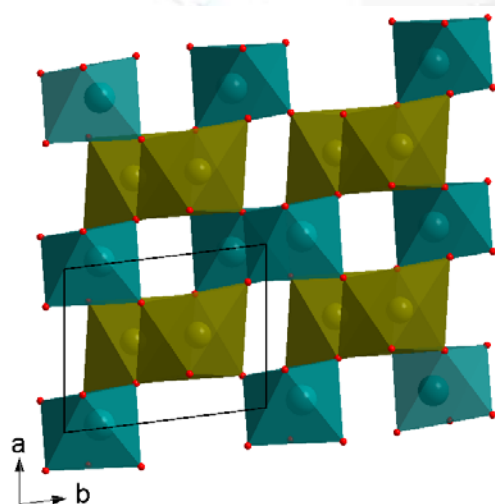
Grupo Laue: 2/m

SG: P2/c (13)

$a = 4,688 \text{ \AA}, b = 5,676 \text{ \AA}, c = 4,927 \text{ \AA}$

$\beta = 90,72^\circ$

$V = 131,09 \text{ \AA}^3, Z = 2$



Grupo Laue: -1

SG: P-1 (2)

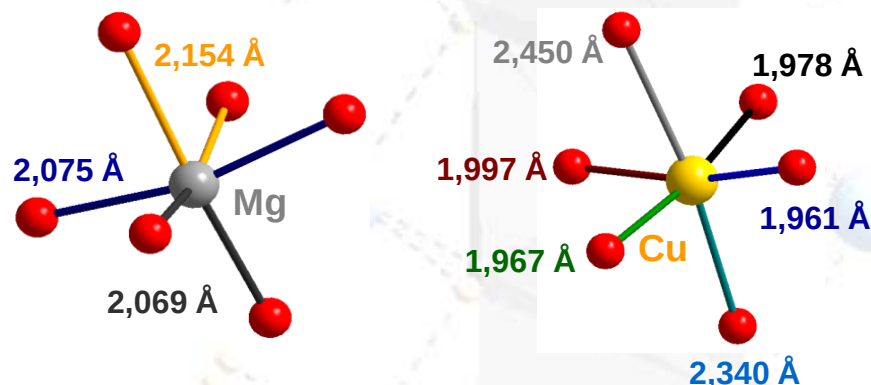
$a = 4,703 \text{ \AA}, b = 5,839 \text{ \AA}, c = 4,878 \text{ \AA}$

$\alpha = 91,68^\circ, \beta = 92,47^\circ, \gamma = 82,81^\circ$

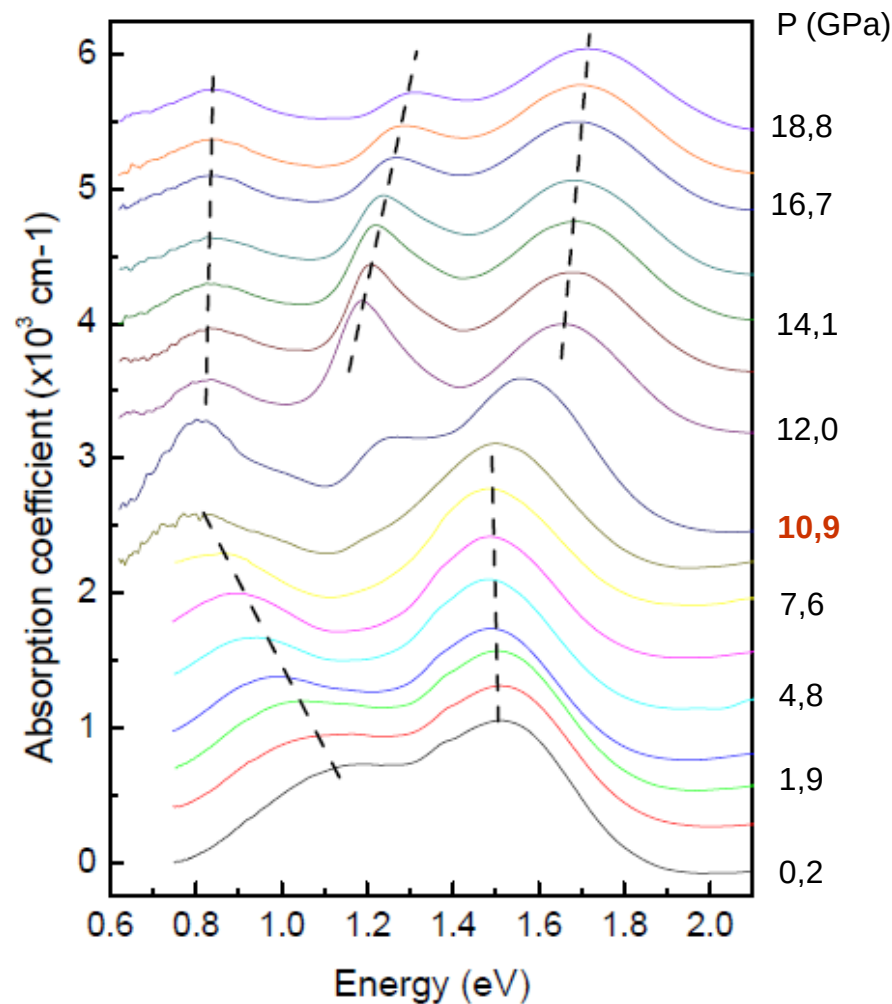
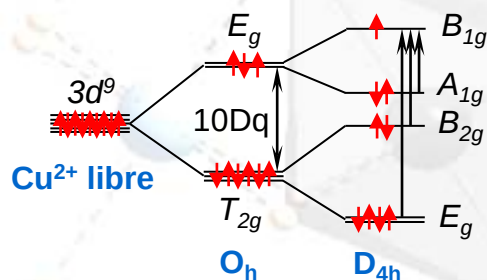
$V = 132,73 \text{ \AA}^3, Z = 2$

Introducción

¿Qué hace al CuWO_4 diferente?

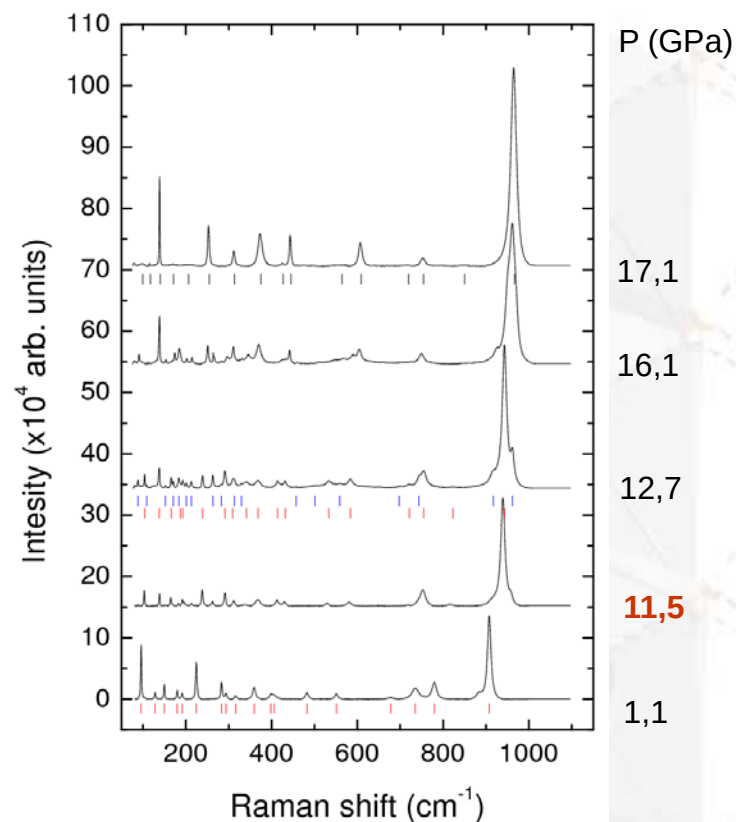


Efecto Jahn-Teller



Ruiz-Fuentes, et. al. J. Phys.: Conf. Ser. **215**, 012048 (2010)

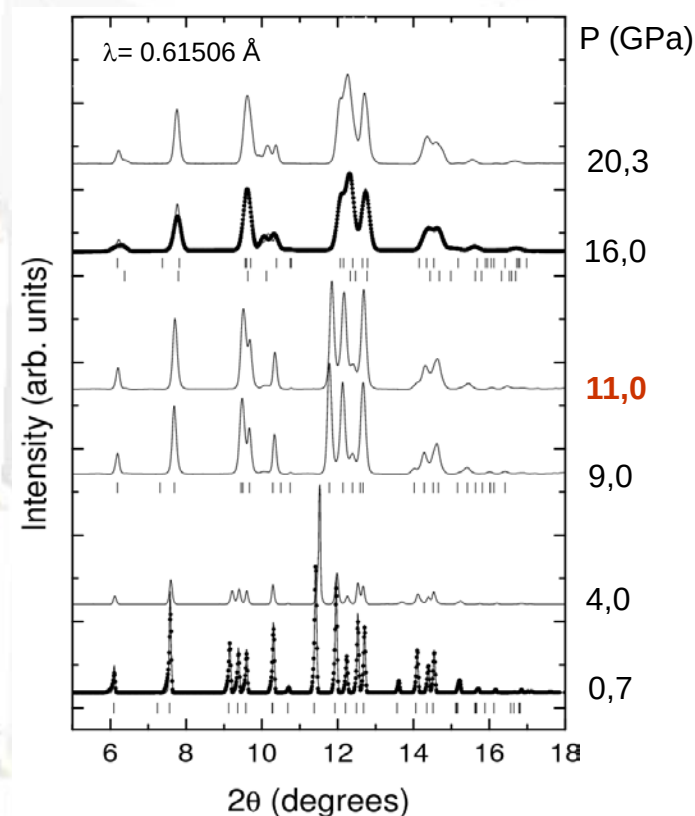
Introducción



Espectroscopía Raman

36 modos Raman a 12 GPa:

18 *P*-1 + 18 *P*2/*c*



Difracción de rayos X con polvo

Ajuste Le Bail a 16 GPa

P-1 + *P*2/*c*

Ruiz-Fuertes, et. al. PRB **81**, 224115 (2010)

¿Estructura de la Fase II?
¿Distorsión Jahn-Teller?

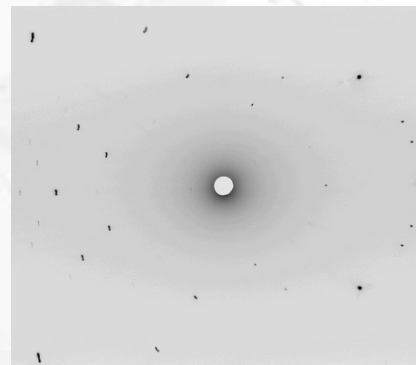
PXRD



1D

Obtención EOS bajo P

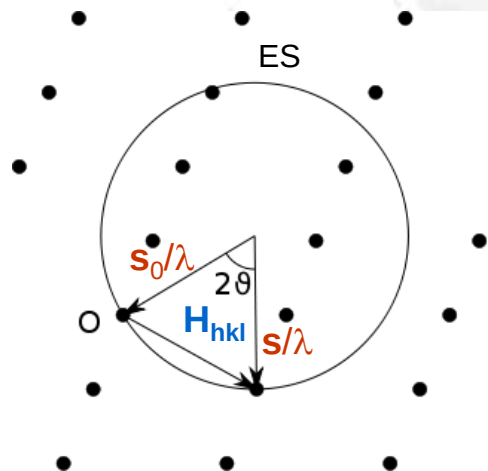
SXRD



3D

Precisión intensidades

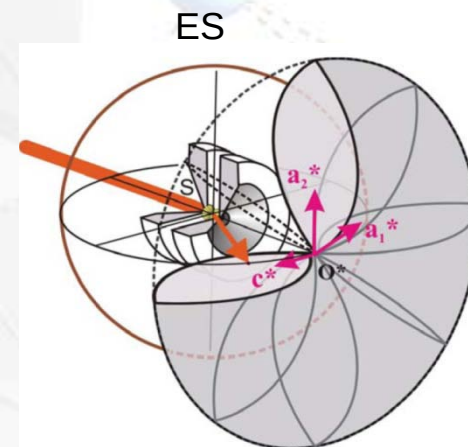
Estrategia del experimento: acceso limitado al espacio recíproco en DAC



Esfera de Ewald

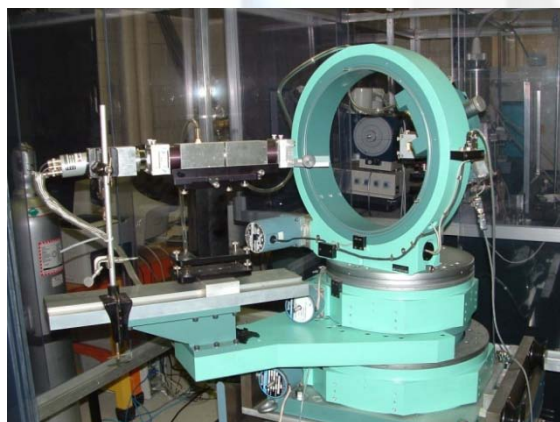
$$(\mathbf{s} - \mathbf{s}_0)/\lambda = \mathbf{H}_{hkl}$$

**Grupo Laue -1: 30%
reflexiones
accesibles**

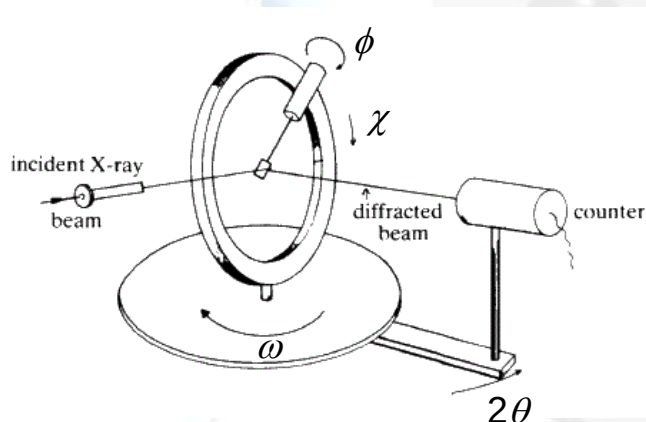


Toroide de acceso
al espacio
recíproco en DAC

Estrategia del experimento: La mejor configuración del difractómetro



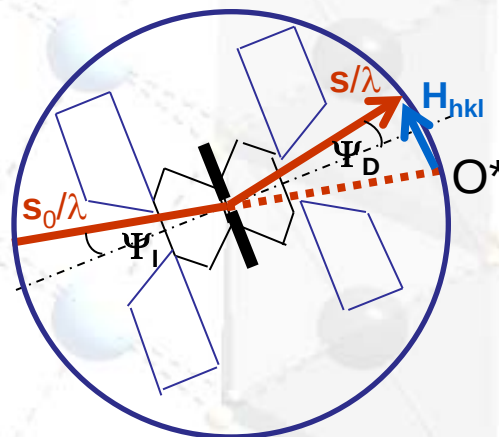
Huber 4 círculos
HASYLAB



$$\mathbf{u} = \begin{pmatrix} \cos \omega \cos \chi \cos \phi - \sin \omega \sin \phi \\ \cos \omega \cos \chi \sin \phi + \sin \omega \cos \phi \\ \cos \omega \sin \chi \end{pmatrix}$$

Una reflexión permanece en condición de Bragg si ω , ϕ y χ cambian de forma que el cristal rote sobre el vector $\mathbf{H}_{hkl}$

Busing and Levy. Acta Cryst. **22**, 457 (1967)



$$\phi = 0$$

$$\Psi_I + \Psi_D = 2\theta$$

Disminuye el recorrido
en la DAC

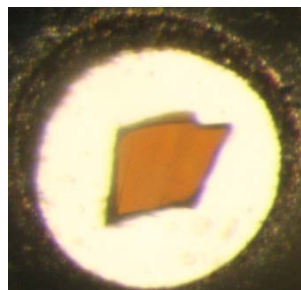
40% reflexiones observadas

Finger and King. Am. Mineral. **63**, 337 (1978)

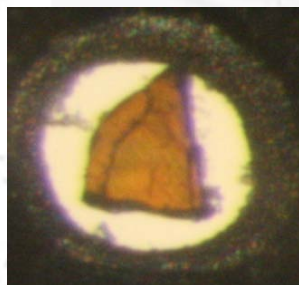
Experimentos para el CuWO_4 a 7,0 y 13,4 GPa

$$\lambda = 0,4 \text{ \AA} \longrightarrow d \sim 2/\mu \sim 30 \text{ \mu m}$$

Imposible plano (111) $\longrightarrow$ **(010)**

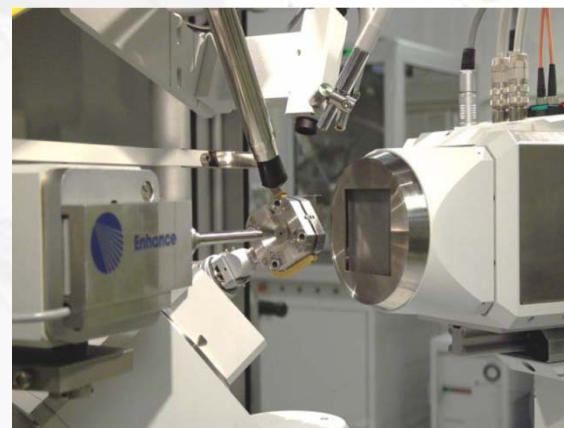


Metanol-etanol
7.0 GPa



Neon
13.4 GPa

Estimación Matriz de
orientación: **UB**



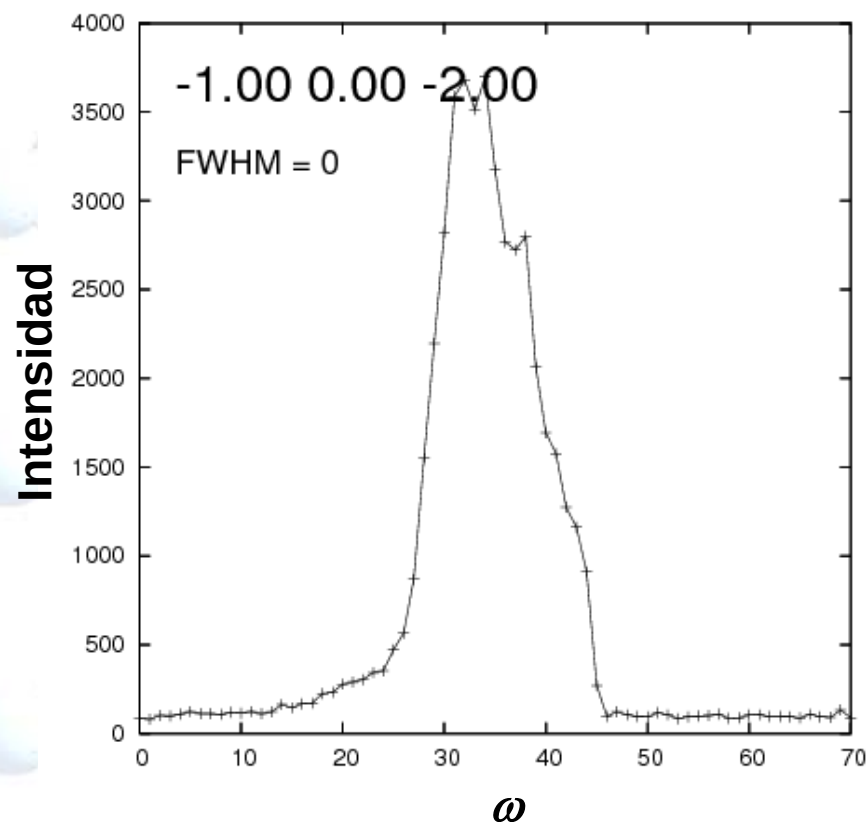
xyz = **UB** hkl

58 reflexiones

$$\begin{array}{ll} a = 4,564 \text{ \AA} & \alpha = 89,7^\circ \\ b = 5,510 \text{ \AA} & \beta = 93,0^\circ \\ c = 4,967 \text{ \AA} & \gamma = 90,0^\circ \end{array}$$

Medidas en el difractómetro Huber con detector puntual

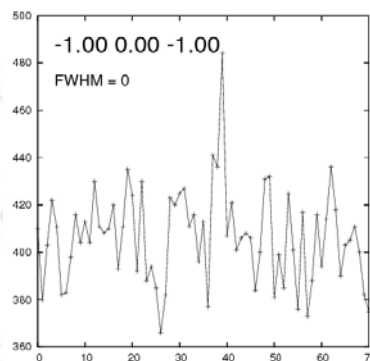
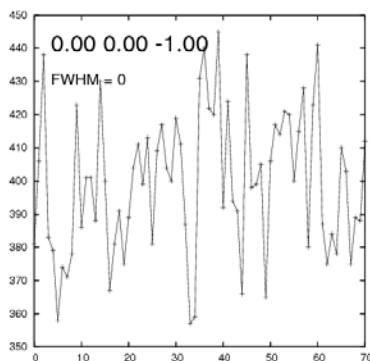
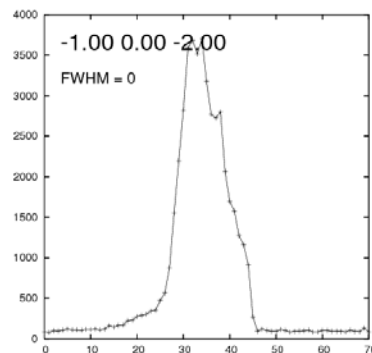
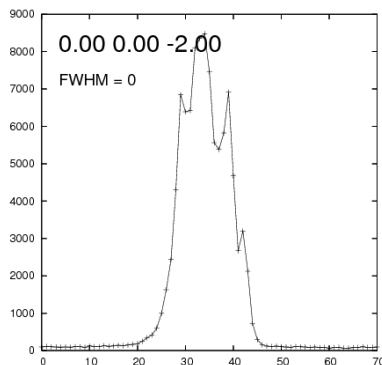
1. **Centrado:** 8 reflexiones para varios valores de los ángulos
2. **Generación de capas hkl de menor a mayor 2θ**
3. **Selección hkl no sombreadas**
4. **Medidas de referencia por variaciones intensidad**



Difracción de Rayos X con monocristal bajo presión

Análisis datos a 13,4 GPa

Extinciones sistemáticas



$00l: l = 2n+1$

$h0l: l = 2n+1$

Grupo Laue: $2/m$

$P2_1/c$

$P2/c$

Eje de tornillo en $b \rightarrow 0k0: k = 2n+1$

Las posiciones atómicas especiales
en la $P2_1/c$

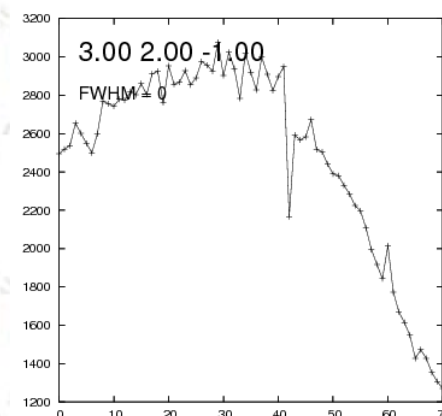
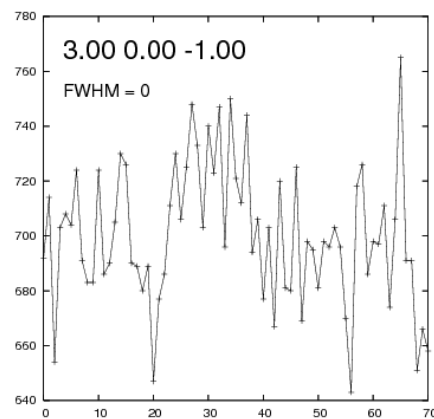
$P2/c$

Análisis datos

Archivo hkl

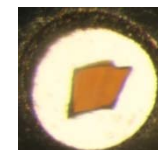
```
*** CuWO4 Drift - beide Standards *** 09:33:14
-1 1 1 5840.94 7.06 1 0.030000 8.85 37.77 -96.37 0.00 869
-1 0 -2 2978.97 4.16 1 0.030000 12.16 7.25 159.57 0.00 1077
1 1 -2 1109.91 7.26 1 0.030000 12.54 28.05 101.49 0.00 29
0 1 -2 66.24 2.04 1 0.030000 11.47 30.82 130.63 0.00 30
-1 1 -2 932.36 6.04 1 0.030000 13.06 29.40 158.76 0.00 31
0 0 -2 5840.45 36.20 1 0.030000 10.44 6.00 131.63 0.00 33
1 0 -2 2307.57 83.81 1 0.030000 11.61 5.47 102.37 0.00 34
1 -1 -2 1082.06 6.99 1 0.030000 12.53 -16.27 103.25 0.00 35
0 -1 -2 66.35 2.02 1 0.030000 11.46 -17.89 132.62 0.00 36
-1 -1 -2 861.55 5.71 1 0.030000 13.06 -13.07 160.08 0.00 37
-2 -1 -1 865.09 5.43 1 0.030000 13.61 -11.29-165.46 0.00 38
-1 -1 -1 5523.00 35.58 1 0.030000 9.22 -24.18 178.00 0.00 39
1 -1 -1 5758.99 33.79 1 0.030000 8.85 -28.93 83.63 0.00 40
2 -1 -1 1146.37 6.92 1 0.030000 13.11 -16.22 64.15 0.00 41
2 0 -1 9.59 2.21 1 0.030000 12.22 4.48 63.64 0.00 42
1 0 -1 2.99 1.55 1 0.030000 7.49 2.68 82.47 0.00 43
0 0 -1 2.87 1.09 1 0.030000 5.22 3.39 131.63 0.00 44
-1 0 -1 1.90 1.68 1 0.030000 7.92 6.00 177.32 0.00 45
-2 0 -1 4.45 2.51 1 0.030000 12.76 8.60-165.66 0.00 48
-2 1 -1 931.65 5.94 1 0.030000 13.61 29.33-165.87 0.00 49
-1 1 -1 5710.01 28.00 1 0.030000 9.22 37.42 176.61 0.00 50
1 1 -1 5996.68 29.03 1 0.030000 8.86 35.51 81.34 0.00 51
2 1 -1 1158.78 6.99 1 0.030000 13.12 26.02 63.15 0.00 52
2 1 0 131.62 1.71 1 0.030000 12.30 26.60 38.27 0.00 53
-2 1 0 151.32 1.73 1 0.030000 12.29 30.87-141.40 0.00 54
-2 0 0 5005.25 58.79 1 0.030000 11.34 7.81-141.57 0.00 55
1 0 0 1042.84 10.57 1 0.030000 5.67 4.06 141.57 0.00 56
```

Deshacerse de las reflexiones malas



Correccion absorcion Programa ABSORB Ross Angel

- Diámetro y grosor del gasket
- Coordenadas xyz de cada punto de la muestra
- Grosor de los diamantes

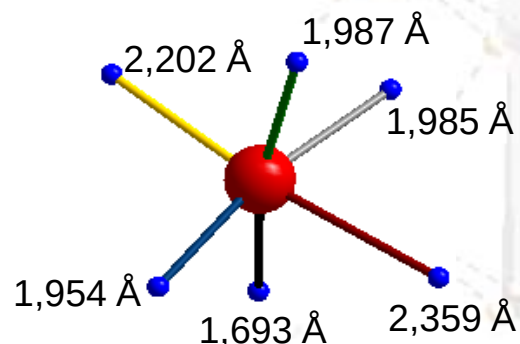
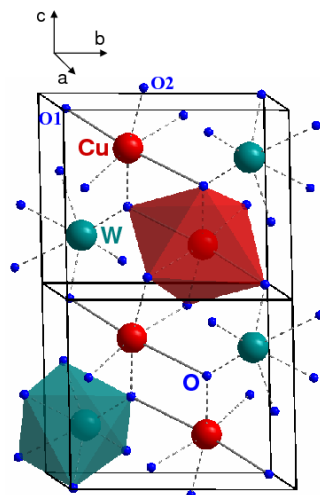


<http://www.crystal.vt.edu/crystal/software.html>

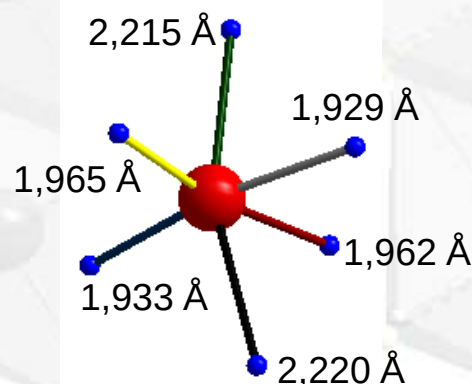
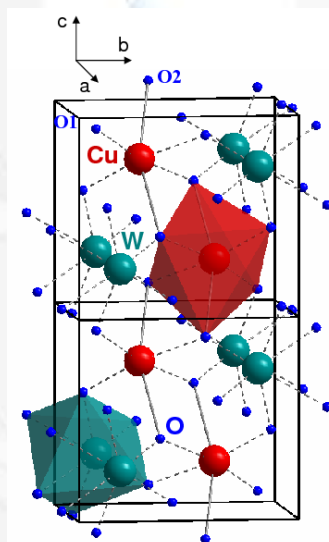
Archivo hkl → SHELX

Resultados de SXRD

P-1
7,0 GPa



P2/c
13,4 GPa



La estructura de alta presión es idéntica a una wolframita

La distorsión Jahn-Teller, aunque reducida, se mantiene

Distorsiones Jahn-Teller

MgWO₄: 0,032 Å

MnWO₄: 0,088 Å

CdWO₄: 0,095 Å

CuWO₄ (P-1,1atm): 0,21 Å

CuWO₄ (P-1,7 GPa): 0,16 Å

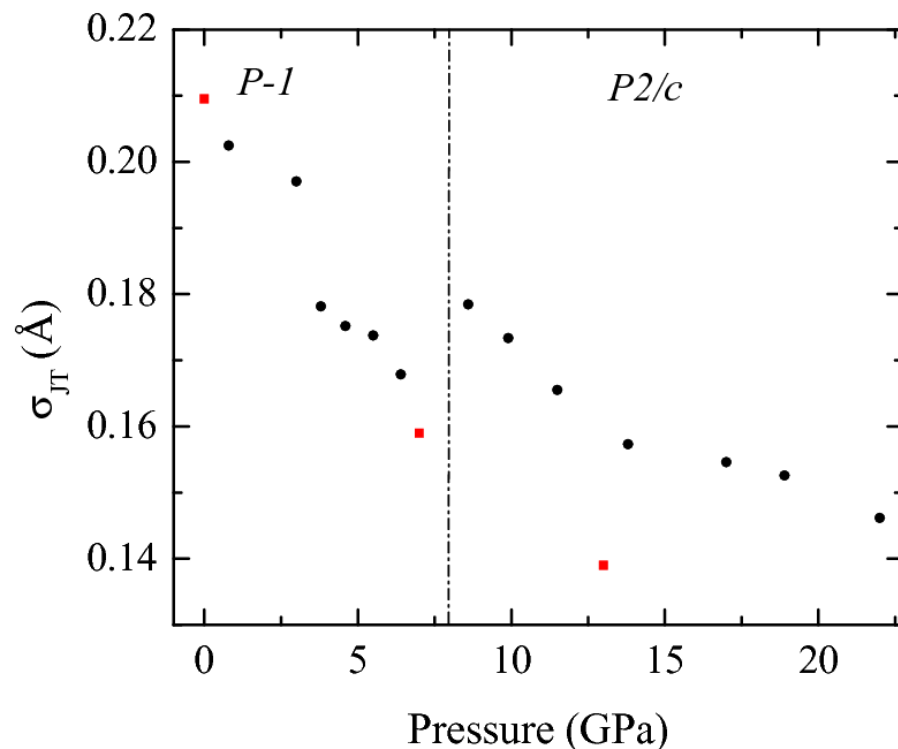
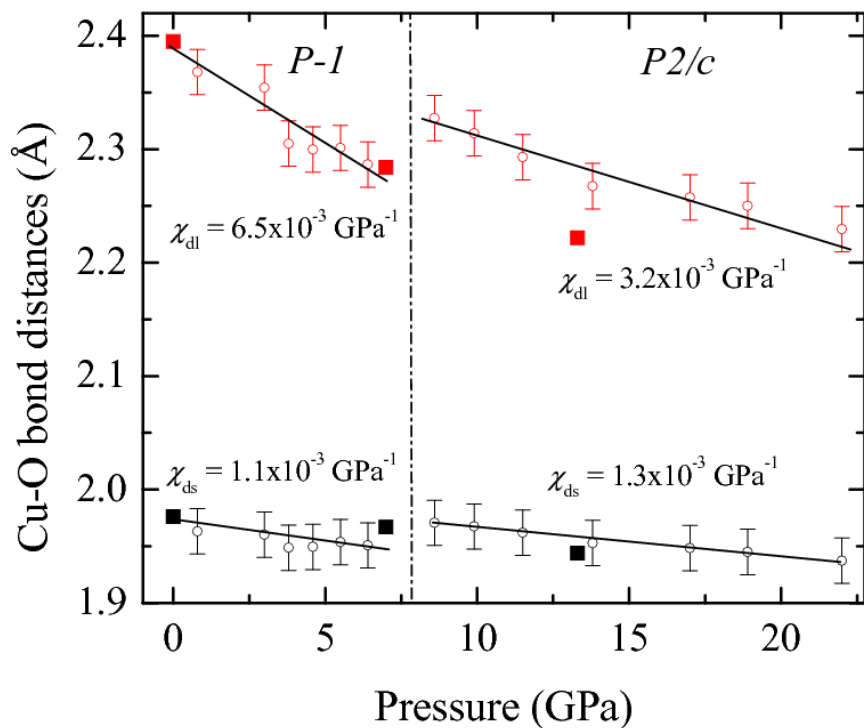
CuWO₄ (P2/c,13 GPa): 0,14 Å

Se ha explicado el procedimiento para hacer una medida de SXRD bajo alta presión con detector puntual

Mediantes SXRD hemos resuelto que la estructura de altas presiones del CuWO_4 a 13,4 GPa es un tipo wolframita

Hemos obtenido que la estructura que la distorsión Jahn-Teller persiste en la estructura de alta presión

Resultados EXAFS CuWO₄ en polvo



Difracción de Rayos X con monocristal bajo presión

Resultados Ajuste

	$P\bar{1}$	$P2/c$
p (GPa)	7.0	13.4
T (K)	293	293
V (Å ³)	128.33	123.33
<i>h</i>	$\bar{8};7$	$\bar{7};7$
<i>k</i>	$\bar{3};3$	$\bar{3};2$
<i>l</i>	$\bar{7};7$	$\bar{7};7$
Observed reflections	1024	681
Unique reflections	487	196
Parameters	26	16
R_{int}	0.0518	0.0603
R_{σ}	0.0490	0.0354
R_1	0.0382	0.0309
wR_2	0.0934	0.0667

	$P\bar{1}$ Kilborg 293 K 1 atm	$P\bar{1}$ (this work) 293 K 7.0 GPa	$P2/c$ (this work) 293 K 13.4 GPa	$P2/c$ <i>ab initio</i> 0 K 10.3 GPa
<i>a</i>	4.7026	4.6200	4.5423	4.5527
<i>b</i>	5.8389	5.7469	5.4607	5.6479
<i>c</i>	4.8784	4.8568	4.9802	4.9002
α	91.677	91.344	90	90
β	92.469	91.482	93.197	90.06
γ	82.805	84.685	90	90
	2i	2i	2f	2f
Cu site	x = 0.49533	x = 0.49768	x = 0.5	x = 0.5
	y = 0.65976	y = 0.66208	y = 0.67014	y = 0.6641
	z = 0.24481	z = 0.24576	z = 0.25	z = 0.25
	2i	2i	2e	2e
W site	x = 0.02106	x = 0.01607	x = 0	x = 0
	y = 0.17348	y = 0.17694	y = 0.18674	y = 0.1802
	z = 0.25429	z = 0.25208	z = 0.25	z = 0.25
	2i	2i	4g	4g
O ₁ site	x = 0.2491	x = 0.25261	x = 0.25341	x = 0.2598
	y = 0.3535	y = 0.35796	y = 0.39652	y = 0.3817
	z = 0.4245	z = 0.42316	z = 0.38516	z = 0.4080
	2i	2i	4g	4g
O ₂ site	x = 0.2145	x = 0.21779	x = 0.22598	x = 0.2251
	y = 0.8812	y = 0.88773	y = 0.89666	y = 0.8940
	z = 0.4309	z = 0.43064	z = 0.42627	z = 0.4302
	2i	2i		
O ₃ site	x = 0.7353	x = 0.73879		
	y = 0.3803	y = 0.38683		
	z = 0.0981	z = 0.09408		
	2i	2i		
O ₄ site	x = 0.7826	x = 0.77633		
	y = 0.9079	y = 0.90434		
	z = 0.0533	z = 0.06128		

Más allá del modelo de Debye

Nuevo módulo de cálculo de efectos térmicos en cristales

David Abbasi Pérez

Miraflores, 26 de Enero de 2011



OBJETIVOS

- Desarrollar una herramienta de cálculo para describir los efectos térmicos en cristales

De manera sencilla

A un bajo coste computacional

- Implementación del método GIBBS-Fleche en el código ***GIBBS***

Modelo de Debye-Einstein

Modelo de Debye-Einstein Extendido

- Examen y comprobación del nuevo código

EOS y propiedades termodinámicas en

MgO, β -C₃N₄, BaWO₄-II

FUNDAMENTOS

- Cristalografía
 - Descripción de los sistemas cristalinos
- Estructura electrónica
 - Cálculos bajo el formalismo de Hartree-Fock y DFT
- Paquetes estándar de cálculo en el estado sólido
 - CRYSTAL ,VASP, Quantum Espresso.
- Programación y métodos numéricos
 - Desarrollo del código en FORTRAN
- Termodinámica estadística
 - Obtención de propiedades termodinámicas a partir de la descripción microscópica (estructura electrónica y vibraciones cristalinas)

MODELOS TÉRMICOS

Energía libre de Gibbs de no equilibrio

$$G^*(V; p, T) = E_{el}^0(V) + pV + A_{vib}(V; T)$$

donde $E_{el}^0(V)$ se obtiene calculando las energías electrónicas a cada volumen de celda del cristal.

$$A_{vib} = \int_0^\infty \left\{ \frac{1}{2} h\nu + k_B T \ln (1 - e^{-h\nu/k_B T}) \right\} g(\nu) d\nu$$

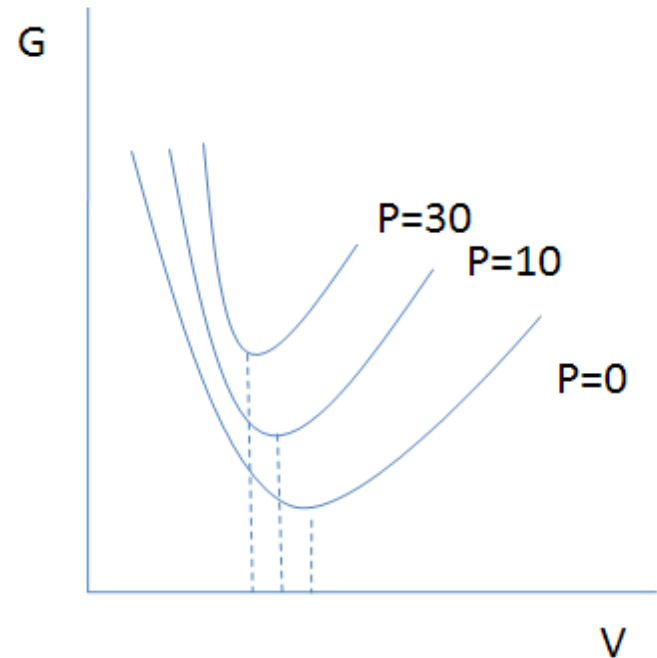
donde $g(\nu)$ es la densidad de estados vibracionales (tanto acústicos como ópticos)

MODELO ESTÁTICO

- $T = 0$ y no se tienen en cuenta las vibraciones del punto cero

$$G_{st}^*(V; p, T) = H_{st}^* = E(V) + pV$$

- Datos de *input* : Conjunto de puntos (E, V) .
- La G_{st}^* se minimiza con respecto a V y se obtiene
 - la EOS $V(p) = V_{opt}(p)$
 - el potencial químico $G(p) = G_{st}^*(V_{opt}(p))$



MODELO DE DEBYE

$$G^*(V; p, T) = E_{el}^0(V) + pV + A_{vib}(V; T)$$

En el modelo de Debye A_{vib} es

$$A_{vib}(\Theta; T) = nkT \left[\frac{9}{8} \frac{\Theta}{T} + 3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right]$$

La integral de Debye

$$D(y) = \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx$$

La temperatura caracterísitica de Debye

$$\Theta = \frac{\hbar}{k} [6\pi^2 V^{1/2} n]^{1/3} f(\sigma) \sqrt{\frac{B_s}{M}}$$

B_s : Bulk modulus adiabático

M : Masa molecular por fórmula unidad

σ : Poisson ratio (aproximamos a una constante)

$$B_S \approx B_{st}(V) = V \left(\frac{d^2 E_{el}^0(V)}{dV^2} \right)$$

MODELO DEBYE

Propiedades termodinámicas que podemos obtener

$$U_{\text{vib}} = nkT \left[\frac{9}{8} \frac{\Theta}{T} + 3D(\Theta/T) \right]$$

$$C_{\text{v,vib}} = 3nk \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right],$$

$$S_{\text{vib}} = nk \left[4D(\Theta/T) - 3 \ln(1 - e^{-\Theta/T}) \right]$$

$$\gamma = - \frac{d \ln \Theta(V)}{d \ln V}.$$

$$\alpha = \frac{\gamma C_{\text{v,vib}}}{B_T V},$$

$$C_{\text{p,vib}} = C_{\text{v,vib}}(1 + \alpha \gamma T),$$

$$B_S = B_T(1 + \alpha \gamma T).$$

MÉTODO DE FLECHE

Separación en contribuciones estática, acústica y óptica.

$$A = A_{st} + A_{vib}, \quad A_{vib} = A_{ac} + A_{op}$$

Se aproxima las ramas de frecuencias acústicas para $\mathbf{k} \neq \mathbf{0}$ con el modelo de Debye

$$\nu_{ac,i}(\mathbf{k}) = (v_i/2\pi) |\mathbf{k}|, \quad i = 1, 2, 3$$

donde v_i es la velocidad de fase de las vibraciones acústicas.

Cada una de las ramas de frecuencias ópticas se aproxima con el modelo de Einstein.

$$\nu_{op,i}(\mathbf{k}) = \nu_i(\Gamma) \quad i = 4, 3n$$

donde $\nu_i(\Gamma)$ son las frecuencias de vibración en el punto Γ , $\mathbf{k} = \mathbf{0}$.

MÉTODO DE FLECHE

Parte estática

Parte acústica

$$A_{st} = E_{el}^0, \quad A_{ac} = Nk_B T \left[\frac{9}{8} \frac{\Theta_D}{T} + 3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right]$$

Parte óptica

$$A_{op} = Nk_B T \sum_{j=4}^{3n} \left[\frac{x_j}{2} + \ln(1 - e^{-x_j}) \right], \quad x_j = \frac{h\nu_j}{k_B T}$$

$$\nu_i(\Gamma) = \nu_{i,0}(\Gamma) \left(\frac{V}{V_{st,0}} \right)^{1/6} \left(\frac{B_{st}}{B_{st,0}} \right)^{1/2} \left(1 - \frac{2p_{st}}{3B_{st}} \right)^{1/2}$$

Otras magnitudes termodinámicas

$$S = S_{ac} + S_{op}$$

$$C_v = C_{v,ac} + C_{v,op}$$

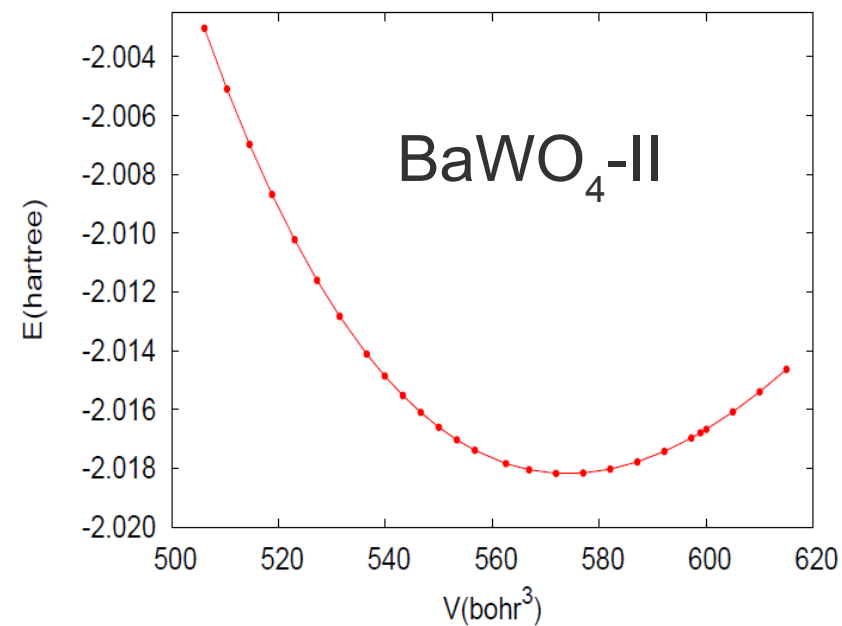
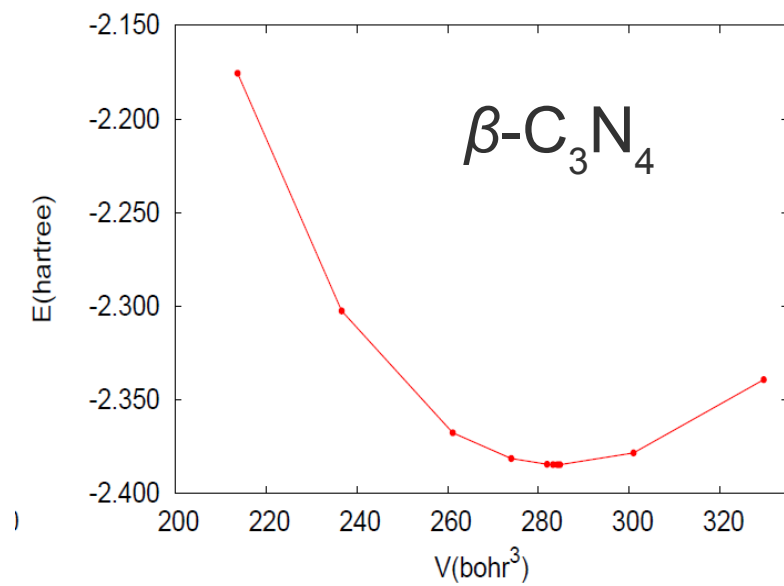
$$S_{ac} = Nk_B \left[4D(\Theta/T) - 3 \ln(1 - e^{-\Theta/T}) \right] \quad C_{v,ac} = 3Nk_B \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right]$$

$$S_{op} = Nk_B \sum_{j=4}^{3n} \left[\frac{x_j}{e^{x_j} - 1} - \ln(1 - e^{-x_j}) \right] \quad C_{v,op} = Nk_B \sum_{i=4}^{3n} \left[\frac{(x_j)^2 e^{x_j}}{(e^{x_j} - 1)^2} \right]$$

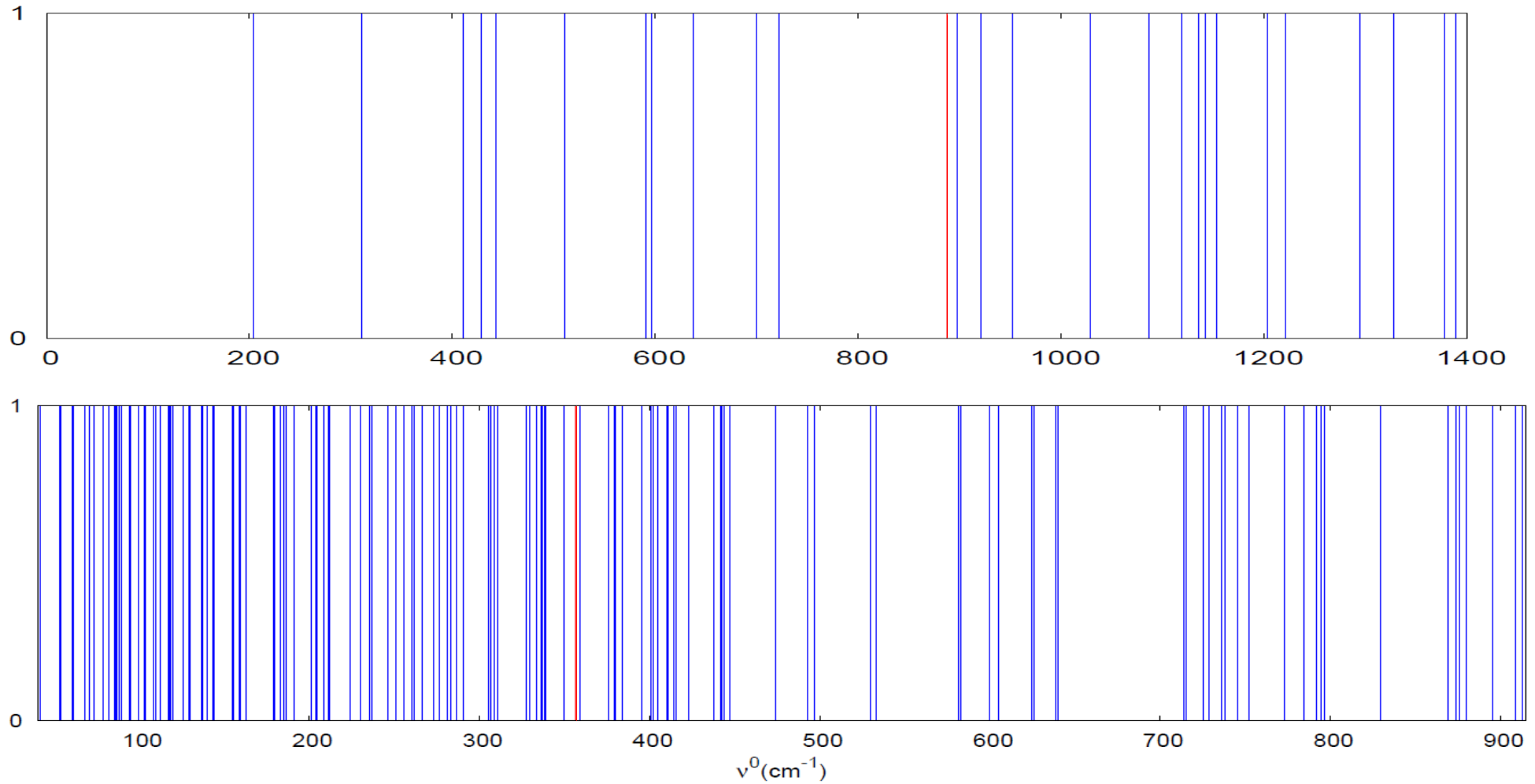
MÉTODO GIBBS-Fleche

- Combinación del método de Fleche con la estrategia computacional de GIBBS
- Descripción de la contribución vibracional como propone Fleche
 - Separación de contribuciones vibracionales en parte acústica y parte óptica
 - Dependencia de las frecuencias ópticas en Γ con V
- Si usamos todas las frecuencias en Γ para la descripción de la contribución óptica hablaremos del modelo de Debye-Einstein Extendido (DEE)
- Si simplificamos el tratamiento de todas las ramas ópticas a una única frecuencia (la frecuencia media) hablaremos del modelo de Debye-Einstein (DE)

CURVAS ENERGÍA-VOLUMEN



DISTRIBUCIÓN DE FRECUENCIAS



Frecuencias ópticas en Γ en la geometría de equilibrio estática a presión cero para el $\beta\text{-C}_3\text{N}_4$ (arriba) y el $\text{BaWO}_4\text{-II}$. En rojo, la frecuencia media (ν_e)

V_0, B_0 y B_0' EN CONDICIONES ESTÁTICAS, 0 K Y 300 K

Valores obtenidos con el método GIBBS-Fleche

Param	$\beta\text{-C}_3\text{N}_4$			$\text{BaWO}_4\text{-II}$		
	Stat	0K	300K	Stat	0K	300K
$V_0(\text{bohr}^3)$	284.86	288.56	288.81	574.06	586.46	594.84
$B_0(\text{GPa})$	441.91	433.92	431.69	83.63	77.37	69.36
B_0'	3.8314	3.7080	3.7169	5.7881	5.7460	6.0333

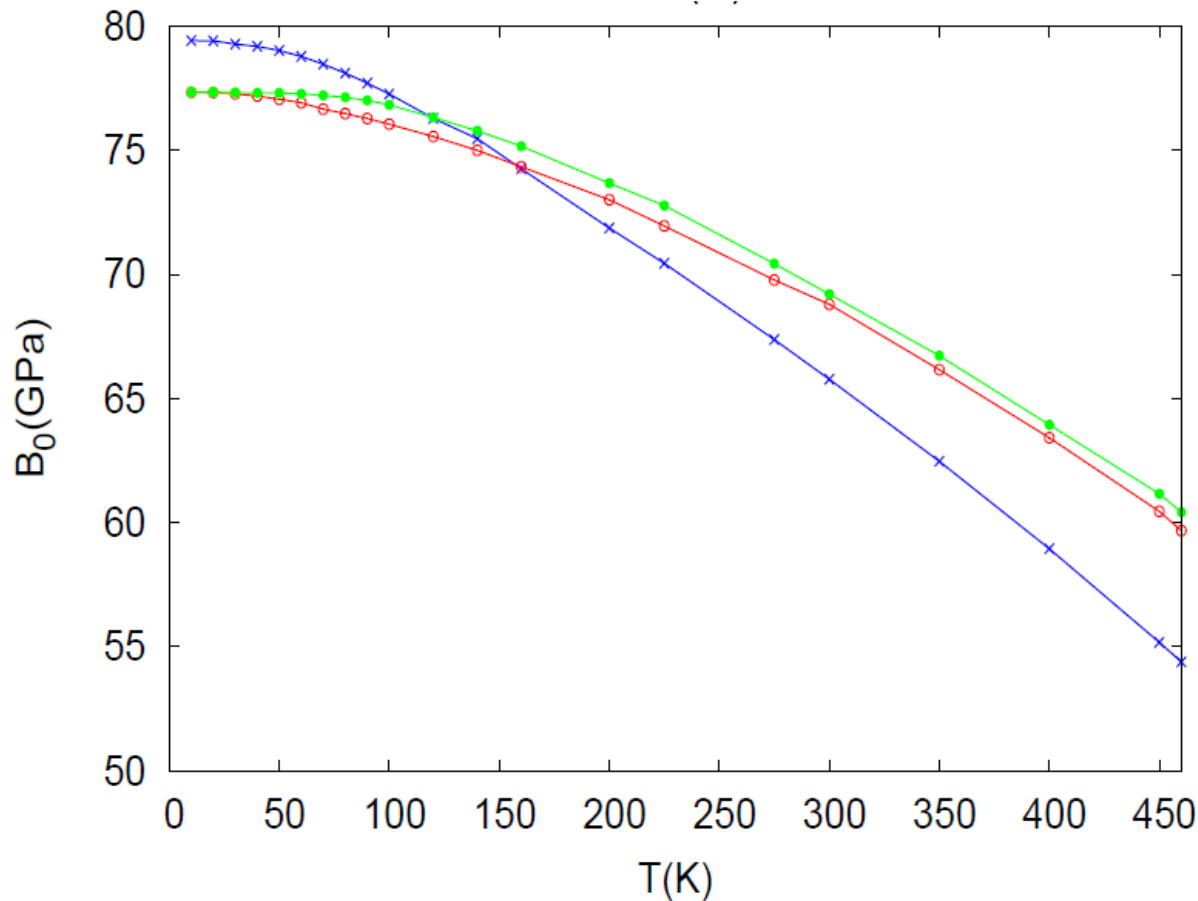
Distinguimos dos factores: vibraciones del punto cero y efecto de la temperatura.

Existe variación del volumen debido a la naturaleza cuasi-armónica del modelo.

El factor más importante en general es la inclusión de las vibraciones de punto cero.

V_0 aumenta y B_0 disminuye al aumentar la temperatura.

COMPORTAMIENTO DE B_0



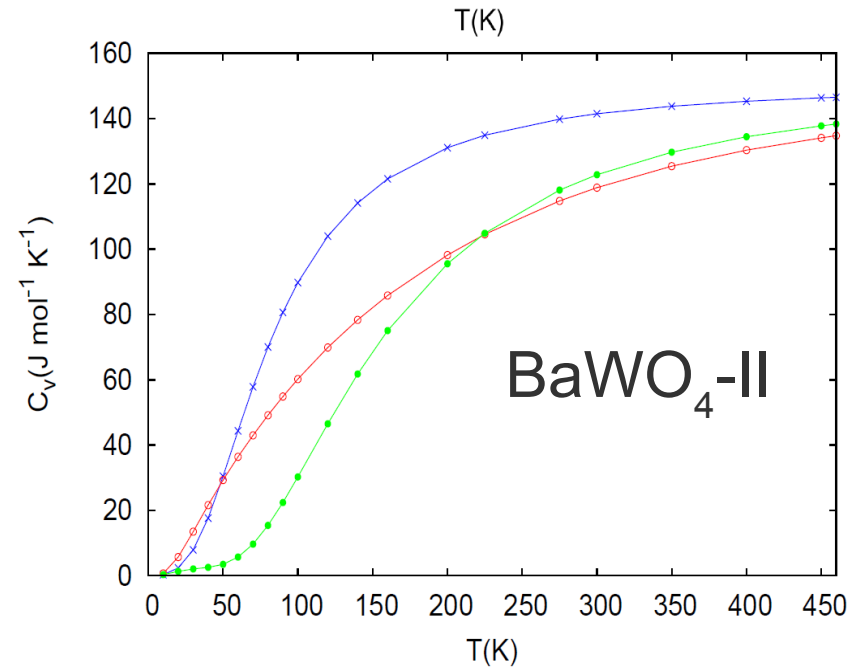
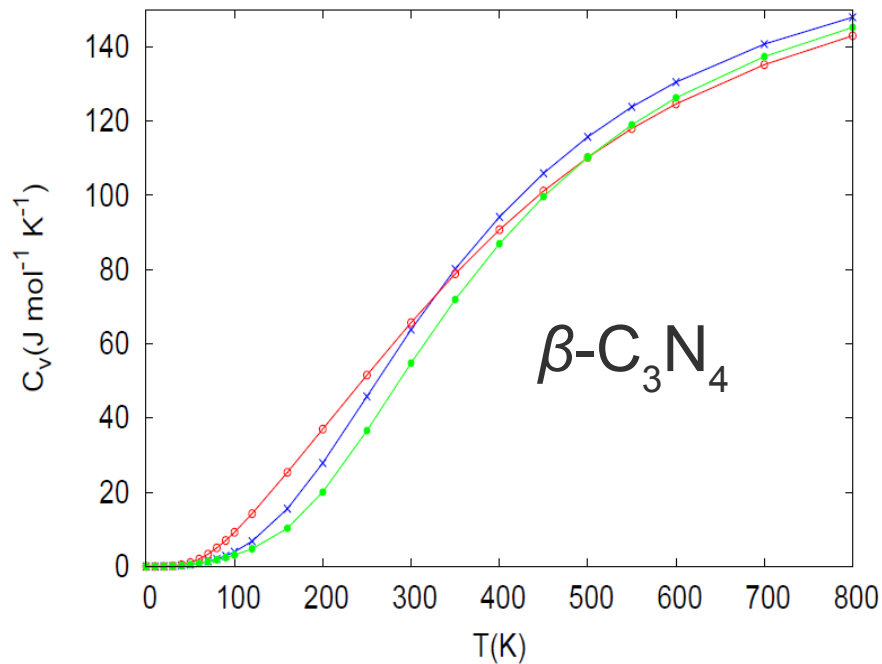
Muestra patrones de variación similares en todos los cristales.

A alta temperatura se obtienen valores mayores con el método de GIBBS-Fleche que con el modelo de Debye.

Representación del bulk módulo isoterma a $p = 0$ para el $\text{BaWO}_4\text{-II}$

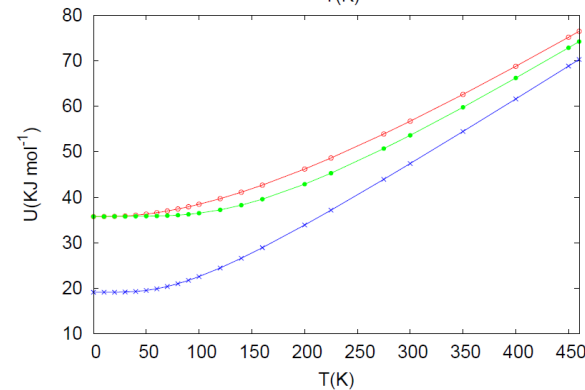
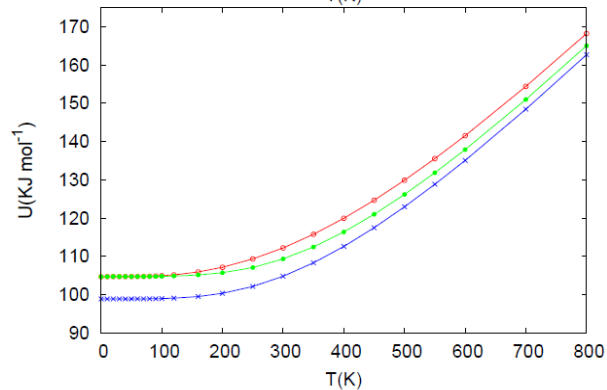
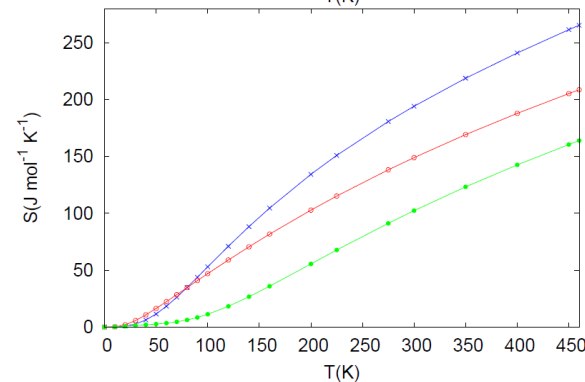
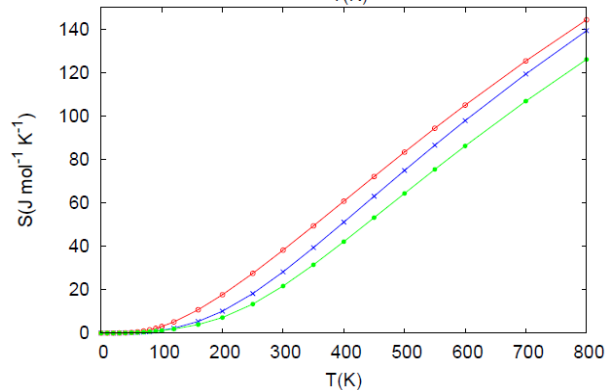
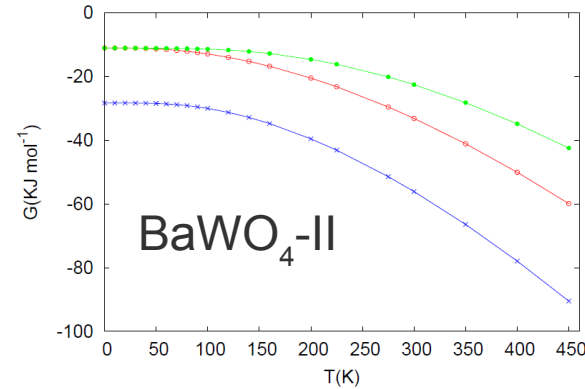
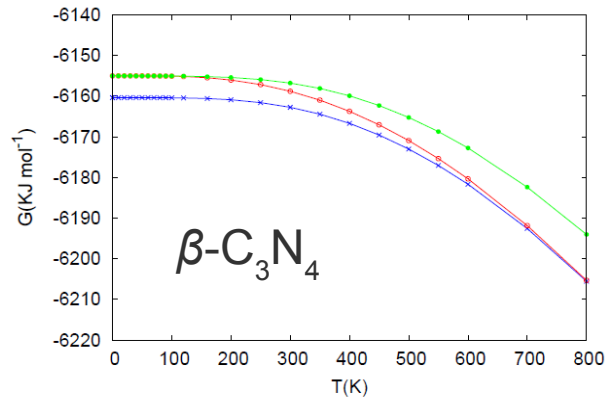
En azul, el modelo de **Debye**, en verde el modelo de **Debye-Einstein** y en rojo el de **Debye-Einstein Extendido**

COMPORTAMIENTO DE C_v



La representación de C_v ha de seguir la ley T^3 de Debye a baja temperatura y la de Dulong y Petit a alta temperatura. El nuevo método se comporta bien.

COMPORTAMIENTO DE G , S y U



Representación de las funciones termodinámicas obtenidas por tres modelos.

En los materiales más blandos las curvas de los diferentes modelos se separan más que en los materiales más duros.

Materiales de alta presión como electrodo para baterías de litio.

M.E. Arroyo y de Dompablo

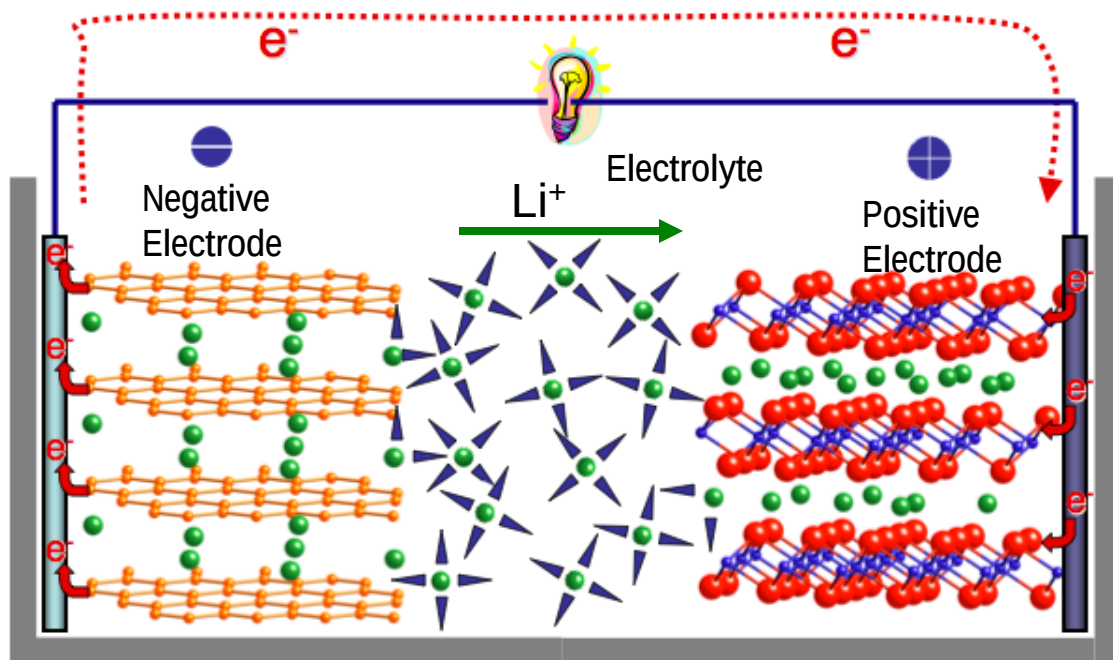
*Facultad de Ciencias Químicas,
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Lithium ion batteries



Positive Electrode

Alto poder oxidante

$V_+ > 3V$ vs. Li^+/Li

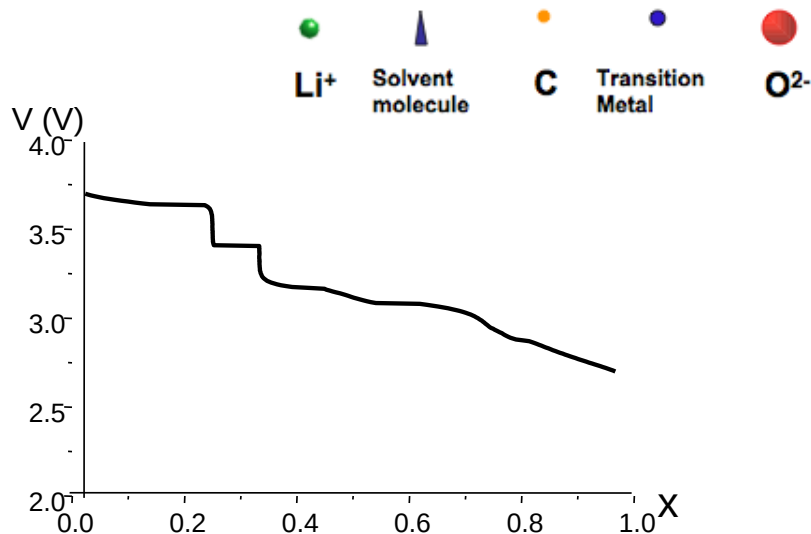
V_2O_5 , LiMn_2O_4 , LiCoO_2 , LiFePO_4

Negative Electrode

Alto poder reductor

$V_- < 1.2\text{ V}$ vs. Li^+/Li

Li_xC_6 , $\text{Li}_{2.6+x}\text{Co}_{0.4}\text{N}$, SnO



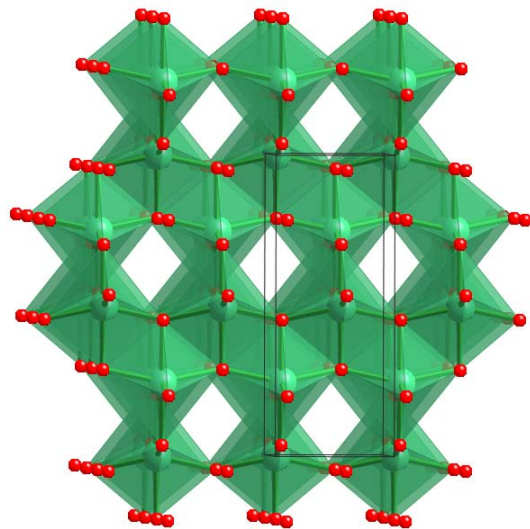
Discharge of the cell: $\Delta G < 0$

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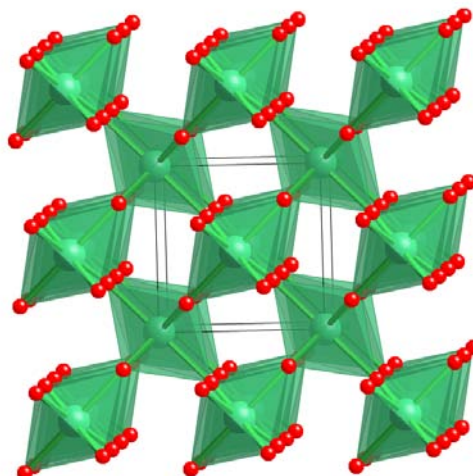
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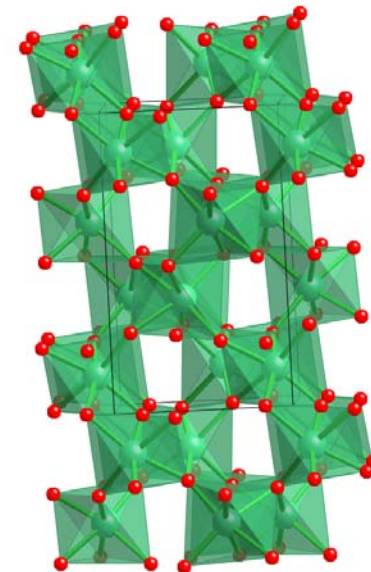
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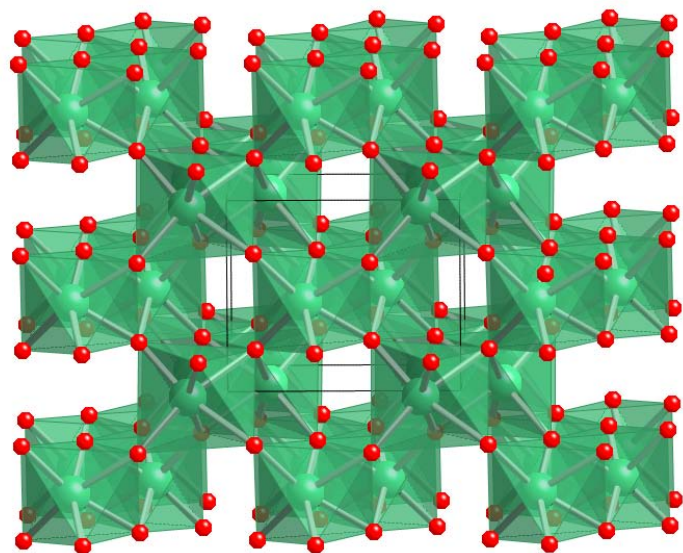


Rutile



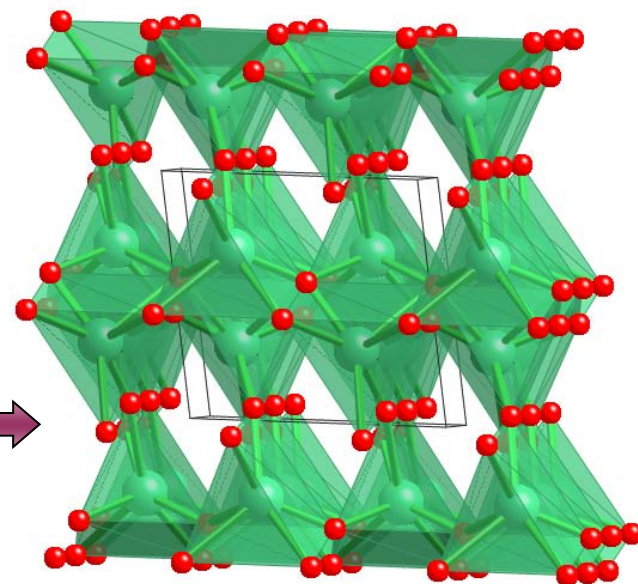
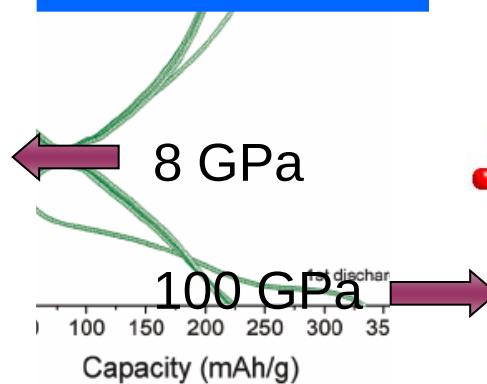
Brookite

TEMPERATURE



Columbite

PRESSURE

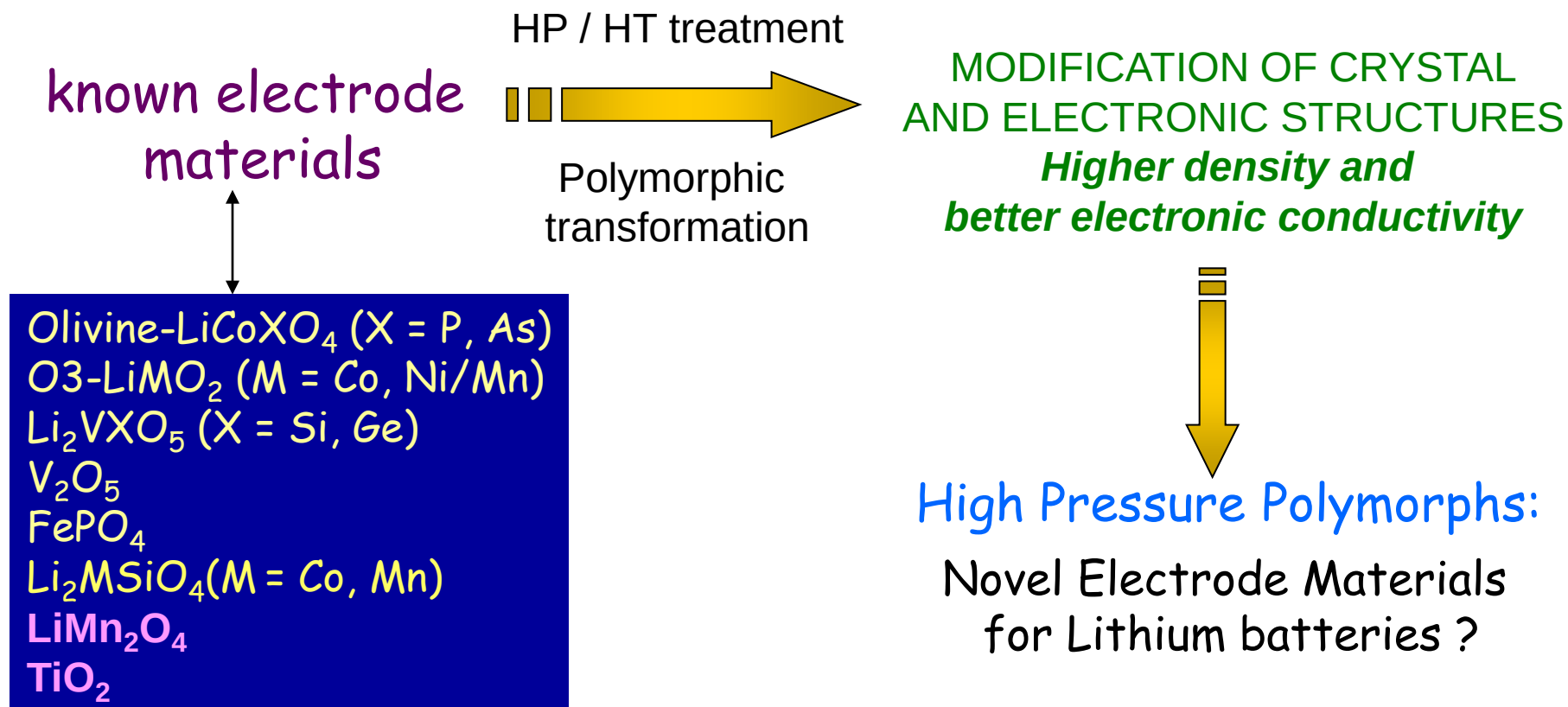


Baddeleyite

© Jambournet, I. Belharouak, and K. Amine, C

High pressure polymorphs

Searching for novel electrode materials



High Pressure/ High temperature Experiments

Belt-type press



AP-polymorph  HP-polymorph

HP / HT

Belt-type press: 1400 °C, 80 kbar
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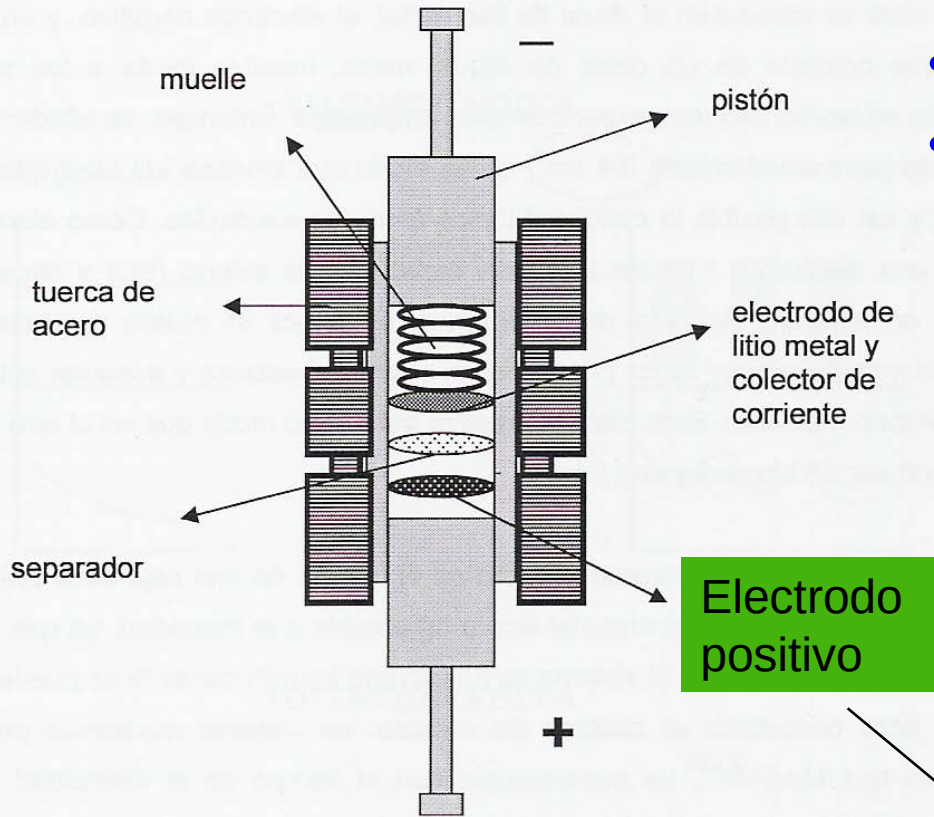
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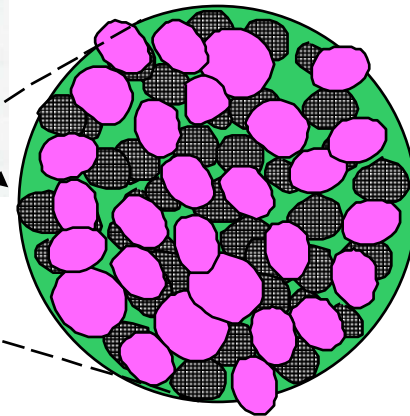
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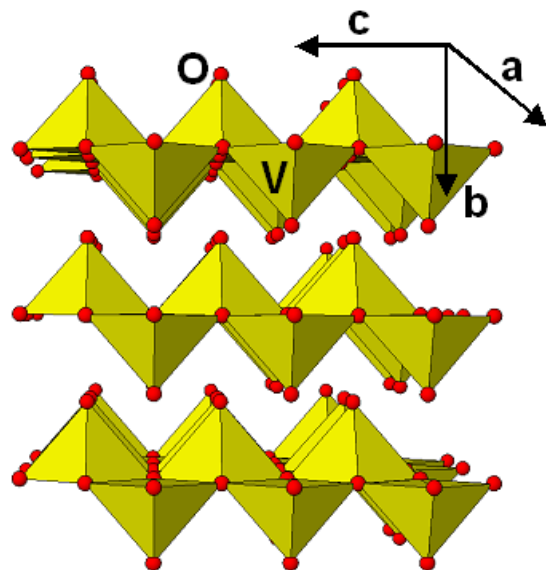
Celda Swagelok





Ambient pressure

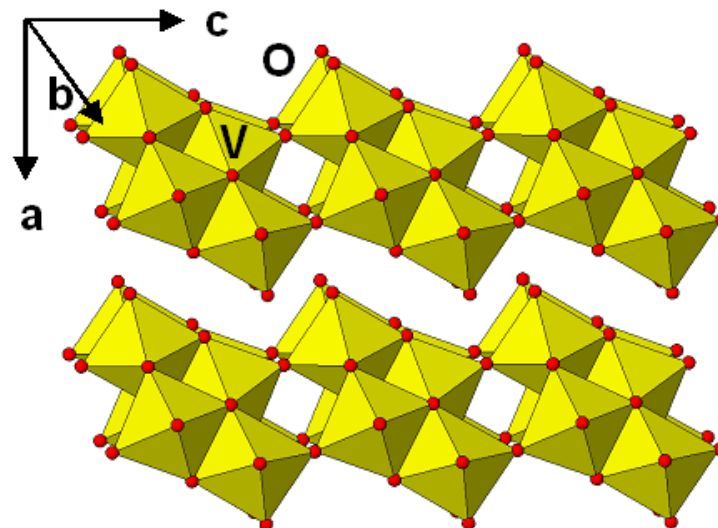
High pressure



6 GPa

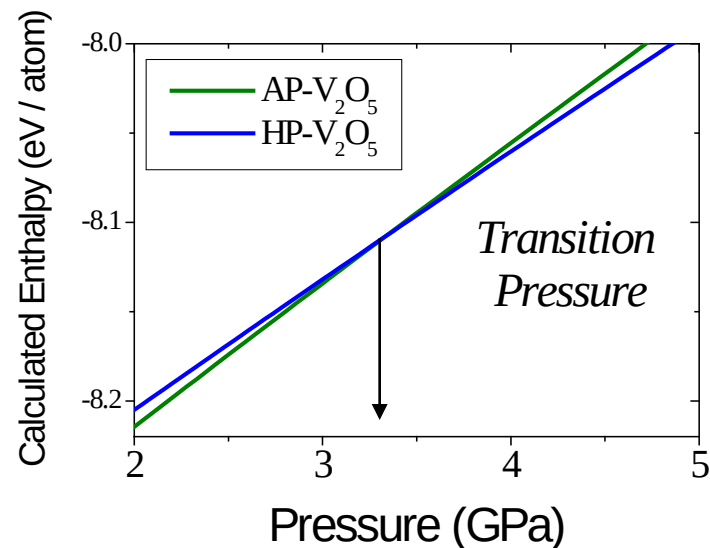
 800°C/90 min

V. P. Filonenko, et al,
 Acta Cryst B, 2004



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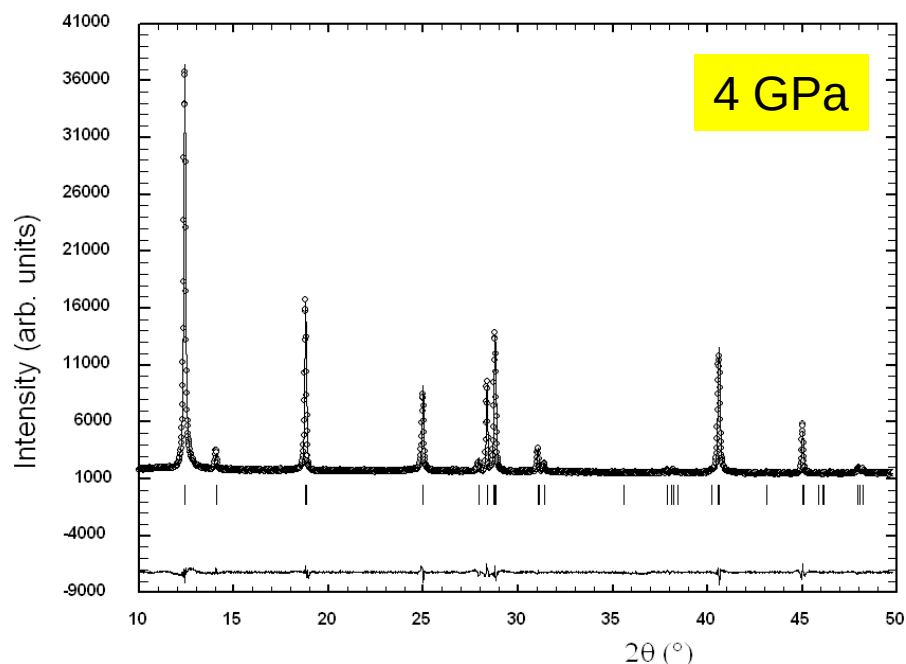
Commercial V_2O_5

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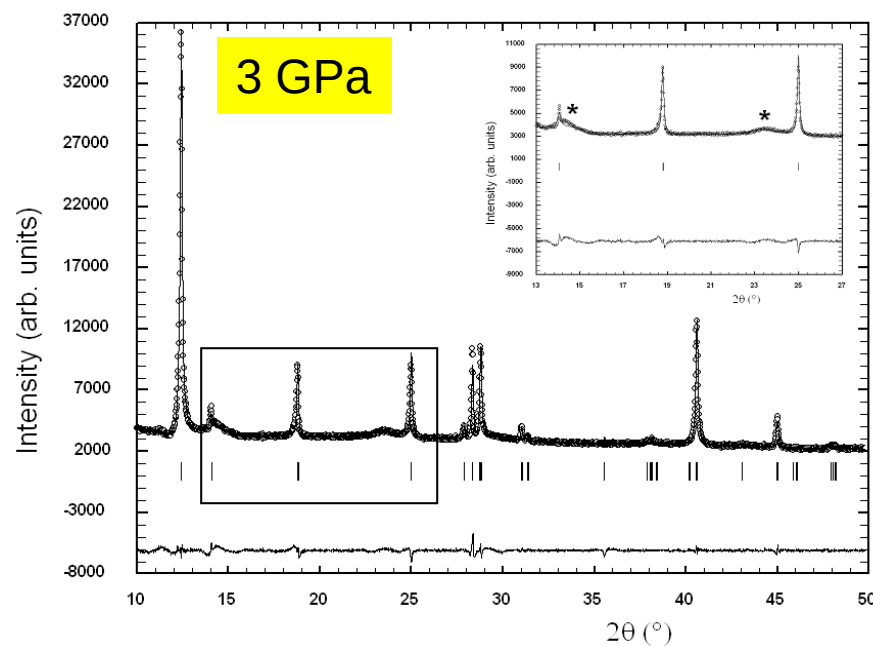


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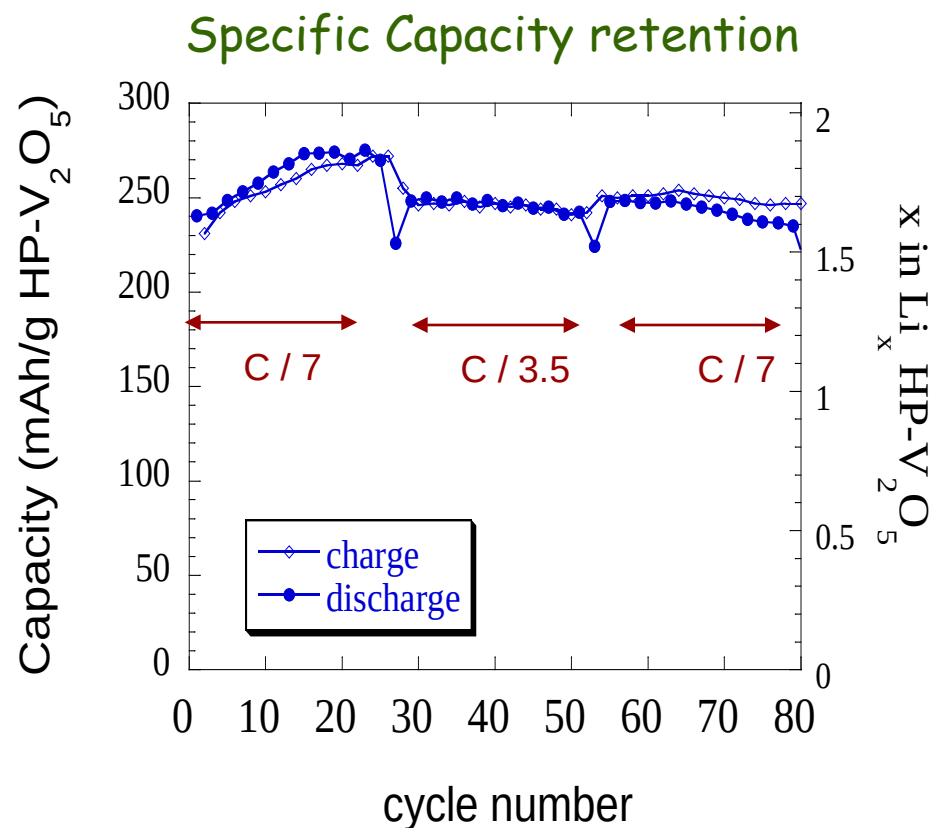
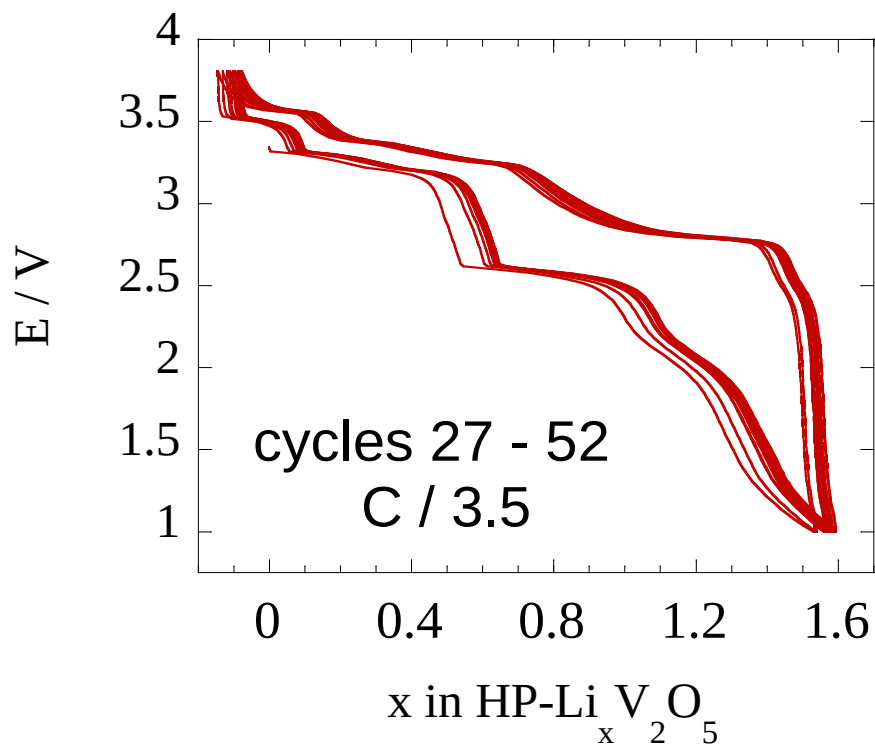
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Good agreement experiments-computations

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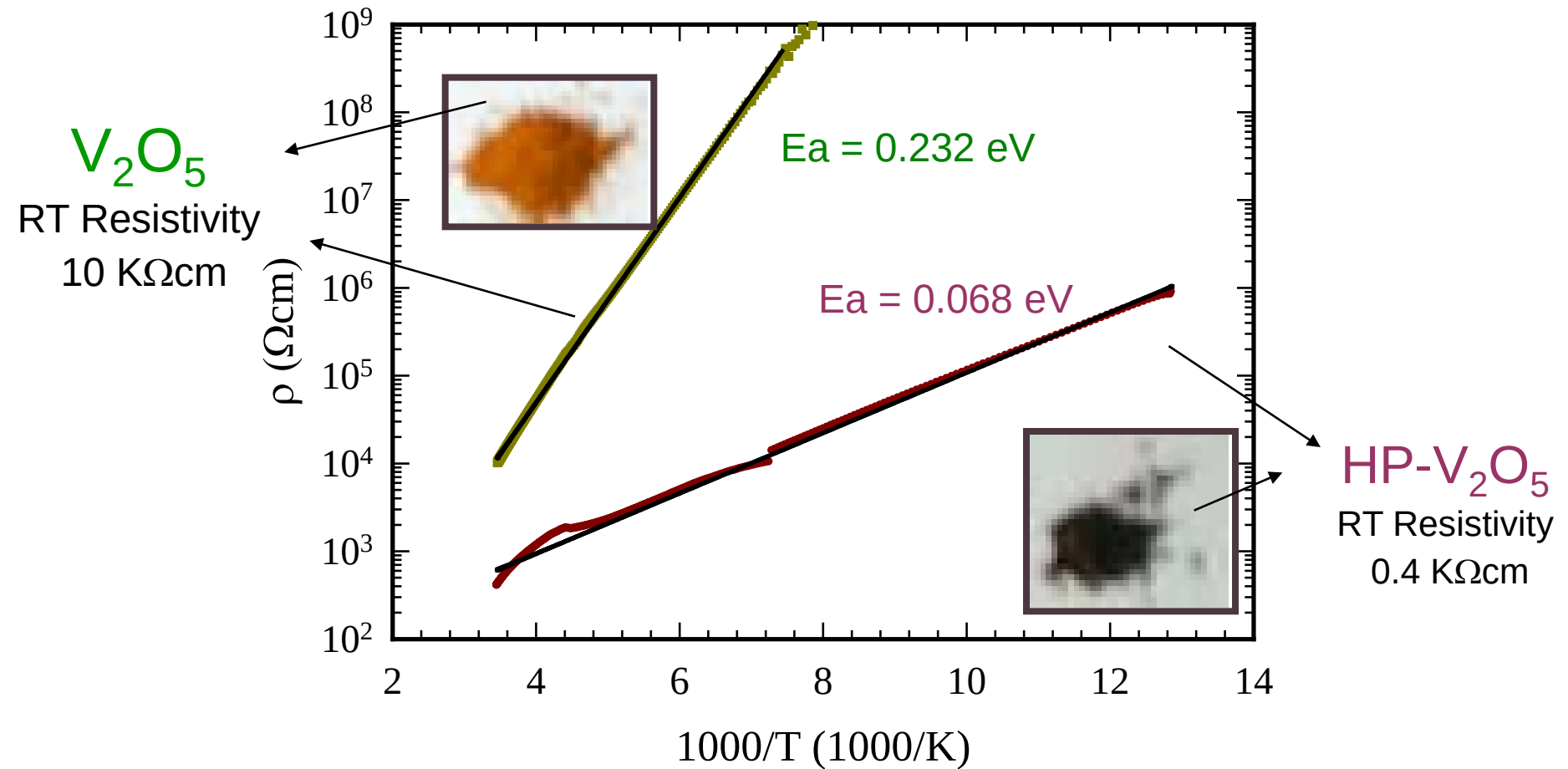


High Specific Capacity and good retention with cycling.
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M.E. Arroyo, J.M. Gallardo-Amores, U. Amador and E. Morán *Electrochem. Comm.*, 2007

M.E. Arroyo y de Dompablo, N. Biskup, J.M. Gallardo-Amores, C. Baethz, U. Amador, and M.E. Arroyo y de Dompablo, *Journal of Physics; Conference Series*, 2008

The advantage of the HP-form

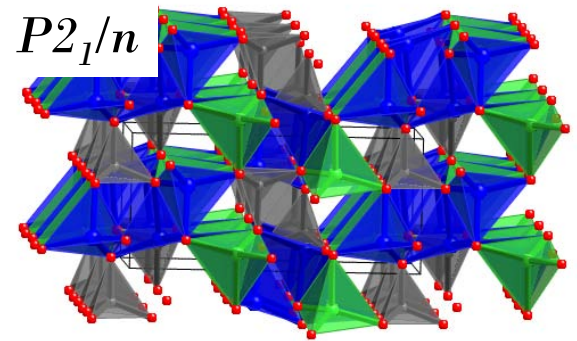
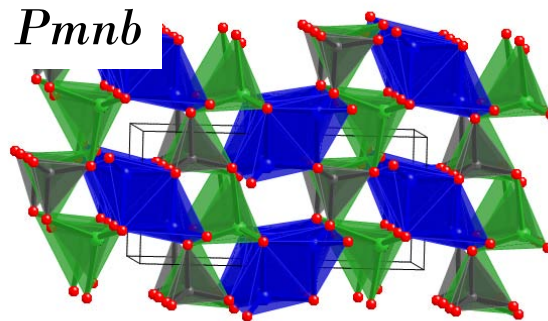
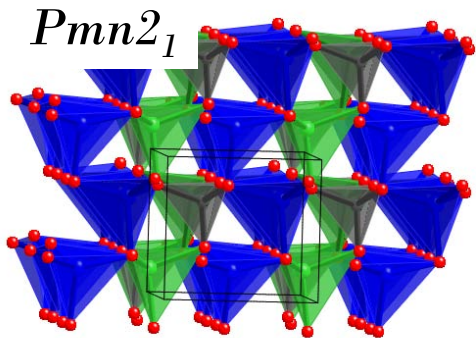
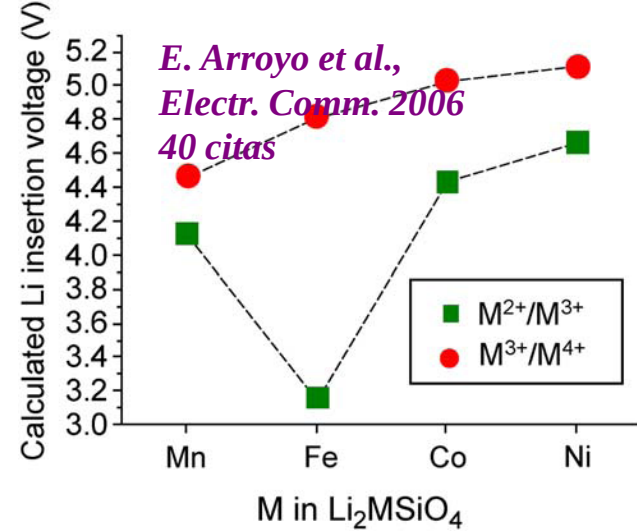
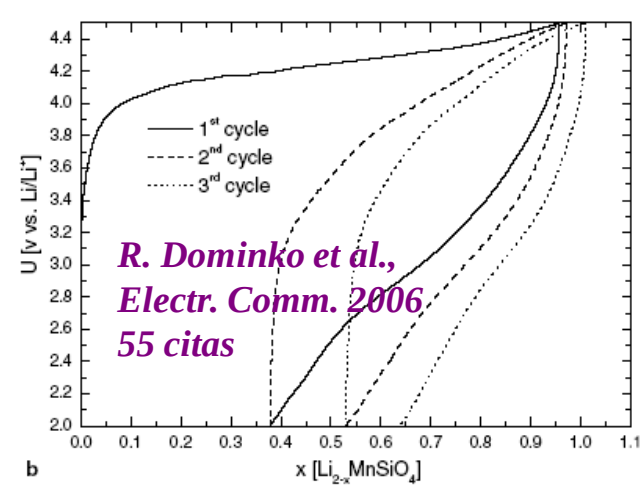


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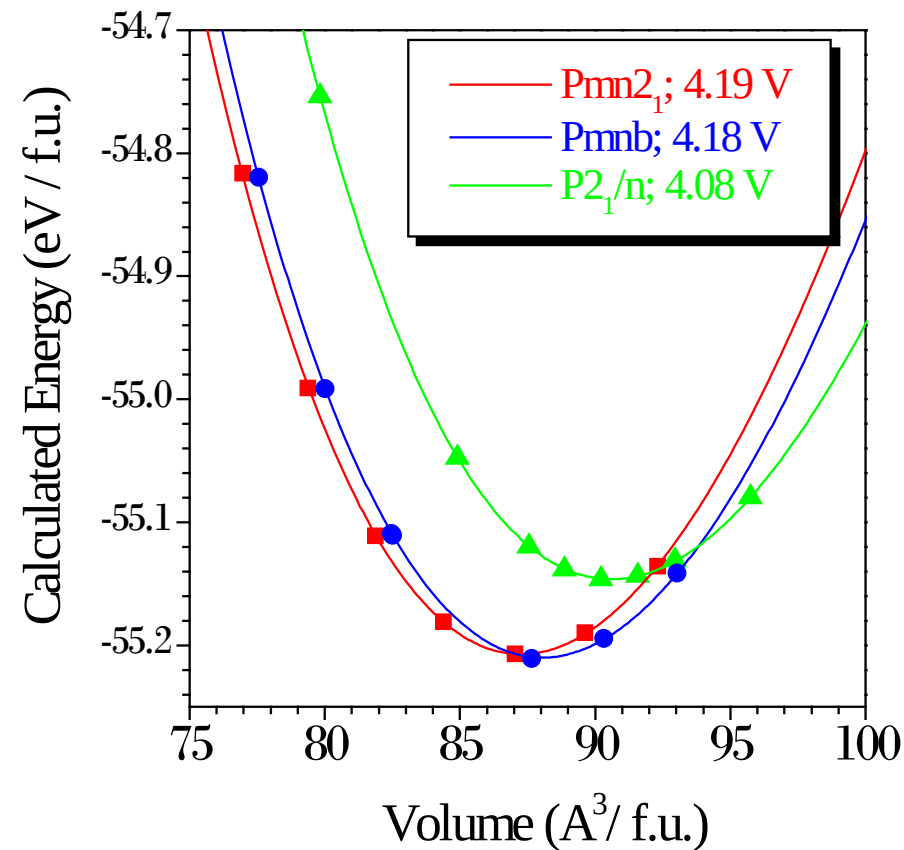
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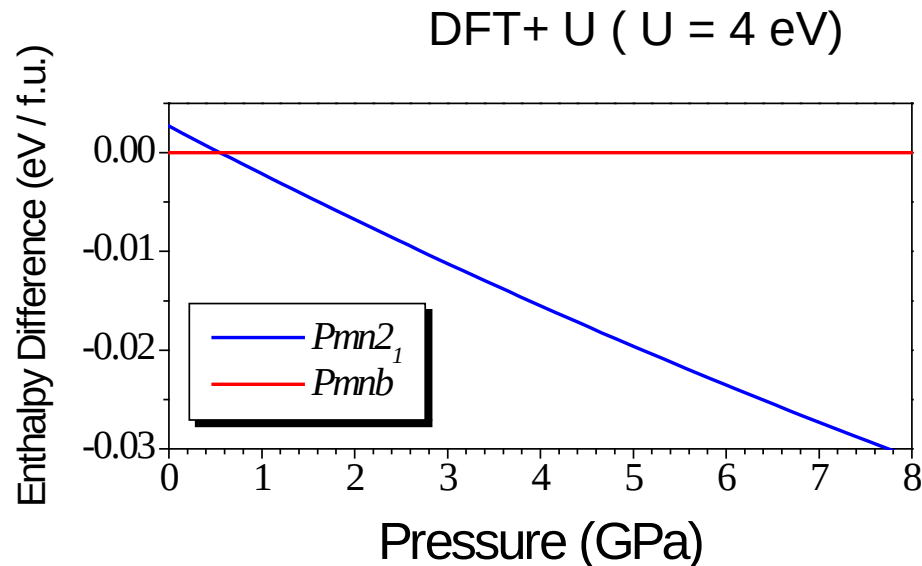
DFT -Li₂MnSiO₄



B = 83 GPa for *Pmnb*

B = 85 GPa for *Pmn2*₁

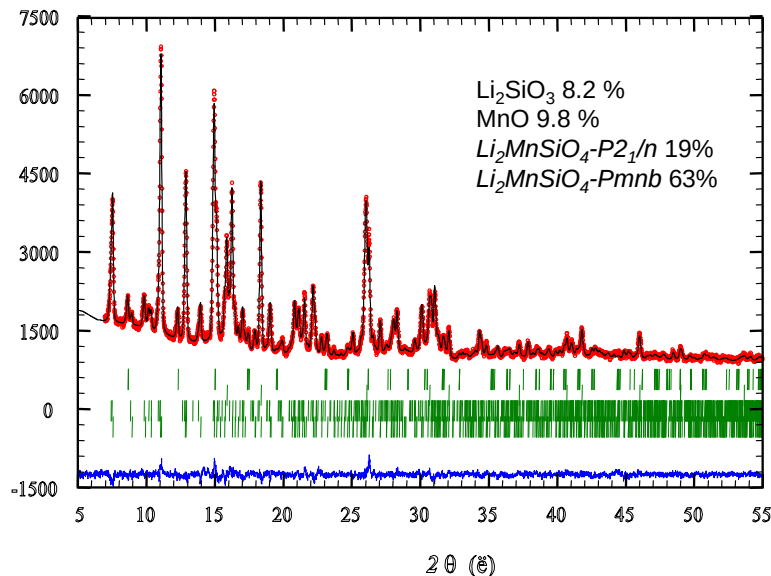
Olivine-Fe₂SiO₄ B = 113 GPa,
Phenakite-Be₂SiO₄ B = 201.8 GPa,
Garnet-Ca₃Fe₂Si₃O₁₂ B = 159 GPa



- Difficult to isolate *Pmn2*₁ and *Pmnb* only by thermal treatments.
- Pressure favors the denser *Pmn2*₁
- Moderate Bulk modulus.
New polymorph at HP?

M.E. Arroyo y de Dompablo, R. Dominko, J.M. Gallardo-Amores, H. Ehrenberg, L. Dupont, G. Mali, J. Jamnik and E. Morán, Chem. Mat, 2008

Intensity (arb. units)



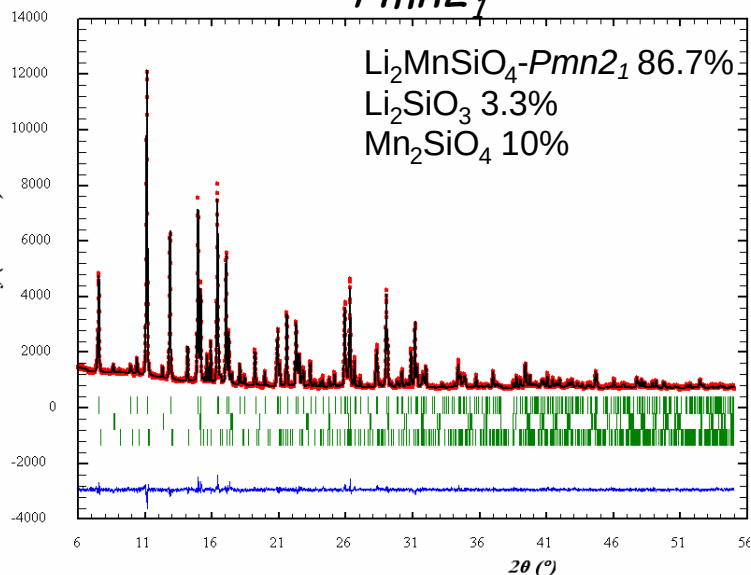
Initial sample Mixture of S.G



HP / HT

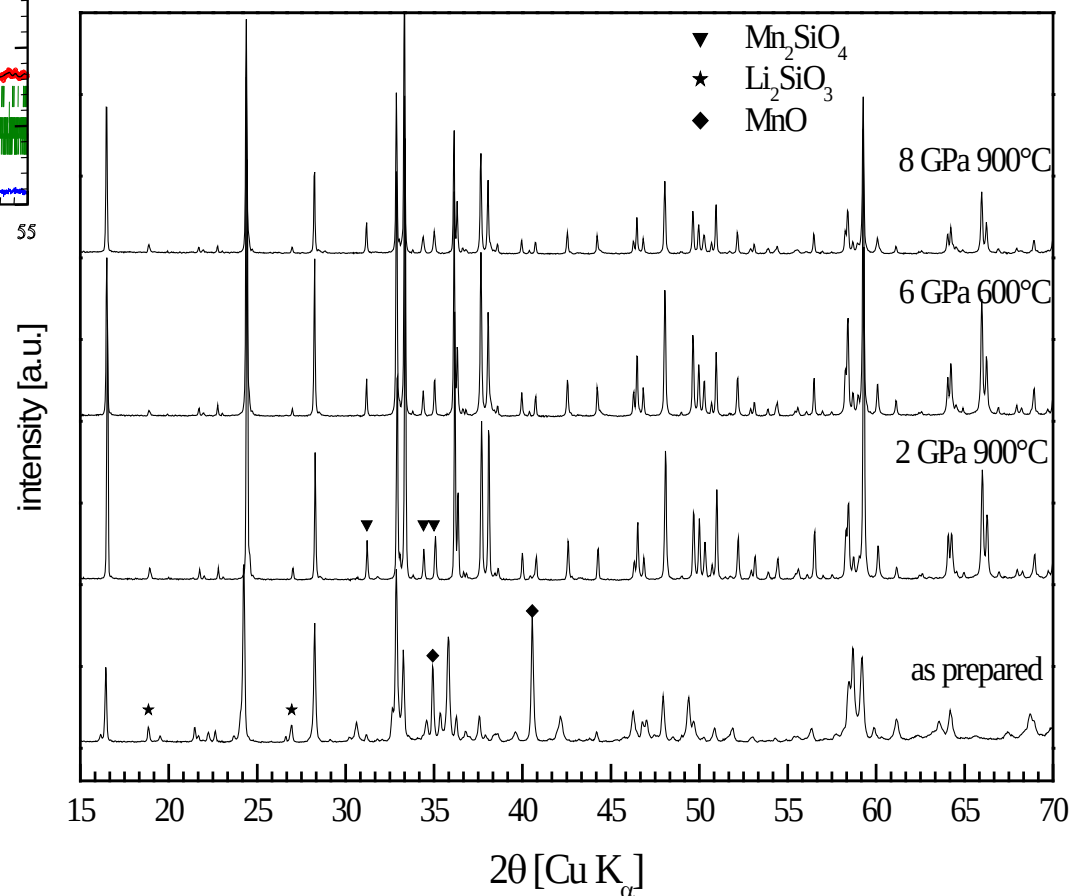
Pmn2₁

Intensity (arb. units)



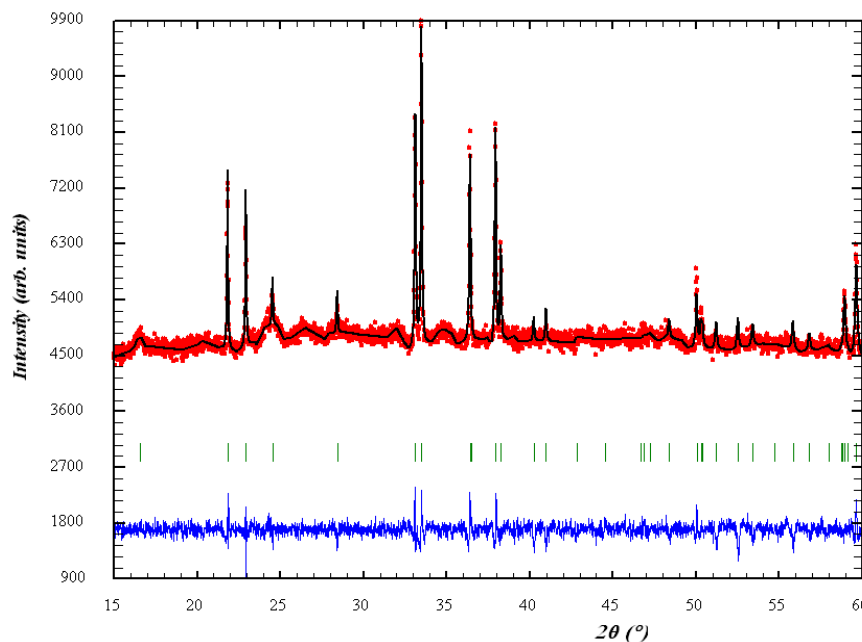
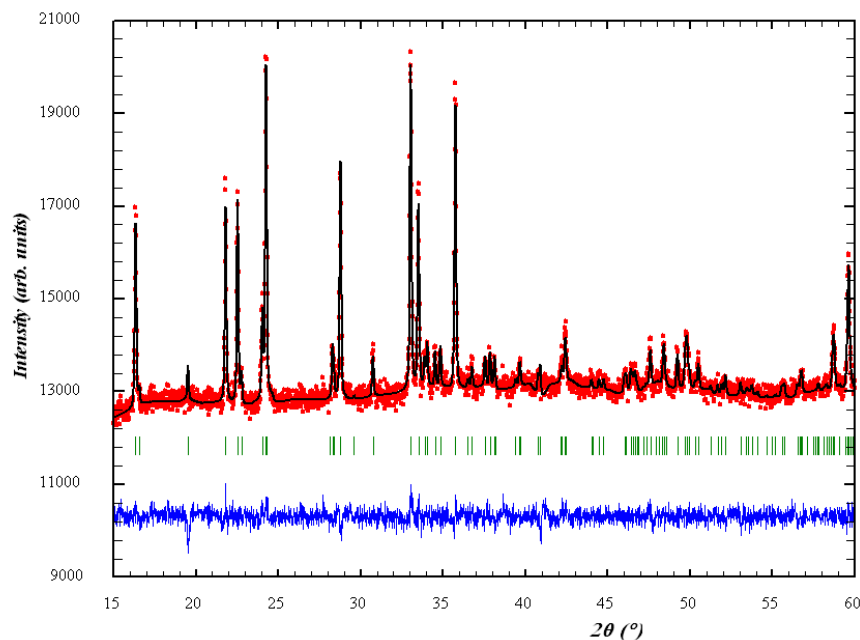
By HP/HT treatment the denser polymorph can be isolated

Confirmed by XRD, SAED, NMR



Transformation at higher pressures?

$\text{Li}_2\text{CoSiO}_4$



$\text{LiNO}_3 + \text{Co}(\text{NO}_3)_2 + \text{SiO}_2$
Combustion (urea)
950°C for 48 hours
quenching

40 kbar, 900 °C

$\text{Li}_2\text{CoSiO}_4 - Pmn2_1$

60 kbar, 900 °C

$\text{Li}_2\text{CoSiO}_4 - P2_1/n$

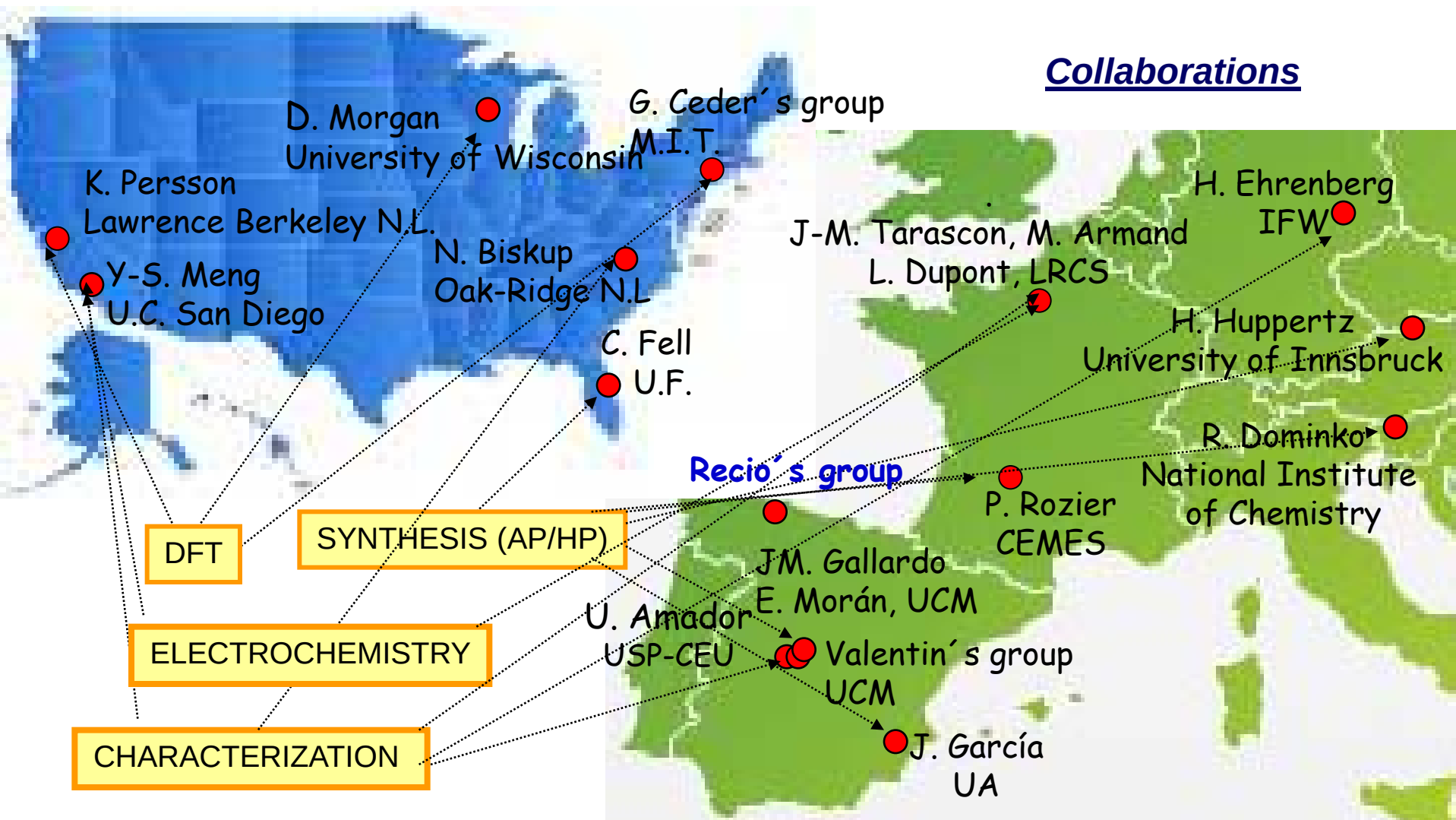
Decomposition of the material

ACKNOWLEDGEMENTS

Funding

- Ministerio de Educación y Ciencia (MAT2007-62929, CSD2007-00046)
- MEC/EGIDE (HF- 2006-0026)
- Universidad Complutense de Madrid/Banco Santander (PR07/1049, PR3407/1854)

Collaborations



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M.E. Arroyo y de Dompablo

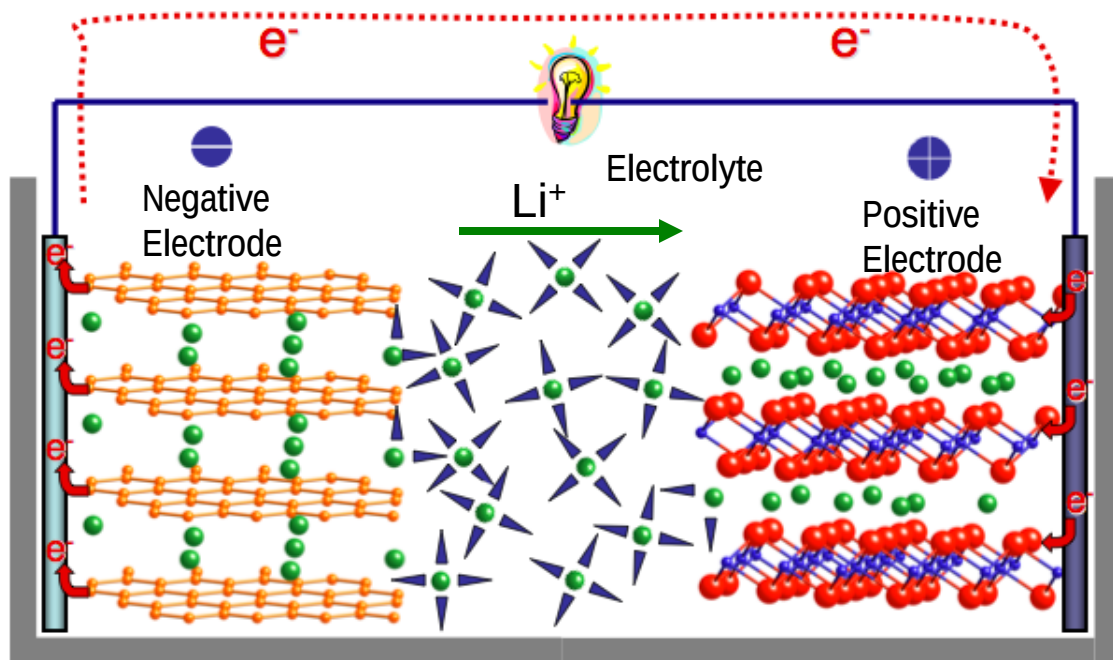
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Lithium ion batteries



Positive Electrode

Alto poder oxidante

$V_+ > 3V$ vs. Li^+/Li

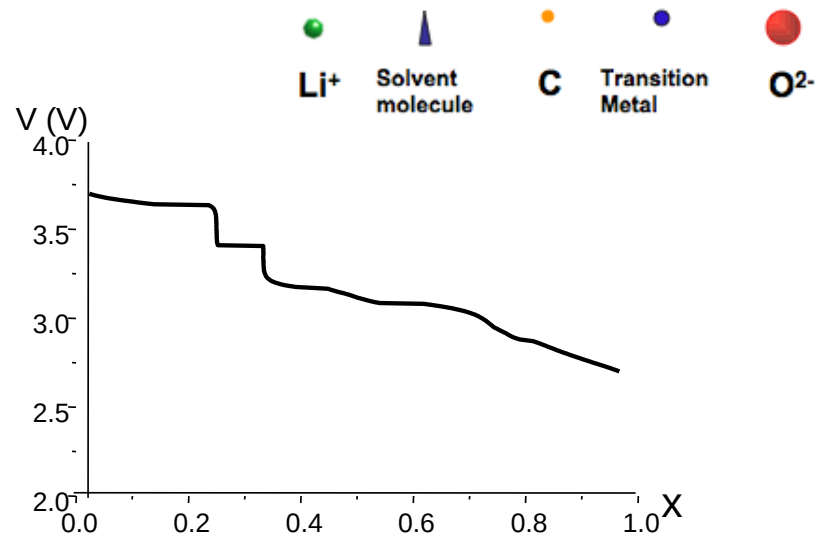
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Alto poder reductor

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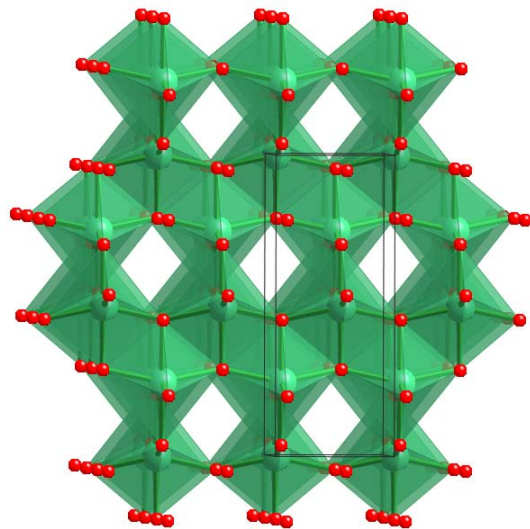
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Energy = Voltage $\times$ Capacity

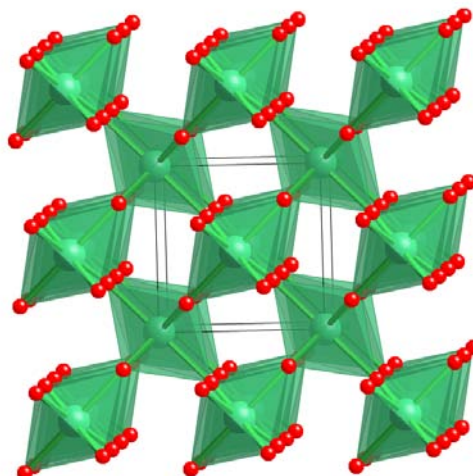
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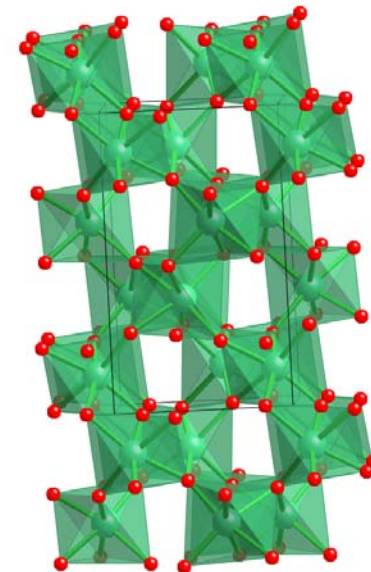
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Anatase

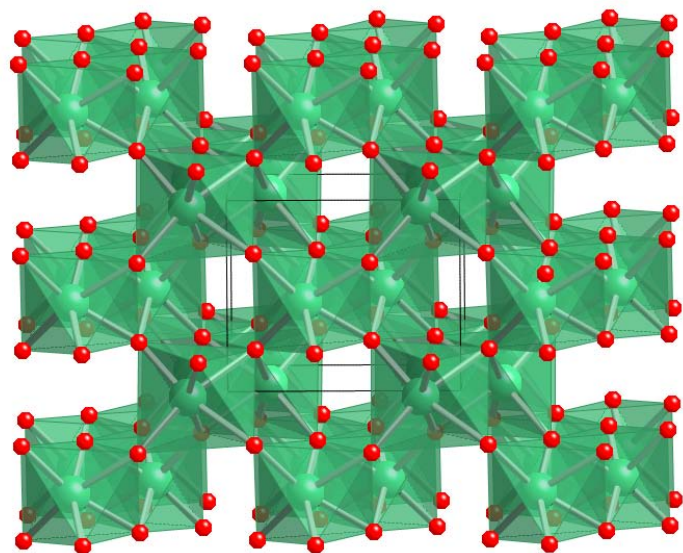


Rutile



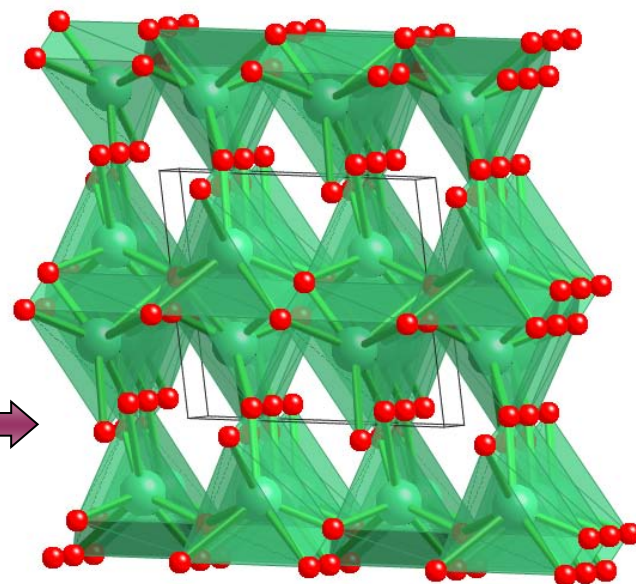
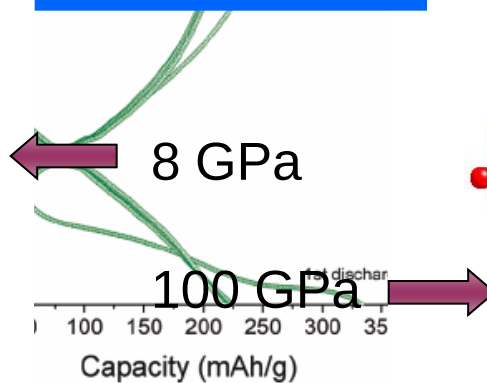
Brookite

TEMPERATURE



Columbite, I. Belharouak, and K. Amine, *Chemistry of Materials*, 2011

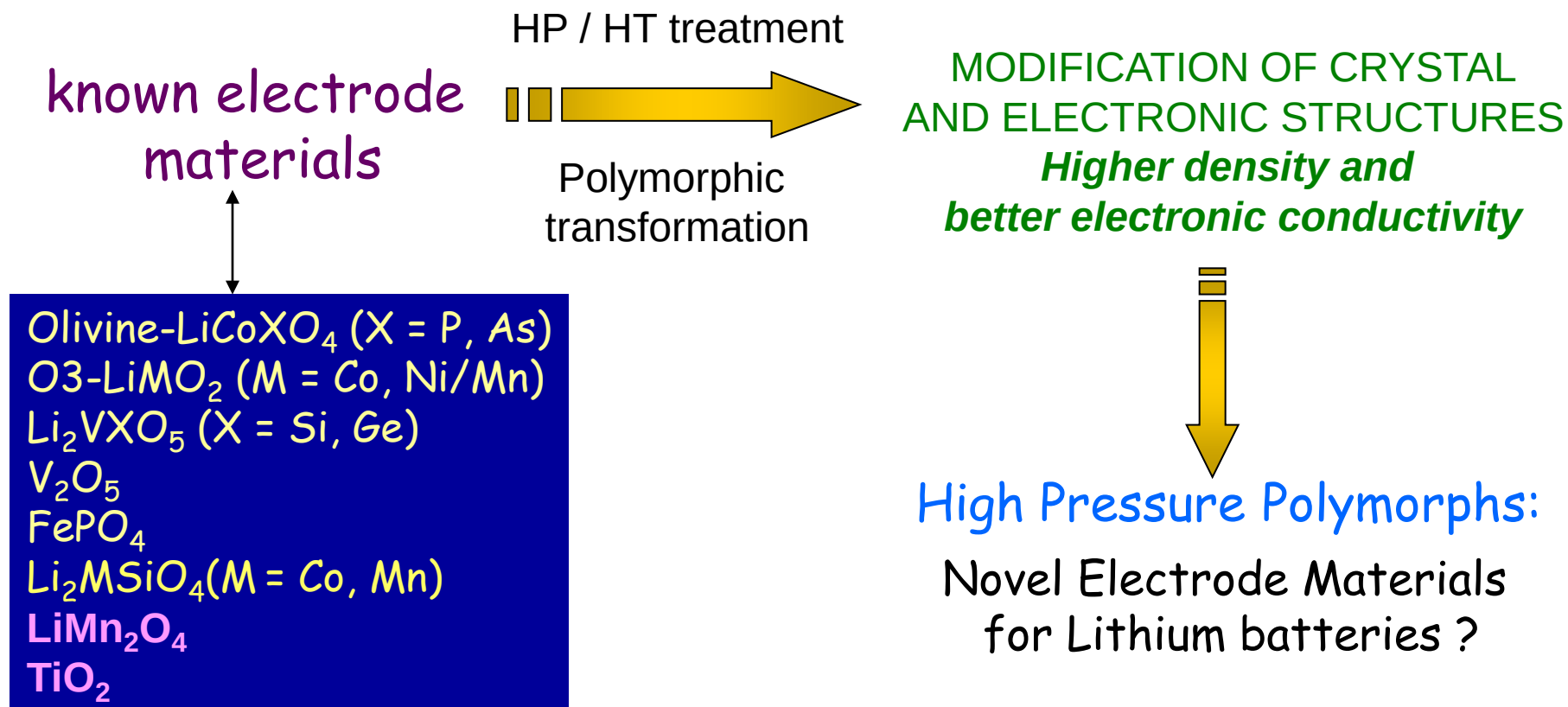
PRESSURE



Baddeleyite

High pressure polymorphs

Searching for novel electrode materials



FIRST PRINCIPLES CALCULATIONS GUIDANCE

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AP-polymorph  HP-polymorph

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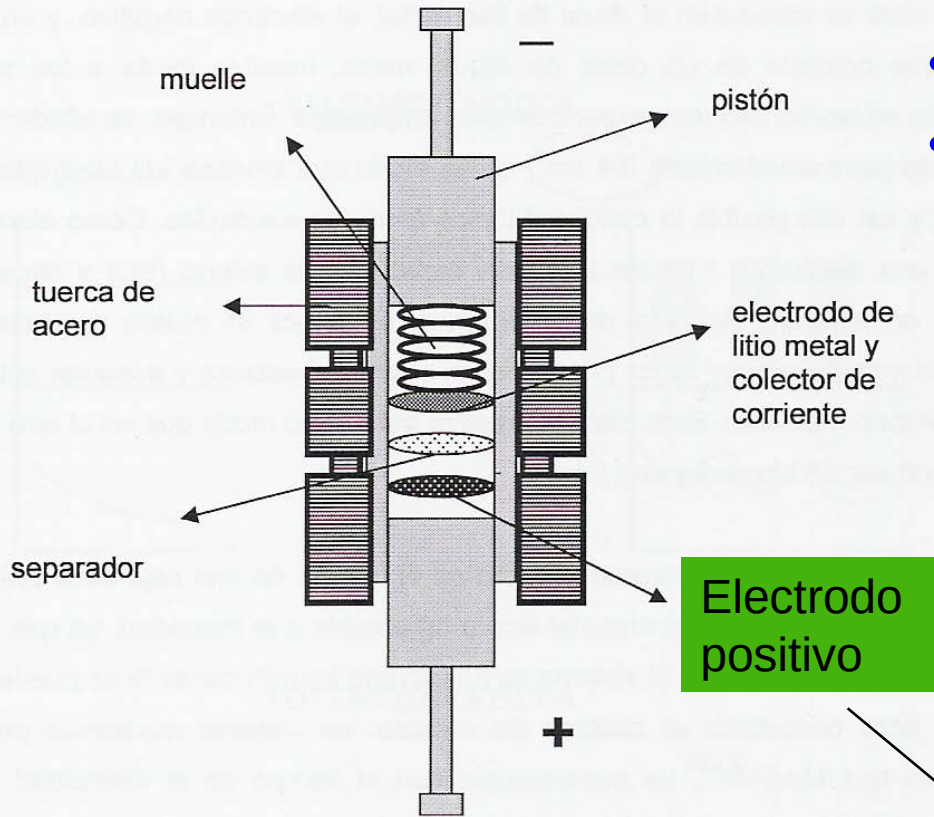
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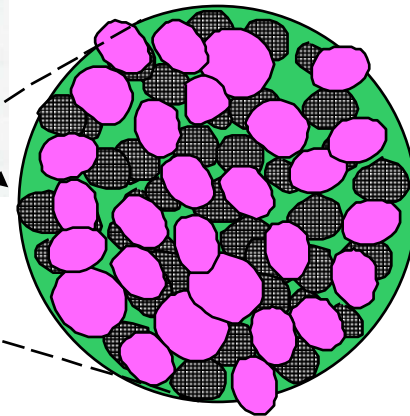
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Lithium batteries-experimental



Celda Swagelok

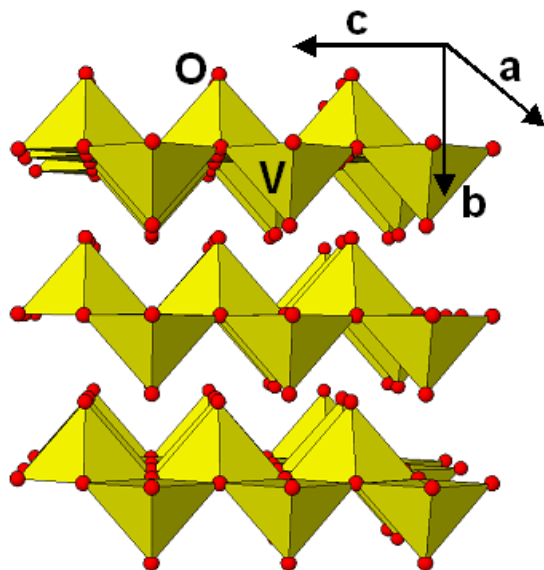
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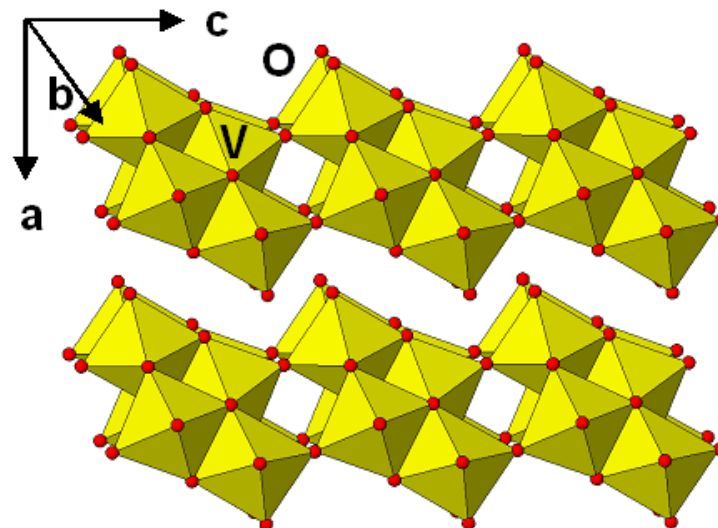
Ambient pressure

High pressure



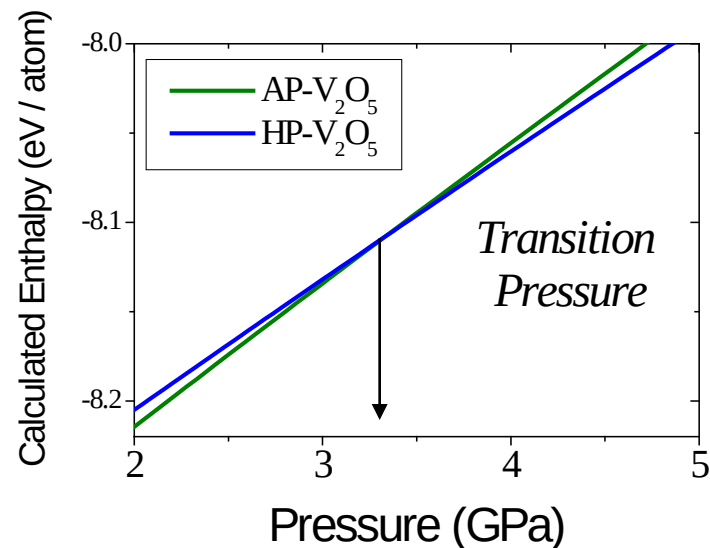
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V. P. Filonenko, et al,
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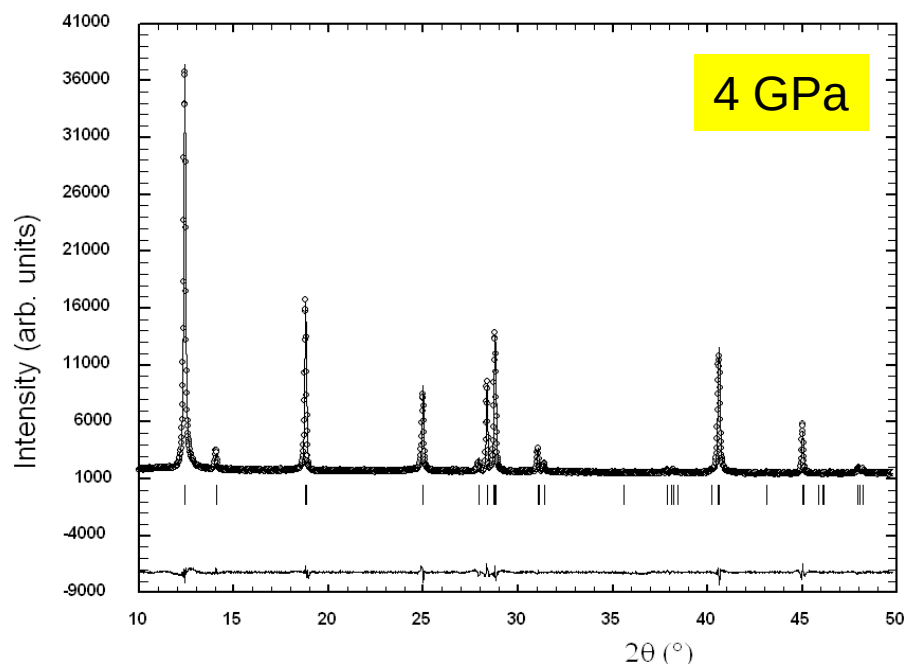
Commercial V_2O_5

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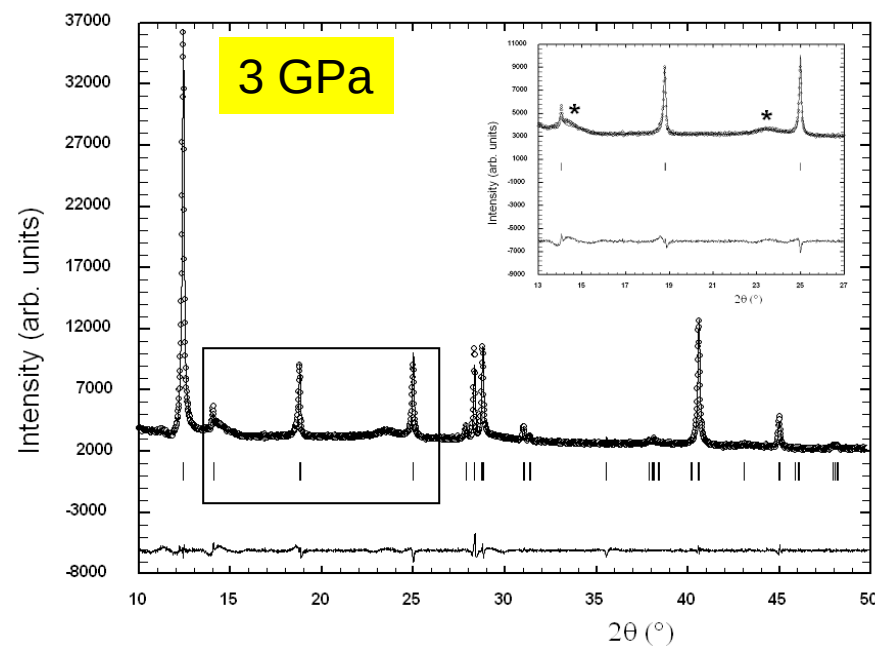


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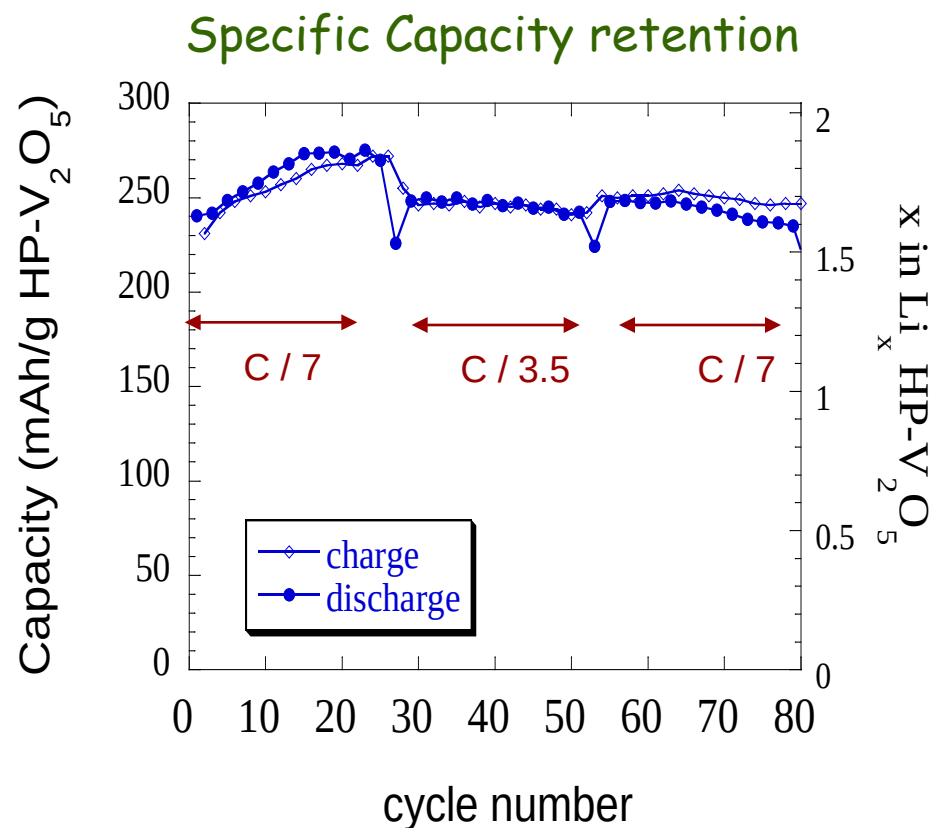
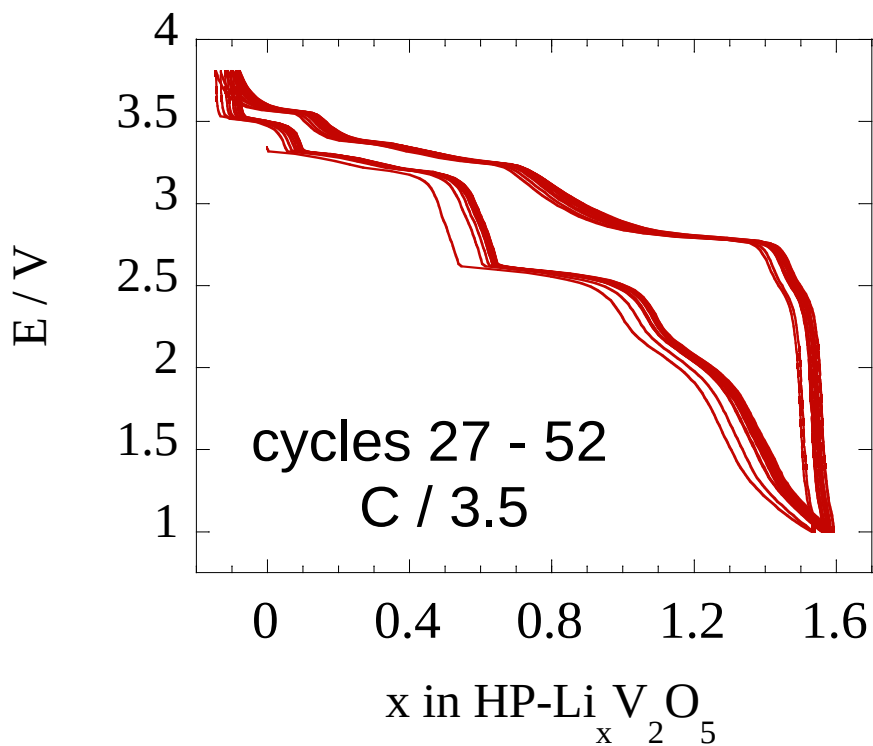
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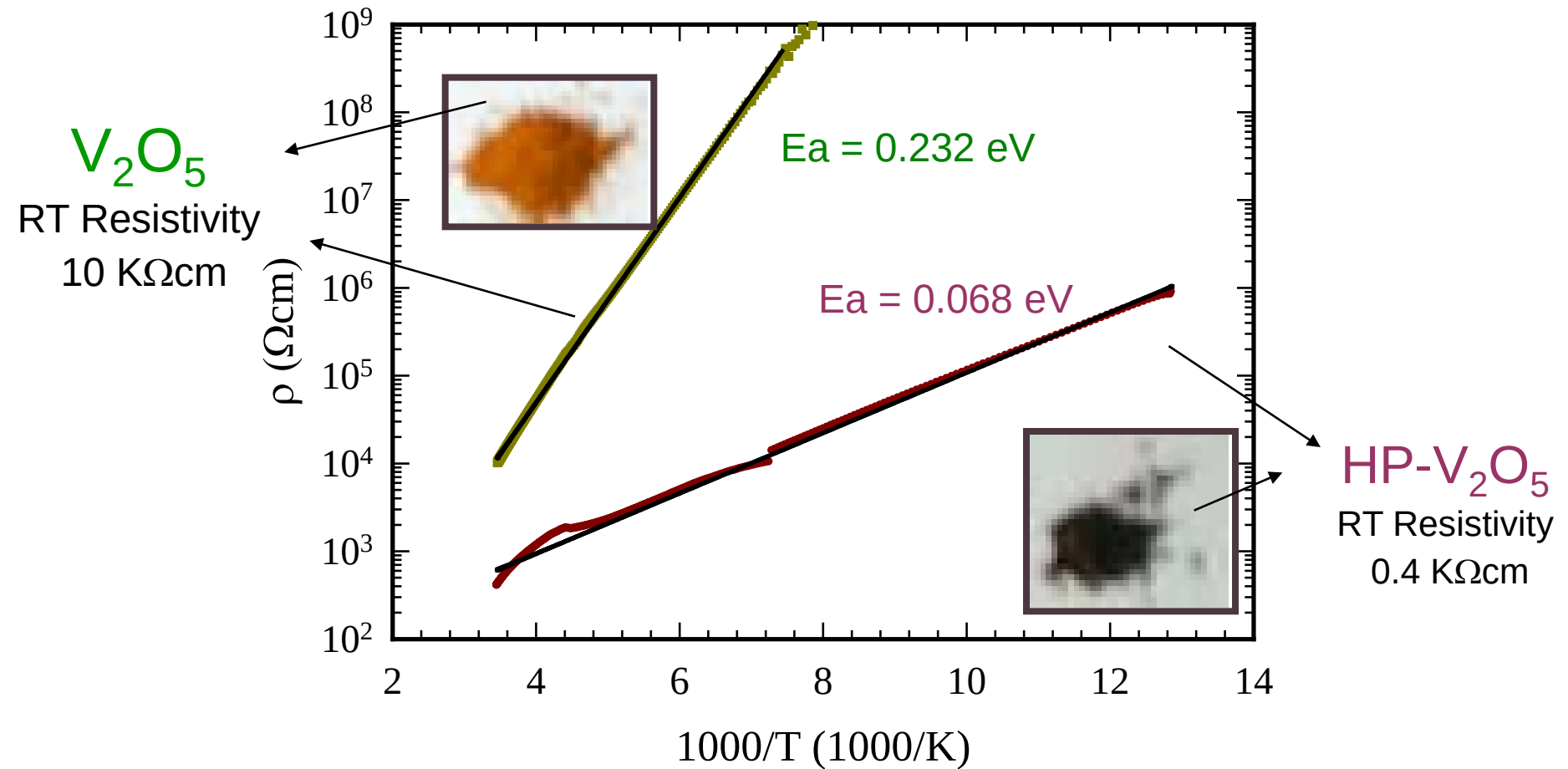


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M.E. Arroyo, J.M. Gallardo-Amores, U. Amador and E. Morán *Electrochem. Comm.*, 2007

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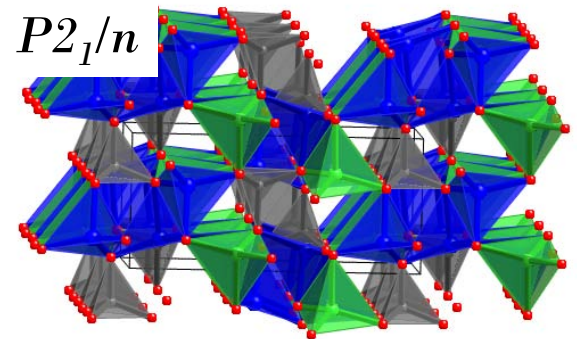
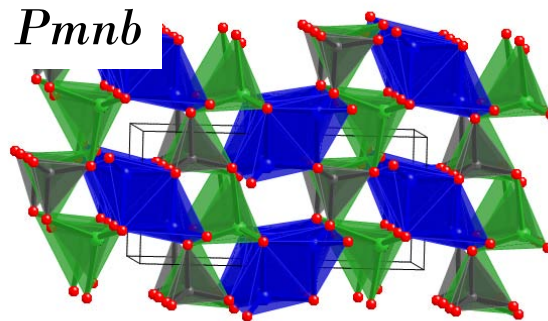
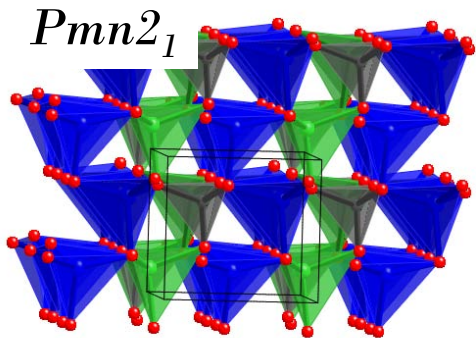
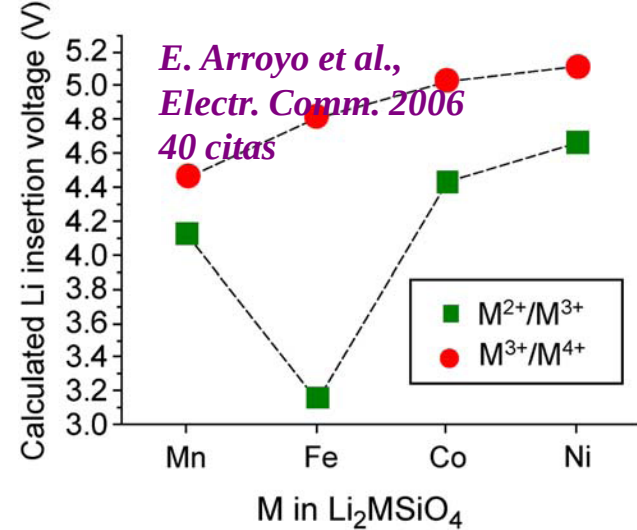
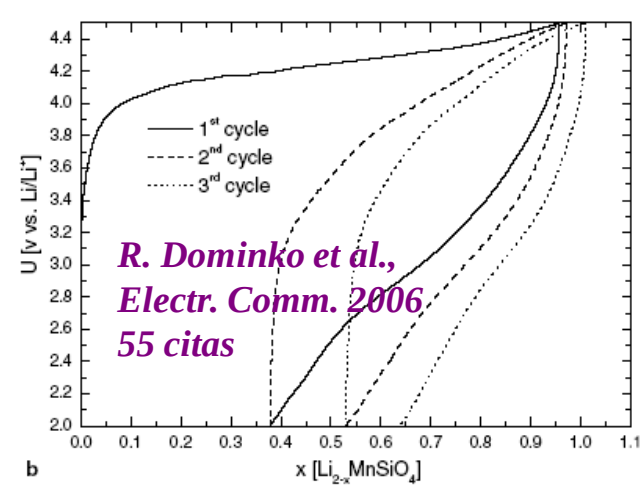


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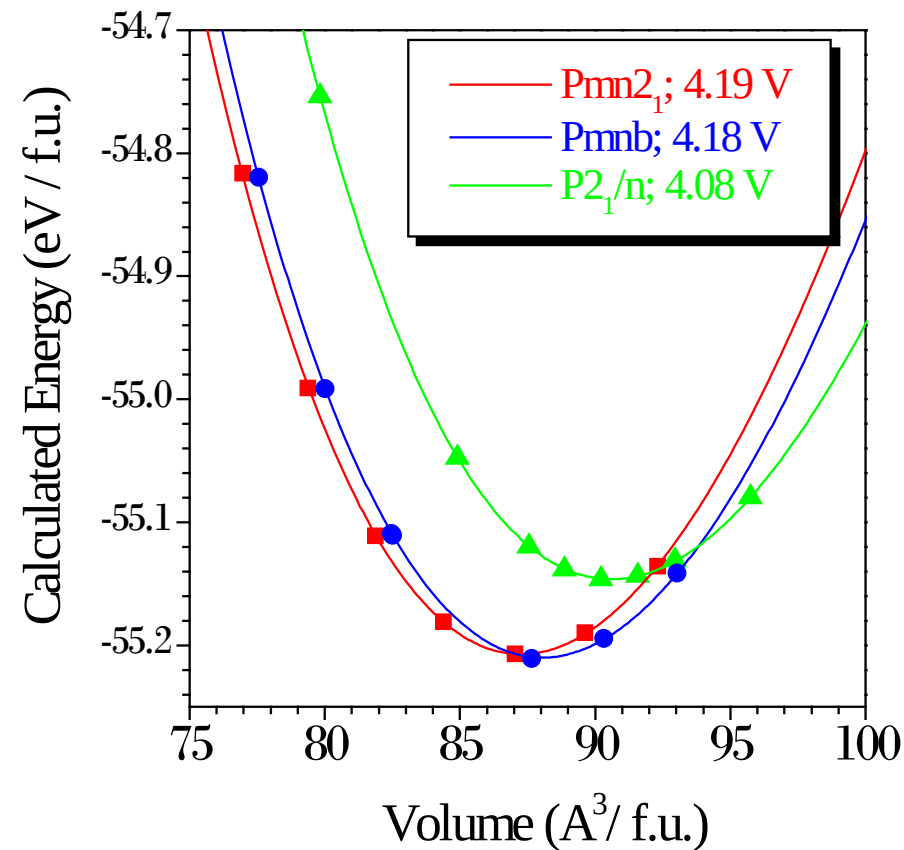
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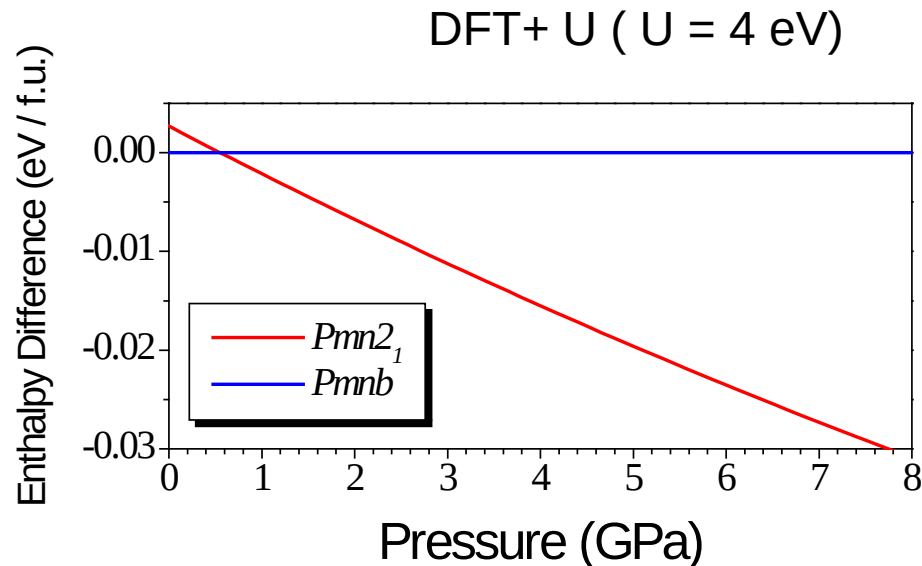
DFT -Li₂MnSiO₄



B = 83 GPa for *Pmnb*

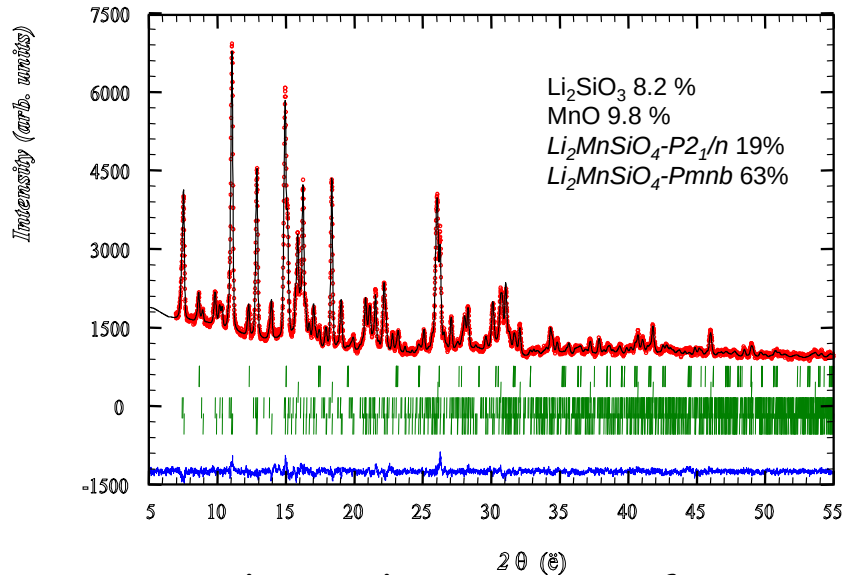
B = 85 GPa for *Pmn2*₁

Olivine-Fe₂SiO₄ *B* = 113 GPa,
 Phenakite-Be₂SiO₄ *B* = 201.8 GPa,
 Garnet-Ca₃Fe₂Si₃O₁₂ *B* = 159 GPa



- Difficult to isolate *Pmn2*₁ and *Pmnb* only by thermal treatments.
- Pressure favors the denser *Pmn2*₁
- Moderate Bulk modulus.
New polymorph at HP?

M.E. Arroyo y de Dompablo, R. Dominko, J.M. Gallardo-Amores, H. Ehrenberg, L. Dupont, G. Mali, J. Jamnik and E. Morán, *Chem. Mat.*, 2008

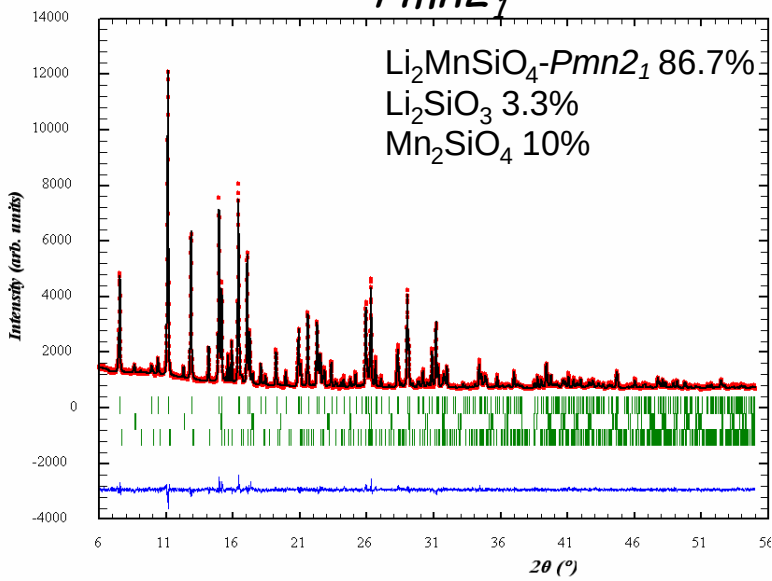


Initial sample Mixture of S.G



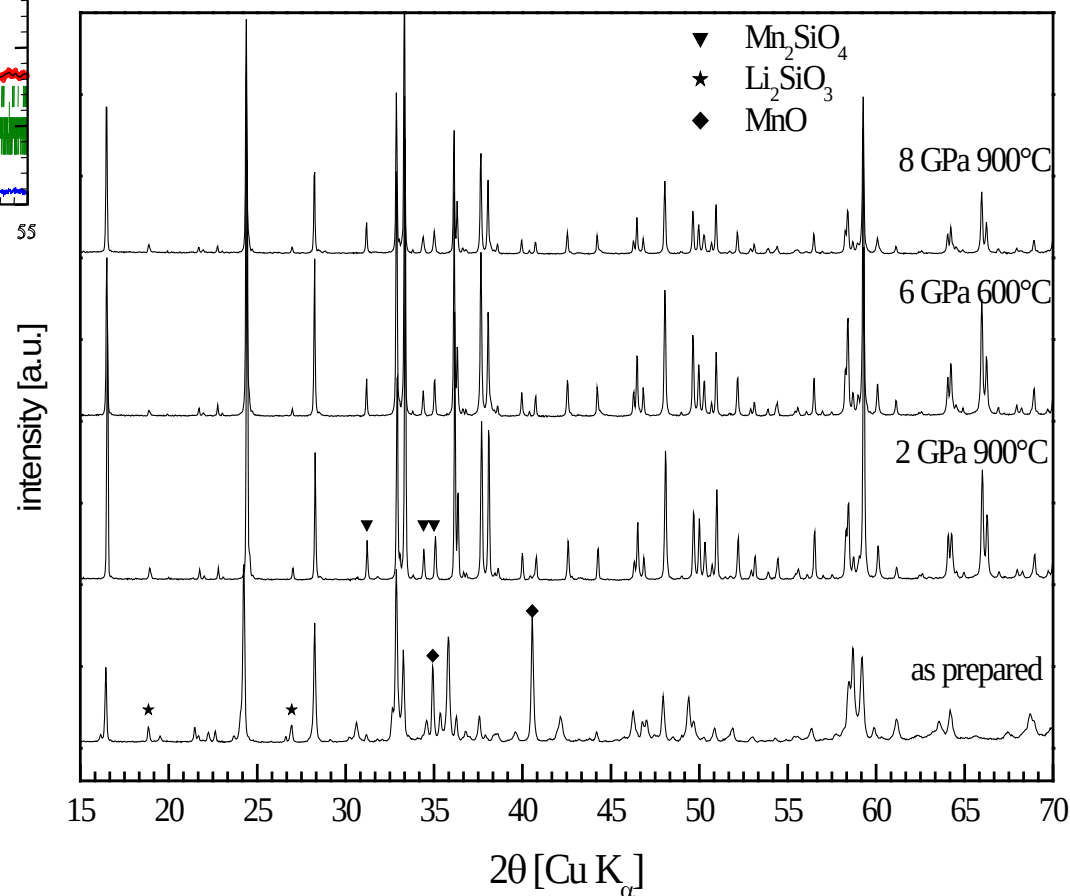
HP / HT

$Pmn2_1$



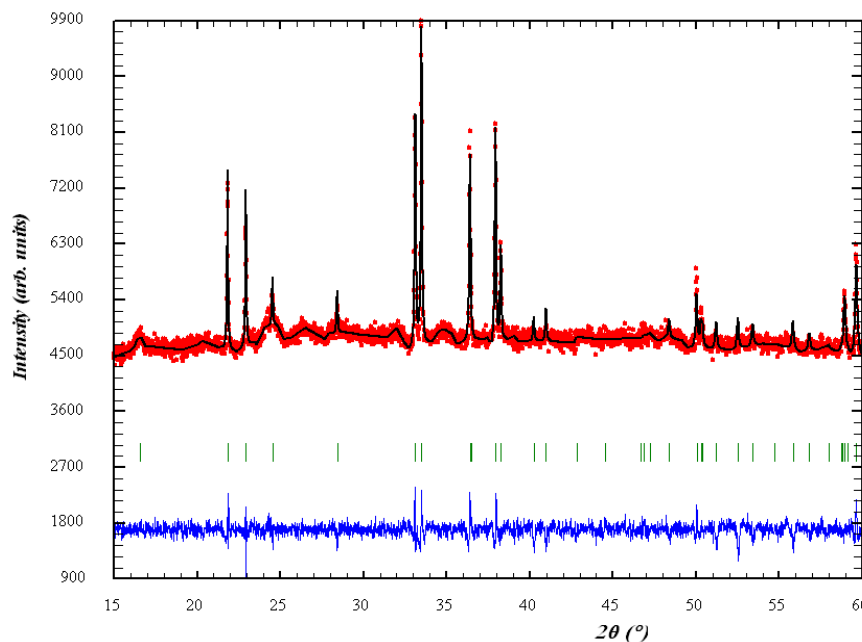
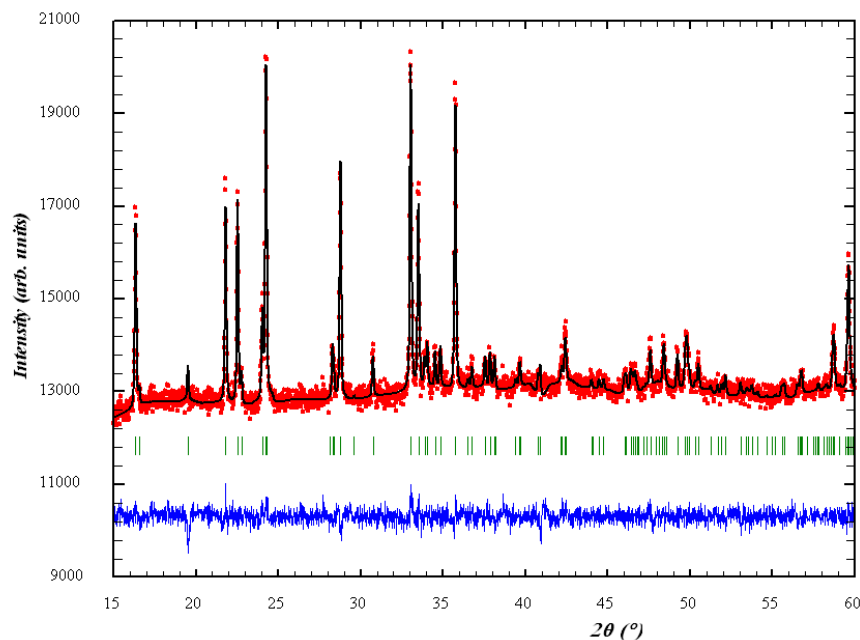
By HP/HT treatment the denser polymorph can be isolated

Confirmed by XRD, SAED, NMR



Transformation at higher pressures?

$\text{Li}_2\text{CoSiO}_4$



$\text{LiNO}_3 + \text{Co}(\text{NO}_3)_2 + \text{SiO}_2$
Combustion (urea)
950°C for 48 hours
quenching

40 kbar, 900 °C

$\text{Li}_2\text{CoSiO}_4 - Pmn2_1$

60 kbar, 900 °C

$\text{Li}_2\text{CoSiO}_4 - P2_1/n$

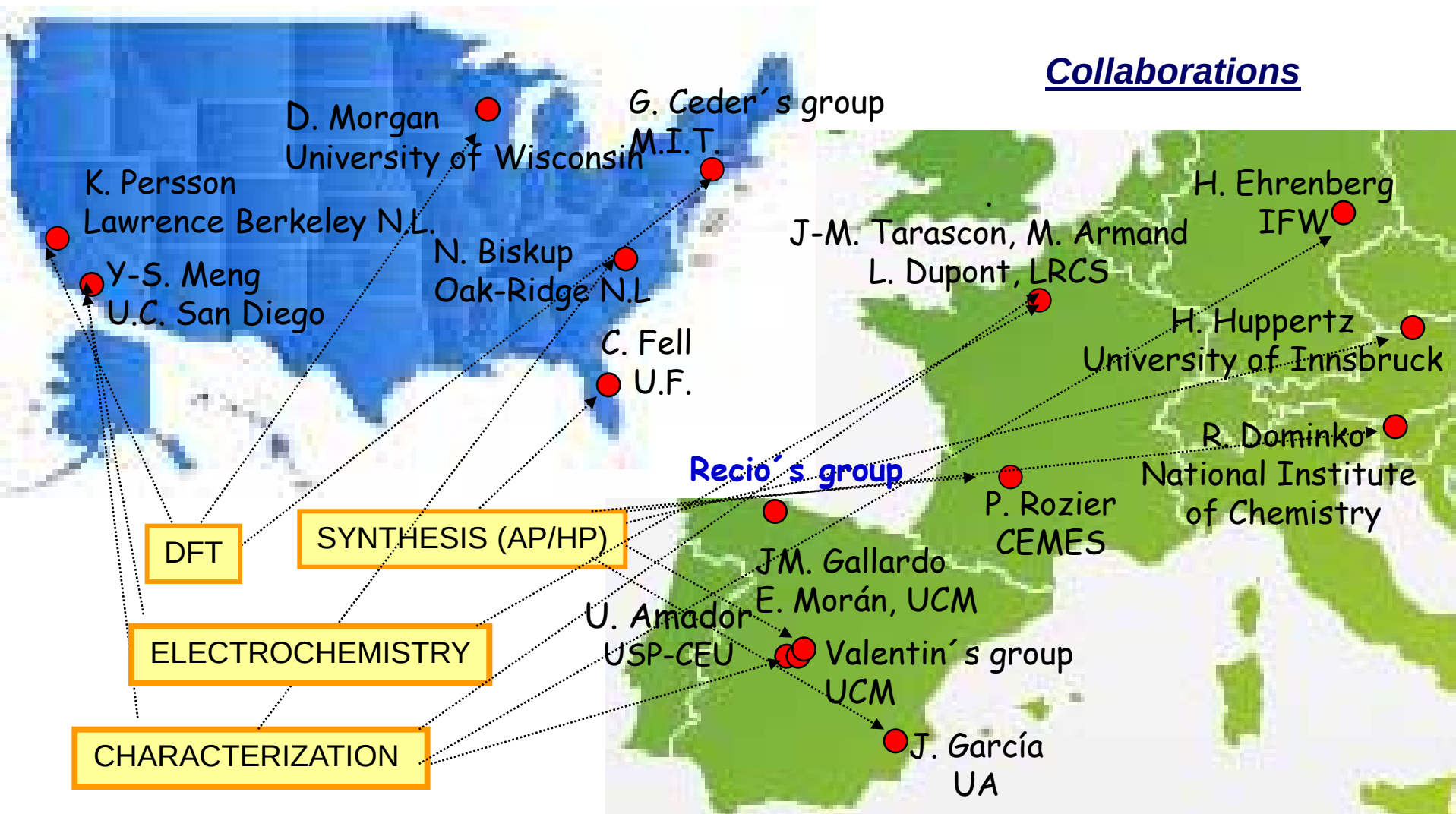
Decomposition of the material

ACKNOWLEDGEMENTS

Funding

- Ministerio de Educación y Ciencia (MAT2007-62929, CSD2007-00046)
- MEC/EGIDE (HF- 2006-0026)
- Universidad Complutense de Madrid/Banco Santander (PR07/1049, PR3407/1854)

Collaborations





Estudio del MnGa_2Se_4 bajo presión

Eduardo Pérez González

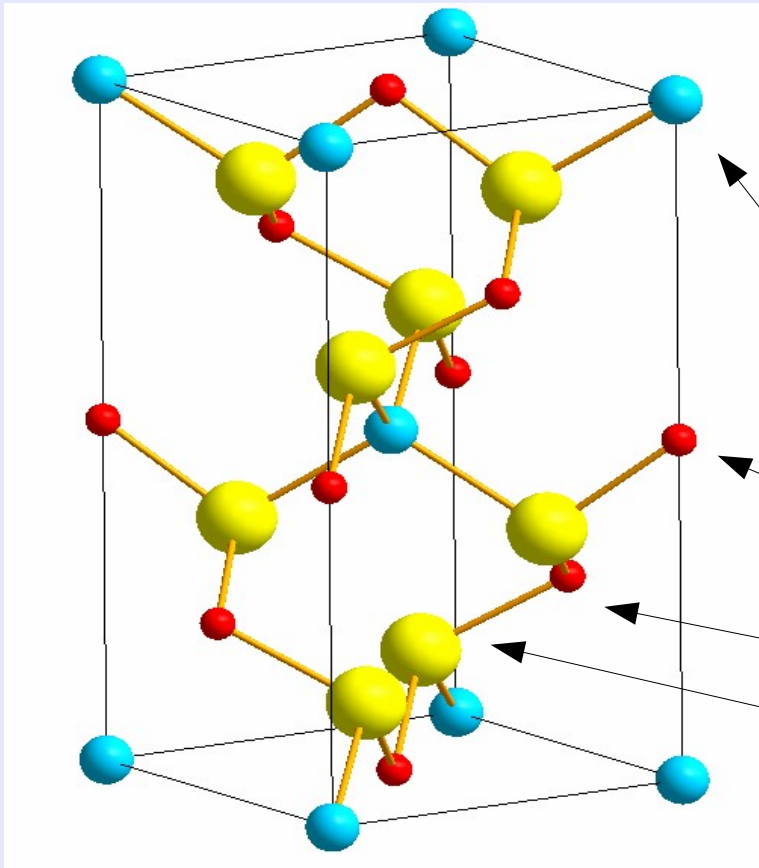
Departamento de Física Fundamental II
Universidad de La Laguna

Plácida Rodríguez Hernández. Universidad de La Laguna
Alfonso Muñoz González. Universidad de La Laguna
Jesús Antonio González Gómez. Universidad de Cantabria

Sumario

- Introducción
- Método de cálculo
- Parámetros estructurales de la fase
- Evolución estructural bajo presión
- Modos normales de vibración en Γ
- Evolución de los modos normales con la presión
- Conclusiones
- Trabajos futuros

Introducción



Calcopirita defectuosa

Estructura tetragonal I-4 (SG 82)

$Z=2$

Posiciones atómicas:

Mn 2a (0 0 0)

Ga I 2b (0 0 $\frac{1}{2}$)

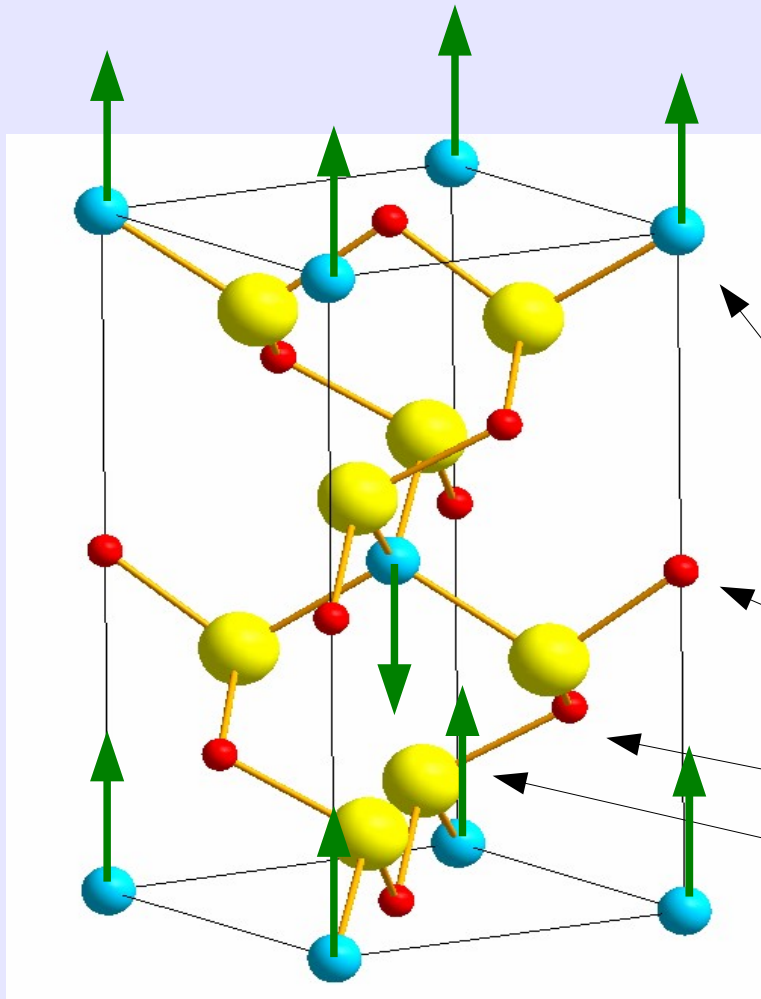
Ga II 2c (0 $\frac{1}{2}$ $\frac{1}{4}$)

Se 8g (x y z)

Vac 2d (0 $\frac{1}{2}$ $\frac{3}{4}$)

Antiferromagnético

Introducción



Calcopirita defectuosa

Estructura tetragonal I-4 (SG 82)

$Z=2$

Posiciones atómicas:

Mn 2a (0 0 0)

Ga I 2b (0 0 $\frac{1}{2}$)

Ga II 2c (0 $\frac{1}{2}$ $\frac{1}{4}$)

Se 8g (x y z)

Vac 2d (0 $\frac{1}{2}$ $\frac{3}{4}$)

Antiferromagnético

Introducción

- Propiedades estudiadas experimentalmente
 - Estructurales
 - Magnéticas
 - Ópticas
 - Vibracionales
- Técnicas utilizadas
 - Difracción de neutrones
 - Rayos X
 - Espectroscopía Raman
- ¿Estudios teóricos? Ninguno (que sepamos...)

Introducción

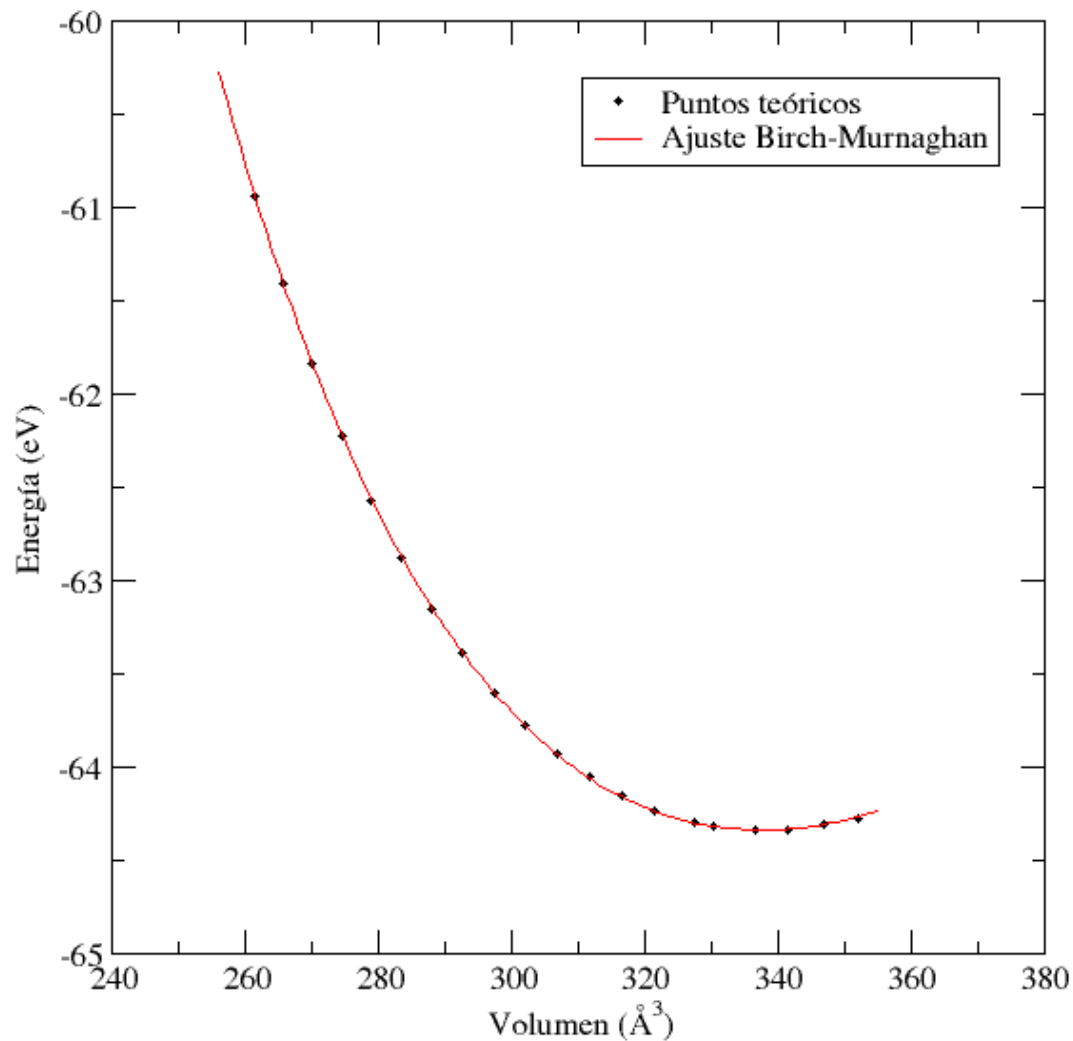
MOTIVACIÓN

- Estudio teórico-experimental de las propiedades bajo presión de la familia de calcopiritas defectuosas, XGa_2Se_4 y XGa_2S_4 (X=Mn, Hg, Cd, Zn)
- Entre la familia de las calcopiritas defectuosas, presenta ordenamiento antiferromagnético
- Medidas experimentales recientes del grupo de Cantabria de MALTA Consolider (Jesús González)
- Altamente resistente y buen fotoconductor según medidas experimentales previas
- Pocos (ninguno?) estudios teóricos sobre el MnGa_2Se_4 en condiciones normales o bajo presión

Método de cálculo

- Código VASP (pseudopotenciales y ondas planas)
- Pseudopotenciales PAW (Projector-Augmented Wave)
- Canje y correlación GGA tipo PBESol (PBE optimizado para sólidos)
- Cut-off en la base de ondas planas: 375 eV
- Grid denso para la integración en espacio recíproco
- Convergencia con el cutoff y el número de puntos de integración
- Cálculos a temperatura nula (movimiento del punto cero no incluido)
- Estructura en configuración antiferromagnética
- Cálculo de fonones en Gamma: método directo (cálculo de las constantes de fuerza aplicando pequeños desplazamientos)
- Construcción de la matriz dinámica y análisis de la simetría de los modos efectuada con el código PHONON.

Energía de la fase



A volúmenes seleccionados, hemos relajado completamente los grados de libertad estructurales (parámetros de celda e internos). Así obtenemos esta curva de energía-volumen.

El ajuste con una ecuación de estado de Birch-Murnaghan de 4º orden permite obtener parámetros estructurales en el equilibrio (volumen, módulo de bulk, ...)

Parámetros estructurales de la fase

	Este trabajo	Ref [1]	Ref [2]	Ref [3]
V_0 (Å ³)	336.51	347.38	346.81	347.64
a_0 (Å)	5.582	5.678	5.677	5.687
c_0 (Å)	10.800	10.775	10.761	10.749
c/a	1.935	1.8975	1.8955	1.894
B_0 (GPa)	38.63	-	-	45
B'_0	4.45	-	-	3.7

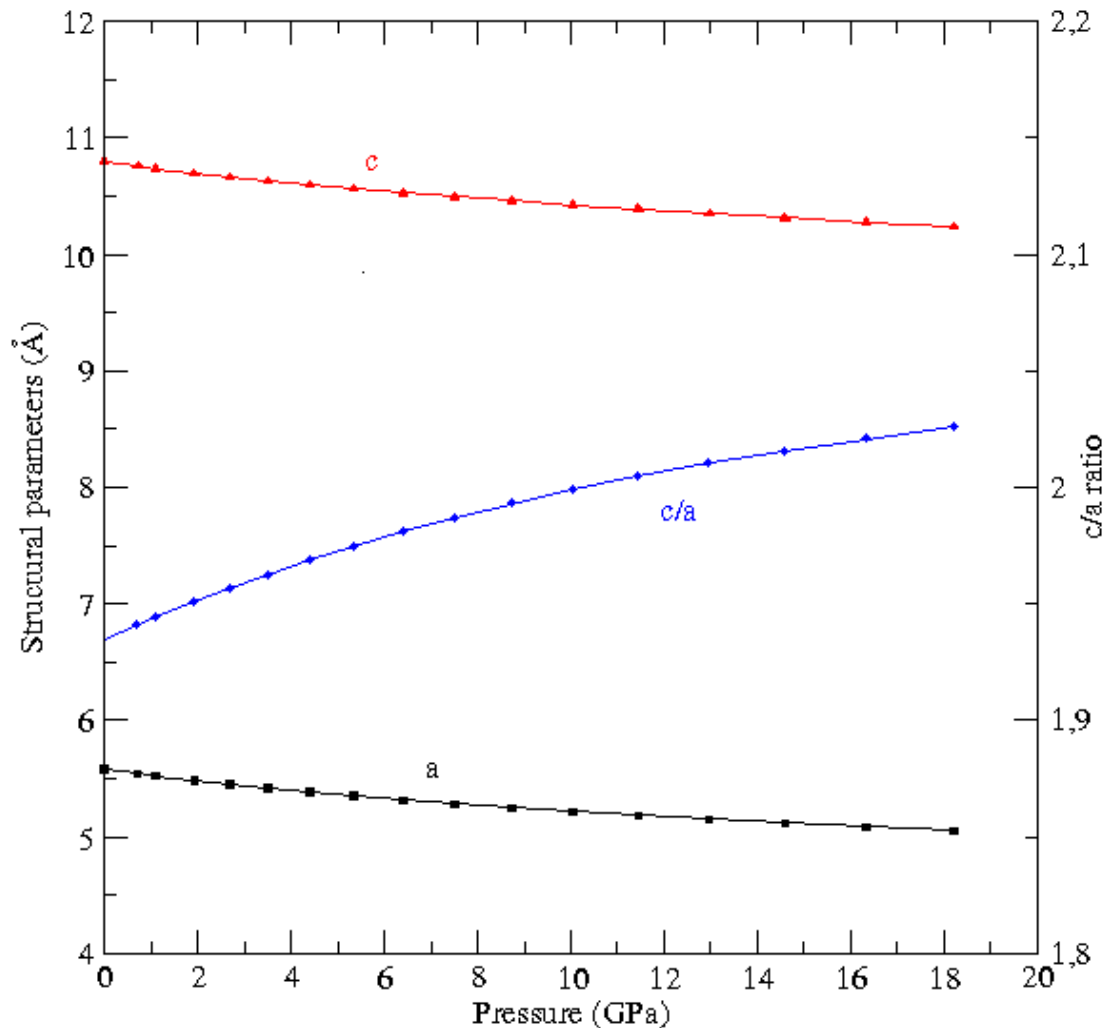
[1] M. Quintero et al. Phys. Stat. Sol. (a), 146, 587 (1994)

[2] M. Cannas et al. Cryst. Res. Technol. 33, 417 (1998)

[3] Tesis doctoral de Jesús R. Marquina C. Mérida, Venezuela (2003)

Diferencias con los resultados experimentales dentro del margen típico de este tipo de cálculos.

Evolución estructural bajo presión

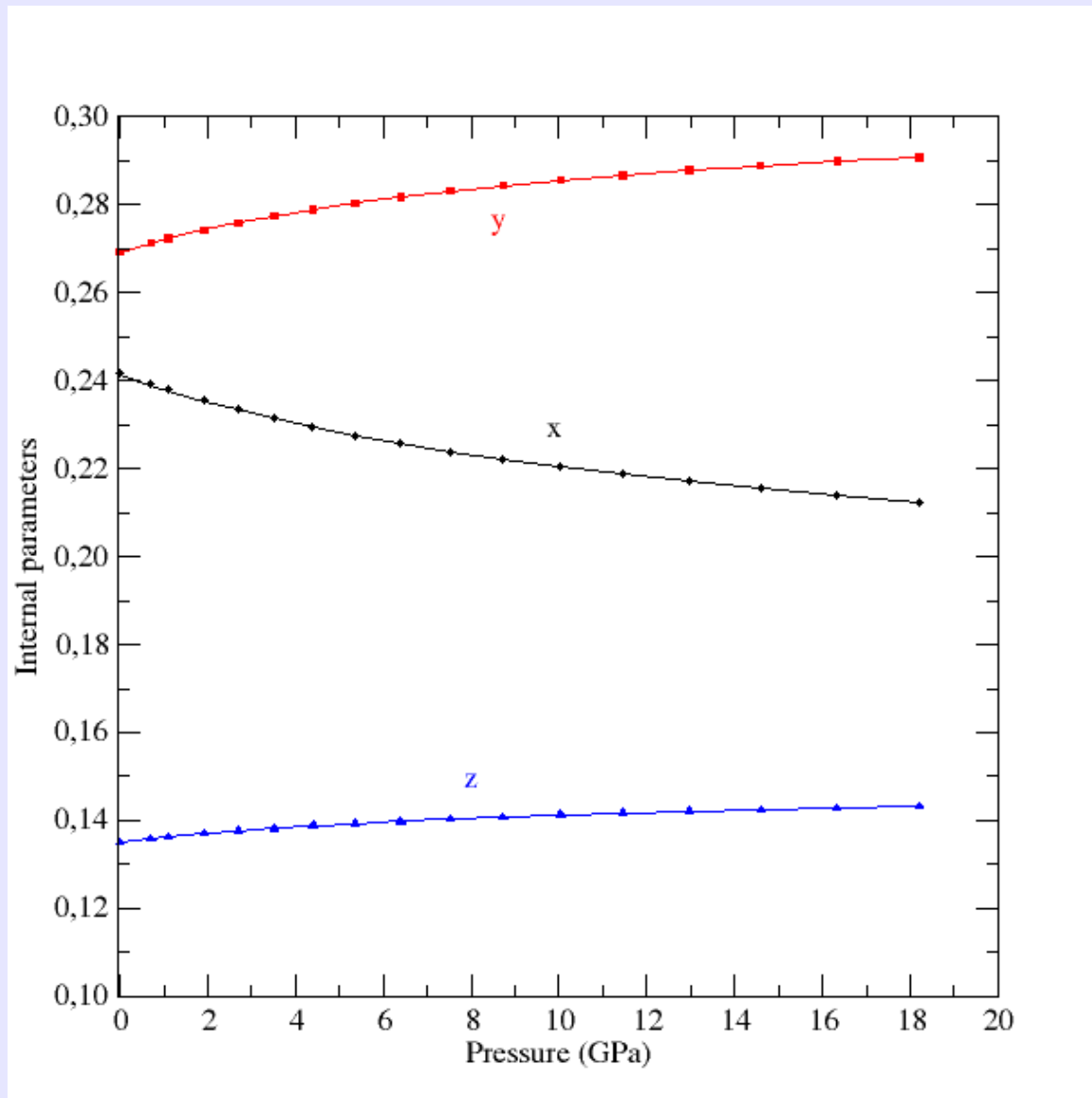


Nuestros cálculos muestran que la celda es más compresible en el plano perpendicular al eje principal.

La variación de c/a con la presión está en excelente acuerdo con el resultado experimental de Marquina:

$$\frac{d c/a}{d p} = 0.06 \text{ kbar}^{-1}$$

Evolución estructural bajo presión



Los cationes Mn y Ga están en posiciones especiales (sin parámetros libres).

Nuestros cálculos muestran la evolución de los parámetros internos asociados a los sitios 8g del anión Se.

No hay resultados experimentales con los que comparar.

Modos normales de vibración en Γ

	Este trabajo			Datos experimentales [1]		
modo	ω_0	$d\omega/dP$	γ	ω_0	$d\omega/dP$	γ
E(RI)	69.8	-0.01	-1.25	76.6	0.2	0.19
B(RI)	87.1	0.6	0.33	91.8	0.83	0.67
E(RI)	95.1	-0.6	-0.38	104.8	-0.1	0.04
B(RI)	113.5	-0.1	0.02	122.7	0.6	0.20
A(R)	131.7	4.9	1.72	134.2	5.3	1.86
A(R)	174.0	2.9	0.74	181.7	3.2	0.89
A(R)	192.9	2.6	0.76	207.0	2.2	0.76
B(RI)	214.4	2.2	0.70	214.0	6.2	1.33
E(RI)	217.6	5.3	1.00	239.3	4.1	0.85
E(RI)	230.9	4.2	0.80	244.9	4.6	1.10
B(RI)	234.9	5.9	1.07	227.0	3.3	0.71
E(RI)	241.8	3.1	0.80	253.5	4.6	0.92
B(RI)	245.9	6.2	1.21	277.9	3.5	0.65

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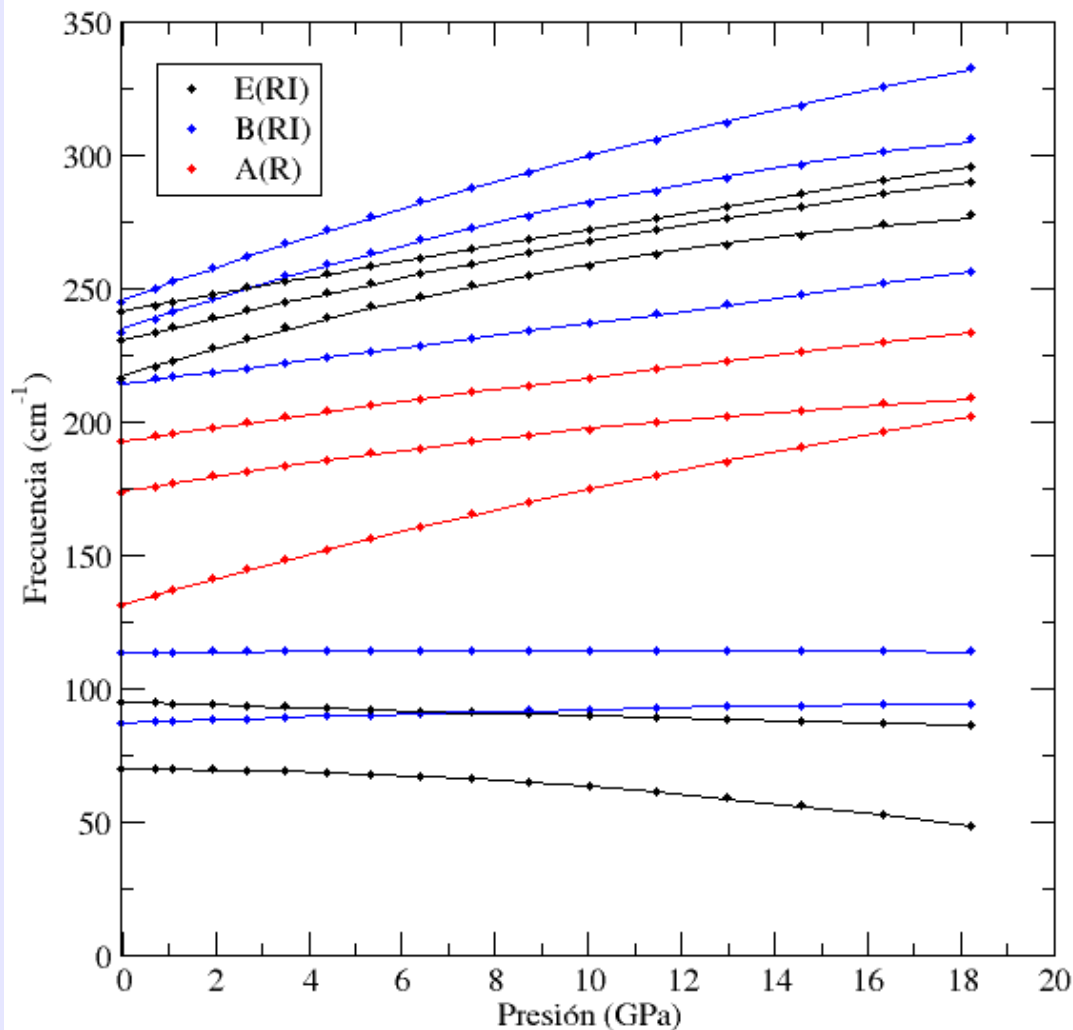
Los modos más bajos son relativamente insensibles a la presión

Modos normales de vibración en Γ

Los modos más altos aumentan con la presión

	Este trabajo			Datos experimentales [1]		
modo	ω	$d\omega/dP$	γ	ω	$d\omega/dP$	γ
E(RI)	68.8	0.01	1.25	76.6	0.2	0.19
				91.8	0.83	0.67
				104.8	-0.1	0.04
B(RI)	113.5	-0.1	0.02	122.7	0.6	0.20
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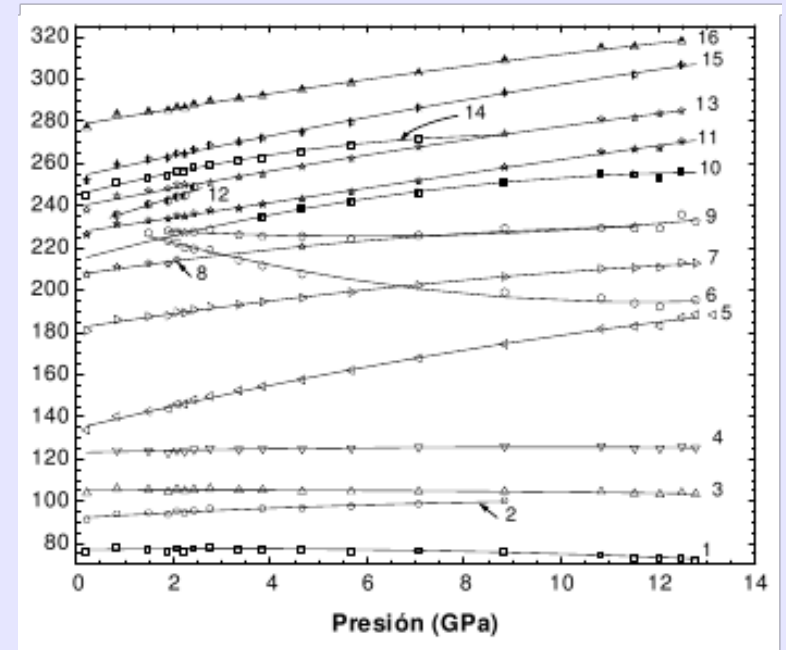
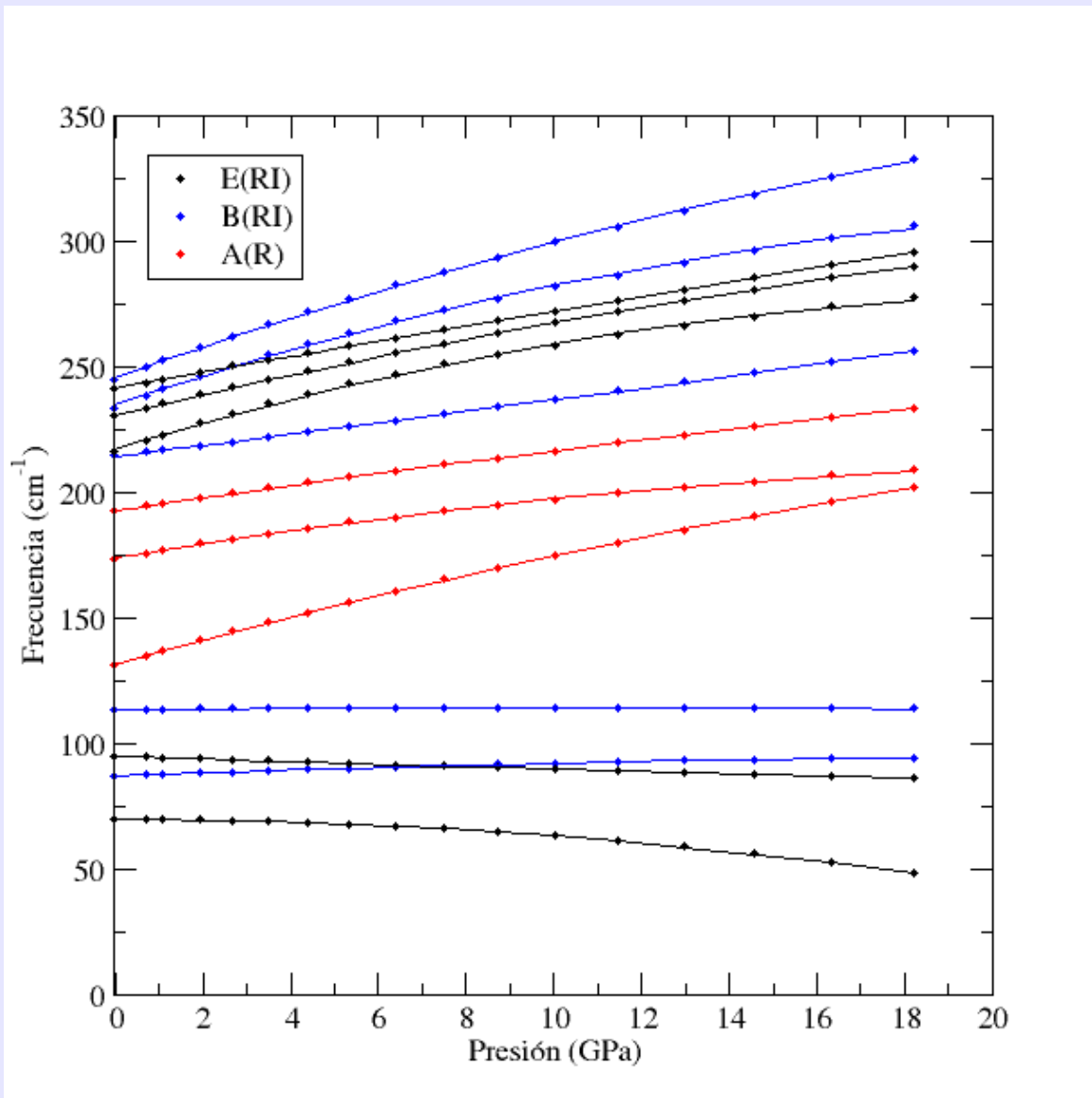
Evolución de los modos normales con la presión



El aspecto cualitativo general de las curvas de evolución de las frecuencias con la presión es el mismo que el obtenido experimentalmente por Marquina (con algunas diferencias cuantitativas).

En los experimentos se observan también unos modos con un fuerte decrecimiento con la presión, que no parecen corresponder a esta fase de acuerdo con nuestros cálculos.

Evolución de los modos normales con la presión



En los experimentos se observan también unos modos con un fuerte decrecimiento con la presión, que no parecen corresponder a esta fase de acuerdo con nuestros cálculos.

Conclusiones

- Estudio teórico del efecto de la presión sobre la calcopirita defectuosa MnGa_2Se_4
- Los parámetros estructurales teóricos están de acuerdo con los experimentales
- Bajo presión, el comportamiento calculado de los modos de vibración es cualitativamente igual al observado experimentalmente

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- Los parámetros estructurales teóricos están de acuerdo con los experimentales
- Bajo presión, el comportamiento calculado de los modos de vibración es cualitativamente igual al observado experimentalmente

Trabajo futuro

- Estructura de bandas y el gap fundamental bajo presión
- Fases de alta presión
- Otros compuestos de la misma familia
- Efecto de la temperatura

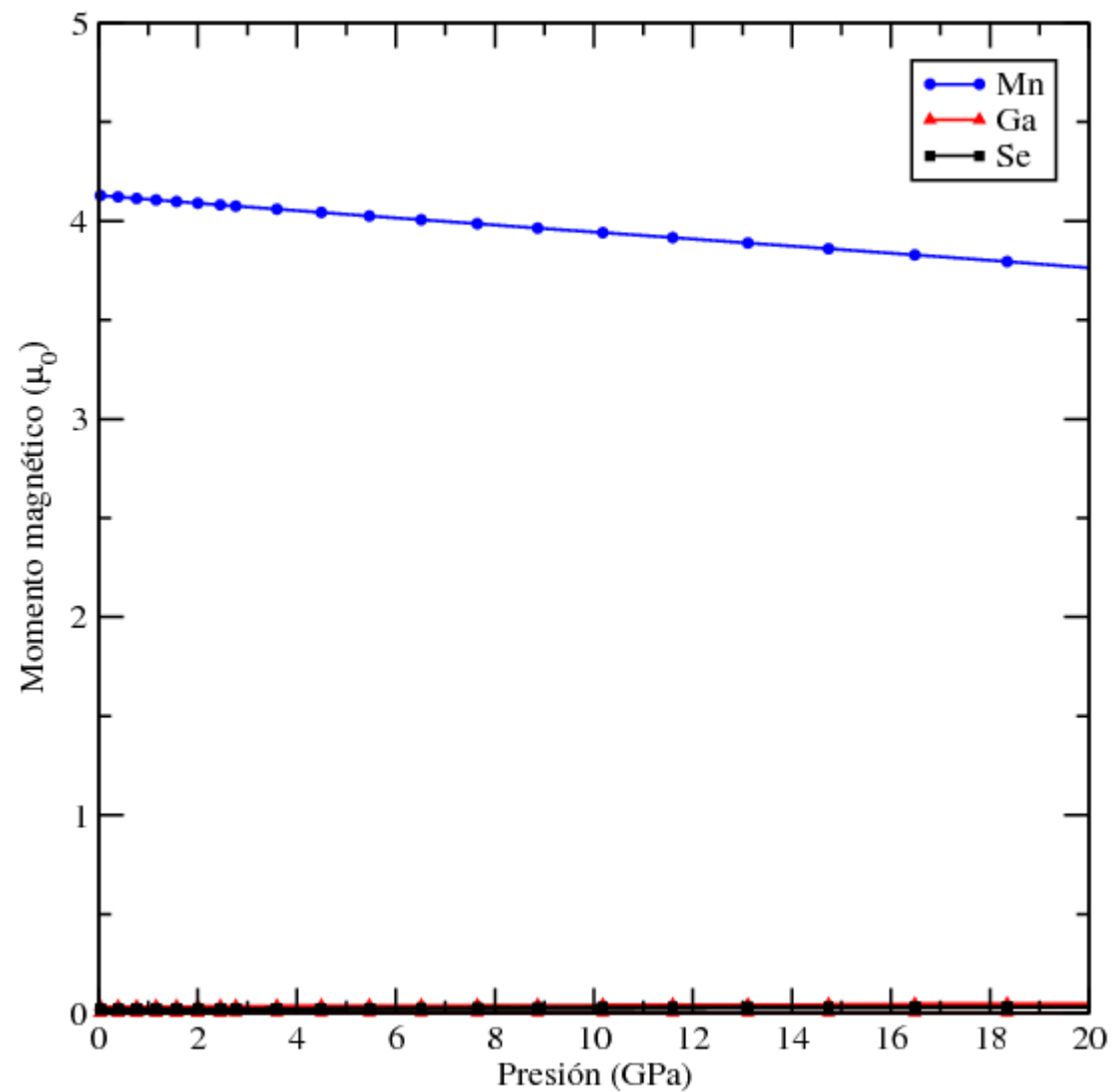
A full-page background image of a sunset at Playa de Benijo. The sky is filled with dramatic, dark clouds tinged with orange and yellow from the setting sun. In the foreground, the calm water of the beach reflects the sky and the silhouettes of the cliffs. To the left, a long, dark cliff line stretches across the horizon. To the right, a large, jagged rock formation stands prominently in the water. The overall mood is serene and majestic.

Gracias por su atención

Playa de Benijo

Gracias por su atención

Momento magnético



Modos normales de vibración en Γ

	Este trabajo			Datos experimentales [1]		
modo	ω	$d\omega/dP$	γ	ω	$d\omega/dP$	γ
E(RI)	70.282	0.26118	0.14	76.6	0.2	0.19
B(RI)	87.0603	0.53415	0.23	91.8	0.83	0.67
E(RI)	95.1	-0.6	-0.38	104.8	-0.1	0.04
B(RI)	112.978	-0.14467	-0.05	122.7	0.6	0.20
A(R)	131.124	5.0427	1.49	134.2	5.3	1.86
A(R)	170.88	0.7665	0.62	181.7	3.2	0.89
				207.0	2.2	0.76
				214.0	6.2	1.33
E(RI)	215.483	5.6737	1.02	239.3	4.1	0.85
B(RI)	230.326	5.4503	0.91	227.0	3.3	0.71
E(RI)	231.66	4.5013	0.75	244.9	4.6	1.10
E(RI)	243.102	3.3287	0.53	253.5	4.6	0.92
B(RI)	244.436	6.1907	0.98	277.9	3.5	0.65

Los modos más bajos son relativamente insensibles a la presión

Modos normales de vibración en Γ

Los modos más altos aumentan con la presión

	Este trabajo			Datos experimentales [1]		
modo	ω	$d\omega/dP$	γ	ω	$d\omega/dP$	γ
E(RI)	70.000	0.00110	0.14	76.6	0.2	0.19
				91.8	0.83	0.67
				104.8	-0.1	0.04
B(RI)	112.978	-0.14467	-0.05	122.7	0.6	0.20
A(R)	131.124	5.0427	1.49	134.2	5.3	1.86
A(R)	173.22	2.7665	0.62	181.7	3.2	0.89
A(R)	192.9	2.4979	0.50	207.0	2.2	0.76
B(RI)	214.115	1.5897	0.29	214.0	6.2	1.33
E(RI)	215.483	5.6737	1.02	239.3	4.1	0.85
B(RI)	230.326	5.4503	0.91	227.0	3.3	0.71
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HgWO_4 under pressure

Javier López Solano

Universidad de La Laguna

Universidad Complutense de Madrid

Universitat Politècnica de València

Universitat de València

Universidad de Oviedo



Overview

1 Introduction

2 Calculation details

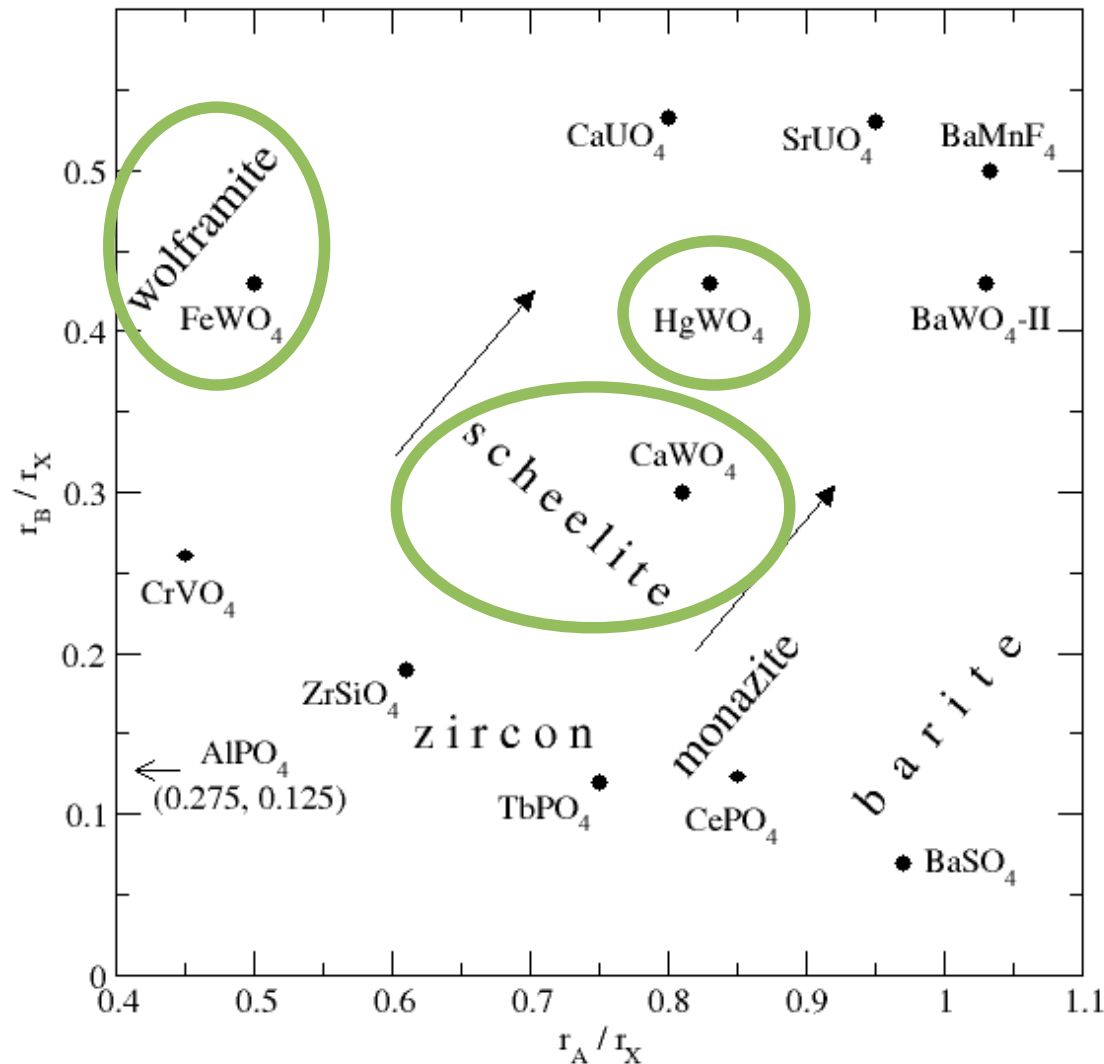
3 Low pressure

4 High pressure

5 Conclusions

1 Introduction

Among the members of the ABO_4 family, $HgWO_4$ is one of the less studied compounds.



However, it's a fairly interesting compound, since it does not crystallize in the scheelite (SG no. 88, $I2/a$, $Z=4$) nor in the wolframite (SG no. 12, $P2/c$, $Z=2$) structures, which the two most usual in tungstates.

1 Introduction

The HgWO_4 -type (SG no. 15, $C2/c$, $Z=4$) structure has some similarities with the wolframite, but in particular the cationic environments are very different. This is reflected by the different coordinations - [6,6] for wolframite and [6+2,6] for HgWO_4 -type.

Thus, we can expect HgWO_4 to have a behaviour under pressure rather different from that of the better-studied scheelite and wolframite compounds, which respectively feature BaWO_4 -II-type ([8-6] coordination) and Cmca ([9-6]) structures under high pressure.

2 Calculation details

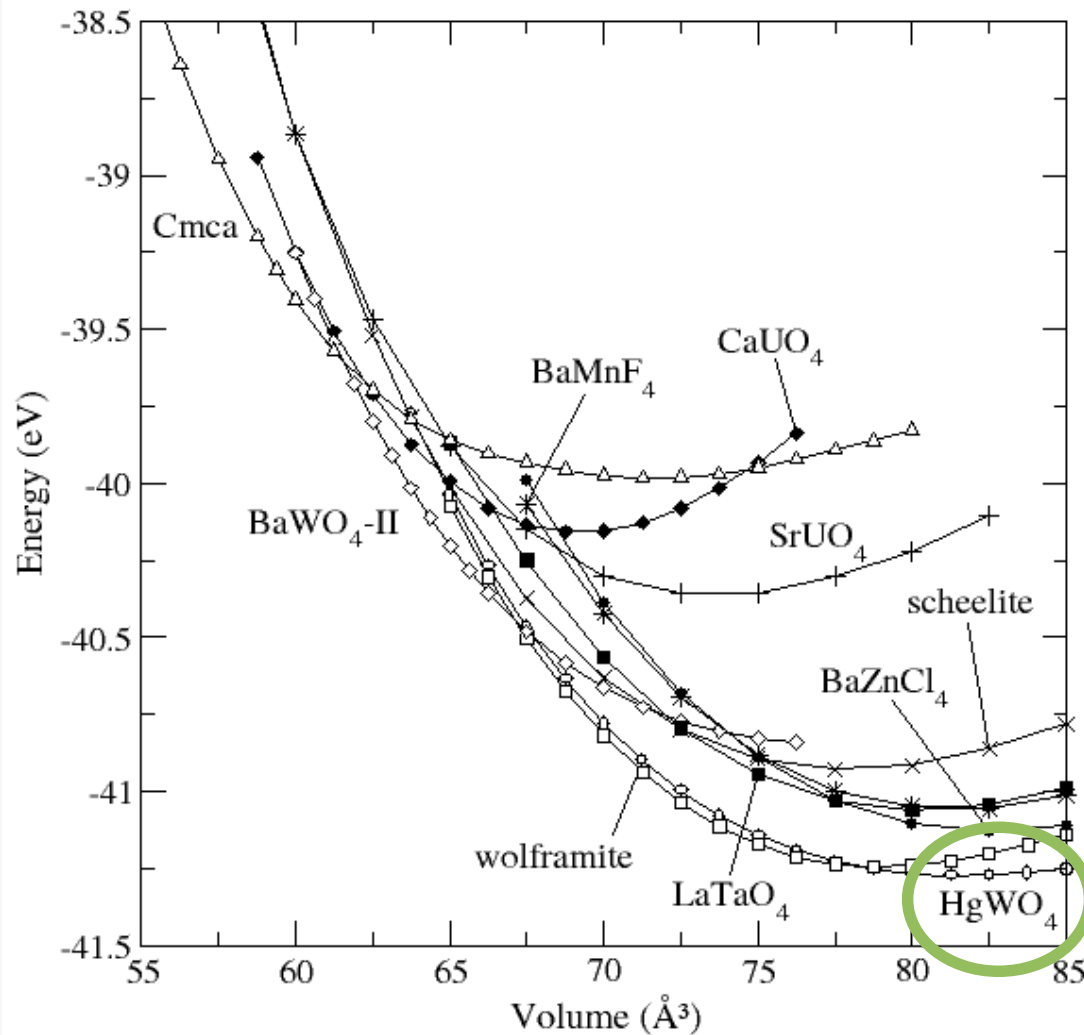
All the calculations have been performed with the VASP *ab initio* code, using PAW PBEsol pseudopotentials.

An energy cutoff of 530 eV and dense Monkhorst-Pack grids ensure an energy convergence of 1 meV per formula unit. All the crystal structures considered were fully optimized.

To include temperature effects we have used the GIBBS code, which allows to calculate the Gibbs free energy within the quasi-harmonic Debye model.

Phonon frequencies at the Γ point were calculated using the direct force constant method as implemented in the PHONON code.

3 Ambient pressure



The HgWO₄-type structure is lowest-energy one among the 11 considered.

Experimental and theoretical values of V_0 , B_0 and B'_0 are in reasonable agreement. In particular, the PBEsol approximation produces a V_0 which is very close to the experimental value ($81.61 \text{ \AA}^3$ vs $81.01 \text{ \AA}^3$)

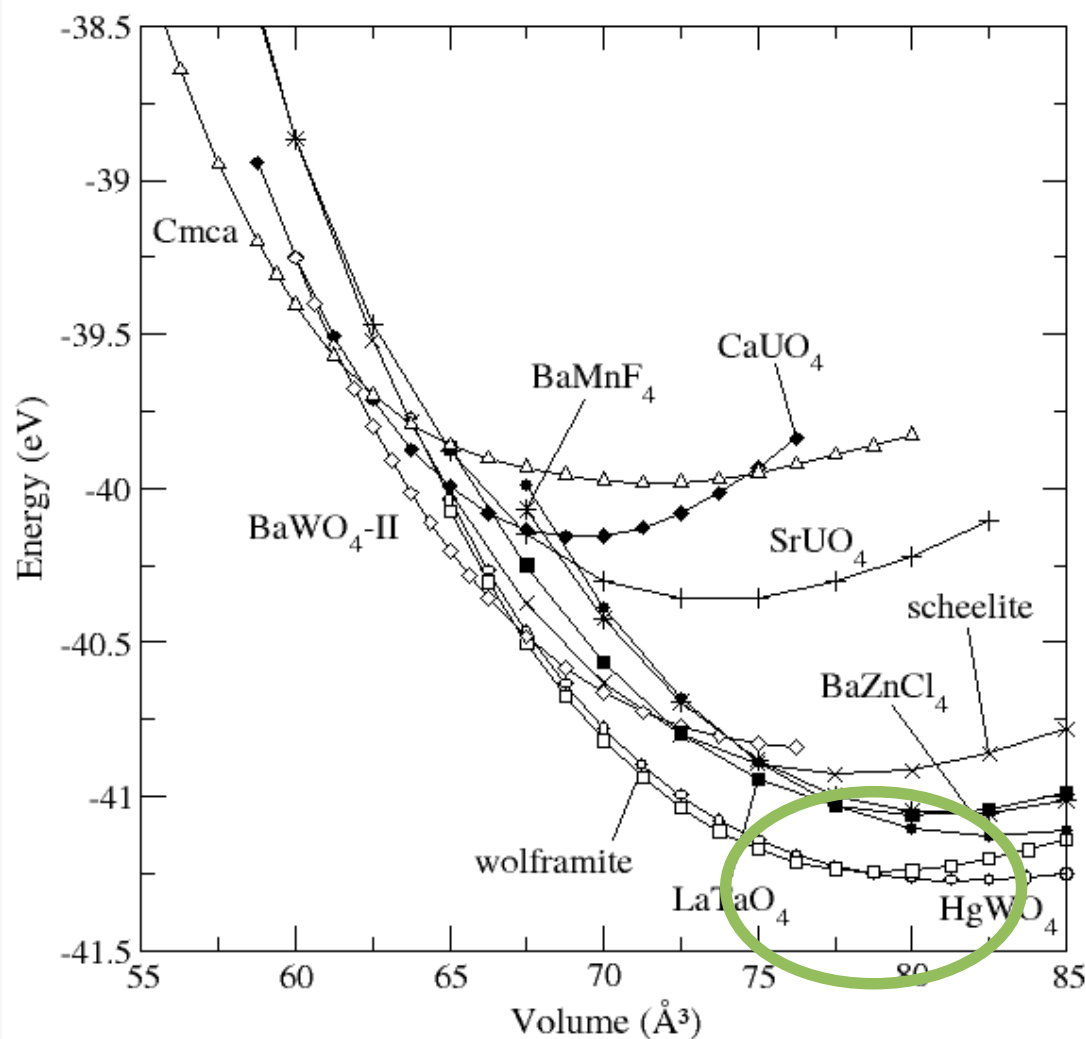
3 Ambient pressure

Mode	ω (th.)	ω (expt.)
B _g	87	89
B _g	133	139
A _g	141	145
A _g	184	193
B _g	200	204
B _g	216	228
A _g	268	278
A _g	353	374
B _g	491	508
A _g	525	537
A _g	683	698
B _g	695	715
B _g	827	842
A _g	907	924

The calculated and experimental Raman frequencies ω (in cm⁻¹) are also in good agreement.

Thus, the ambient pressure phase is clearly determined as HgWO₄-type

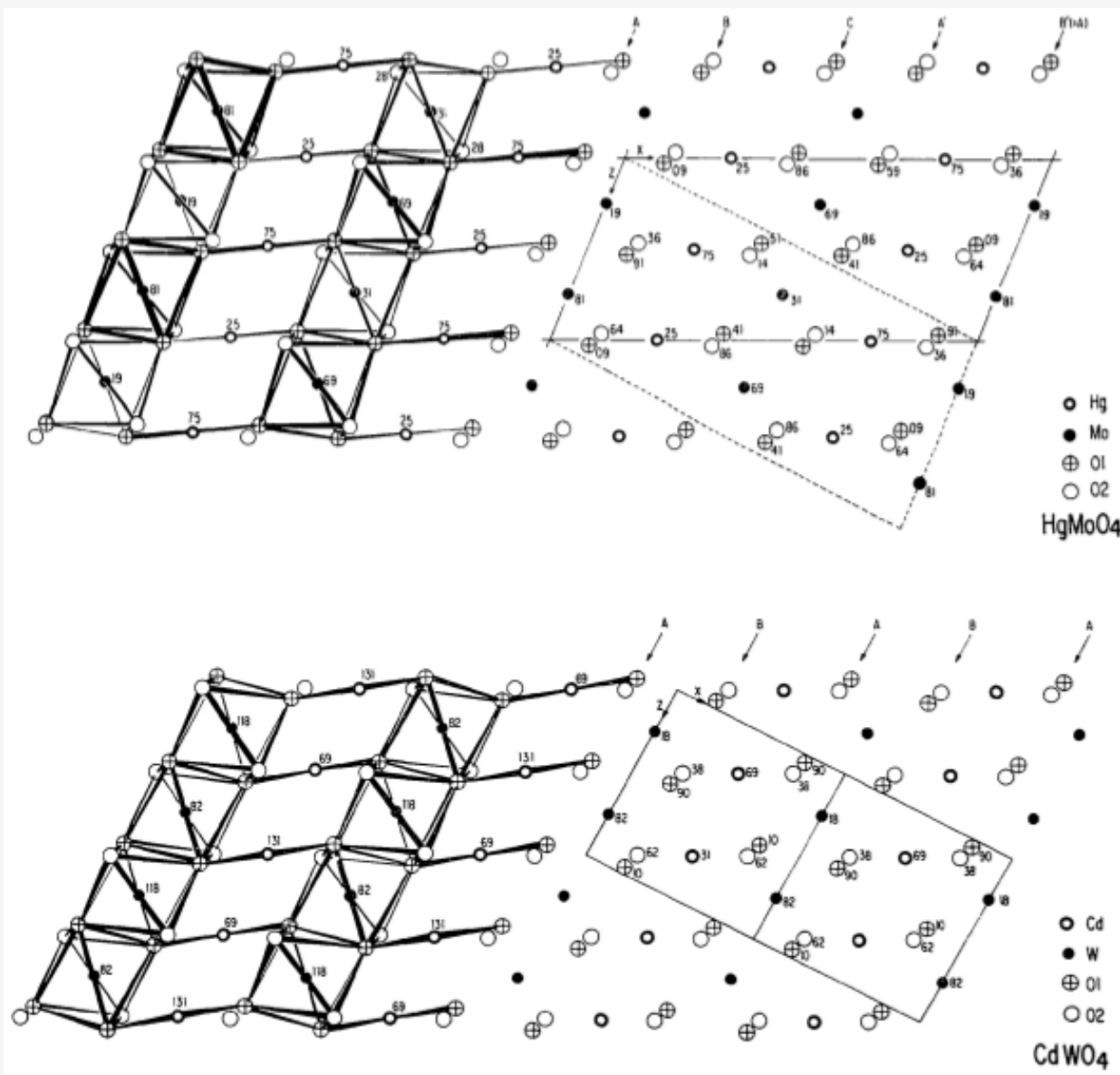
4 Transition to wolframite?



Upon compression, we find that wolframite becomes lower in energy than the HgWO₄-type structure.

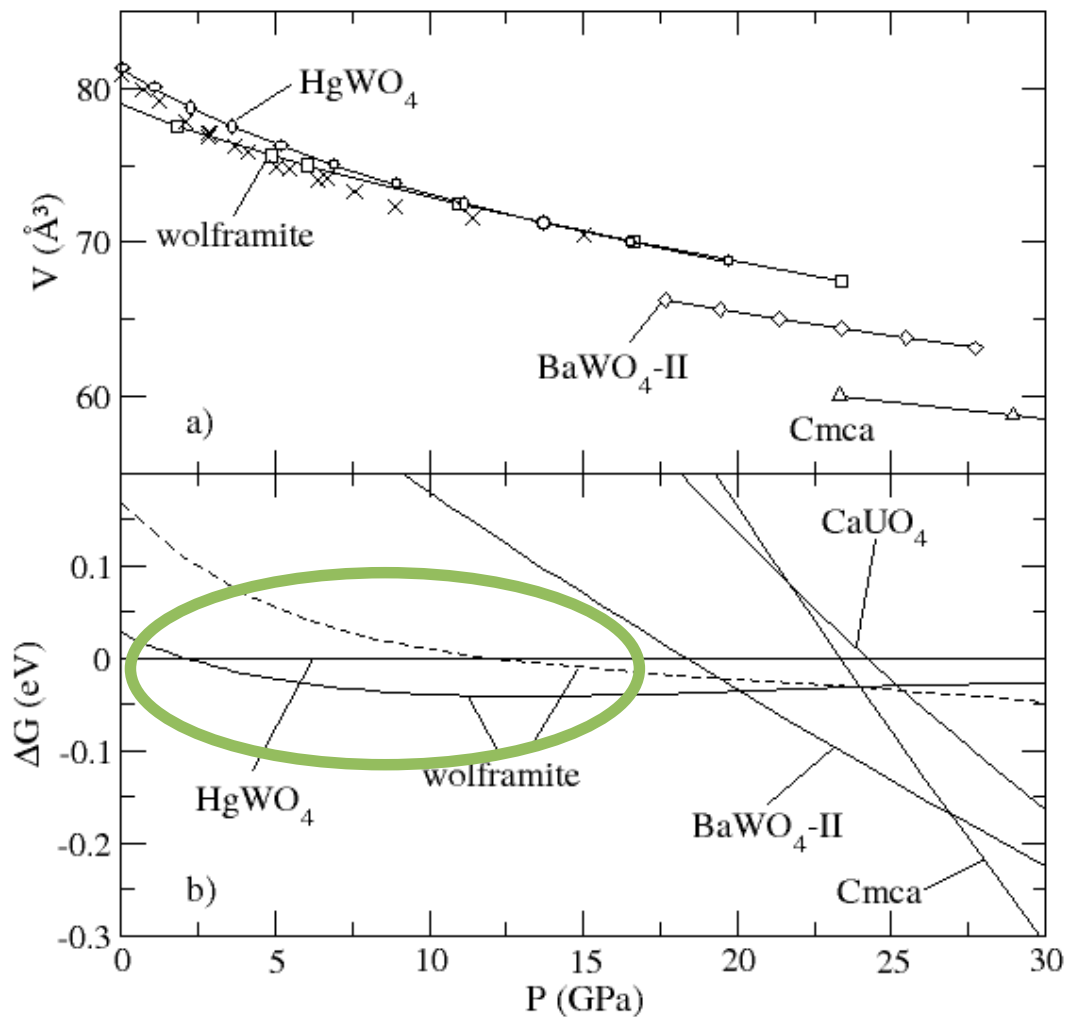
However, we have good quality experimental data up to 16 GPa, and wolframite was not observed.

4 Transition to wolframite?



The HgWO_4 -type and wolframite structures are very similar. However, as Jeitschko and Sleight noted in their study on HgMoO_4 , the packing of oxygens is fairly different. This results in somewhat distorted coordination polyhedra for the cations of the HgWO_4 -type structure.

4 Transition to wolframite?

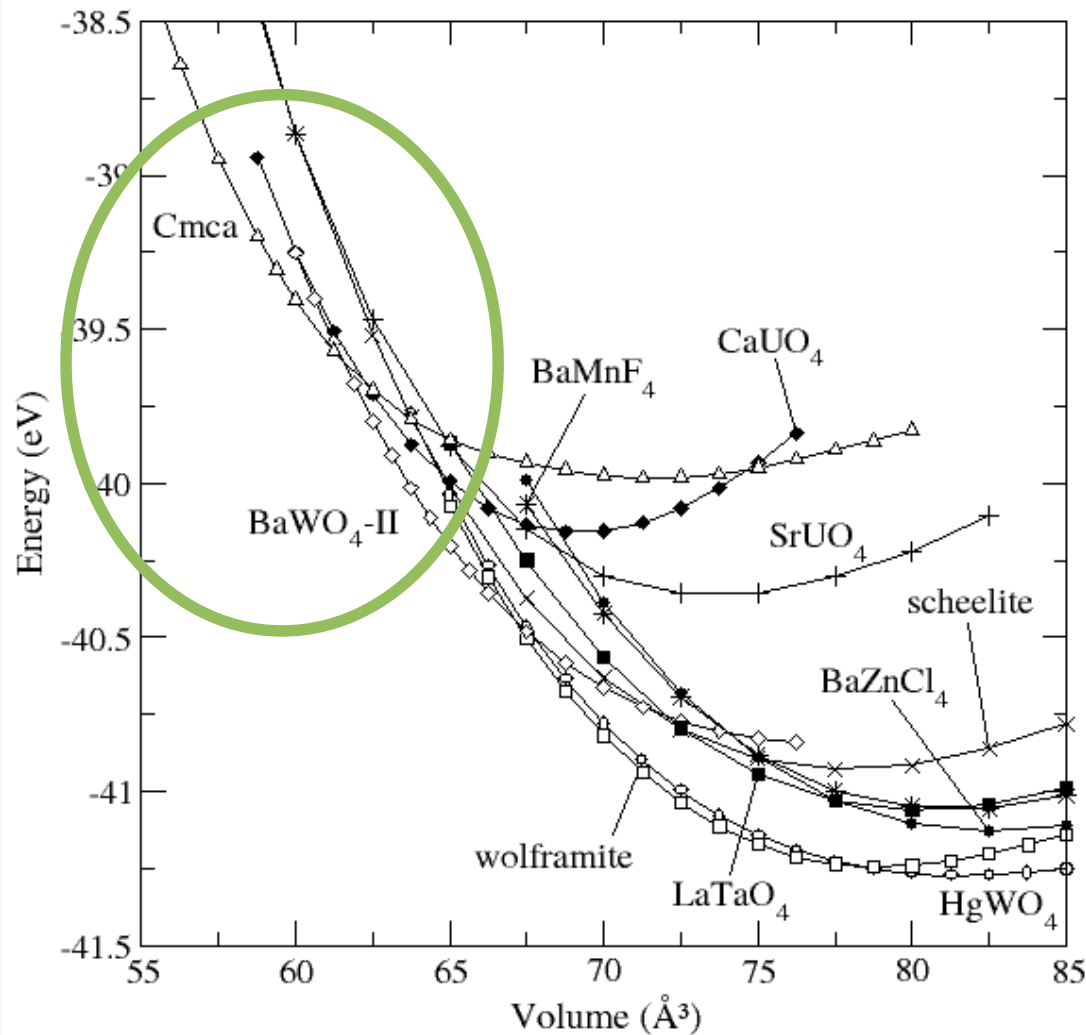


We suspected this difference between theory and experiment could be related to the lack of temperature effects in our calculations.

Using the GIBBS code, we calculated the Gibbs free energy of the HgWO_4 -type and wolframite phases at 300K.

Temperature makes wolframite more unfavourable with respect to HgWO_4 -type – the transition pressure increases from 2 to 11 GPa.

5 Further transitions



At pressures above the maximum reached in experiments, first the BaWO₄-II-type and then the Cmca become the most stable structures.

The BaWO₄-II-type structure is a usual high pressure structure of scheelite compounds, while the Cmca has been found in wolframites.

6 Conclusions

At ambient pressure, theory and experiment are in good agreement.

Temperature plays an important role in the stability of the HgWO_4 -type vs the wolframite structures.

The sequence of phases under pressure bears similarities to the sequence of both scheelite and wolframite tungstates.

Further experimental work would be necessary to confirm the high pressure behaviour.



Title

Text

Estudio bajo presión de óxidos ternarios: Zircon, Monazite, Scheelite y minerales relacionados

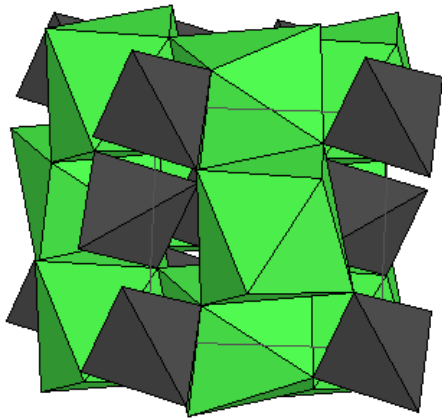
Daniel Errandonea
Universidad de Valencia

Introduction

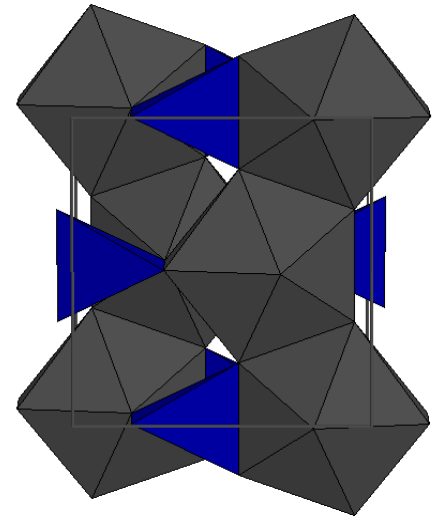
- ✓ Study of pressure effects on structural properties
- ✓ Phase transitions induced by pressure (amorphization, decomposition?)
- ✓ Scheelite-structured oxides (AWO_4 , $AMoO_4$)
- ✓ Wolframite-structures oxides ($CdWO_4$, $MgWO_4$, $ZnWO_4$, ...)
- ✓ Zircon-structured oxides (AVO_4 , APo_4 , $AGeO_4$...)
- ✓ Monazite and other minerals (barite, anhydrite, $AgClO_4$...)
- ✓ Other oxides (spinel, columbite, ...)
- ✓ Differential bond compressibility
- ✓ Systematic behavior?

Why we are interested in these oxides?

Many crystal structures of ABO_4 compounds consists AO_8 bisdisphenoids and BO_4 tetrahedra. They include important mineral structures, e.g. zircon ($ZrSiO_4$), anhydrite ($CaSO_4$), silver perchlorate ($AgClO_4$), and scheelite ($CaWO_4$).



scheelite



zircon

These oxides, because of their compositional diversity and structural simplicity, played a key role in developing comparative crystal chemistry.

Systematically Studied: $P > 50 \text{ GPa}$ (HP-HT)

CaWO_4 , SrWO_4 , BaWO_4 , PbWO_4 , EuWO_4 ,

SrMoO_4 , PbMoO_4 , CdMoO_4 , EuMoO_4

CuWO_4 , CdWO_4 , MgWO_4 , ZnWO_4 ,

YVO_4 , ScVO_4 , EuVO_4 , LuVO_4 , CeVO_4 , NdVO_4 , ...

YPO_4 , ScPO_4 , ErPO_4 , TbPO_4 , EuPO_4 , LaPO_4 , ...

ThGeO_4 , YAsO_4 , YCrO_4

BaSO_4 , CaSO_4 , AgClO_4 , HfTiO_4

ZnGa_2O_4 , selenates, sulphates, nitrides, silicides

✓ ADXRD

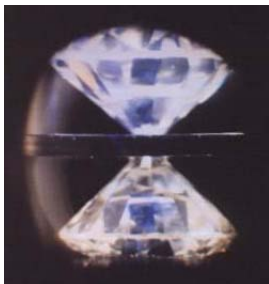
✓ single-crystal diffraction ✓ XANES & EXAFS

✓ Optical absorption ✓ Raman spectroscopy

✓ *Ab initio* total-energy & lattice dynamics calculations

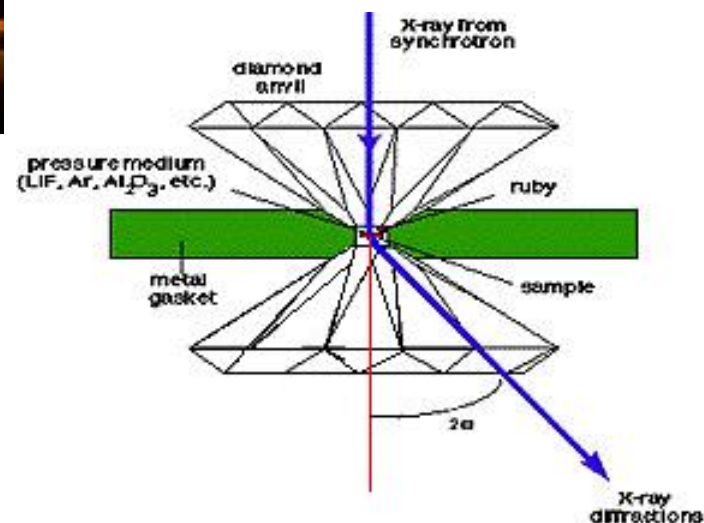
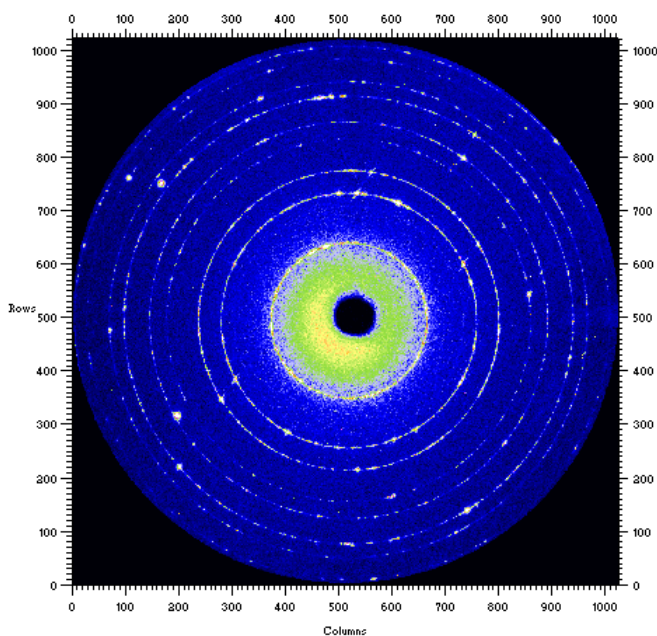
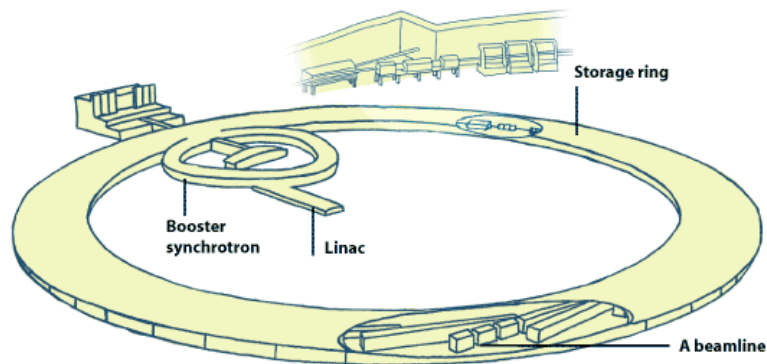
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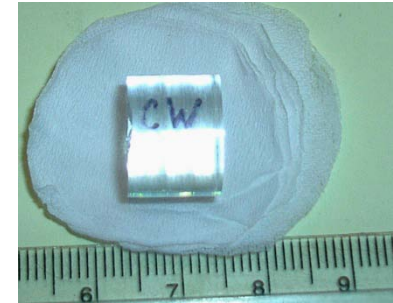
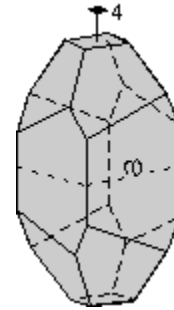
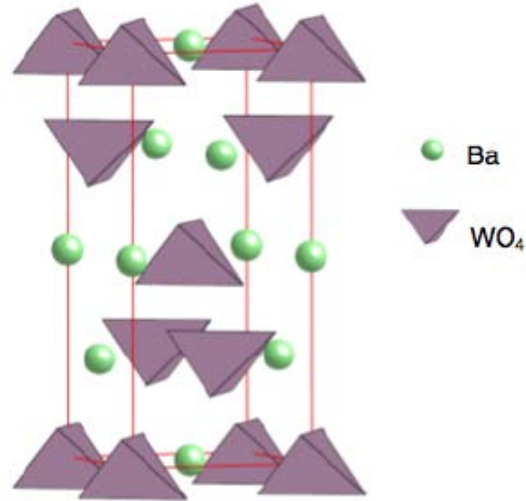
ADXRD

ESRF(ID27) – APS(HPCAT) – Diamond (I15) - MALTA



Pressure media: neon, argon, silicone-oil, methanol-ethanol, no-medium, etc.

scheelites



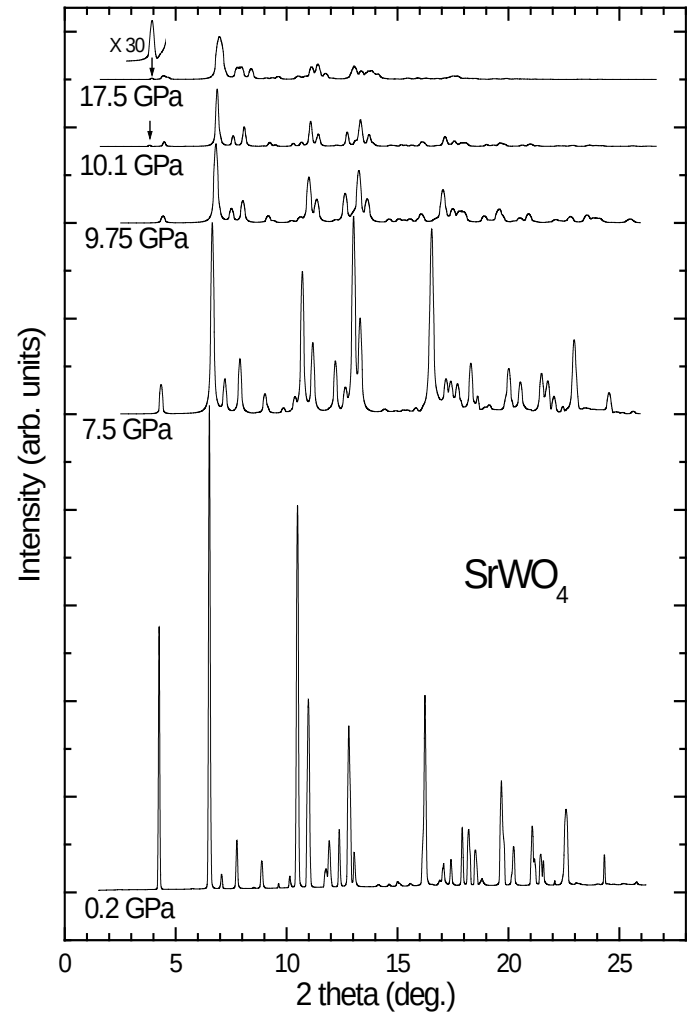
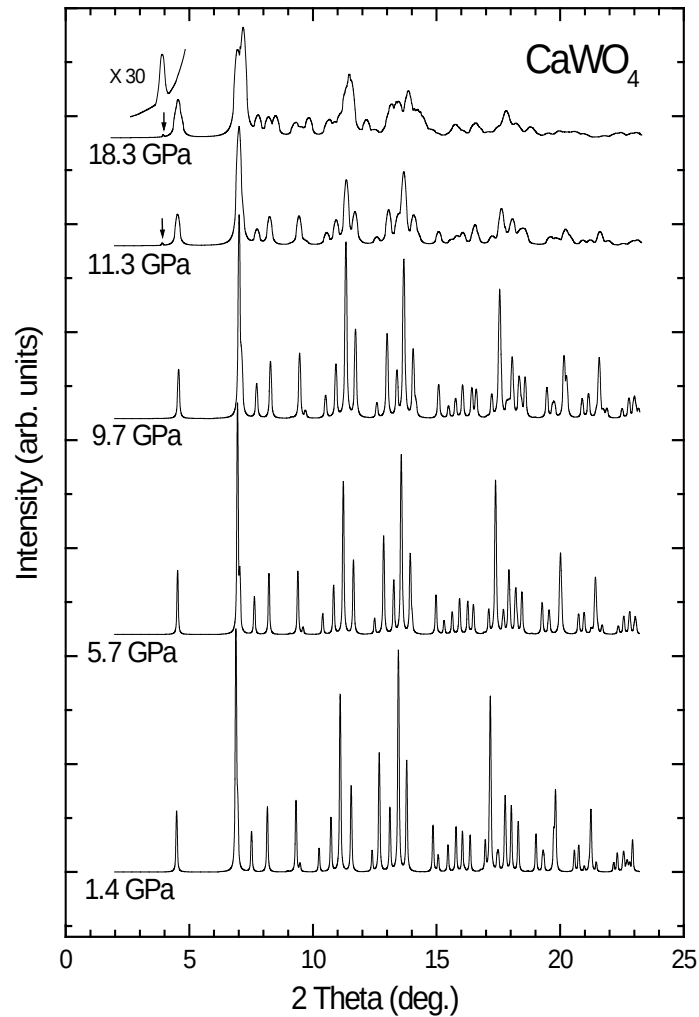
Structural sequence:

scheelite → fergusonite → monoclinic $P2_1/n$ → orthorhombic

Amorphous $P > 40$ GPa

scheelites

ADXRD $\lambda = 0.3738 \text{ \AA}$



scheelites

No volume
discontinuity at the
transition pressure

fergusonite structure:

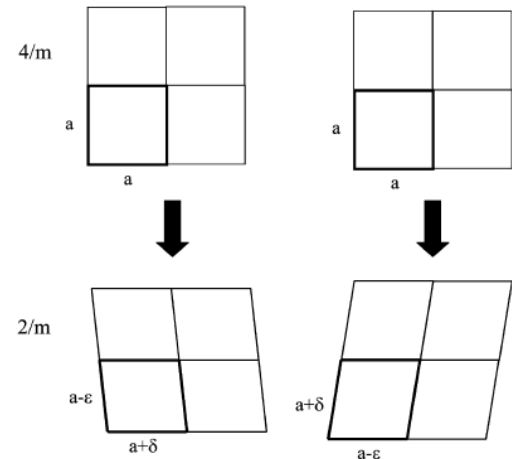
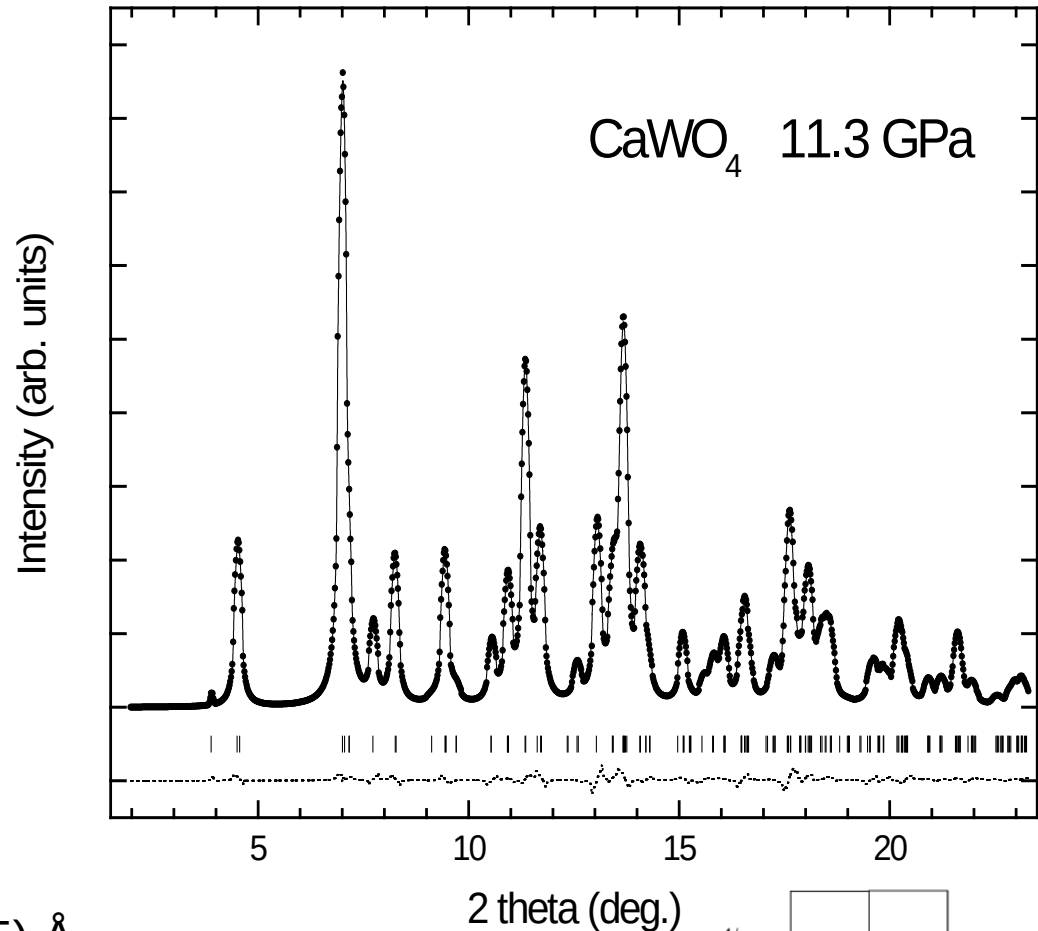
$I2/a$ [# 15] – $Z = 4$

$a = 5.069(2) \text{ \AA}$, $b = 10.851(5) \text{ \AA}$,

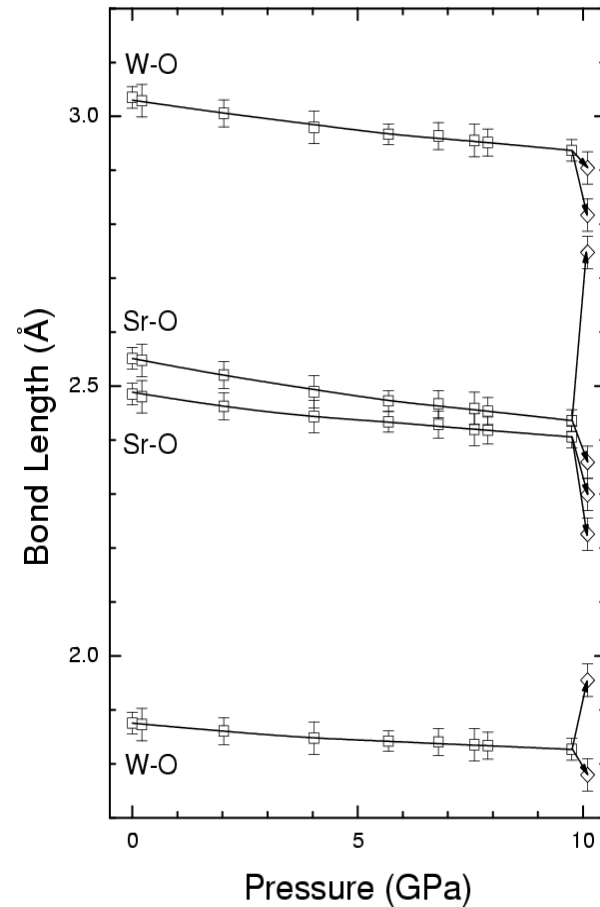
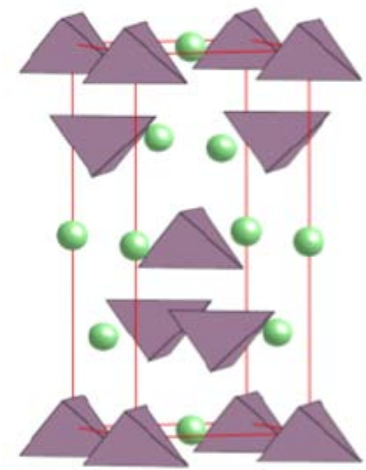
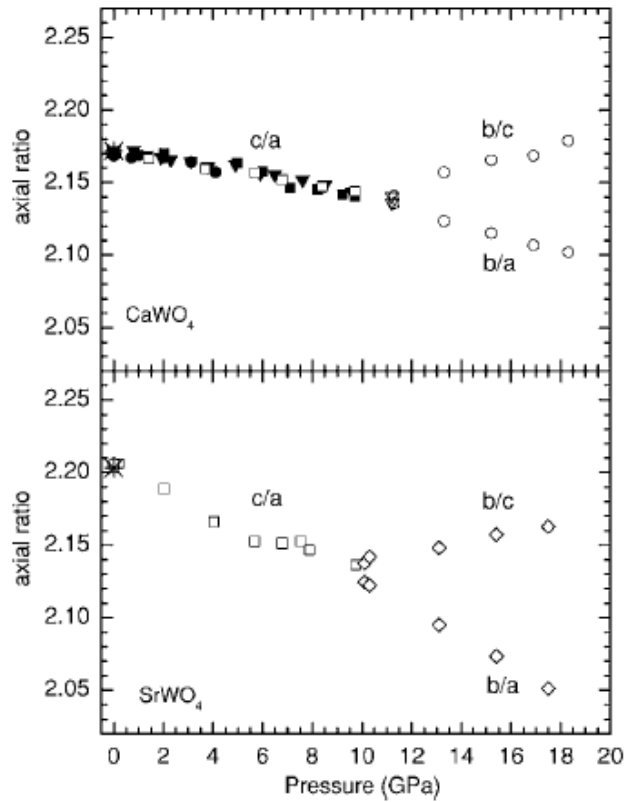
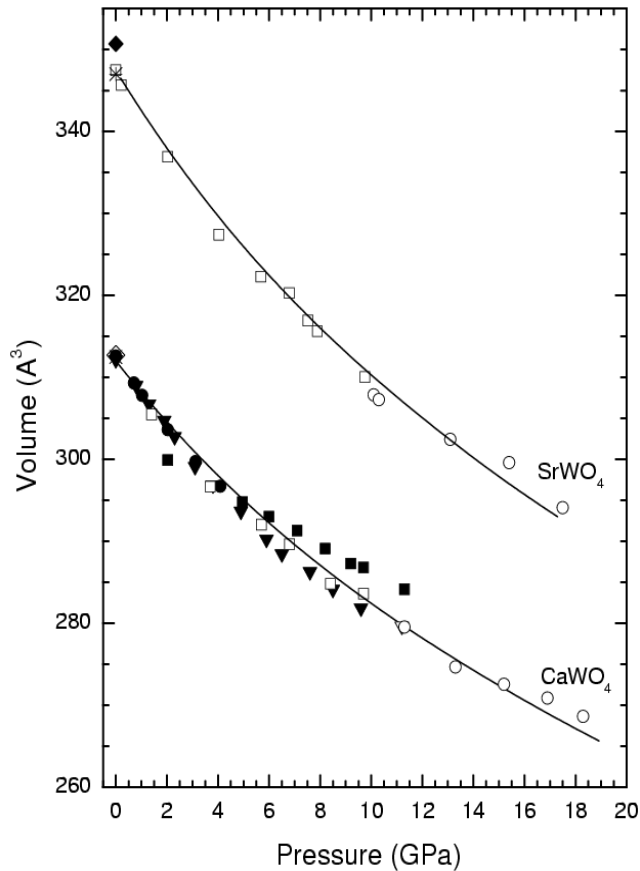
$c = 5.081(7) \text{ \AA}$, $\beta = 90.091(9)^\circ$

Lowering point-group symmetry from $4/m$ to $2/m$

Second-order ferroelastic transition



scheelites



✓ W tetrahedra are rigid structural elements that undergo little change with P

✓ Bulk modulus determined by A-O bond compression

scheelites

EOS Parameters

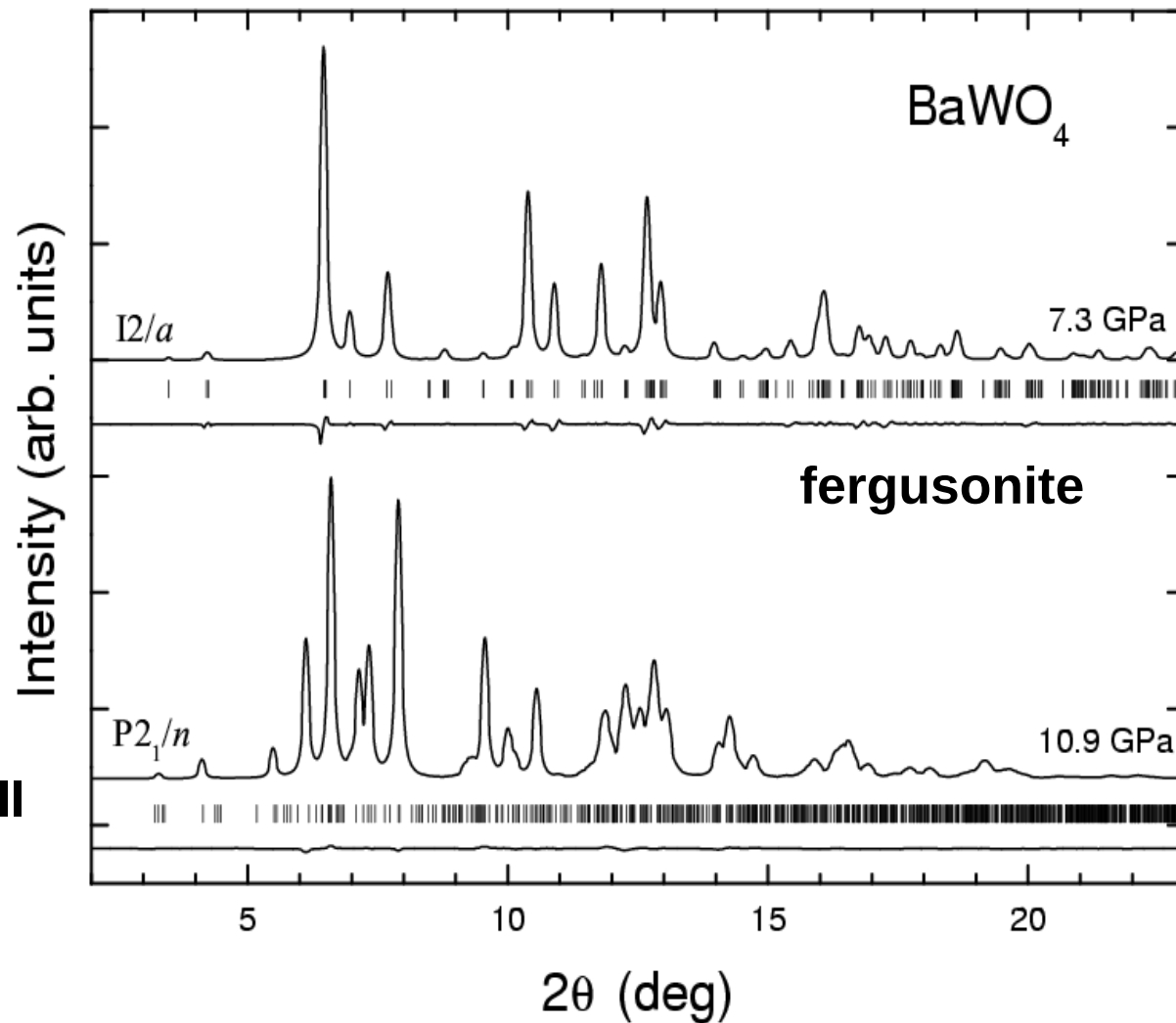
	V_0	B_0	B_0'	P_T (GPa)
CaWO_4	$312 \text{ \AA}^3$	74 GPa	5.6	11
SrWO_4	$347.4 \text{ \AA}^3$	63 GPa	5.2	12
EuWO_4	$348.9 \text{ \AA}^3$	65 GPa	4.6	9
PbWO_4	$357.8 \text{ \AA}^3$	66 GPa	5.6	7
BaWO_4	$402.8 \text{ \AA}^3$	52 GPa	5	5

Bulk modulus correlated with A-O distance at ambient pressure

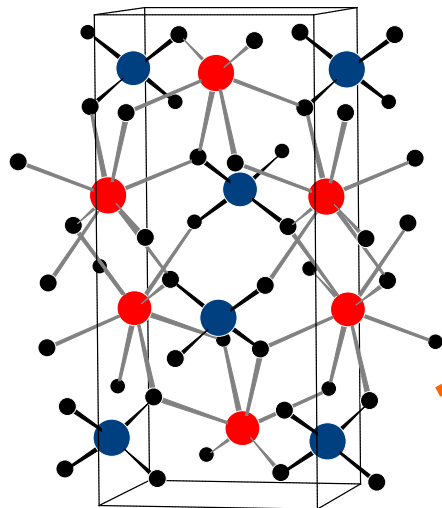
scheelites

Second
transition

BaWO₄-II

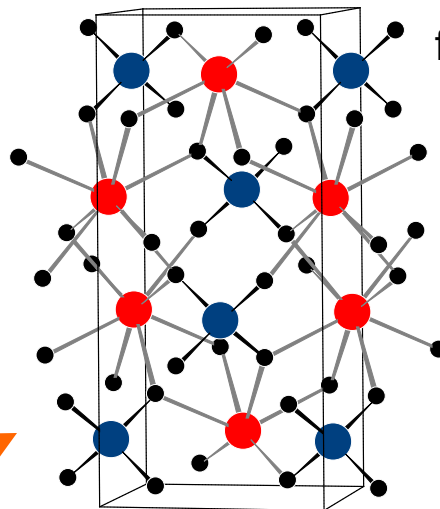


PbWO₄-BaWO₄



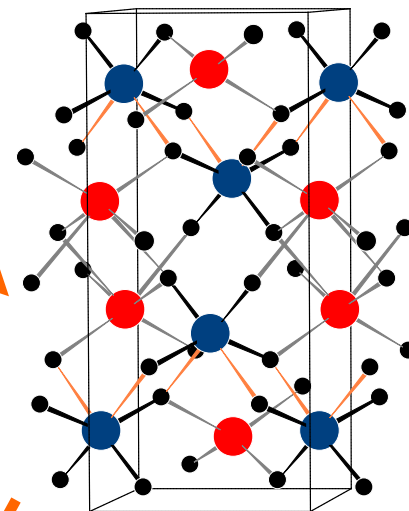
scheelite (I4₁/a) – 1 bar - W-O coordination = 4

Second-order transition



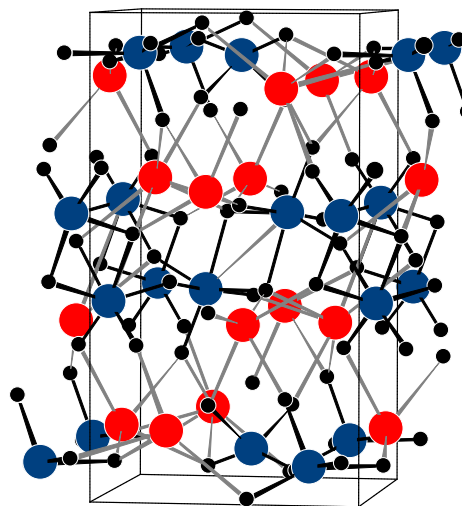
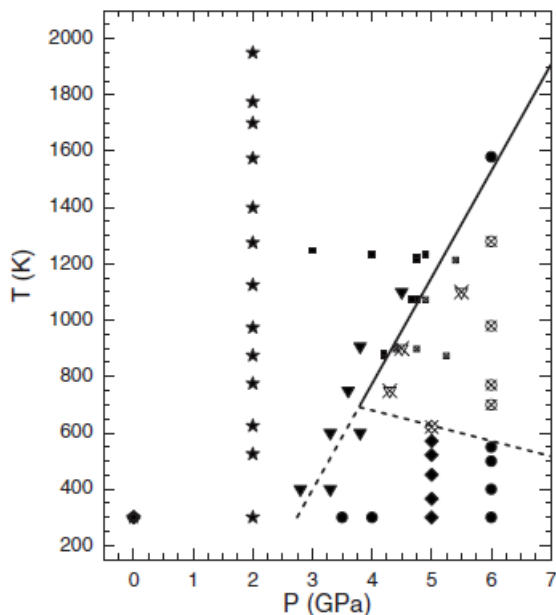
fergusonite (I2/a) – 7.9 GPa

W-O coordination = 4



fergusonite (I2/a) – 9.5 GPa

W-O coordination = 4+2



PbWO₄-III (P2₁/n) – 12 GPa

W-O coordination = 6

$\Delta V/V = 8\%$

Scheelites (tungstates and molybdates)

- ✓ WO_4 (MoO_4) tetrahedra → rigid structural units (undergo little change with P)
- ✓ Bulk modulus determined by A-O bond compression
- ✓ Transition pressure increases as the packing ratio of the anionic WO_4 (MoO_4) units around the A cations increases

High-pressure phases

- ✓ The nine compounds undergo a scheelite → fergusonite transition
- ✓ Fergusonite: W environment distorted (4 → 4+2 coordination)
- ✓ More compact monoclinic structures found in BaWO_4 & PbWO_4
- ✓ Orthorhombic structures at higher P?

Nanocrystals

- ✓ Transition pressure and compressibility increases

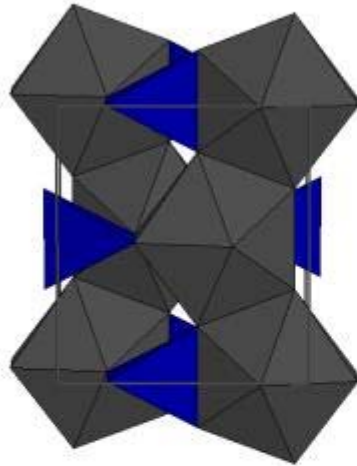
CdMoO_4 (first study in EuMoO_4)

- ✓ Contradict previous studies scheelite to fergusonite (not to wolframite)

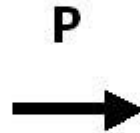
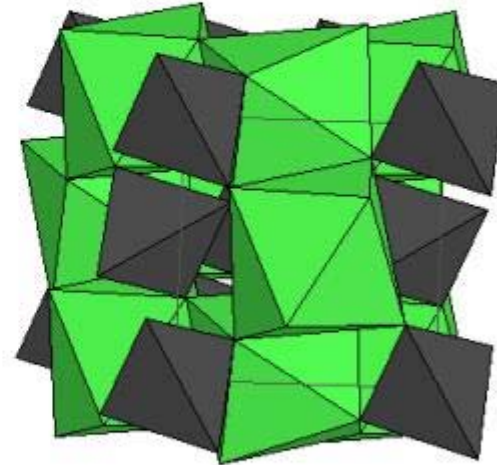
Zircon-type oxides

Vanadates, phosphates, arsenates, chromates, silicates, germanates

zircon ($I4_1/amd$)

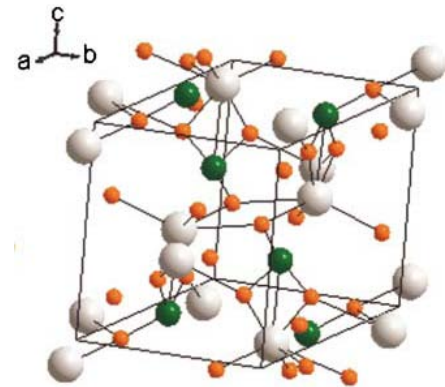
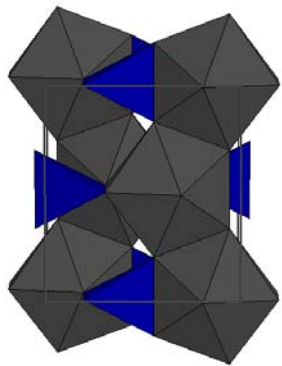
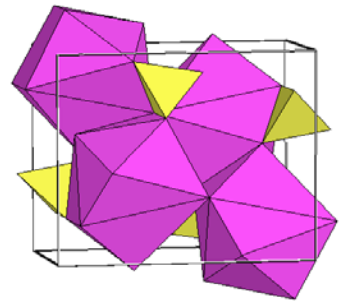
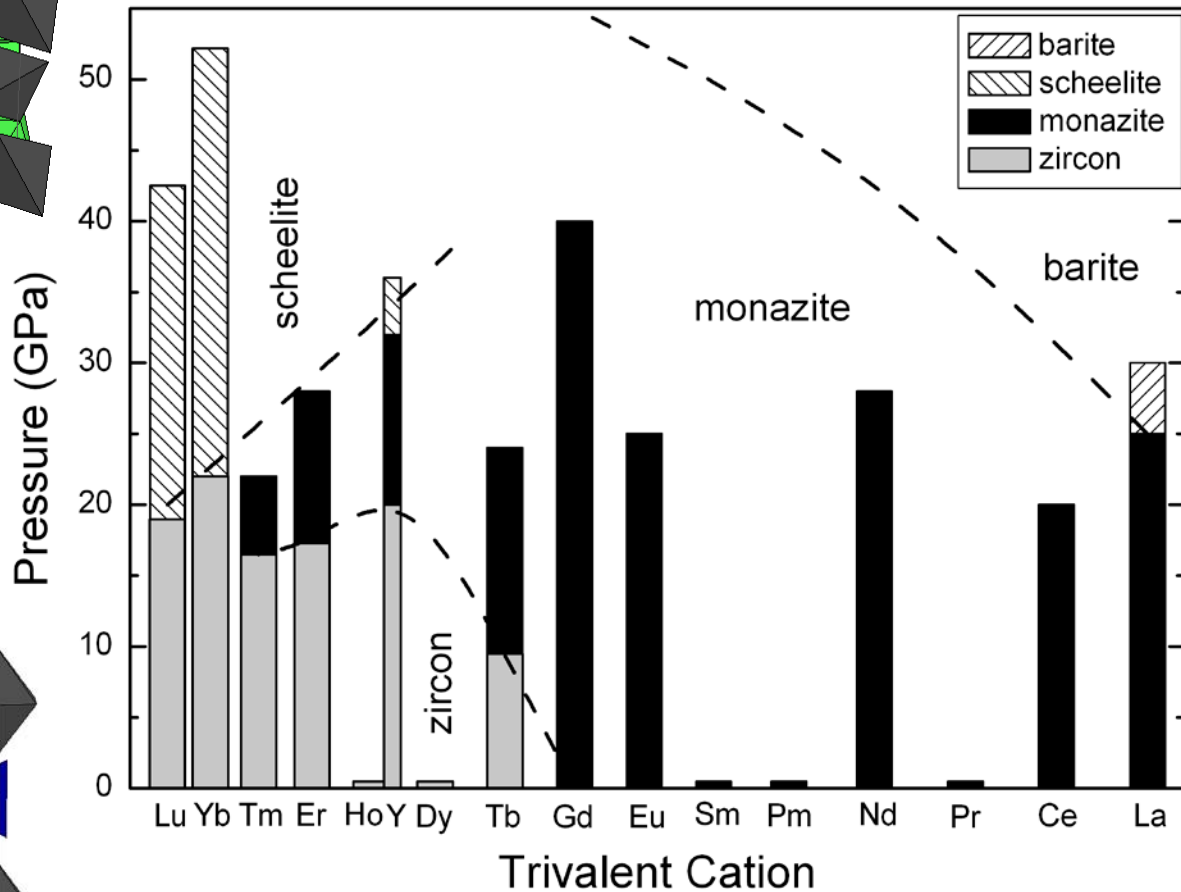
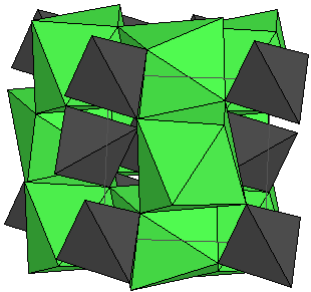


scheelite ($I4_1/a$)



Symmetry reduction (group-subgroup relationship)

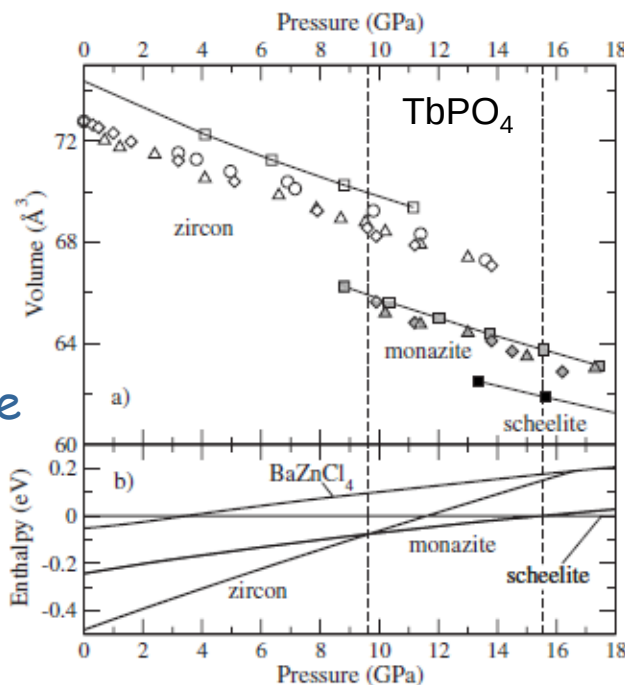
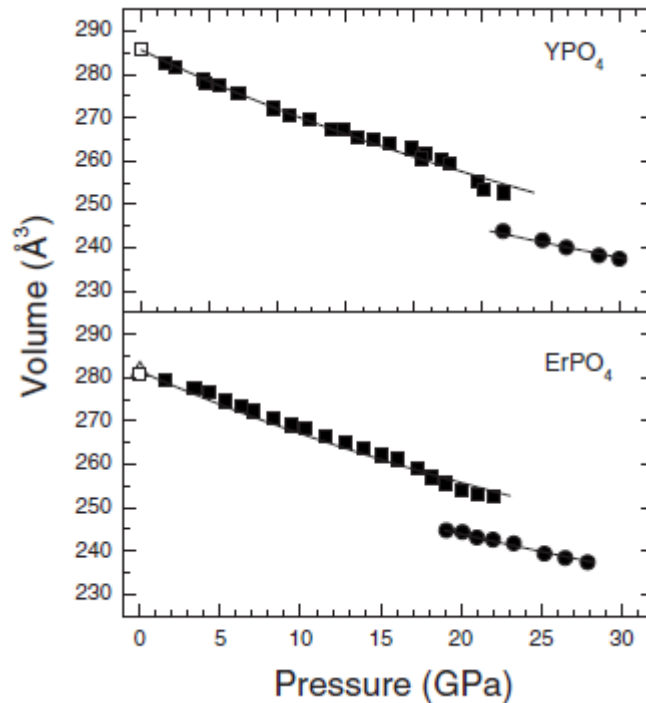
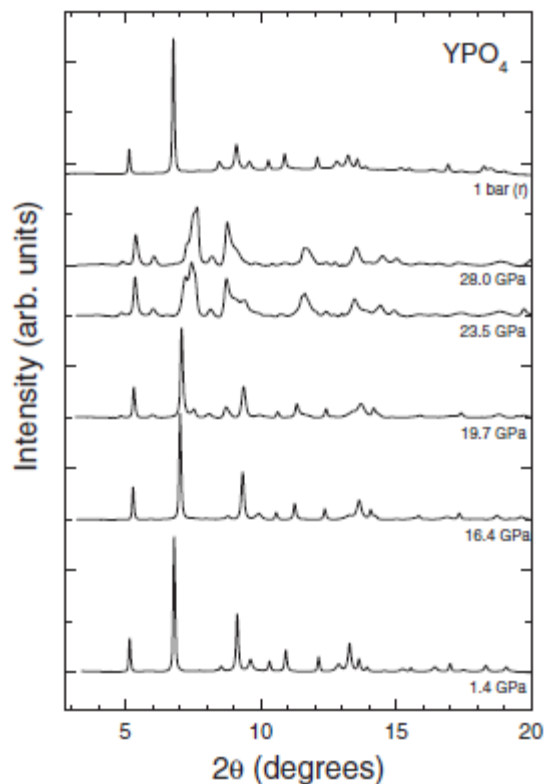
Phosphates



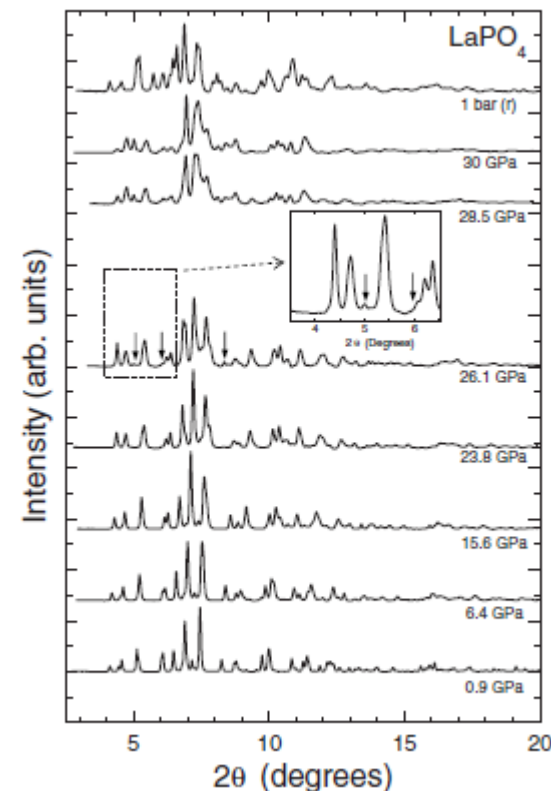
Mechanism of transition?: Single-crystal diffraction

Phosphates

ADXRD $\lambda = 0.3746 \text{ \AA}$



First-order transitions



monazite $\rightarrow$ barite

zircon $\rightarrow$ monazite $\rightarrow$ scheelite

or

zircon $\rightarrow$ scheelite

Phosphates

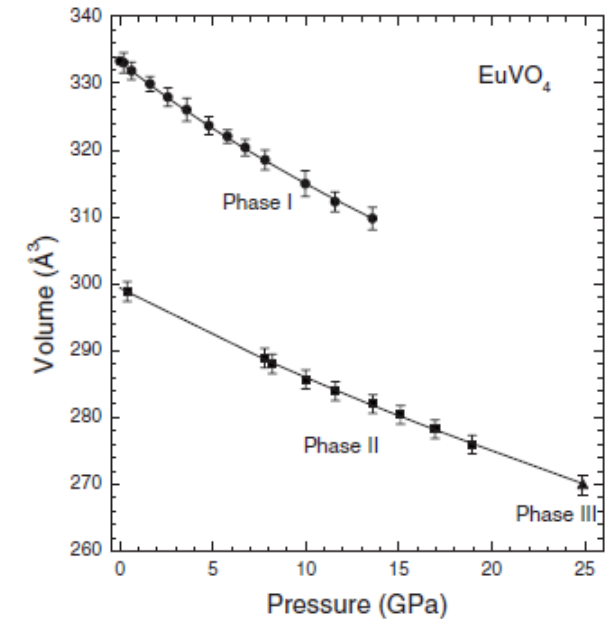
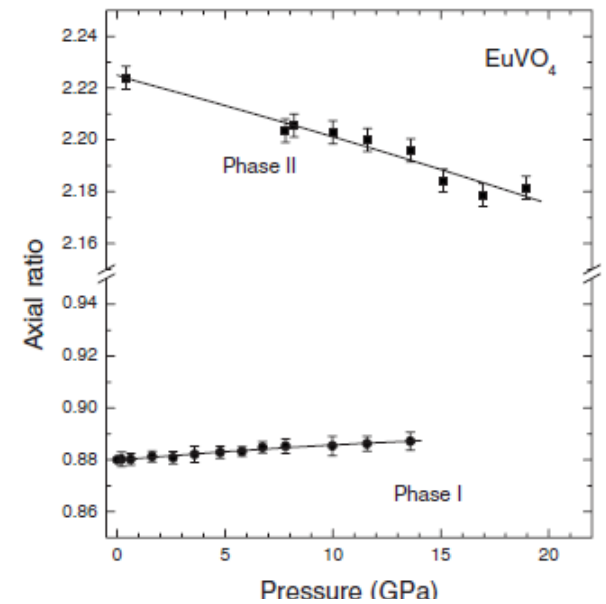
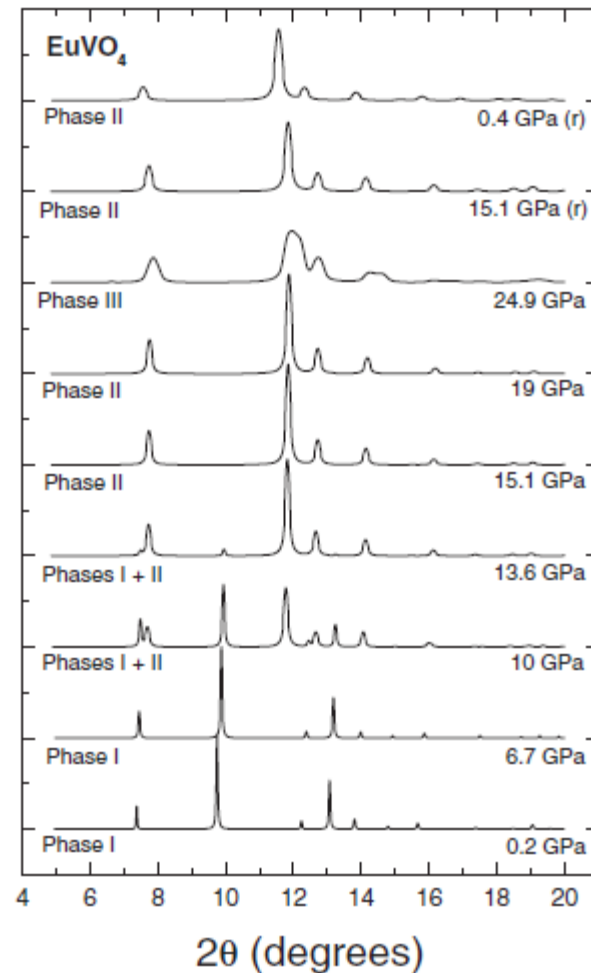
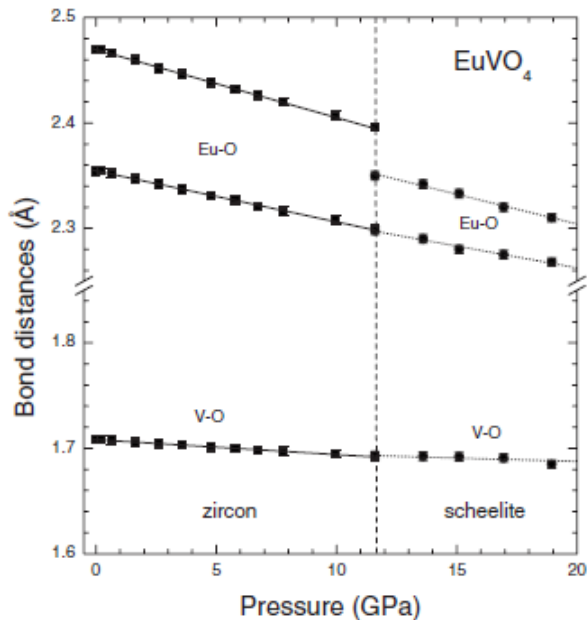
EOS Parameters

Compound	Structure	Unit-cell volume	Bulk modulus		
			Experiments	Theory	Empirical model
ScPO ₄	Zircon	252.1	203(7) ^a	175.1 ^f –183 ^a	169
ScPO ₄	Scheelite		376(8) ^a	334 ^a	
LuPO ₄	Zircon	273.7	184(4) ^b –166 ^c	152.8 ^f	150
LuPO ₄	Scheelite		226(3) ^b		
YbPO ₄	Zircon	276.5	150(5) ^b	150 ^f	147
YbPO ₄	Scheelite		218(2) ^b		
TmPO ₄	Zircon	278.9		147.2 ^f	146
ErPO ₄	Zircon	281.5	168(4) ^e	146.1 ^f	145
ErPO ₄	Monazite		208(6) ^e		
YPO ₄	Zircon	286.5	132 ^d –149(2) ^e –186(5) ^a	144.4 ^f –165 ^a	143
YPO ₄	Monazite		206(4) ^e –260 ^a	190 ^a	
YPO ₄	Scheelite			213.7 ^a	
HoPO ₄	Zircon	284.6		143.4 ^f	142
DyPO ₄	Zircon	287.9		141.5 ^f	141
TbPO ₄	Zircon	291.4		138.8 ^f –128 ^h	139
GdPO ₄	Monazite	279.1	160(2) ^e	149 ^f	120
EuPO ₄	Monazite	281.6	159(2) ^e	147.1 ^f	118
SmPO ₄	Monazite	284.4		146 ^f	117
NdPO ₄	Monazite	291.4	170(2) ^e	142.3 ^f	114
PrPO ₄	Monazite	295.3		139.7 ^f	112
CePO ₄	Monazite	299.5		137.2 ^f	110
LaPO ₄	Monazite	305.7	144(2) ^e	134 ^f –100 ^g	107
LaPO ₄	Barite	296.2	143(4) ^e		

Bulk modulus correlated with A-O distance at ambient pressure

Vanadates

ADXRD $\lambda = 0.6149 \text{ \AA}$



zircon $\rightarrow$ scheelite $\rightarrow$ fergusonite sequence

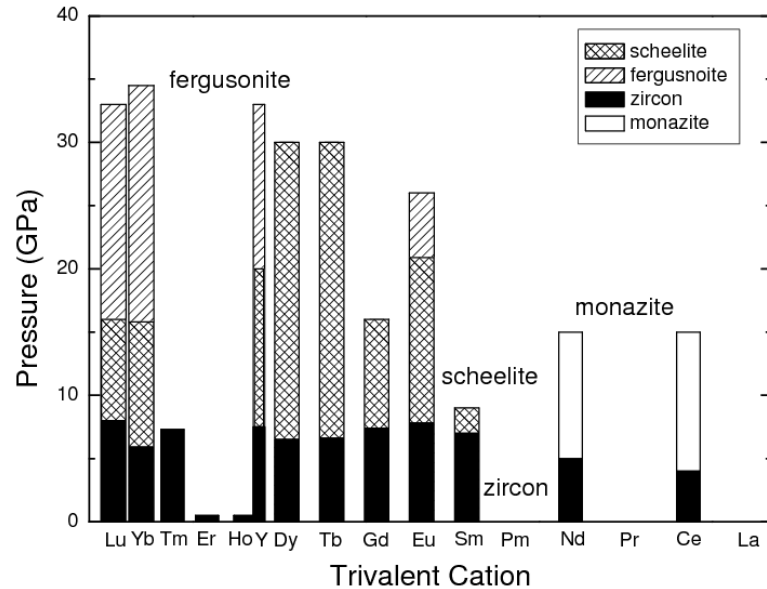
found in YVO_4 , ScVO_4 , EuVO_4 , LuVO_4

Compounds with large trivalent cation (NdVO_4 , CdVO_4) transform to monazite and subsequently to denser phases with VO_6 octahedra.

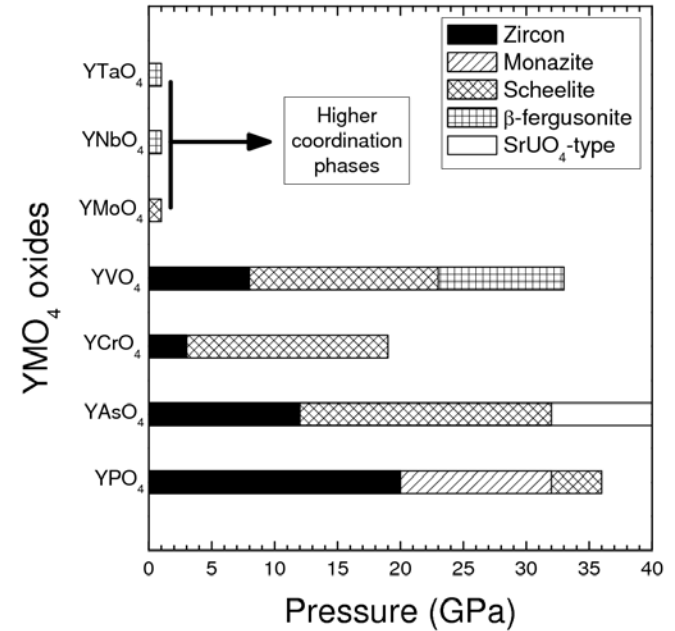
Compound	Structure	V_0 [Å ³]	B_0 [GPa] This work	B_0 [GPa] Experiments	B_0 [GPa] <i>Ab initio</i>	B_0 [GPa] Empirical model
EuVO ₄	Zircon	333.4	149(6)			134(26)
DyVO ₄	Zircon	325.9		140(5) ^a		135(26)
TbVO ₄	Zircon	322.2		129(5) ^a		137(26)
HoVO ₄	Zircon	319.1		142(9) ^a		138(26)
YVO ₄	Zircon	318.7		130(3) ^b		138(26)
ErVO ₄	Zircon	315.9		136(9) ^a		140(27)
LuVO ₄	Zircon	307.7	166(7)	147 ^c	166 ^c	145(28)
ScVO ₄	Zircon	282.2	178(9)			162(30)
BiVO ₄	Scheelite	311.2		150(5) ^d		142(27)
EuVO ₄	Scheelite	299.4	199(9)			158(29)
YVO ₄	Scheelite	284.5		138(9) ^b		160(29)
LuVO ₄	Scheelite	271.4	195(9)	194 ^c	173 ^c	166(30)
ScVO ₄	Scheelite	256.9	210(12)			185(35)

Bulk modulus correlated with A-O distance at ambient pressure

Vanadates



Other zircons



$YAsO_4$: zircon $\rightarrow$ scheelite $\rightarrow$ fergusonite?

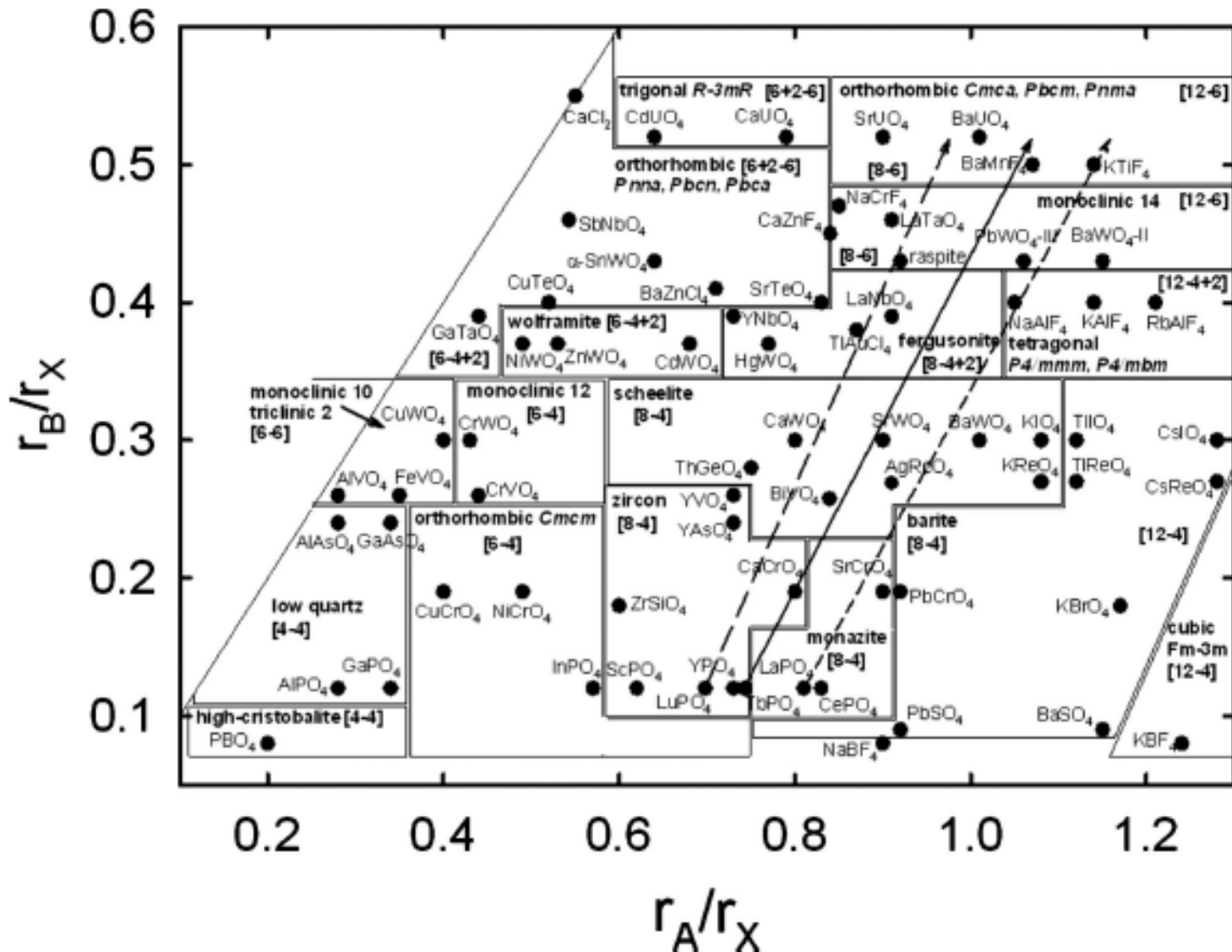
$YCrO_4$: zircon $\rightarrow$ scheelite $\rightarrow$ fergusonite?

$ThGeO_4$: zircon $\rightarrow$ scheelite $\rightarrow$ fergusonite

$ZrSiO_4$ & $HfSiO_4$: zircon $\rightarrow$ scheelite

$TbPO_4$: zircon $\rightarrow$ monazite $\rightarrow$ scheelite $\rightarrow$ orthorhombic (six coordinated P)

Crystal chemistry



Crystal chemistry

Support to phase diagram

AgClO_4 transforms to barite structure

CaSO_4 : anhydrite $\rightarrow$ monazite $\rightarrow$ barite

CrVO_4 transforms to wolframite

Wolframites (MgWO_4 , CdWO_4 , ZnWO_4) follows same systematic

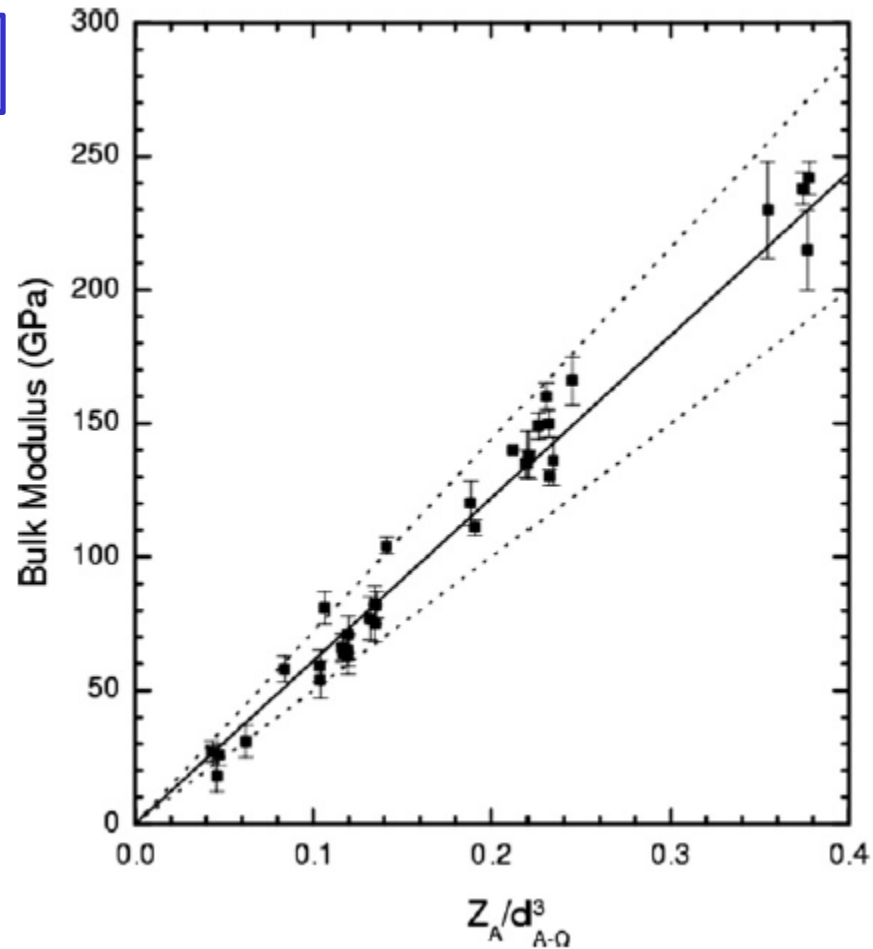
CuWO_4 transforms to wolframite

HfTiO_4 & ZrTiO_4 : columbite-cottunite

HgWO_4 to orthorhombic structure?

Compressibility

$$B_0 \text{ (in GPa)} = 610 Z_i / d^3$$



D. Errandonea & F. J. Manjon, Progress in Materials Science 53 (2008) 711–773

ABO ₄ compound	Space group	Mean A–O bond distance (Å)	Cation formal charge	B_0 (GPa)	Reference
HfGeO ₄	$I4_1/a$	2.196	4	242(6)	[135]
ZrGeO ₄	$I4_1/a$	2.203	4	238(6)	[135]
ZrSiO ₄	$I4_1/a$	2.243	4	230(18)	[144]
ZrSiO ₄	$I4_1/amd$	2.198	4	215(15)	[136,144,201,202]
LaNbO ₄	$I4_1/a$	2.505	3	111(3)	[154]
YVO ₄	$I4_1/a$	2.387	3	138(9)	[139]
TbVO ₄	$I4_1/amd$	2.369	3	149(5)	[203]
BiVO ₄	$I4_1/a$	2.350	3	150(5)	[205]
DyVO ₄	$I4_1/amd$	2.354	3	160(5)	[204]
YCrO ₄	$I4_1/amd$	2.391	3	135(5)	[116]
YVO ₄	$I4_1/amd$	2.348	3	130(3)	[139]
ErVO ₄	$I4_1/amd$	2.341	3	136(9)	[206]
LuPO ₄	$I4_1/amd$	2.306	3	166(9)	[207]
YLiF ₄	$I4_1/a$	3.044	3	81(6)	[80]
BaSO ₄	$Pnma$	2.879	2	58(5)	[208,209]
BaWO ₄	$I4_1/a$	2.678	2	57(4)	[15,19]
BaMoO ₄	$I4_1/a$	2.679	2	59(6)	[20]
PbWO ₄	$I4_1/a$	2.579	2	64(2)	[19,21,60]
PbMoO ₄	$I4_1/a$	2.576	2	64(2)	[60]
SrWO ₄	$I4_1/a$	2.557	2	63(7)	[17]
EuWO ₄	$I4_1/a$	2.557	2	71(6)	[32]
SrMoO ₄	$I4_1/a$	2.556	2	73(5)	[134,210]
NaY(WO ₄) ₂	$I4_1/a$	2.478	2	77(8)	[211]
CaMoO ₄	$I4_1/a$	2.458	2	82(7)	[16,60]
CaWO ₄	$I4_1/a$	2.457	2	75(7)	[14,17,60,68,209]
SrSO ₄	$Pnma$	2.452	2	82(5)	[210]
CdMoO ₄	$I4_1/a$	2.419	2	104(2)	[60]
ZnWO ₄	$P2/c$	2.112	2	140	[70]
CdWO ₄	$P2/c$	2.197	2	120(8)	[62]
KReO ₄	$I4_1/a$	2.791	1	18(6)	[212]
TlReO ₄	$Pnma$	2.765	1	26(4)	[57]
AgReO ₄	$I4_1/a$	2.524	1	31(6)	[147]
NaAlH ₄	$I4_1/a$	2.850	1	27(4)	[180]

Concluding remarks

- ✓ Recent HP studies on structural properties of ABO_4 oxides.
- ✓ The occurrence of pressure-induced phase transitions in scheelites, zircons and related materials have been discussed in detail.
- ✓ Discover new phases.
- ✓ Comparative analysis of crystal chemistry of ABO_4 compounds under HP in order to present the whole body of structural studies available in the literature in a consistent fashion (opportunities for future work).
- ✓ Related axial and bulk compressibility with bonds strength.
- ✓ Results have implications for technological applications and in geophysics.
- ✓ 2008 -2010: 20 articles involving XRD (10 PRB) - 6 using MALTA XRD.
- ✓ Many collaborations (within MALTA and abroad).

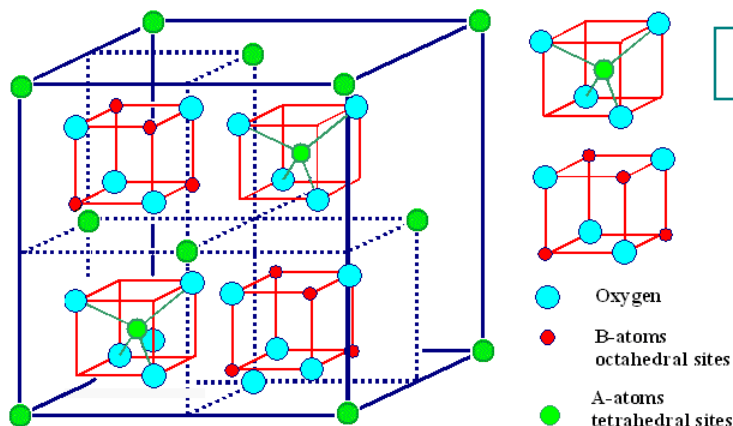
Post-spinel transformations in zinc gallate (ZnGa_2O_4)

SG: $Fd\bar{3}m$ (227) $u = 0.26$

Zn at 8a ($1/8, 1/8, 1/8$); Ga at 16c ($1/2, 1/2, 1/2$); O at 32e (u, u, u) $u \approx 1/4$

Discontinuidad sísmica 400 – 900 Km. (30 GPa) manto superior
Olivine $(\text{Mg,Fe})_2\text{SiO}_4 \rightarrow$ Spinel $\rightarrow$ Post-spinel or
Perovskite MgSiO_3 + Periclase MgO
Hardness?

MgAl_2O_4 – Orthorhombic post-spinel at 35 GPa
 ZnAl_2O_4 spinel stable up to 50 GPa



AB_2O_4 spinel The red cubes are also contained in the back half of the unit cell

ADXRD up to 65 GPa – 16IDB HPCAT – $\lambda = 0.3682 \text{ \AA}$ (Silicone oil & Ar)

Two phase transitions:

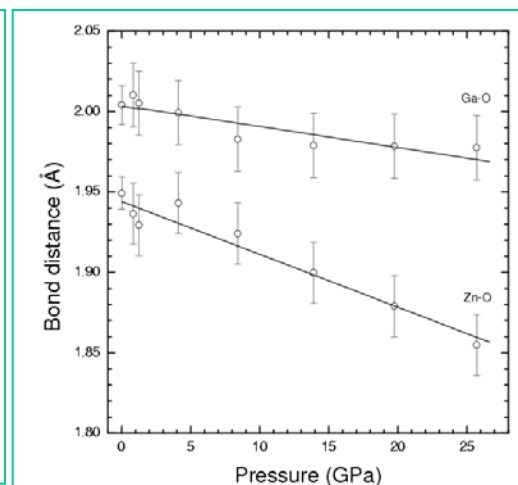
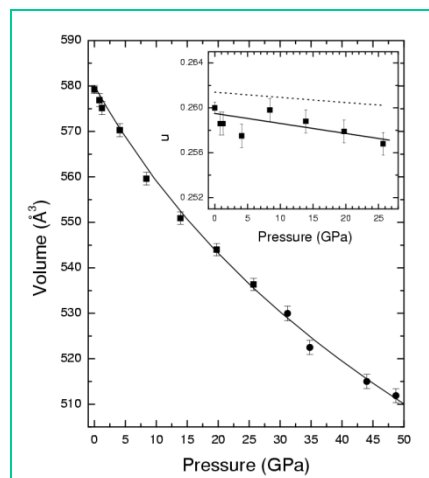
31.2 GPa tetragonal spinel ($I4_1/amd$)

55 GPa orthorhombic CaMn_2O_4 -type (Pbcm)

EOS: $V_0 = 580.1 \text{ \AA}^3$, $B_0 = 233 (8) \text{ GPa}$, $B_0' = 8.3(4)$
Least compressible spinel?

Octahedral compressibility: 265(9) GPa
Tetrahedral Compressibility 155(9) GPa

Future: MgGa_2O_4 - Raman: spinel (5 modes);
Tetragonal (10); Orthorhombic (24 – 24 – 18)



$$R_{\text{Zn-O}} = \sqrt{3}(u - 0.125)a$$

$$u = 0.2625$$

$$R_{\text{Ga-O}} = \sqrt{(3u^2 - 2u + 0.375)}a$$

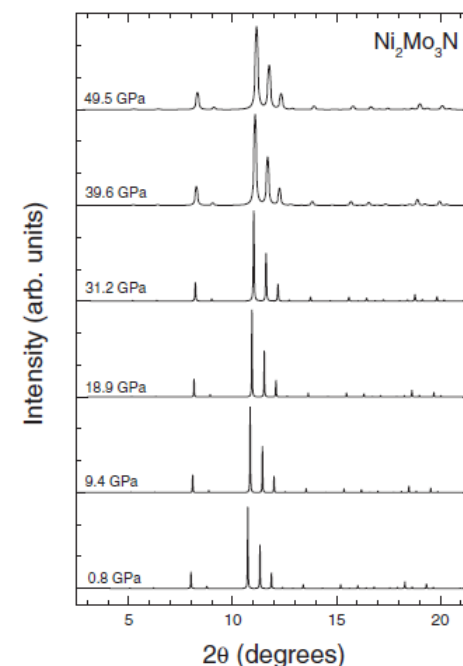
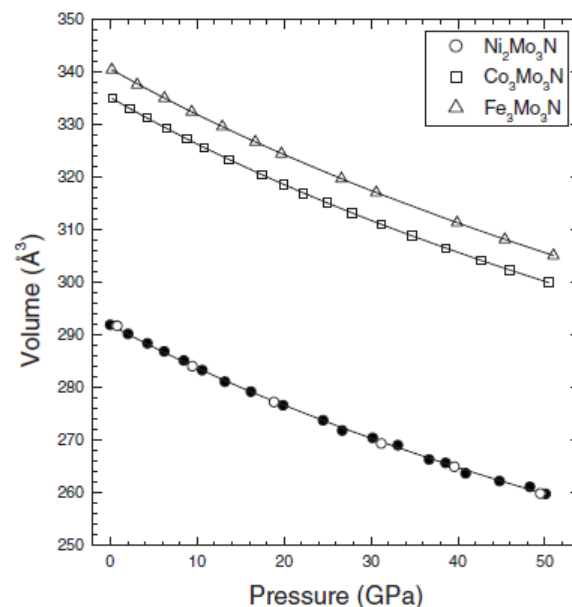
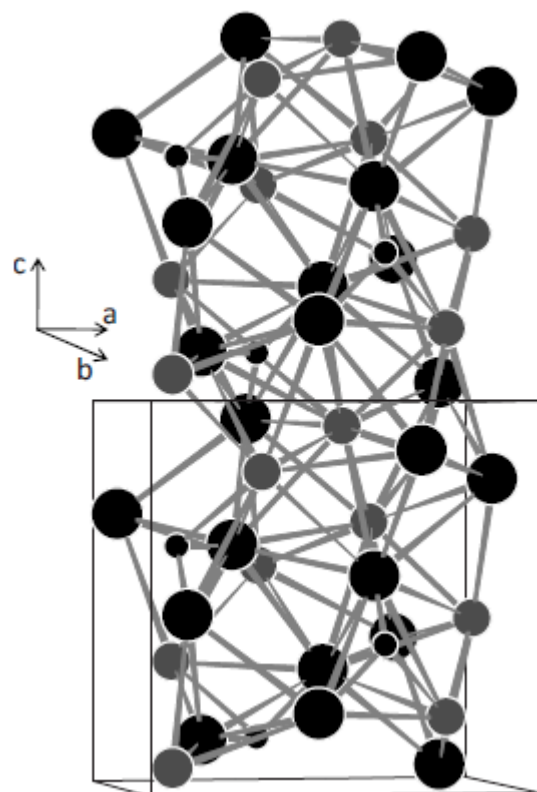
$$R_{\text{Zn-O}} = R_{\text{Ga-O}}$$

$$u = 0.25 \quad \frac{\partial R_{\text{Zn-O}}}{\partial u} = \sqrt{3}a$$

$$\frac{\partial R_{\text{Ga-O}}}{\partial u} = -a$$



High-pressure x-ray diffraction and *ab initio* study of $\text{Ni}_2\text{Mo}_3\text{N}$, $\text{Pd}_2\text{Mo}_3\text{N}$, $\text{Pt}_2\text{Mo}_3\text{N}$, $\text{Co}_3\text{Mo}_3\text{N}$, and $\text{Fe}_3\text{Mo}_3\text{N}$: Two families of ultra-incompressible bimetallic interstitial nitrides



Compound		V_0 ($\text{\AA}^3$)	B_0 (GPa)	B'_0	B''_0 (GPa^{-1})
$\text{Ni}_2\text{Mo}_3\text{N}$	Experiment	291.96(2)	330(8)	4.5(5)	-0.014 ^a
	Theory	282.131	317.53	4.54	-0.016
$\text{Pd}_2\text{Mo}_3\text{N}$	Experiment	316.89 ^b			
	Theory	310.046	312.11	4.94	-0.028
$\text{Pt}_2\text{Mo}_3\text{N}$	Experiment	319.43 ^c			
	Theory	314.966	341.80	4.81	-0.020
$\text{Co}_3\text{Mo}_3\text{N}$	Experiment	1340.8(6)	350(8)	4.7(6)	-0.014 ^a
	Theory	1265.24	333.26	4.74	-0.028
$\text{Fe}_3\text{Mo}_3\text{N}$	Experiment	1362.4(6)	368(9)	4.2(4)	-0.011 ^a
	Theory	1273.79	351.35	3.62	-0.0006



9:30	15'	Óxidos y Minerales I –Estructura y Reactividad 1: Presentación del Moderador		Alfredo Segura García del Río
9:45	4x15'	Ponencias Óxidos y Minerales I – 1	<i>Aplicación de la absorción de rayos X al estudio de las delafositas bajo presión</i>	Julio Pellicer Porres
			<i>Estudio estructural de la distorsión Jahn-Teller del CuWO_4 bajo presión</i>	Javier Ruiz Fuentes
			<i>Transiciones de fase en Rb_2S a alta presión. Comparación estructural de los sulfuros alcalinos y sus óxidos correspondientes</i>	David Santamaría Pérez
			<i>Estudio bajo altas presiones de la estructura de minerales de la corteza y de la capa superior del manto</i>	Daniel Errandonea
10:45	45'	Conferencia Invitada	<i>Difracción de Neutrones en Condiciones Extremas: XTREMED</i>	Javier Campo Ruiz

III. Structure, stability, and reactivity of minerals,

III.a- PTC Diagrams / Specific Goals

- Target systems: ABO_3 ($AO - BO_2$; $A_2O_3 - B_2O_3$), ABO_4 ($AO_2 - BO_2$) and AB_2O_4 ($AO - B_2O_3$) oxides, with lightest A-B elements and, in particular, compounds involving carbon.
- Influence of inclusions of transition metal ions like Co, Fe, Cr, Ni, upon the structural and physical properties of these materials.
- Study of the influence of these oxides in geodynamics and prospects on new materials applications

III.b- Structure and reactivity / Specific Goals

- High pressure structure and properties of Ni, Fe, and their alloys, sulphides and oxides (topic III. a)
- Catalytic properties of Ni, Fe, and their alloys, sulphides and oxides
- Kinetics and stability of methane clathrates (topic I.a.)
- High pressure reactivity of methane and other small hydrocarbons in presence of oxides of metals (topic II.b.)

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- High pressure reactivity of methane and other small hydrocarbons in presence of oxides of metals (topic II.b.)

PTC Diagrams

- **J. Pellicer:** ABO_2 delafossites : XRD and XAS
- **J. Ruiz-Fuertes:** CuWO_4 , single crystal XRD y XAS
- **D. Santamaría-Pérez:** Rb_2S , XRD
- **D. Errandonea:** ABO_4 , AB_2O_4 , XRD

Resultados no presentados: materiales ultraduros (nitruros intersticiales y ReB_2)

XtremeD: a new neutron diffractometer for high pressures and magnetic fields

Javier Campo

José Alberto Rodríguez Velamazán

Pedro Noguera



fmc.unizar.es/people/jcampo

Outline



- **History and Motivation**
- **Basic Concepts on Neutron Scattering**
- **Overview of the Scientific Case**
- **Benchmarking**
- **Requirements**
- **Implantation**
- **Budget**
- **Project Organization**
- **Administrative framework**
- **Project team and Scientific Advisory Committee**

Motivation



Science under
extreme conditions



- High P +
- High H
 - Low/High T
 - Extreme chemical environments
 -

Strong interest for these problems reflected in:

- Extreme conditions scientific programs in the major large facilities (e.g. PECS at ESRF/ILL)
- New instruments in neutron scattering centres
- Number of proposed experiments
- High impact publications

Motivation



**Strong high pressure
community**

(MALTA group)

Crystallography /
geosciences area

**Spanish
interest**
on neutron
diffraction
under
extreme
conditions

**Magnetism
/solid state sciences
community**
(major part of Spanish
neutron diffraction users)

- Other major groups in Europe (Edinburgh, Paris, LLB, ...) have shown their interest participating as scientific advisors
- Also a number of groups proposing an European Science Foundation (ESF) Research Networking Programme on Magnetic Materials under Extreme Conditions (MAGMATEC)

History



- **2008:** After the Dracula project was discarded, new ideas for instrumentation came up in the Diffraction Group and CRG's
- **2008:** A new MICINN-ILL contract was signed for the period 2009-13
- **2008:** Contacts with the community of extrem conditions. The Spanish CRG's team shows its interest on leading the project.
- **May 2009:** Creation of the Scientific Advisory Committee (1st meeting 27th May in Grenoble)
- **May-November 2009:** Preparation of the Project Initiation Document and the Scientific Case Document
- **October 2009:** Contract with AVS company for the development of the technical project
- **November 2009:** Presentation to the Scientific Council and Steering Committee of ILL



History

Conclusions of the Scientific Council



- The SciCo rated the proposal as “**exciting, science driven and challenging**”
- It was particularly appreciated that the low-Q part of the structure factor will be covered by the thermal neutron beam, which is important for magnetic structure analysis.
- The **site** for the instrument is **available**.
- **The SciCo endorses the science case** of the *XtremeD* instrument.
- At the same time the SciCo raises concerns with respect to CRGs in general about financial commitments.
- Assuming that these concerns are ungrounded, **the SciCo recommends its installation**



History



- **10/2009 → 09/2010: Pre Construction Phase**
Development in parallel of the Technical project with distribution of tasks, timing and cost estimation.
- **07/2010: Spanish Ministry of Science and Innovation (MICINN)** shown its interest at the SETN meeting in Gijón
- **09/2010.** MICINN requests ILL for a decision on the **change of the H24 guide as a prior condition** to going ahead with the XtremeD instrument.
- **09/2010 → 02/2011.** A feasibility study on H24 guide should be completed.



Next steps



- The **decision to launch the execution** phase for the H24 guide project will be taken by the ILL management in February 2011 (meeting **03/02/2011**)
- **9/2010 → 3/2011** Negotiations with ILL
- Negotiations with other CRG partners (<30%)

03/2011 → 08/2014: Construction Phase

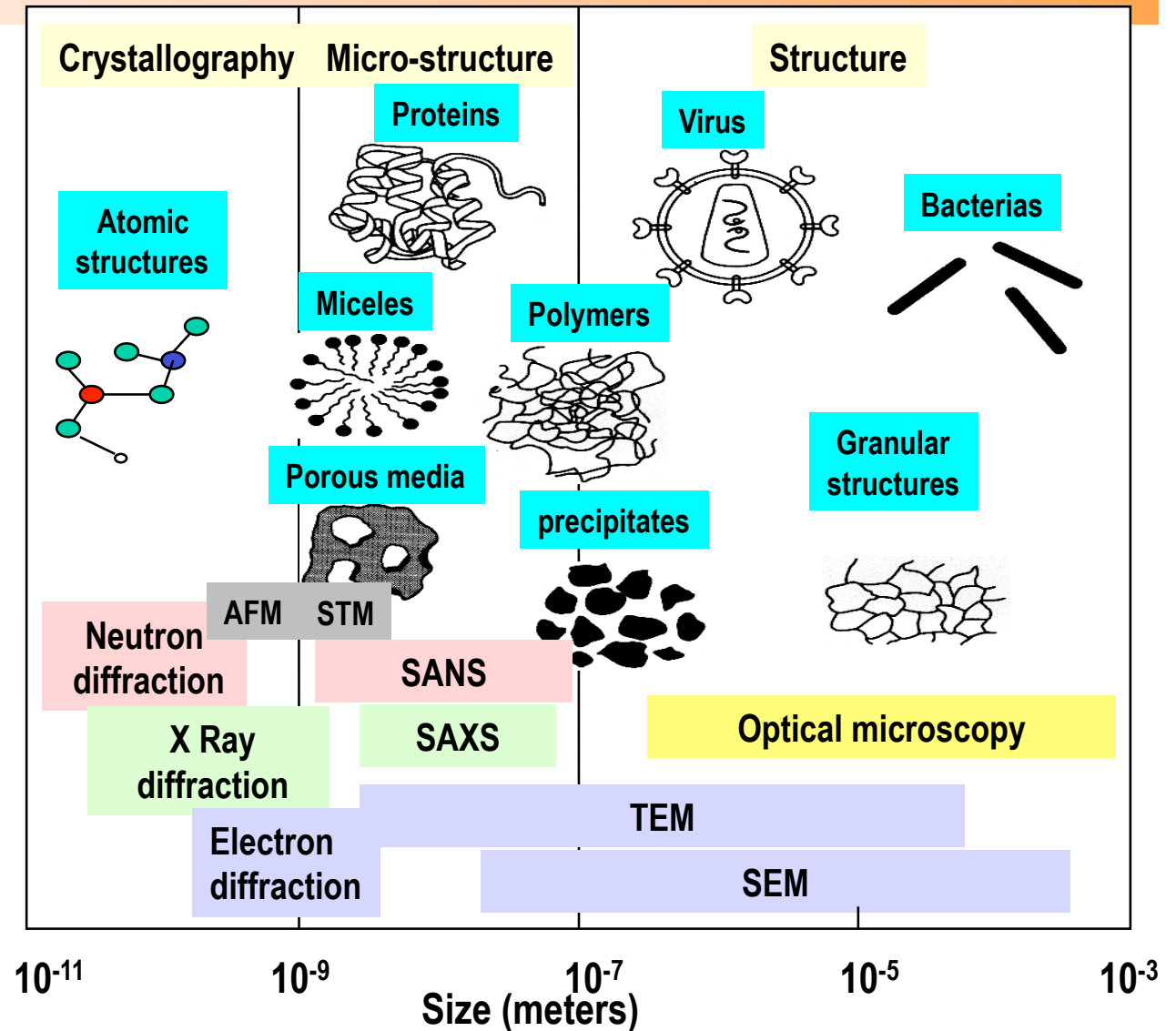
~09/2014: Commissioning and operation phases.

Basic Concepts

Accessible Length scales

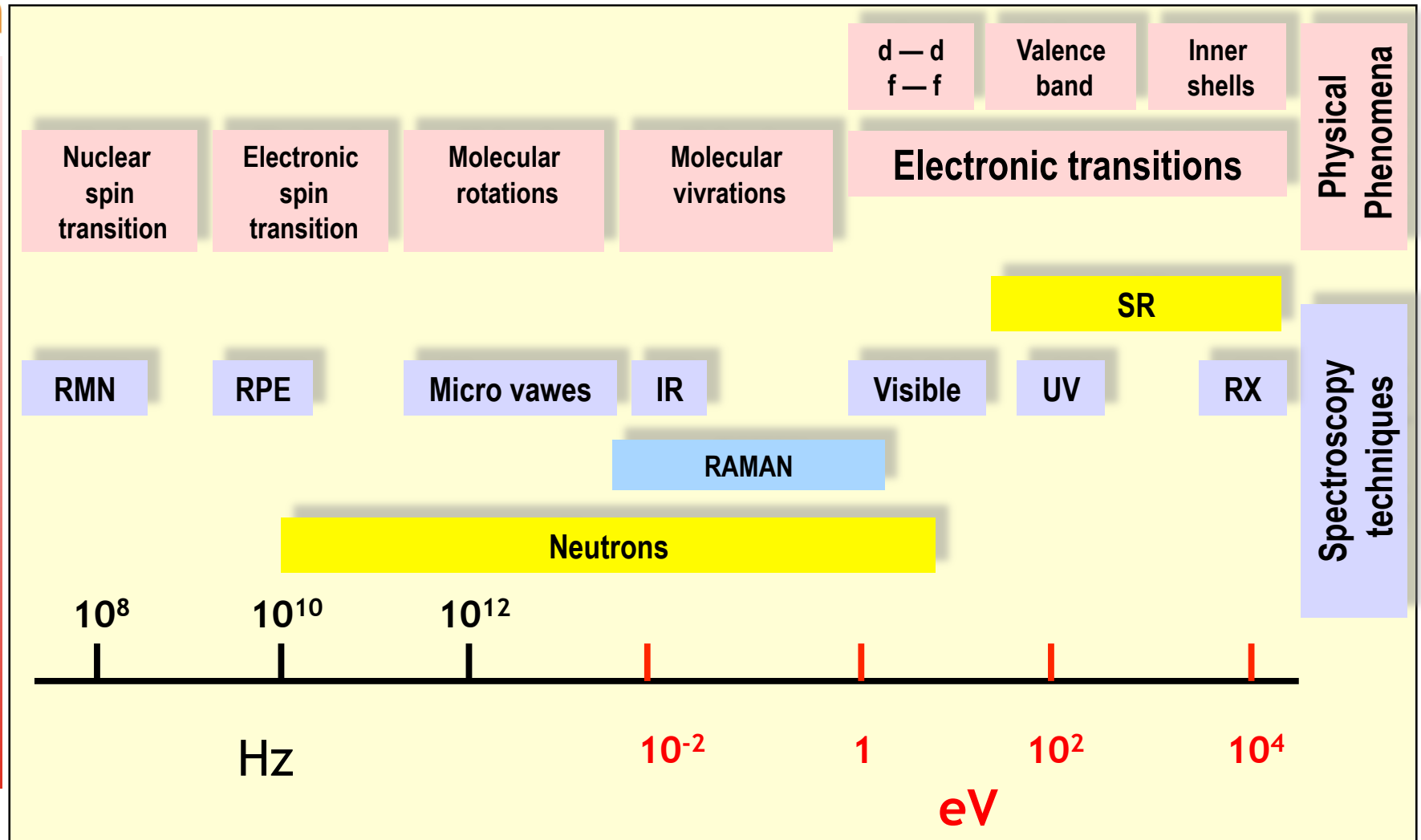
Length scale

Techniques



Basic Concepts

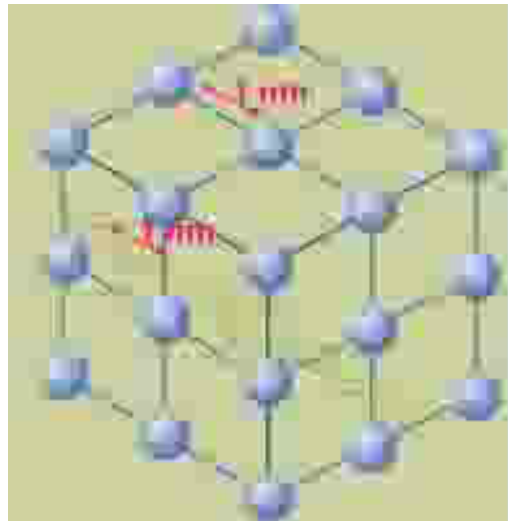
Accessible Energy range



Basic concepts on neutron scattering

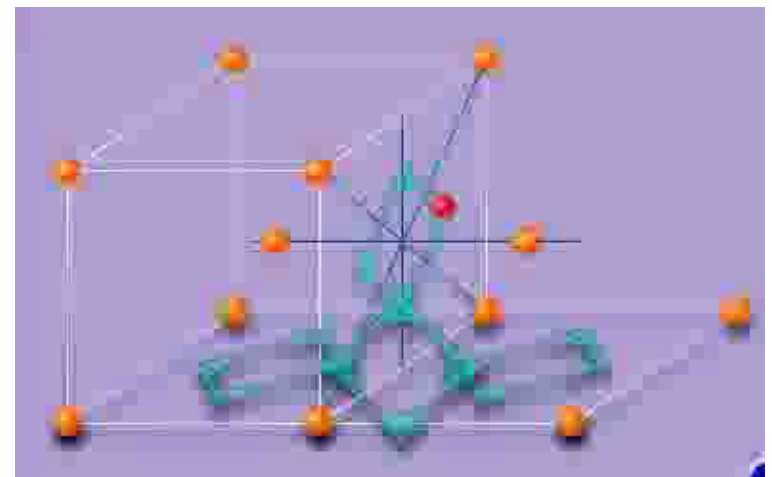
- Neutrons have similar wavelengths that the interatomic distances and therefore they can diffract

- Wide range of wavelengths (0.05 to 20 Å)
- To observe different length scales



- Same energy range that the atomic and electronic processes (meV a eV) with the possibility to detect changes of μeV

- *Tunneling*,
- Rotations
- Vibrations
- Electronic Transitions
- Diffusion.



Basic concepts on neutron scattering

- The interaction neutron-matter is *via* nuclei (**strong interaction**) and not with the electronic cloud

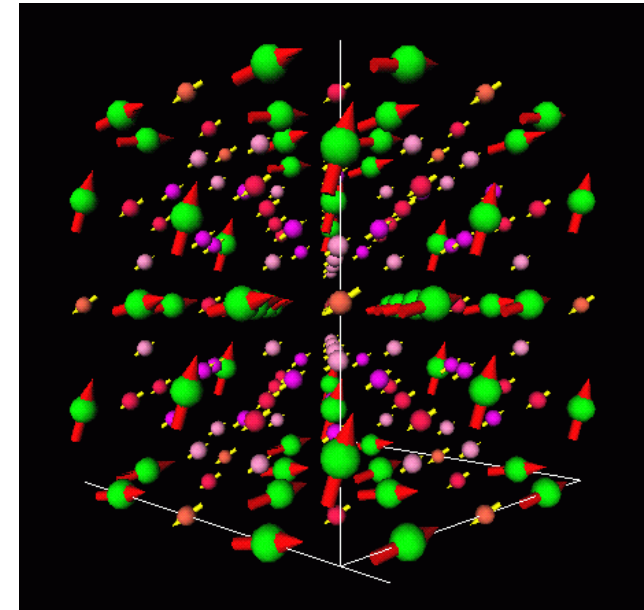
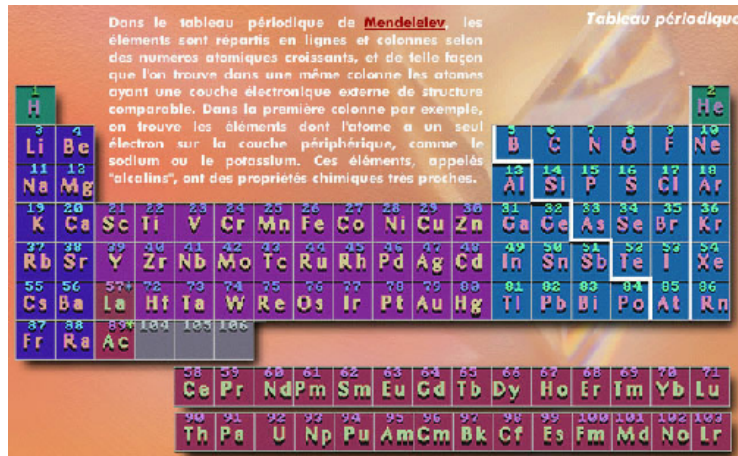
- Scattering length for atoms does not depend on the atomic number Z
 - Easy to see **light atoms** (H, Li) in presence of heavy atoms
 - Easy to distinguish **next neighbors** atoms in the periodic table (Cr, Mn, Fe Co, Ni, etc...)
 - **Isotopic substitution**

- Neutrons carry magnetic moment then they “see” (**via the magnetic dipolar interaction**) the magnetism present in the matter; unpaired electrons, nuclei

- To study magnetic structures
- Magnetic excitations

Dans le tableau périodique de Mendeleev, les éléments sont répartis en lignes et colonnes selon des numéros atomiques croissants, et de telle façon que l'on trouve dans une même colonne les atomes ayant une couche électronique externe de structure comparable. Dans la première colonne par exemple, on trouve les éléments dont l'atome a un seul électron sur la couche périphérique, comme le sodium ou le potassium. Ces éléments, appelés "alcalins", ont des propriétés chimiques très proches.

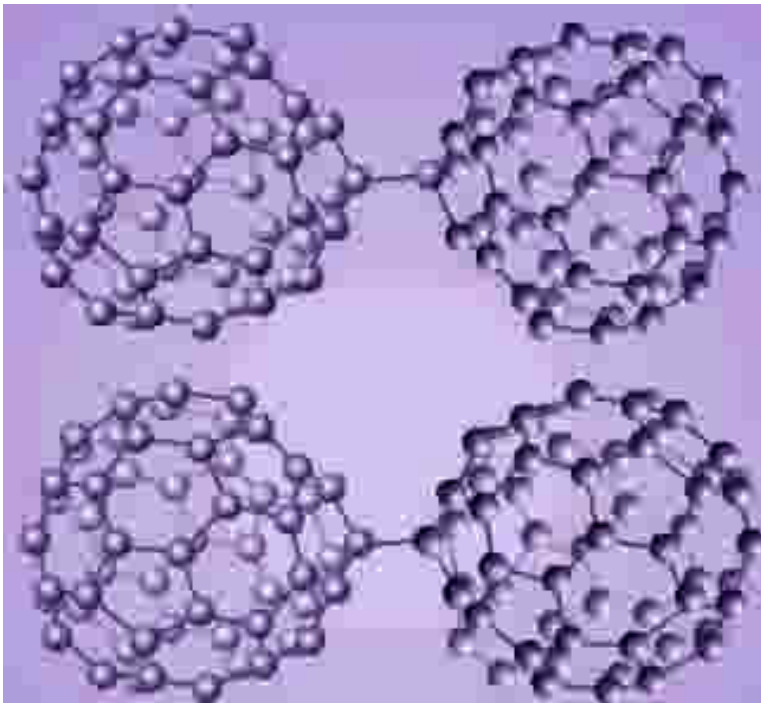
Tableau périodique



Basic concepts on magnetic neutron scattering

- With neutrons we can measure simultaneously the structure and the dynamics

Phonons



Magnons



Scientific case



Some examples of what have been recently done

Boost extreme conditions in neutron science and technology

XtremeD

High interest on the field!

Open opportunities for new scientific breakthroughs

Scientific case



Study of matter under extreme conditions

Necessary for progress in Condensed Matter Physics, Solid State Chemistry and Geosciences, and even in Molecular Biology

Understanding mechanisms ...

3 representative topics:

- Water-related systems
- Molecular chemistry
- Magnetic materials under extreme conditions



Scientific case



Water-related systems

What would be the *XtremeD* contribution?

The study of these systems implies systematic studies of hydrogen bonding and clustering, host-guest interactions in clathrate hydrates and the role of water in crystals.

Far ranging implications in physics, chemistry, planetary sciences and geochemistry

- Planetary ices (water, methane, ammonia) and clathrates
- Segregation and related phenomena in water solutions at extreme conditions
- Mineral hydration: implications for the water cycle in Earth crust and mantle



Scientific case



Molecular chemistry

Exciting physical phenomena and problems with high social contribution for an extreme conditions diffractometer

- Simple molecular systems
- Energetic materials
- Production and characterization of new phases: pharmaceutical applications / molecular materials
- Extreme conditions studies on established phases: material applications, phase transformations, chemical reactions (green chemistry)

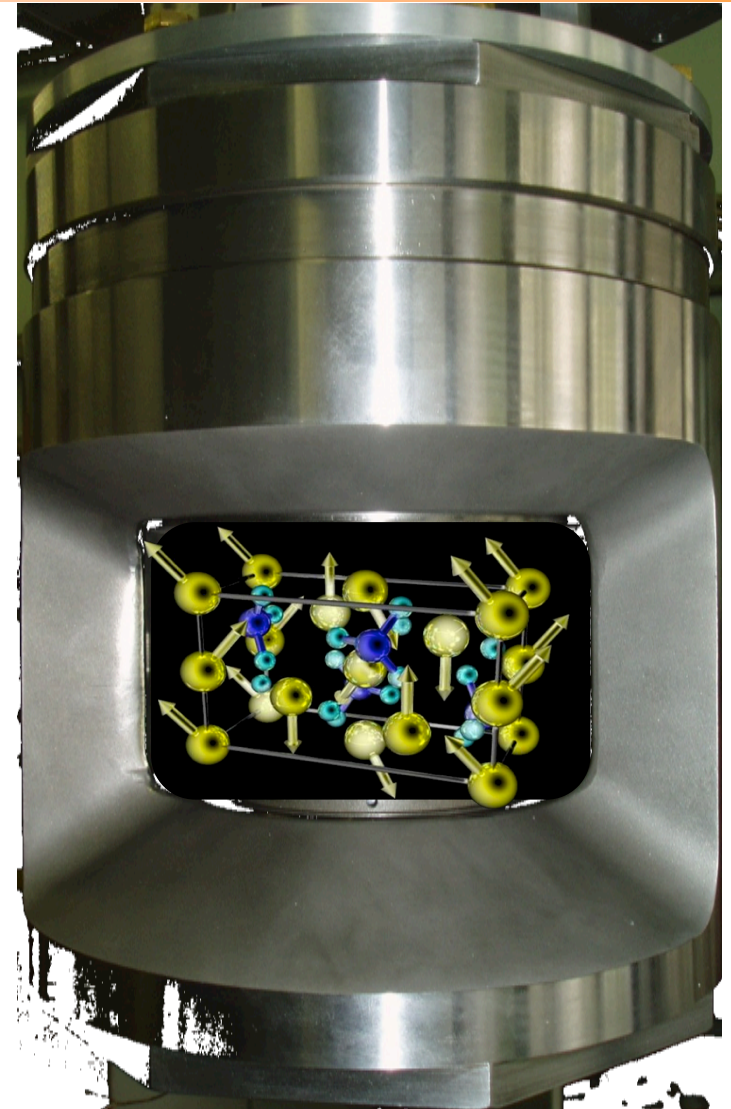


Scientific case



Magnetism under extreme conditions

- Transition metal oxides
- Multiferroics and magneto-electric materials
- Exotic magnetic states in magnetically frustrated materials
- Magnetic molecular materials



Benchmarking

Internal Competition

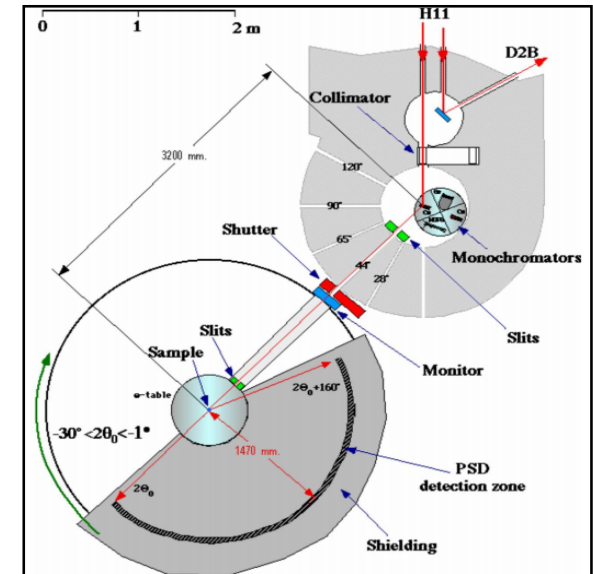


D20

- Its extremely high flux opens up the possibilities for experiments with very small samples.

Technical solutions:

- Vertical focusing monochromators
- Paris-Edinburgh cell (25GPa)
- Continuous magnet (9T)
- PS ^3He detector

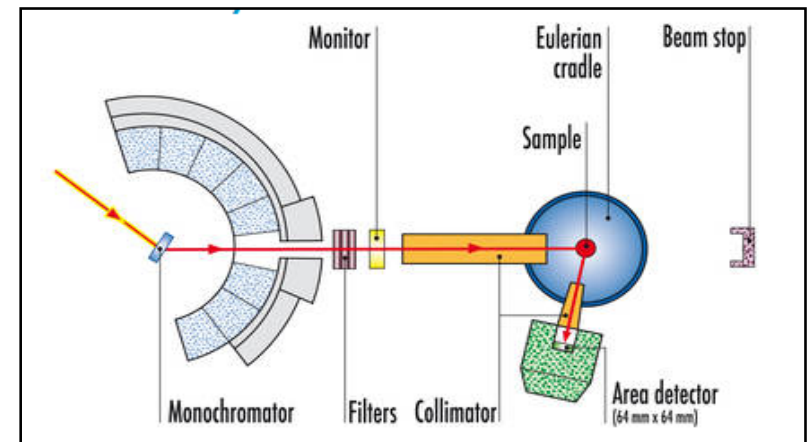


D9

- Often used to study single crystals under high pressure

Technical solutions:

- No focusing: Collimation
- Paris-Edinburgh cell (10GPa)
- Continuous magnet (9T)
- Small two dimensional detector



Benchmarking

External Competition

Paul Scherrer Institut (SINQ)



DMC

- Cold neutrons
- Powder
- Very flexible
- Magnetic structures
- FUTURE UPGRADING

Technical solutions:

- Vertical focusing (HOPG and Ge)
- CP 1.5 GPa
- CM 4T
- PS BF₃ detector

HRPT

- High resolution
- Powder diffraction
- Small samples.

Technical solutions:

- Vertical focusing (Ge)
- CP 1.5 GPa
- CM 4T
- PS 3He detector

Trics

- Single crystal
- Magnetic structures

Technical solutions:

- NO FOCUSING
- CP 3 GPa
- CM 6T
- PS 3He detector



CP=Clamp pressure cell CM=Continuous Magnet PM= Pulsed Magnet

Benchmarking

External Competition

Hemholtz Zentrum Berlin (HZB) & SNS



Hemholtz Zentrum Berlin (HZB)

Exed

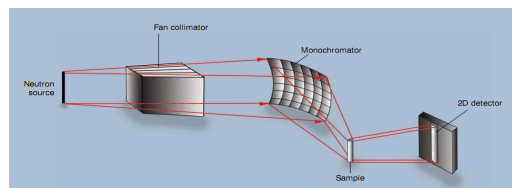
- High resolution
- Powder
- Extreme conditions of magnetic field

Technical solutions:

- Ballistic elliptical guide
- CP 1.5 GPa
- PM 30T
- Four banks with PS 3He detector

E6

- Optimized for small samples



Technical solutions:

- Fan collimator + Focusing HOPG monochromator
- CP 1.5 GPa
- CM 16T
- PS detector

SNS

Snap

- Extreme conditions of P and T
- Powder and single crystal

Technical solutions:

- Large volume pressuring cells (up to 50GPa)
- PS detector

Benchmarking

External Competition

ISIS



Wish

- Main application is powder diffraction
- single crystal

Technical solutions:

- Ballistic elliptical guide + Collimation
- PE 25GPa
- CM 15T
- ZnS scintillator detectors

Pearl

- High pressure facility
- Optimized for PE

Technical solutions:

- NO FOCUSING
- PE 25GPa
- 11 detector modules
 - Scintillators with photomultipliers

SXD

- Single crystal

Technical solutions:

- NO FOCUSING
- PE 10GPa
- 11 ZnS scintillator detectors



PE=Paris-Edinburgh cell

Benchmarking

External Competition

LLB & ANSTO



LLB

G6-1

- High intensity powder diffractometer
- Long wavelengths
- Magnetic structures and high pressure

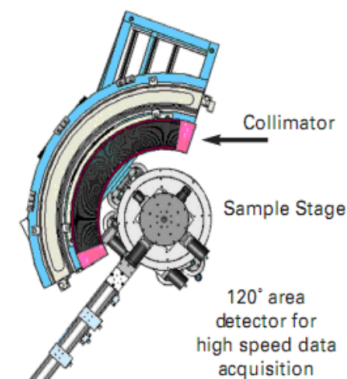
Technical solutions:

- Focusing trumpet
- Sapphire pressure cells
- CM 10T
- PS BF3 detector

ANSTO

Wombat

- High flux powder diffractometer



Technical solutions:

- Vertical focusing (Ge)
- CM 7.4T
- Large solid-angle PSD

Benchmarking

Extracted Ideas



Focusing optics:

- Focusing mosaic monochromators are the most common system
- New instruments (SNAP...) are developing new systems
- Collimation plays an important role due to the preservation of the resolution

Sample environment:

- Presently, the highest pressure is reached at the Paris-Edinburgh pressure cell (~25GPa)
- Most of the magnets for high magnetic field used in diffraction are continuous field magnets.

Detector:

- PSD are the most typical detection systems in continuous sources
- ^3He is the most used of the detection gases
- At ISIS, scintillators with photomultipliers are used for extreme conditions.



Benchmarking

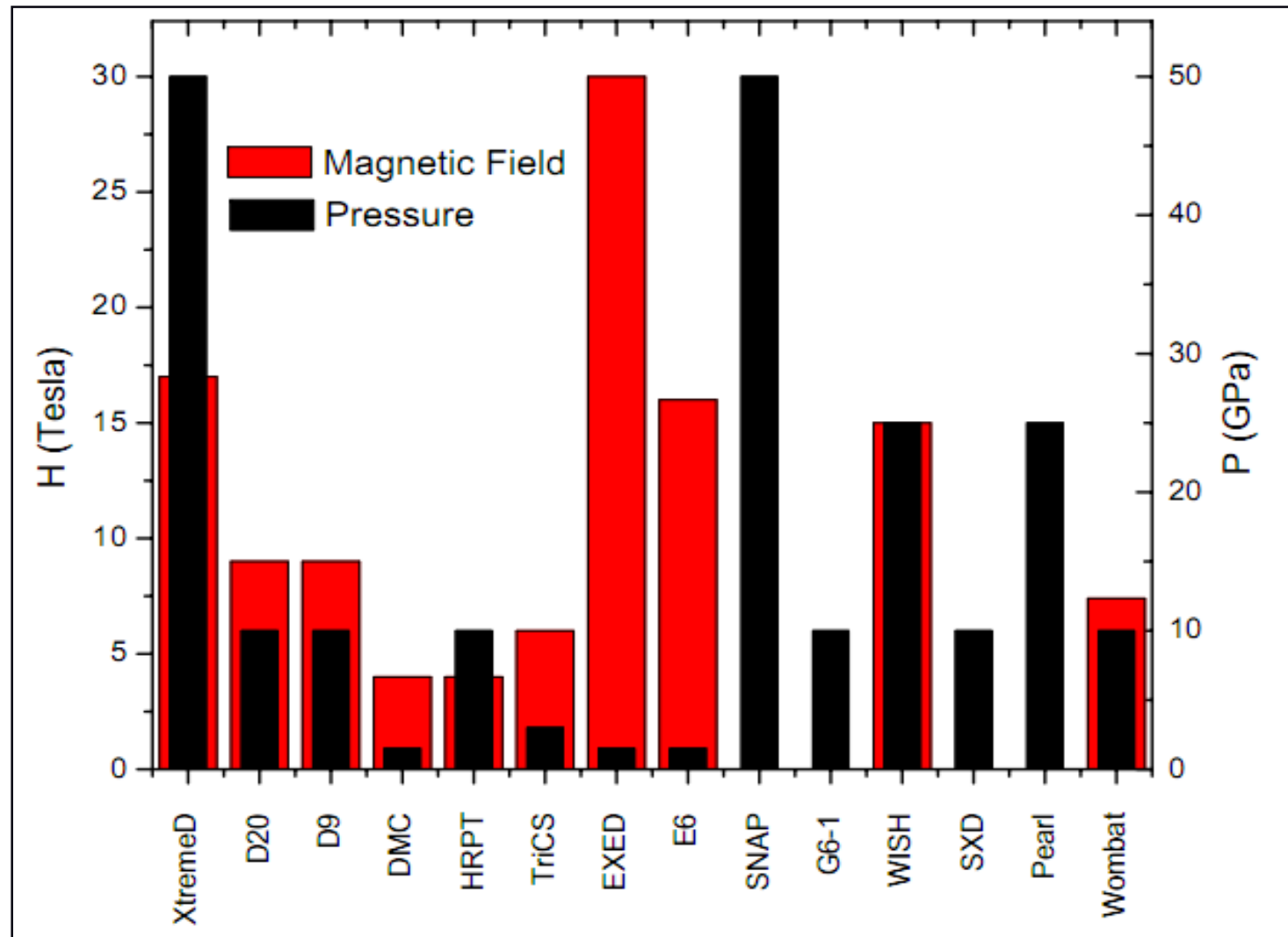
Comparative performance with other instruments



Facility	Instrument	Source	Application	Dedicated to extreme conditions	Pmax (GPa)		Hmax (Tesla)	
ILL	XtremeD	CON	Both	YES	50		17	CON
	D20	CON	Powder		10	PE	9	CON
	D9	CON	Single crystal		10	PE	9	CON
SINQ	DMC (DMC-2)	CON	Powder (Both)	(YES)	1,5	CC	4 (17)	CON
	HRPT	CON	Powder		10	PE	4	CON
	TriCS	CON	Single crystal		3	CC	6	CON
HZB	EXED	CON	Powder	YES	1,5	CC	30	PUL
	E6	CON	Both		1,5	CC	16	CON
SNS	SNAP	PUL	Both	YES	50	LS	-	
LLB	G6-1	CON	Powder	YES	10	SC	-	
ISIS	WISH	PUL	Both		25	PE	15	CON
	SXD	PUL	Single crystal		10	PE	-	
	Pearl	PUL	Both	YES	25	PE	-	
ANSTO	Wombat	CON	Powder		10		7,4	CON
CON - CONTINUOUS PUL - PULSED				PE - PARIS-EDINBURGH PRESSURE CELL CC - CLAMPED CELL LS - LARGE SAMPLE CELL SC - SAPHIRE CELL				

Benchmarking

Comparative performance with other instruments

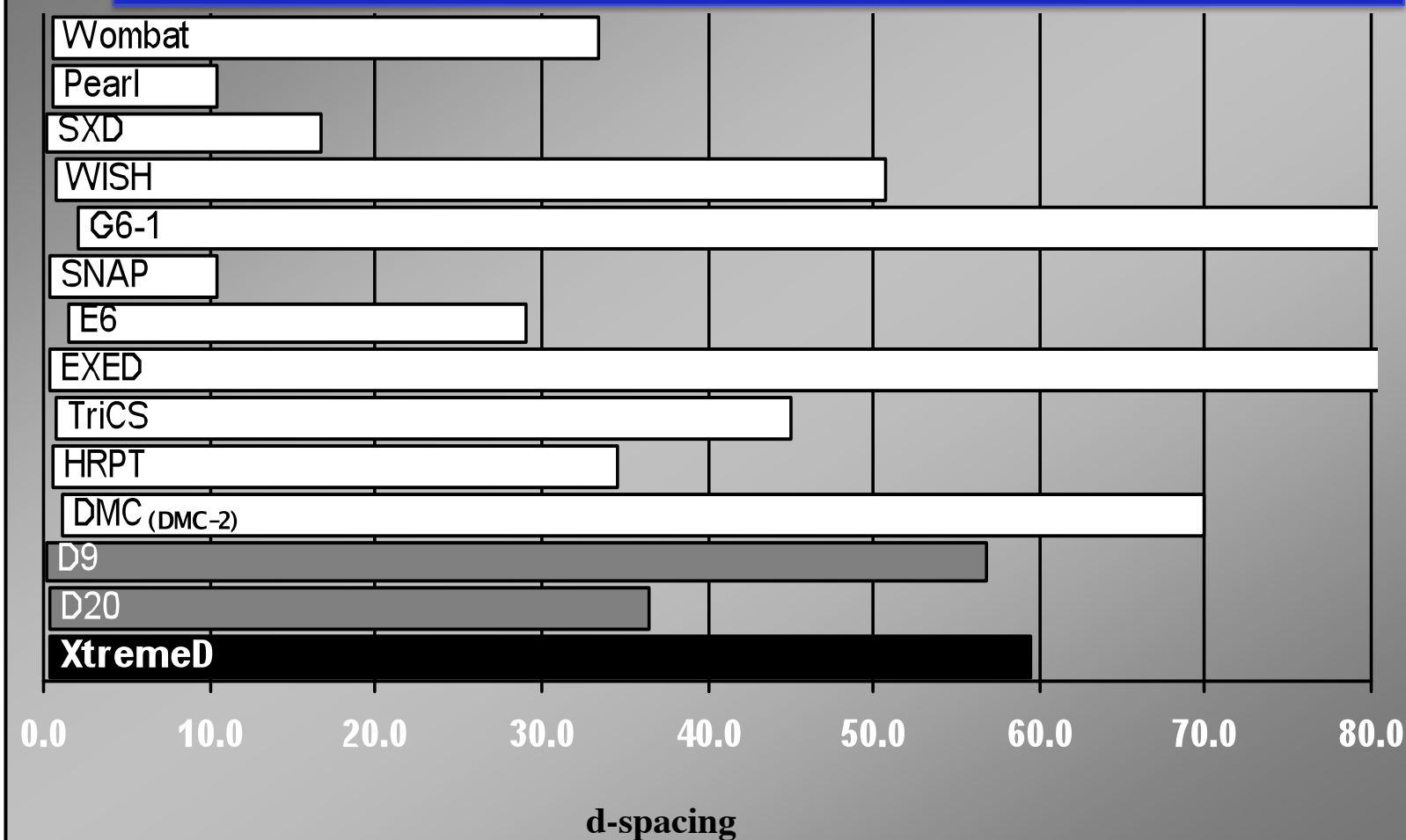


Benchmarking

Comparative performance with other instruments



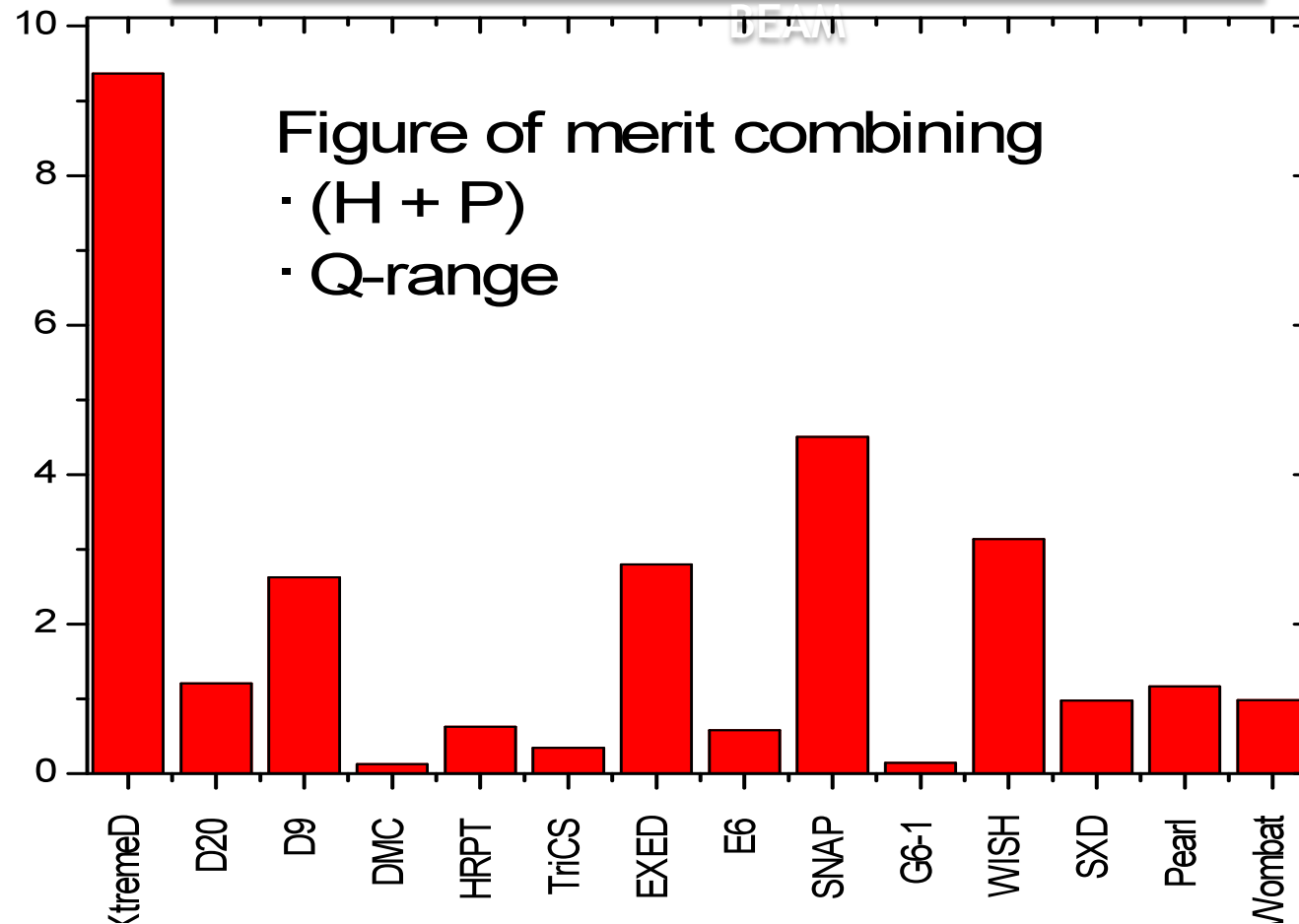
Short Pulse Spallation source = Inaccessibility to low Q-reflections
VERY IMPORTANT FOR MAGNETISM



Benchmarking

Comparative performance with other instruments

Magnetism + High pressure + Single crystal
BETTER HANDLED WITH INTENSE CONTINUOUS



Requirements

General description



MAIN IDEA:

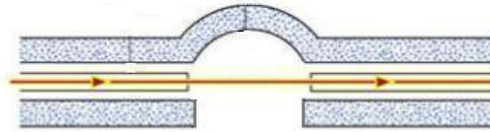
To combine a large solid-angle detector with an optional highly-focused beam on the sample, thus providing high flux while maintaining low background.

- Skeleton of a typical diffractometer →
 - Monochromator
 - Sample
 - Detector
- Conceived in a modular way → High flexibility
 - OPERATION: switch between take-off angles
 - CONSTRUCTION: progressive installation
 - RECYCLING: decommissioned components of IN3, D1A...

Requirements

General description

Instrument Lay-out



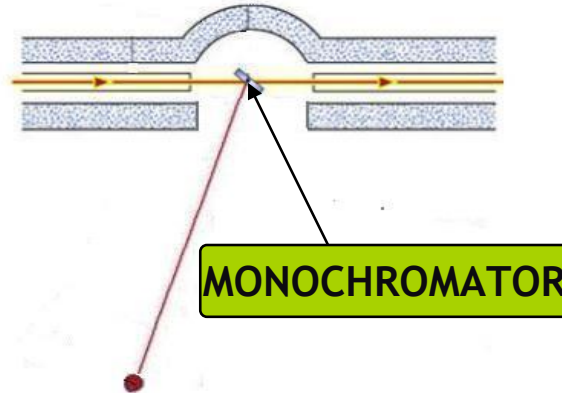
Guide H24

- Technical definition of the guide (Feasibility Phase)
- Optimization of the instrument will take it into account the guide
- A future refurbishment project is foreseen
- From the Feasibility Phase on, the guide will be managed in a separate project

Requirements

General description

Instrument Lay-out



Monochromator:

- Two monochromators:
 - Si or Ge (BPC)
 - HOPG (mosaic)
- A third Cu monochromator optional
- A set of filters (to suppress harmonics)

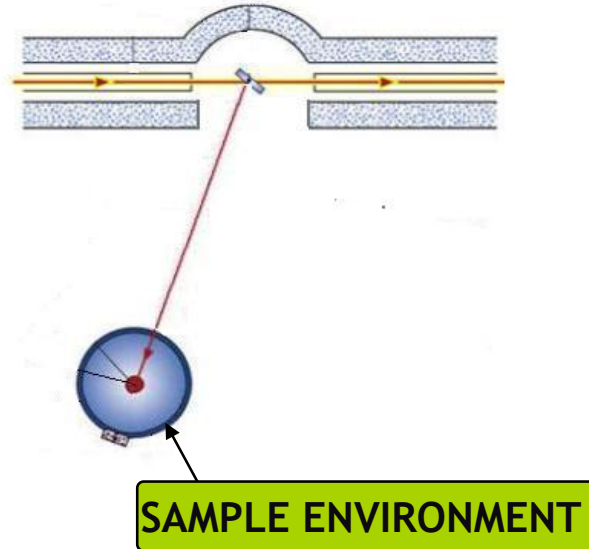
Monochromators	
lambda	0.8 - 4.1 Å
Q	0.1 - 15.6 Å ⁻¹
d-spacing	0.4 - 47 Å
take-off angle	40 - 120°

Requirements

General description

Instrument Lay-out

Sample stage	
Work vol. (X-Y-Z)	200x200x100mm
Linear accuracy	$\pm 0.05\text{mm}$
Angular accuracy	$\pm 0.01^\circ$
Admissible weight	1500kg



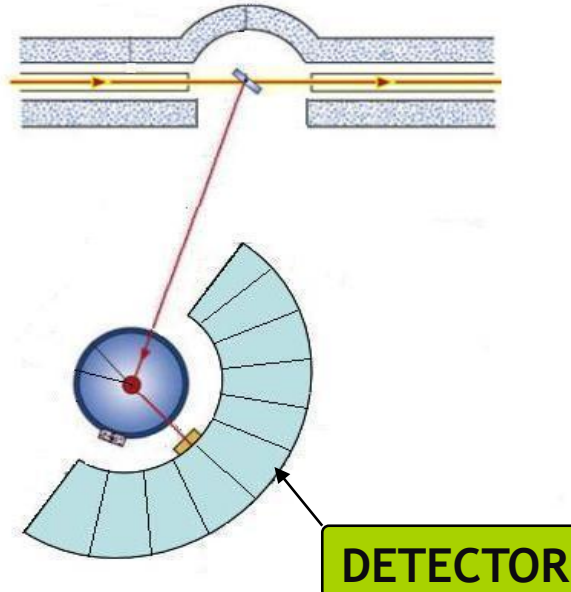
Sample environment

- Sample size 1mm^3
- 17T continuous magnet
- Set of pressure cells (50GPa ?)
- Other provisional equipment:
 - High field pulsed magnet (LNCMI -Toulouse)
 - Paris-Edinburgh pressure cell (25GPa)
- Non-magnetic mechanics

Requirements

General description

Instrument Lay-out



Detector

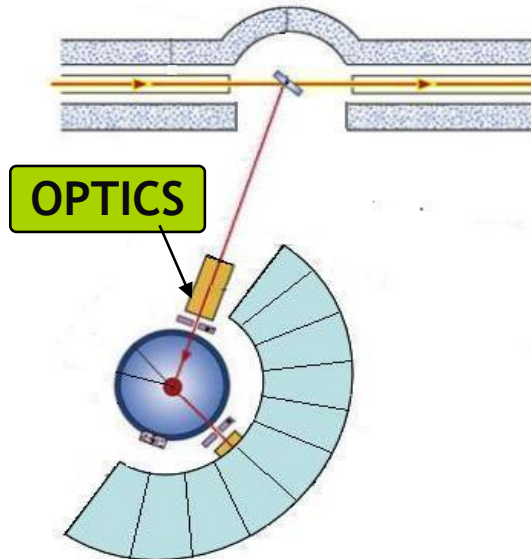
- “Banana” position sensitive detector
- Technology:
 - ^3He detector
- Radial oscillating collimator to suppress background

Detector	
2q (horizontally)	150°
2q (vertically)	$\pm 10^\circ$
Resolution (HxV)	0.1 x 0.2°
Counting rate	~ x5 D20

Requirements

General description

Instrument Lay-out



Optics

- Adjustable focusing capabilities:
 - Divergence
 - Size of the sample
- Removable system
- Strong implication required

Optics	
Sample size	1mm ³
Focal distance	2-3m
Resolution (Dd/d)	10 ⁻³

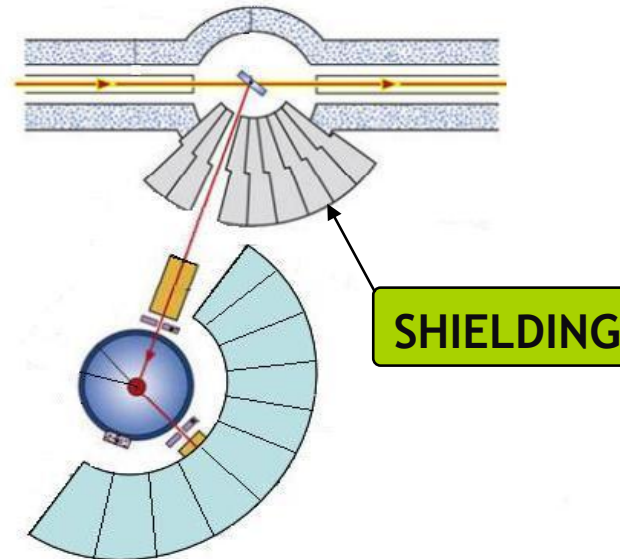
Requirements

General description

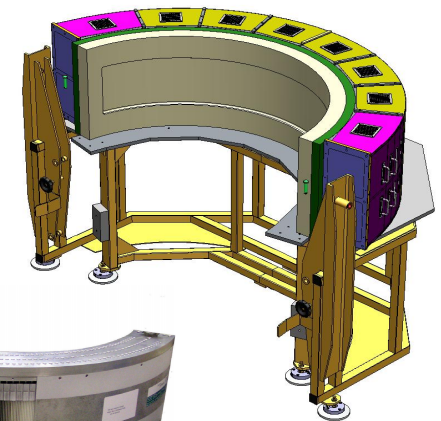
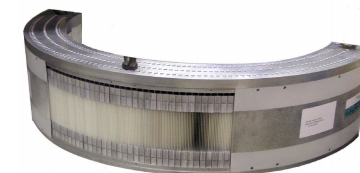
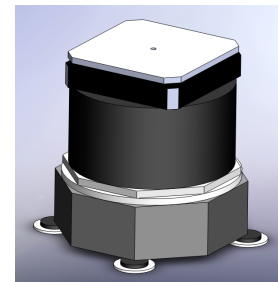
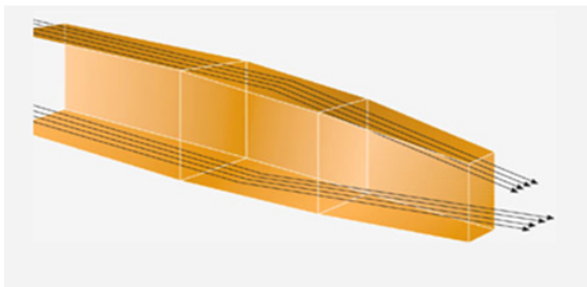
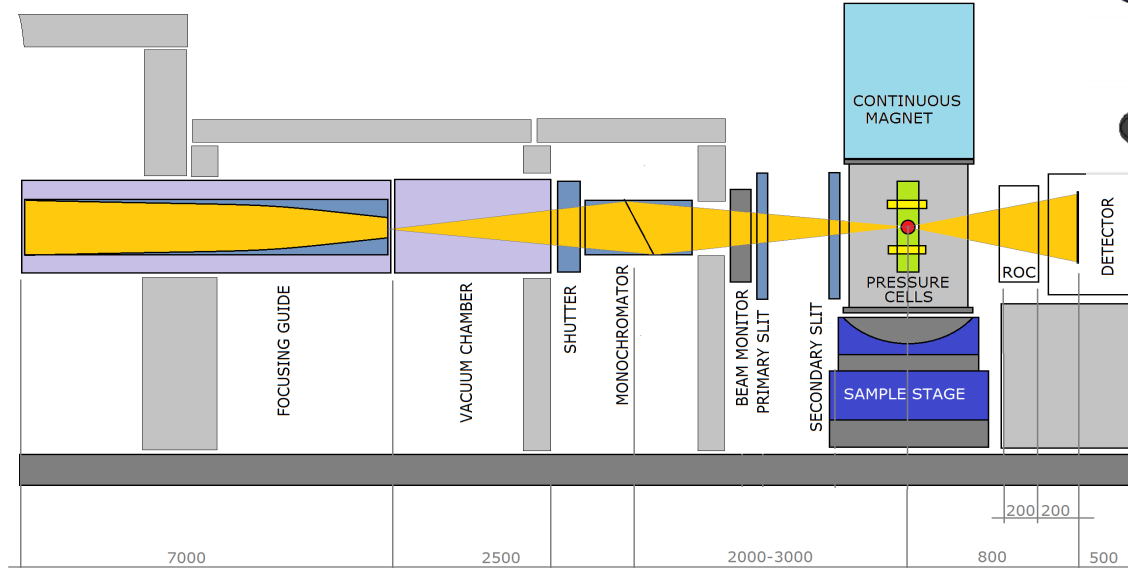
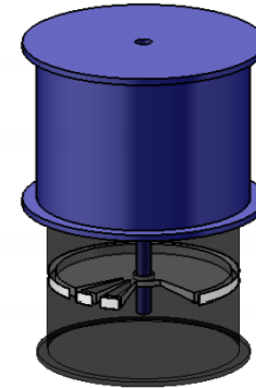
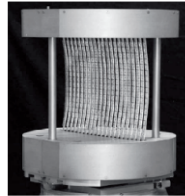
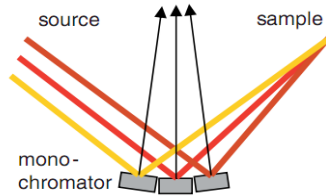
Instrument Lay-out

Shielding

- Very important for the background
- Advantages of the well prepared site of IN3



Outline of the project



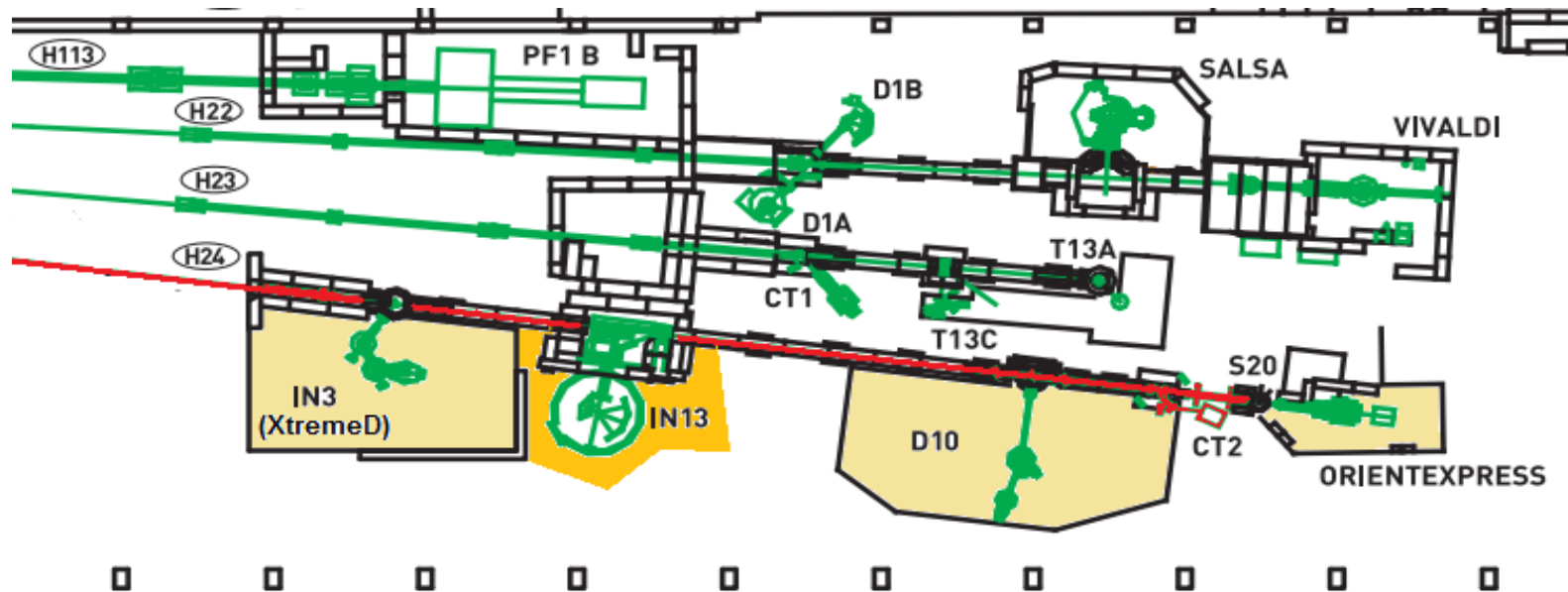
Requirements

General description

Guide H24



- XtremeD will be placed at the guide H24 at the position where now the three-axis spectrometer IN3 stands
- It will share the guide with another three-axis instrument, IN13, and with the diffraction instruments D10, Cyclops and OrientExpress
- It will occupy the first position along the guide



Requirements

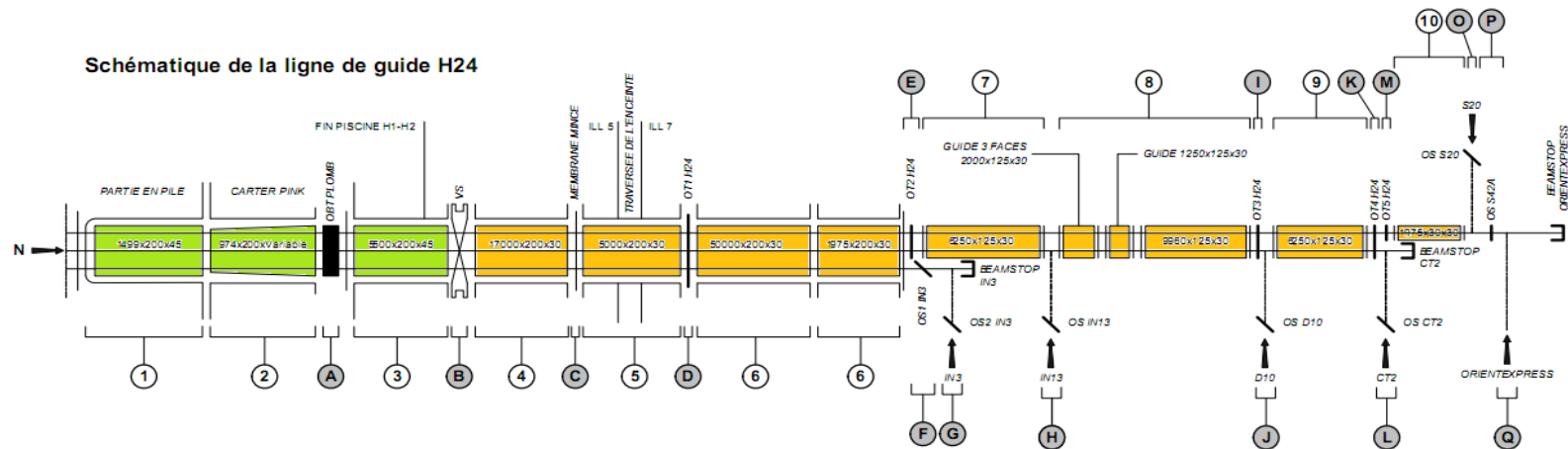
General description

Guide H24



- First modules of the guide: renewed in 2006.
(however, this part of the guide is renewed every ten years)
 - Main properties
 - $m = 2$
 - straight guide
 - $a = 45 \text{ mm}$
- Rest of the guide: without change since 1972.
 - Main properties
 - $m = 1$
 - $R = 14000 \text{ m}$
 - $a = 30 \text{ mm}$

Schématique de la ligne de guide H24



Requirements

Optics

General view

HIGH PRESSURE



Small samples

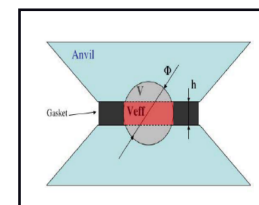
XtremeD

SAMPLE SIZE: 1 mm³

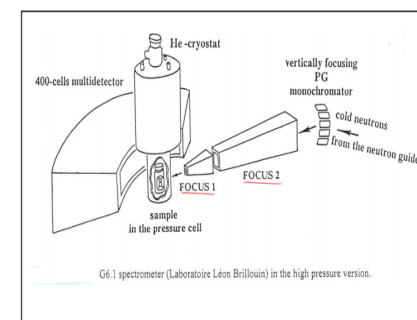
DIMENSIONALITY: 2D Focusing

WAVELENGTHS: 0.8 to 4.1 Å

FOCAL LENGTH: 2 to 3 m



$V_{\text{sample}} \sim 1 \text{ mm}^3$



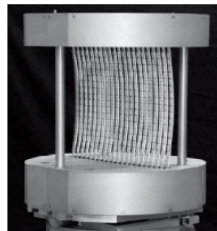
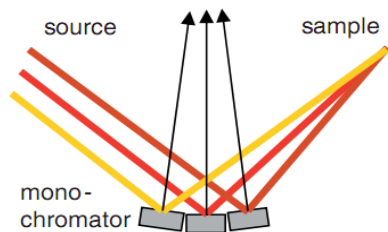
Requirements

Optics

Alternatives

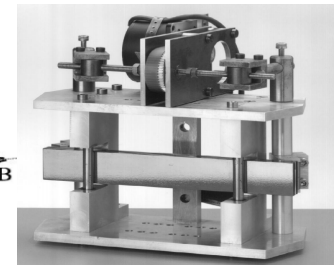
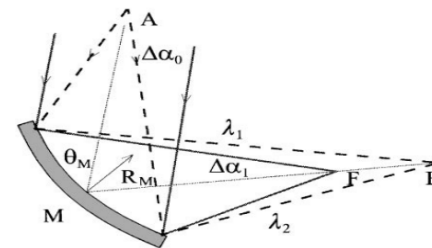
MOSAIC MONOCHROMATORS:

- Graphite HOPG monochromators
- High efficiency
- Limitation $\rightarrow 10\text{mm}$ (V_{sample})
- Quite expensive
- Vertical and horizontal focusing



BENT PERFECT CRYSTAL MONOCHR.:

- Silicon monochromator.
- No limitation at the sample spot
- Excellent horizontal resolution
- Limited vertical focusing (degraded vert. resolution)
- Avoid 2° order contamination
- Transparent to non-diffracted



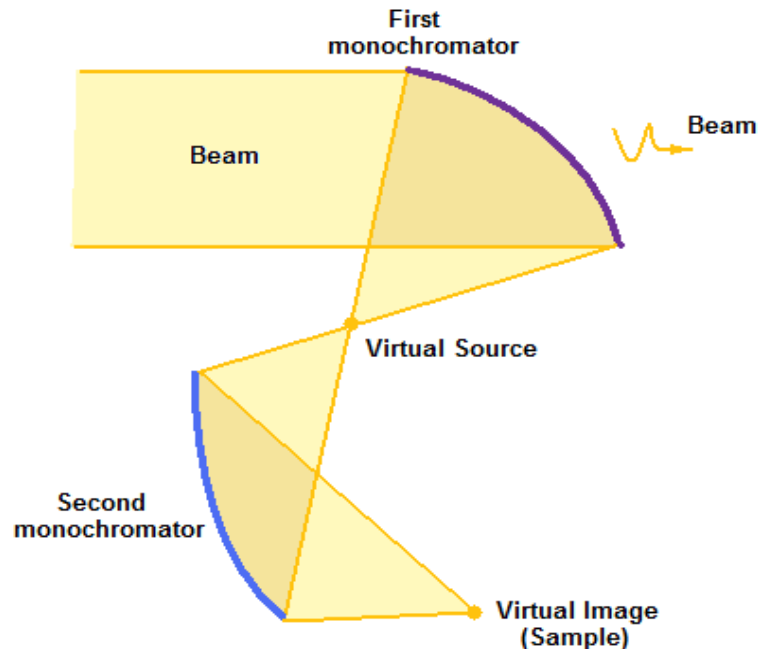
Requirements

Optics

Alternatives



- **Combination of two focusing monochromators**
 - Double focalization
 - Transparency of the first focusing monochrom



Q-space focusing effect:

- Appears when focusing with a monochr. in the plane of scattering
- Compensation of the gain in divergence after the scattering at the sample

Requirements

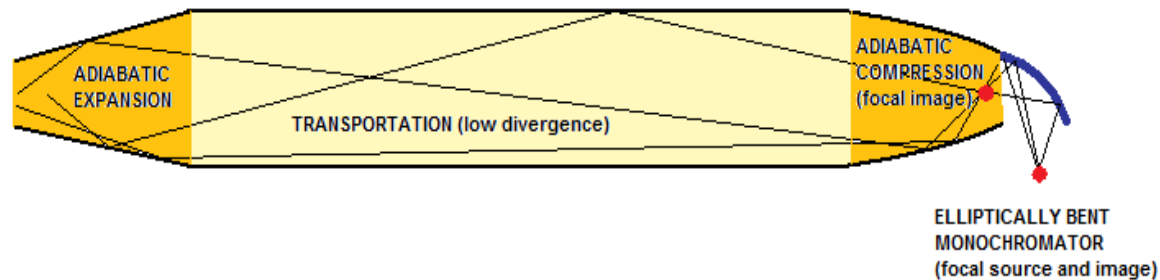
Optics

Alternatives



FOCUSING GUIDES

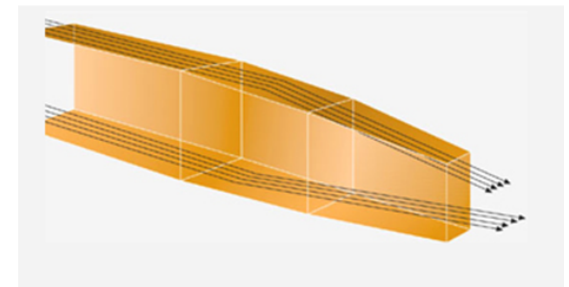
- It creates a “punctual” source for the focusing monochromator



- Ballistic guide: widening of the guide in order to reduce the divergence, minimize the number of reflections and thus maximize the flux
- Before monochromator

TRUMPET:

- Focuses vertically the beam to reduce it to the sample size
- Horizontally, only at expense of resolution: maintenance of the Q-space focusing effect.
- Very important: dist. exit-sample.
- Analysis of the interface sample environment - guide.



Requirements

Sample Environment

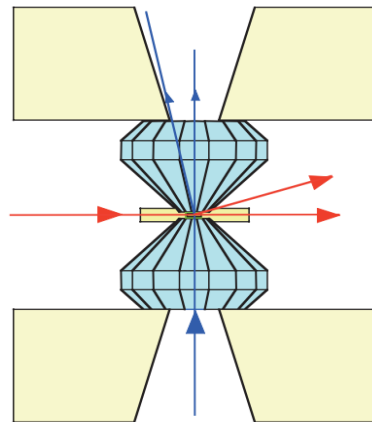
Pressure cells



Performance:

XtremeD is going to have the option high magnetic field with high pressure up to a limited pressure ($\sim 10\text{GPa}$) at the first stages. For pressures higher than this value, the experiments must be carried out without magnetic field

GEOMETRY



- ✓ Following the typical setting at continuous neutrons sources: transversal config.

NON-MAGNETIC PRESSURE CELL

- ✓ Non-magnetic materials
- ✓ Size: 40mm.
- ✓ Pressure: The objective is 10GPa.
- ✓ Sample size: Not smaller than 1mm^3 .

VERY HIGH PRESSURE CELL

- ✓ Pressure: Initial pressure limit will be 30GPa. After developments, the goal is to reach 50GPa.
- ✓ Sample size: Not smaller than 1mm^3 .

Requirements

Sample Environment

Pressure cells



Pressure cells will be developed in the frame of a collaborative partnership between the most important institutions dedicated to high pressure research

Paris-Edinburgh cells

- Toroid-type high pressure devices
- Large volume pressure cells (40mm³).
- Pressures up to 30GPa
- One of this devices could be used at the first stages of XtremeD

Goncharenko cells

- Sapphire cells (sample size 10mm³)
- Very focused beams
- His knowledge went lost with him

Other potential partnerships

- Carnegie Institution of Science & SNS
- J PARC facility

MALTA group

- Spanish research network
- Strongly linked to the development of new pressure cells

- A project is been initiated for the development of the new generation very high pressure cells (>50GPa)

- MALTA group also leads a project of design and fabrication of non-magnetic pressure cells for moderate pressure (10GPa)
- XtremeD's team is going to collaborate at this project

Requirements

Sample Environment

Magnet



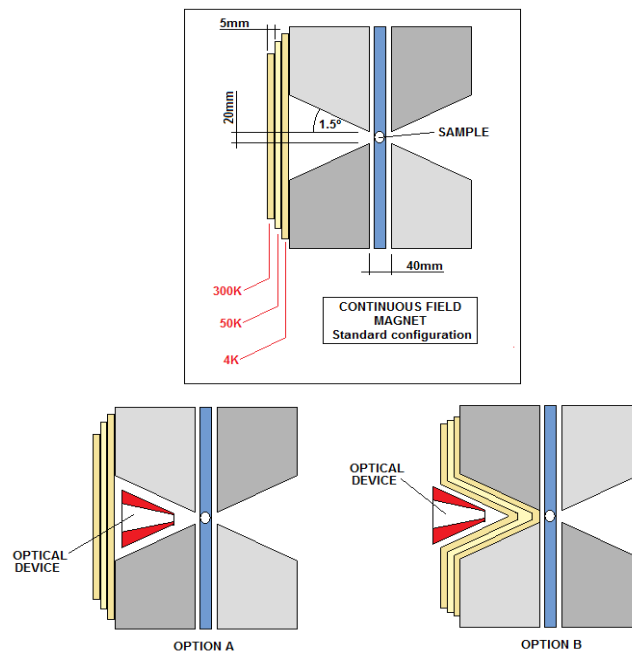
PERFORMANCE

XtremeD is going to generate continuous magnetic fields of 17 T with a dedicated continuous magnet.

The possibility of using a pulsed magnet is going to be considered for the long term.

CONTINUOUS FIELD MAGNET

- ✓ Field: Generates a continuous magnetic field up to 15T
- ✓ Main problem = SPACE
- ✓ Objective: Development of a magnet with an integrated focusing guide
- ✓ Booster: a special sample bearer that increases the field in 2T
 - Dysprosium
 - Superconductor

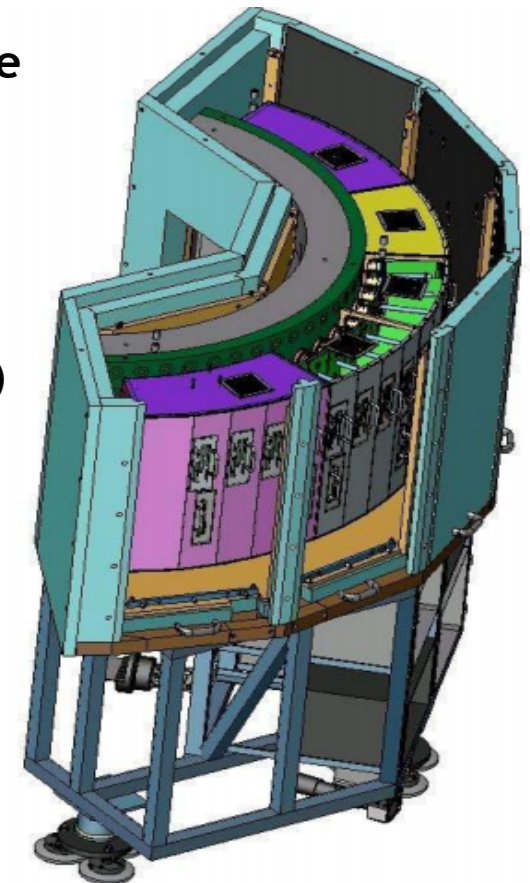


Requirements

Detector Specifications



- Powder and monocrystal
- Solid-angle:
 - 150° in the horizontal plane
 - Low vertical degree: $\pm 10^\circ$. (It is a compromise between the instability at bigger angles and the needs at singlecrystal experimentation)
- Definition:
 - 0.1° in horizontal
 - 0.2° in vertical (D19 has a resolution of 0.15°)
- Sample environment: ~600 mm in diameter. Magnetic field, pressure cell. This means a detector of around 800 mm in radius.
- Counting rate: 5 times higher than D20.
- Radial Oscillating Collimator
- ^3He technology: Optimisation of the volume of ^3He in the detector



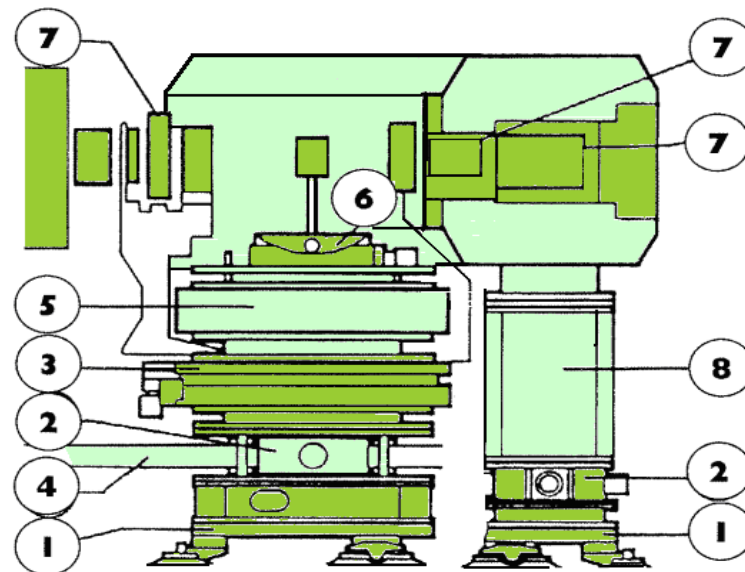
Requirements

Mechanics



- Non-magnetic materials
- Air-cushion pads (tanzboden)
- Displacement:
 - Translational: focusing optics
 - Rotational (w)
 - Positioning: X-Y-Z
 - Tilt ($\pm 20^\circ$)
- Other mechanics: ROC, optical devices, monochromators...

Sample stage	
Work vol. (X-Y-Z)	200x200x100mm
Linear accuracy	$\pm 0.05\text{mm}$
Angular accuracy	$\pm 0.01^\circ$
Admissible weight	1500kg



- 1 - GROUND MODULES
- 2 - TRANSLATIONAL MODULES
- 3 - ROTATIONAL MODULES
- 4 - COUPLING ARMS
- 5 - STAGE
- 6 - ADJUSTMENT DEVICES
- 7 - COMPONENTS FOR BEAM OPTICS
- 8 - INTERCONNECTIONS

Siting: Implantation Study

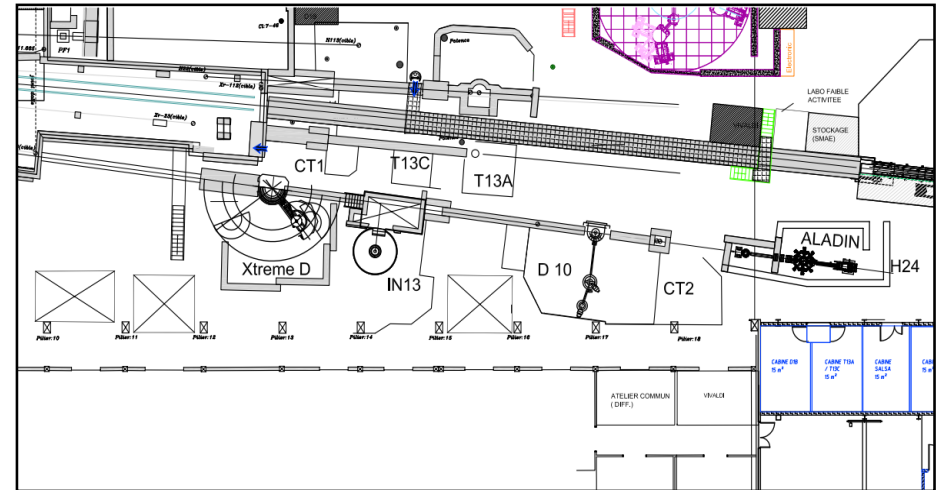


COHABITATION WITH IN3

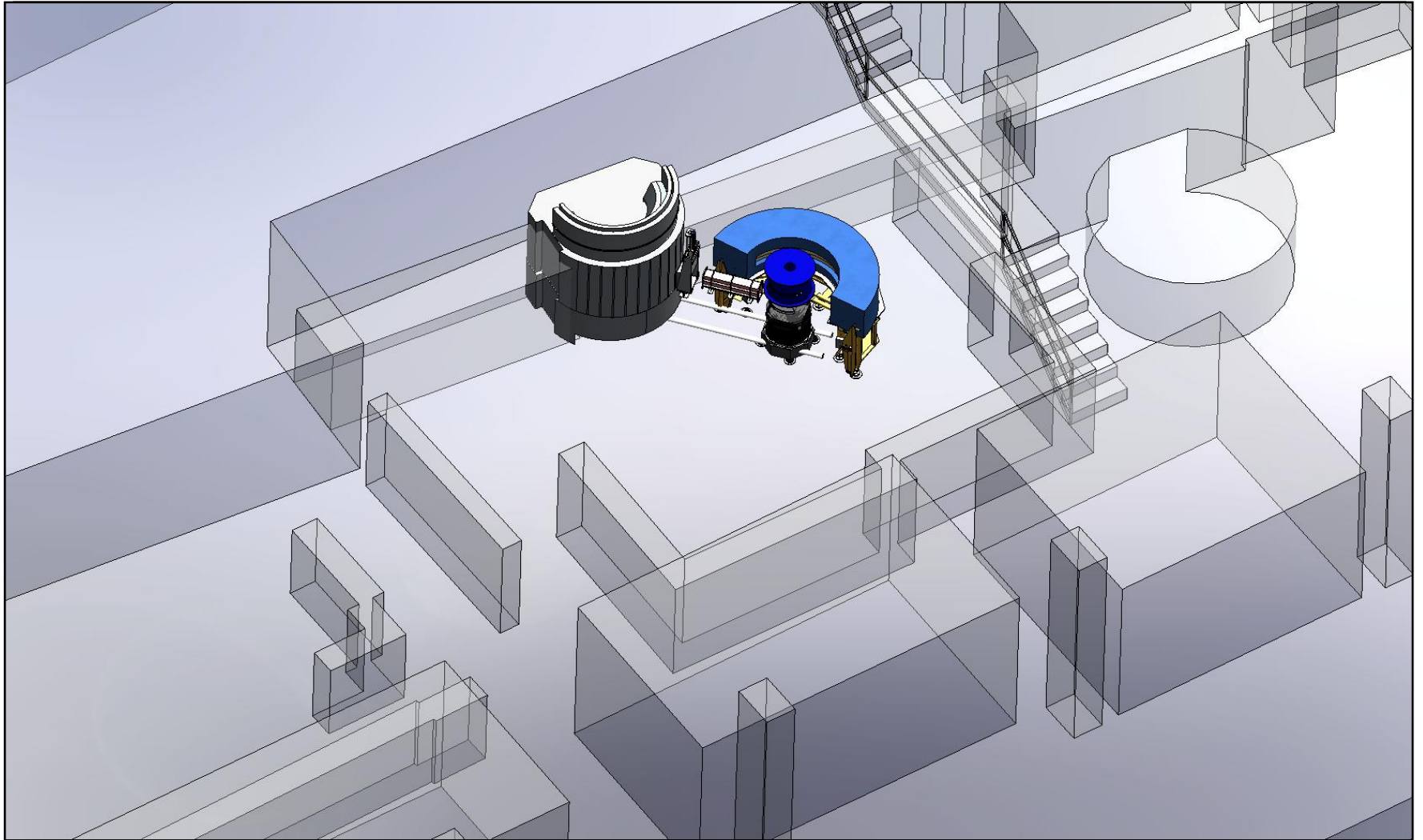
- The installation of XtremeD can start in 2011 (before that date, IN3 will be operational)
- XtremeD will have access to the site
- No technical support for tests

RECYCLING OF IN3

- Sequential installation of XtremeD: recycling of decommissioned components:
 - Non-magnetic omega table with displacement X-Y-Z
 - Guide, monochromator and casemate
 - Possible problems with the monochromator shielding at the first stages



Siting: Implantation Study

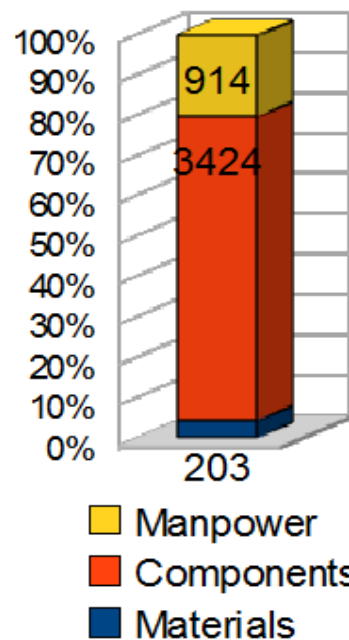


Projected Budget

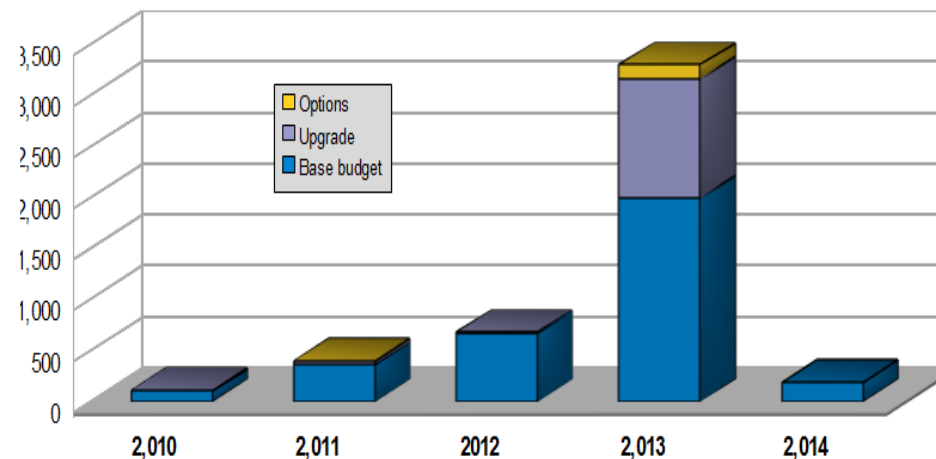


BASE BUDGET (k€)		3,318
+ UPGRADE		1,223
+Optional equipment		135
Units per element	Specific cost	TOTAL

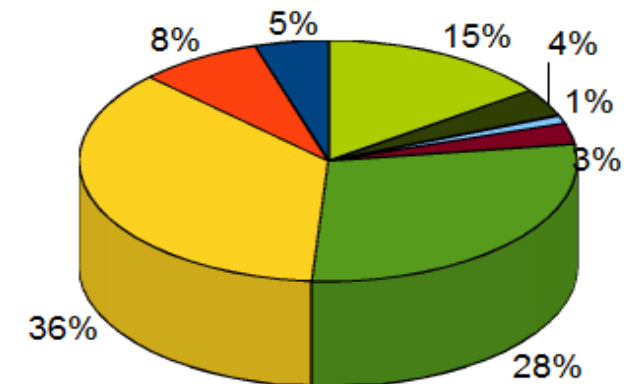
Expenditure per type
(upgraded version)



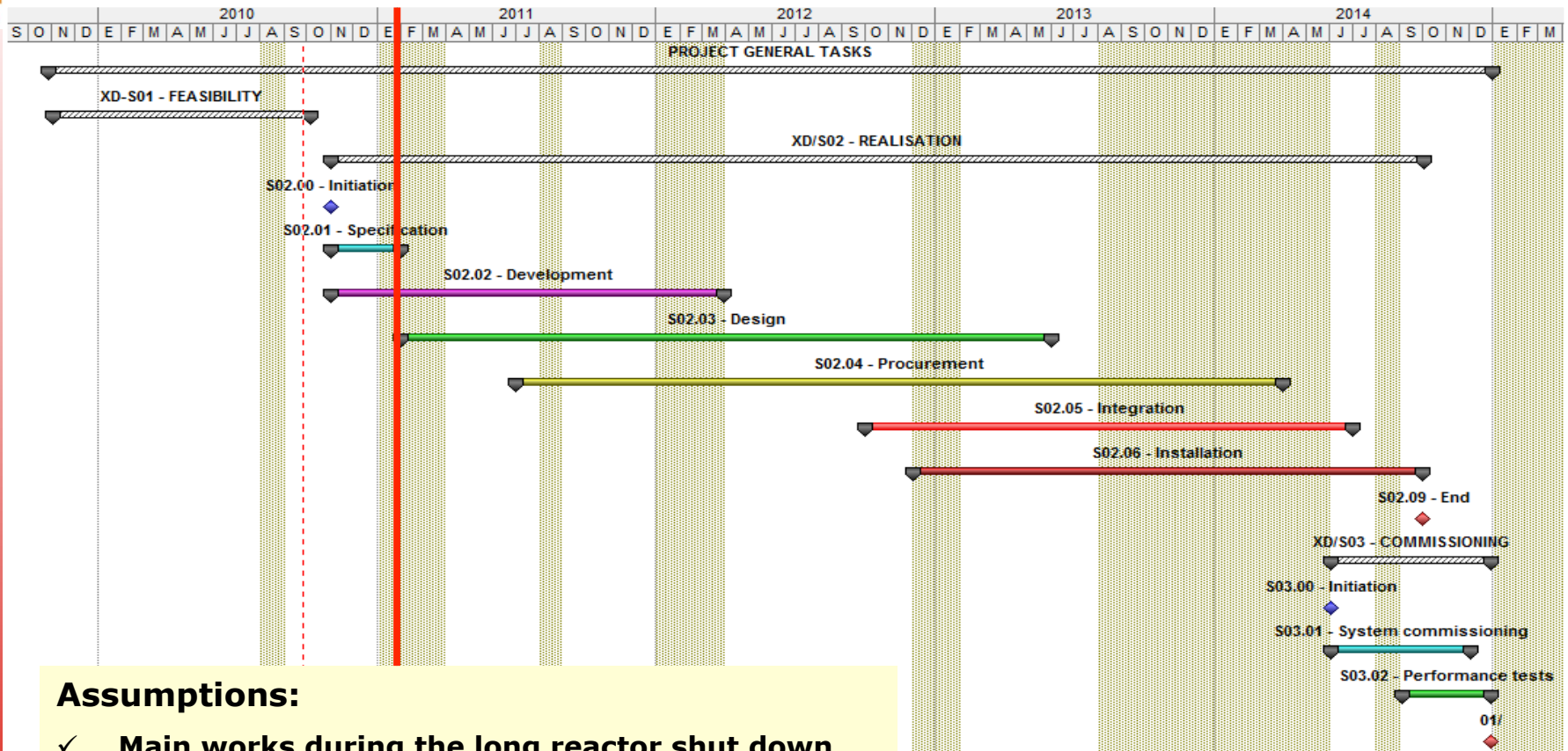
Cost per year



Expenditure per lot
(upgraded version)

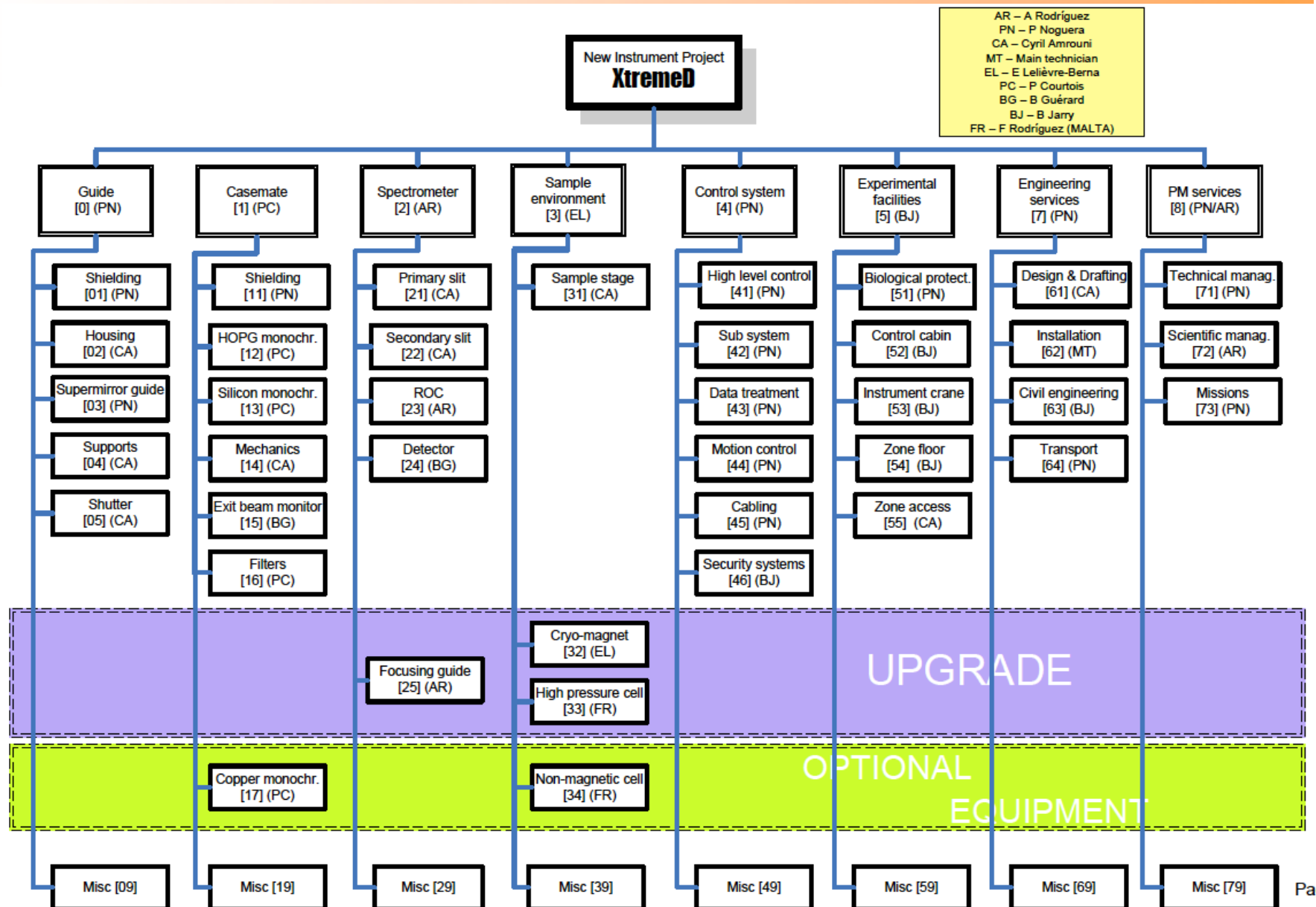


Project organisation



Assumptions:

- ✓ Main works during the long reactor shut down (August 2013 – June 2014)
- ✓ New guide will be operational after the long shut down.



Project organisation

Risk Analysis



Cause	Consequence	Effect	Crit	Preventive Actions	Curative actions			
Single supplier magnet	Delays in manufacturing, high prices	Schedule, budget	60	Identify alternative suppliers and split procurement	Identify alternative suppliers and split procurement			
Delays in the H24 guide project	Delays in the installation and full efficiency	schedule	60	H24 project should prioritize all the task related with XtremD	Re-Schedule			
Cancellation of the H24 guide project	Deep degradation of the instrument	performance	54	Give special attention to this point during negotiations				
Resolution/ background worse than expected	Degradation of the instrument's performance	performance	54	Simulate the instrument as soon as possible	Adapt the objectives in terms of flux/ resolution/ background			
Detector's specifications can not be reached	Degradation of the instrument's performance	PERFORMANCE	3	5	2	30	Launch feasibility study over the different options	Redo the specifications of the instrument. Re-study the options of polivelence for single crystal
Resolution/background are worse than expected	Degradation of the instrument's performance	PERFORMANCE	3	6	3	54	Simulate the instrument as soon as possible	Adapt the objectives in terms of flux/resolution/background

Administrative framework

A CRG instrument



- CRGs help to establish strong and durable relationships with other national or international research organisations.
- CRGs **increase and complement ILL's facilities** and instruments, overcoming the limitation of public instruments.
- **CRGs offer more opportunities for exploring new techniques and for carrying out adventurous or difficult experiments.**
- No cost for ILL in human resources. External teams can operate, **expanding the human and material scientific resources** that contribute to the reputation of the ILL.



Administrative framework

A CRG instrument



- CRG « B » team operating on an ILL beam an instrument which is not the property of the ILL (30%-70%)
- The new contract MICINN-ILL & MICINN - partners (<30% CRG-Beam Time):

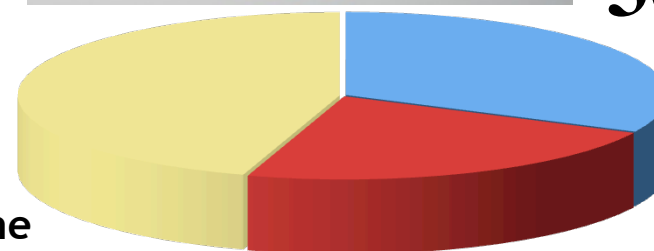


49%

70% CRG-Beam time



30 %



Partners 21%

30% CRG-Beam Time

SpINS management



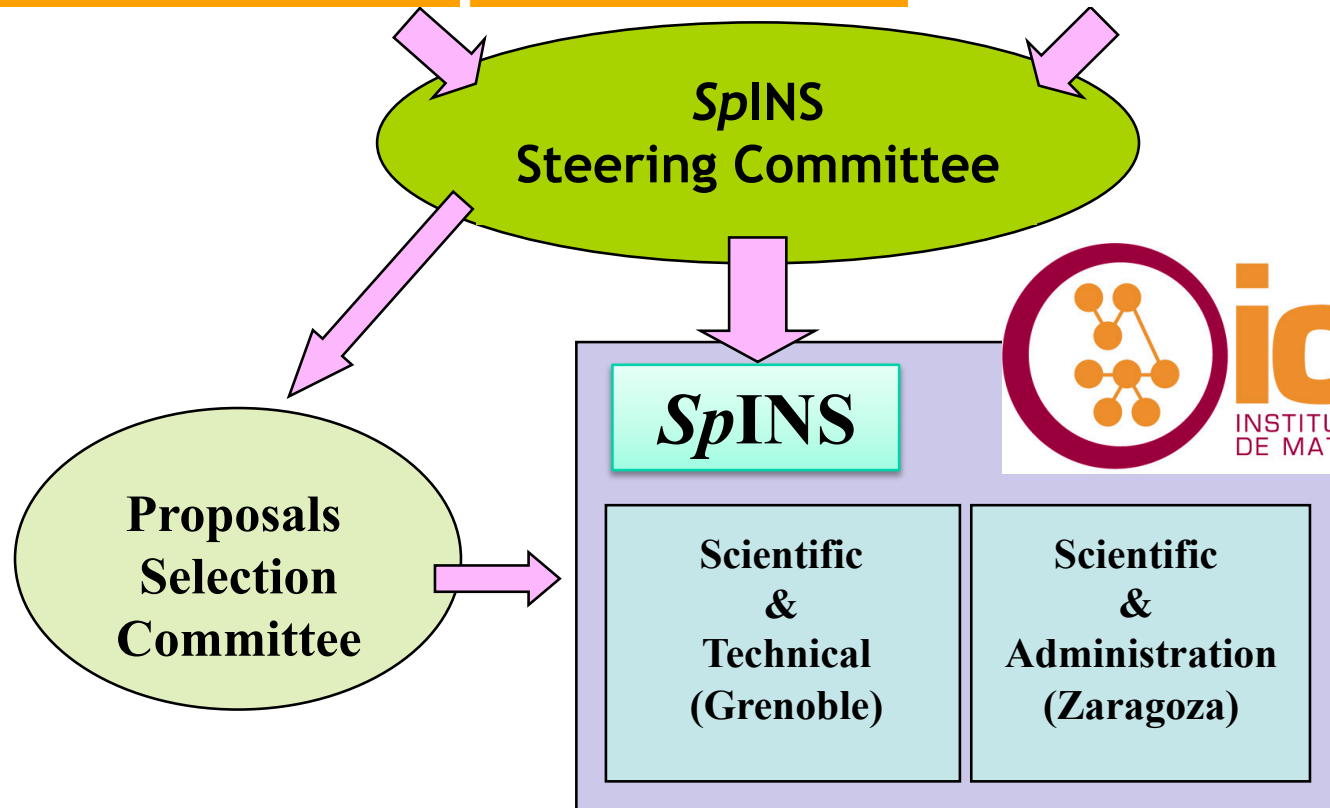
GOBIERNO
DE ESPAÑA

MINISTERIO
DE CIENCIA
E INNOVACIÓN



CSIC

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS



Project team and Scientific Advisory Committee



Project team:

General Project Leader

- J. Campo (ICMA)

Scientific

- J.A. Rodríguez Velamazán (ICMA) *Scientific Project Leader*
- H. Fischer (ILL)
- T. Hansen (ILL)
- C. Ritter (ILL)

Engineering

- P. Noguera (AVS) *Technical Project Leader*

Scientific advisory committee:

- J. Rodríguez-Carvajal (ILL) *Chair*
- E. Lelièvre-Berna (ILL)
- L.R. Falvello (U. Zaragoza, Spain)
- V. García Baonza (MALTA group, U. Complutense de Madrid, Spain)
- J.L. García-Muñoz (ICMAB -CSIC, Spain)
- P. Gorria (U. Oviedo, Spain)
- S. Klotz (CNRS, France)
- J.E. Lorenzo (CNRS, France)
- R. Nelmes (U. Edinburgh)
- I. Mirebeau (LLB)
- L-P. Regnault (CEA, France)
- F. Rodríguez (MALTA group, U. Cantabria, Spain)

MICINN, ILL and All of them are acknowledged for their contributions



Thank you for your attention



Óxidos y Minerales I- Estructura y Reactividad (3/4)

Simposio MALTA-Consolider

23-27 Enero 2011, Miraflores de la Sierra



www.malta-consolider.com

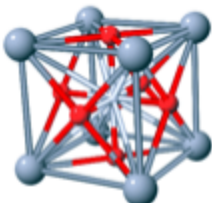
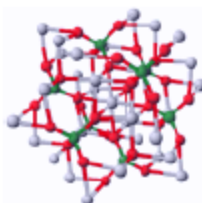
Moderador: J. Manuel Recio (UOVI)

Ponentes:

1. **Alberto Otero de la Roza (UOVI)**
Rigorous treatment of first principles data for quasiharmonic thermodynamics of solids
2. **David Abbasi Pérez (UOVI)**
Más allá del modelo de Debye. Nuevo módulo de cálculo de efectos térmicos en cristales
3. **José Manuel Menéndez (UOVI)**
Estudio sistemático de las ecuaciones de estado de las perovskitas KMF_3
4. **Ángel Morales (UCM)**
Estudio de polimorfos de TiO_2 . DFT+U
5. **Miriam Marqués Arias (CSEC)**
Metales alcalinos a altas presiones

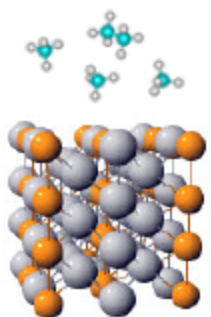
III. STRUCTURE, STABILITY AND REACTIVITY OF MINERALS

a. Pressure-Temperature-Composition (PTx) diagrams and physical properties of:
 ABO_3 ($AO-BO_2$; $A_2O_3-B_2O_3$), ABO_4 (AO_2-BO_2) and AB_2O_4 ($AO-B_2O_3$) oxides

Work Plan III. a.	SCIENTIFIC SCOPE	Example
Field Coordinators A Vegas / FJ Manjon	Scientific Questions - Further understanding the structure and stability of crystal phases at high pressure - Exploring new phases in materials which can only be stabilized under given conditions of pressure and temperature - Deeper understanding of C-Si analogies and its influence of the carbon cycle - Synthesis of new materials with tailored properties of technological interest - <i>In situ</i> determination of the physico-chemical properties of new phases	 
Leading Groups IQFR - UPV UCAN - UV		
Supporting Groups All	Specific Goals - Target systems: ABO_3 ($AO-BO_2$; $A_2O_3-B_2O_3$), ABO_4 (AO_2-BO_2) and AB_2O_4 ($AO-B_2O_3$) oxides, with lightest A-B elements and, in particular, compounds involving carbon. - Influence of inclusions of transition metal ions like Co, Fe, Cr, Ni, upon the structural and physical properties of these materials: structure and phase stability, transport properties (electrical and thermal), optical and magnetic properties (spin transition phenomena and electronic structure modification) and mechanical properties (hardness and elasticity) - Study of the influence of these oxides in geodynamics and prospects on new materials applications	
Related Fields Molecular systems P-T sensors		

III. STRUCTURE, STABILITY AND REACTIVITY OF MINERALS

b. Catalytical properties of minerals on abiotic organic synthesis

Work Plan III. B.	SCIENTIFIC SCOPE	
Field Coordinators A Muñoz / J Andrés	Scientific Questions - Pressure-induced chemical reactivity in minerals - High pressure properties of the catalysts - Formation of methane clathrates at deep sea	
Leading Groups ULL2 – UJI		
Supporting Groups All	Specific Goals - High pressure structure and properties of Ni, Fe, and their alloys, sulphides and oxides (topic III. a) - Catalytic properties of Ni, Fe, and their alloys, sulphides and oxides - Kinetics and stability of methane clathrates (topic I.a.) - High pressure reactivity of methane and other small hydrocarbons in presence of oxides of metals (topic II.b.)	
Related Fields Clathrates Oxides		

2.4. SCIENTIFIC PROGRAM

SUPPORTING THEORETICAL AND COMPUTATIONAL SCIENTIFIC PROGRAM FOR MALTA

1. FUNDAMENTALS

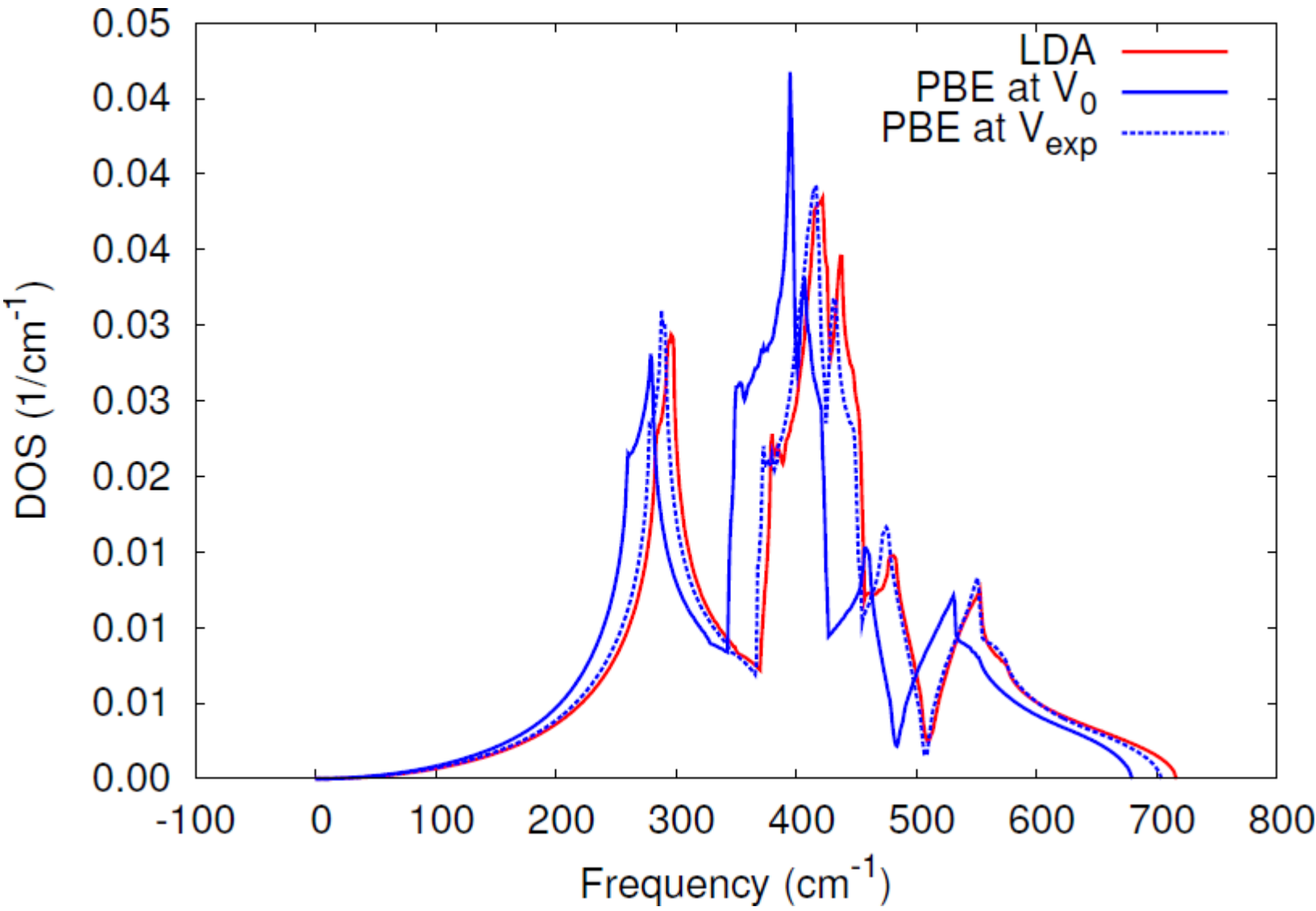
- a) Chemical bonding. Topological analysis of the electron density and ELF.
- b) Thermal effects and dynamics. Vibrations in crystals.
- c) Transition mechanisms. Semi-empirical, martensitic, and nucleation and growth models.
- d) Developments in DFT calculations.
- e) Development of interpretative models for the analysis of high pressure phenomena.

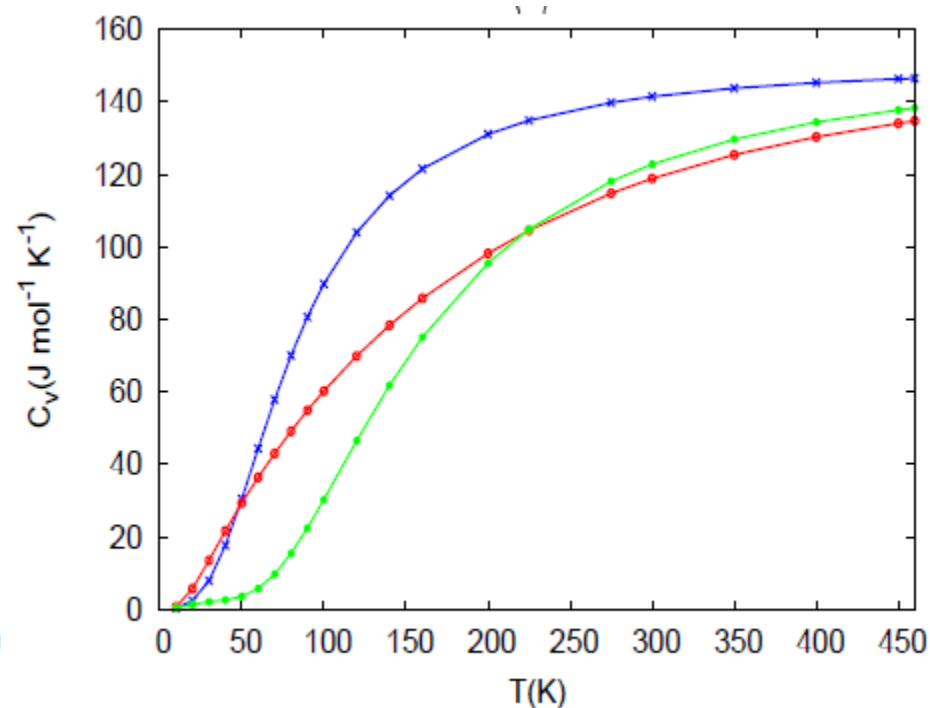
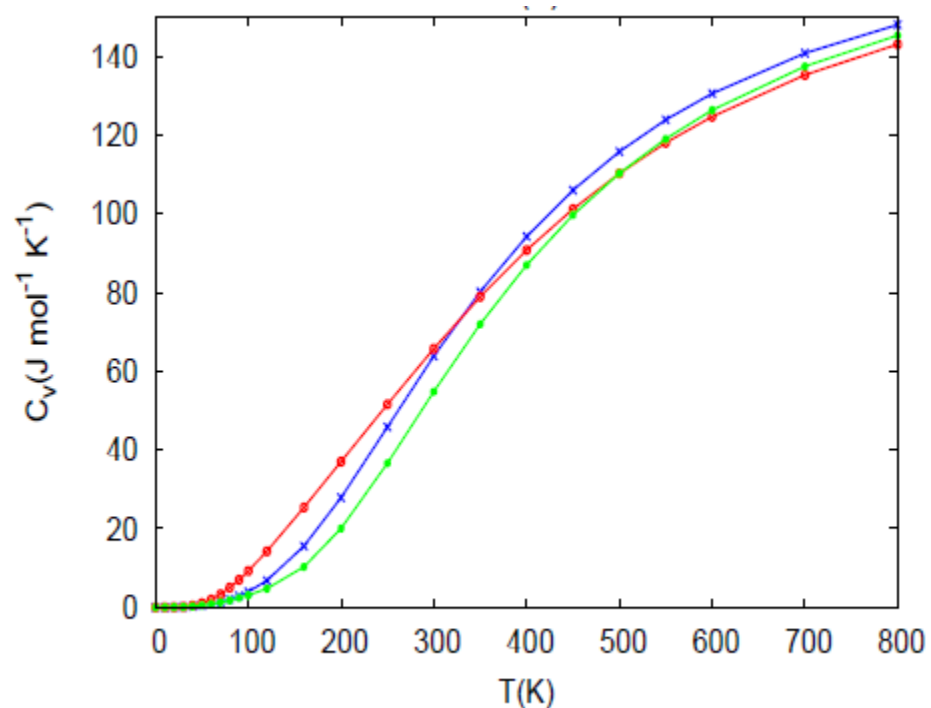
2. METHODOLOGICAL DEVELOPMENTS

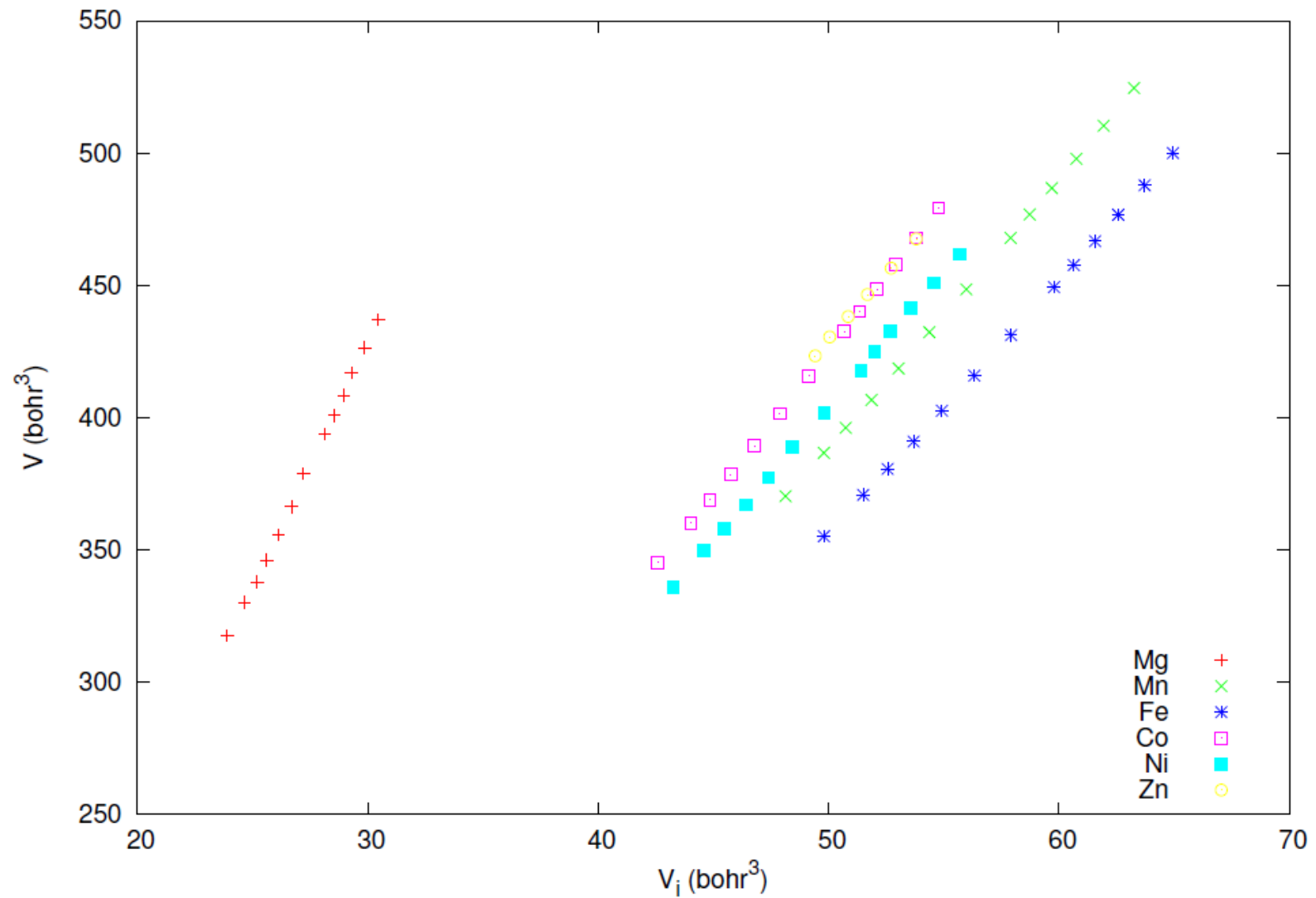
- a) Development of a new code for the analysis of ELF in crystals.
- b) Extension of the GIBBS code in order to improve the evaluation of thermodynamic properties of crystals at finite temperatures. The Fleche model.
- c) Analysis of schemes of different complexity to the calculation of energetic profiles in solid-solid phase transitions.
- d) Analysis of different exchange and correlation functionals in DFT calculations: equations of state of simple molecular solids.

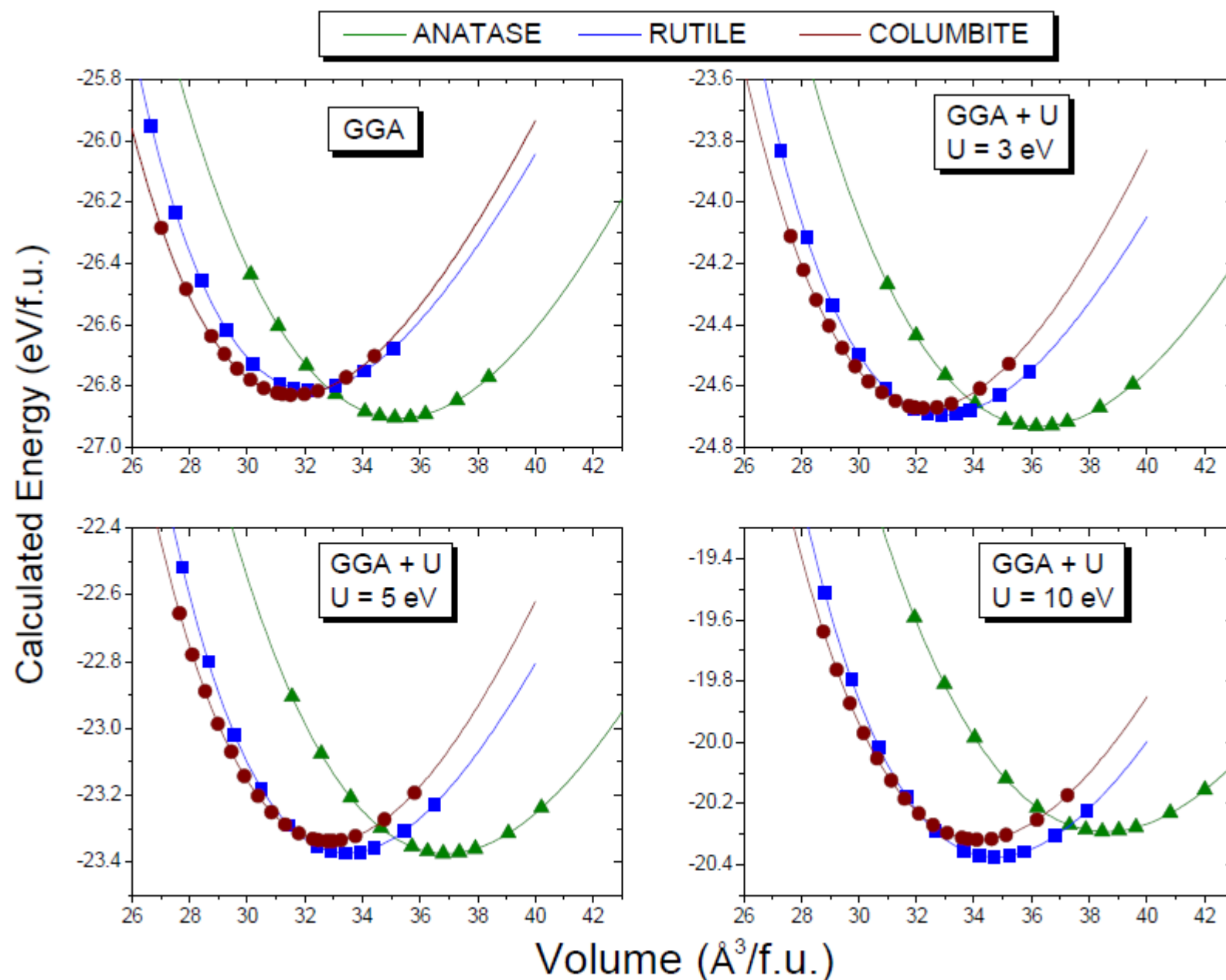
3. APPLICATIONS – INTERPRETATIVE MODELS OF HIGH PRESSURE PHENOMENA

- a) Chemical decomposition of the compressibility.
- b) Determination of the phase diagrams for simple **NOCH** molecular crystals with multiple bonds.
- c) Determination of phase diagrams in silver halides and silicates.
- d) Molecular to polymeric transformations in CO₂, dimethyl-acetylene, and other **NOCH** compounds.
- e) Mechanisms of pressure induced phase transitions in simple NOCH compounds.
- f) Mechanisms of the pressure induced transformations in silver halides and silicates. The zircon to reidite transformation in ABO₄ compounds (including ZrSiO₄ as a model). Post-reidite phases.
- g) Theoretical interpretation of the model of anions in metallic matrices. Topological analysis of the ELF in metals, inter-metallic compounds, and inorganic crystals containing metallic elements.
- h) Rare gas solids as test materials for the testing of the exchange and correlation functionals.
- i) Computer simulation of aqueous solutions of proteins.



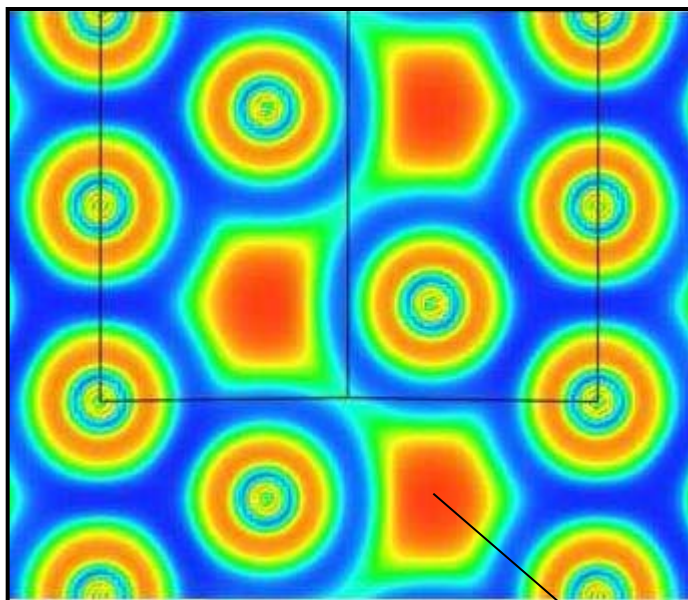
$\beta\text{-C}_3\text{N}_4$ y $\text{BaWO}_4\text{-II}$ 





K → Alkali chalcogenide

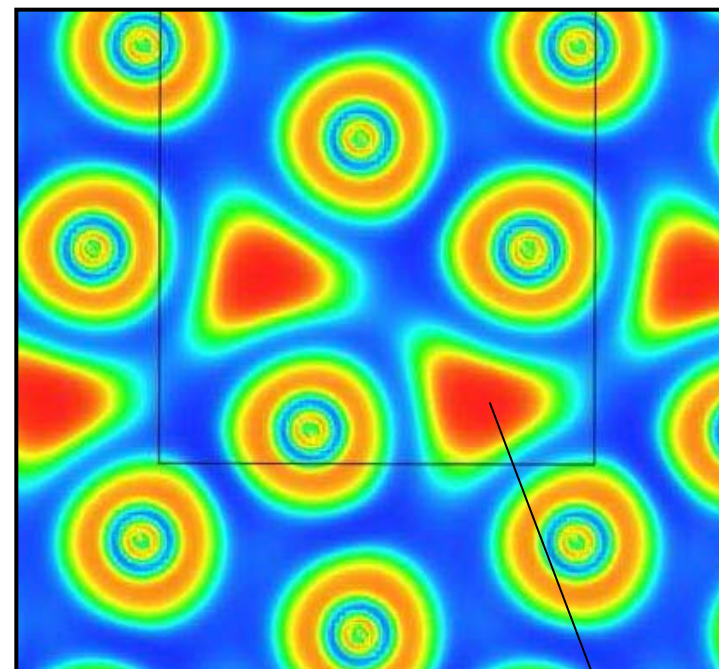
Same structure as A_2X
(Ni_2In)



25 GPa
(ELF ≈ 0.95)
hP4 phase of K.

Chalcogenide
position

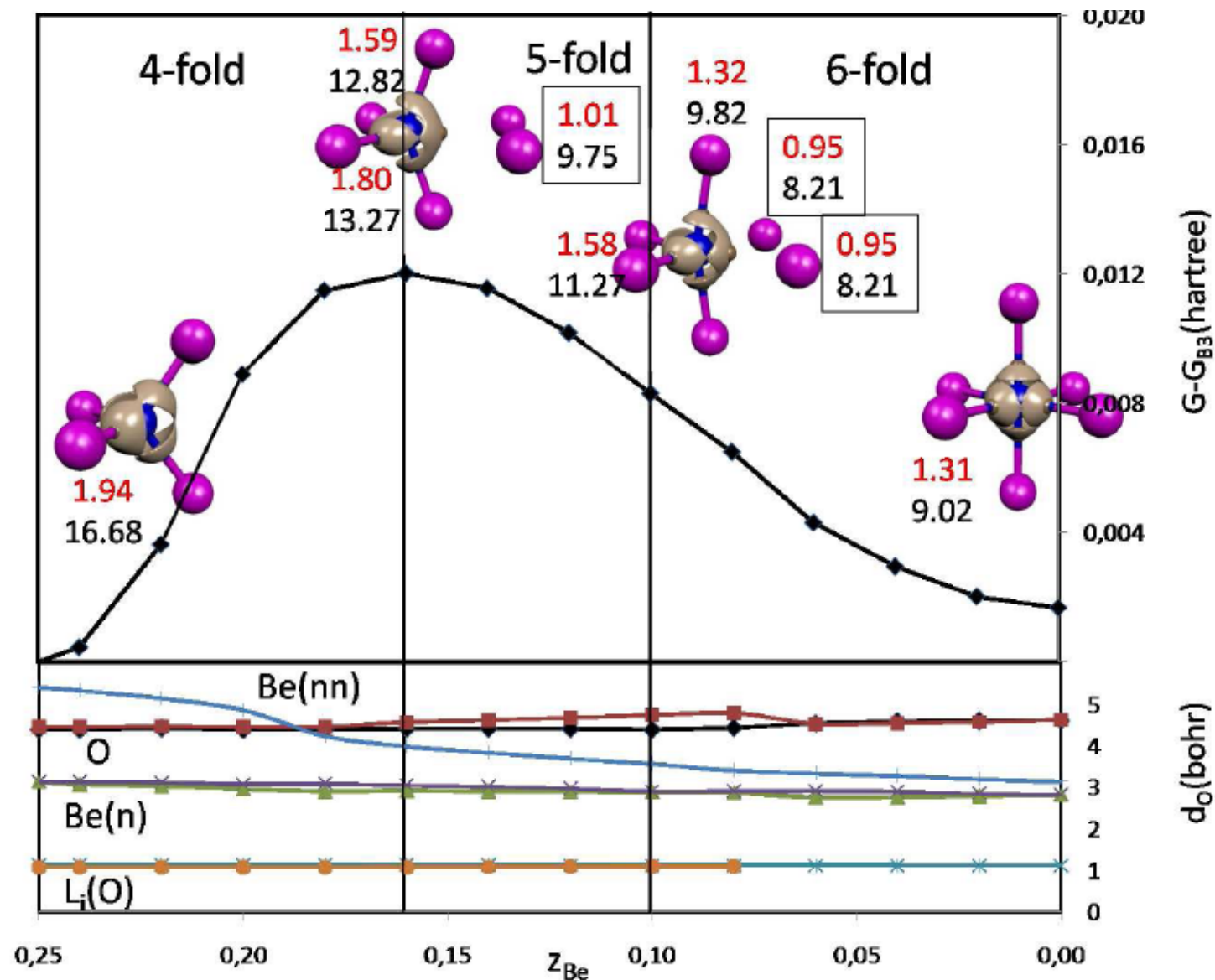
Same structure as A_2X
(anticotunnite)

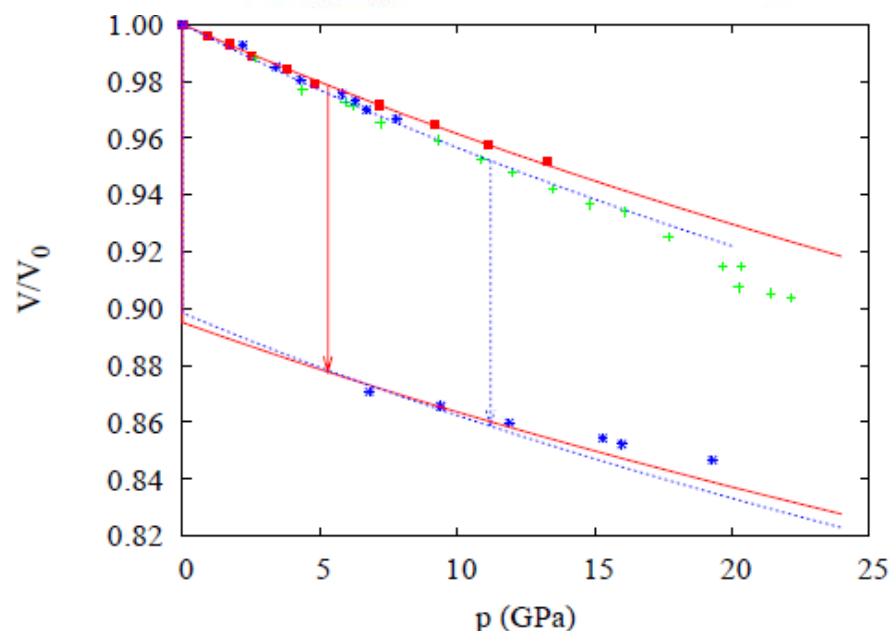
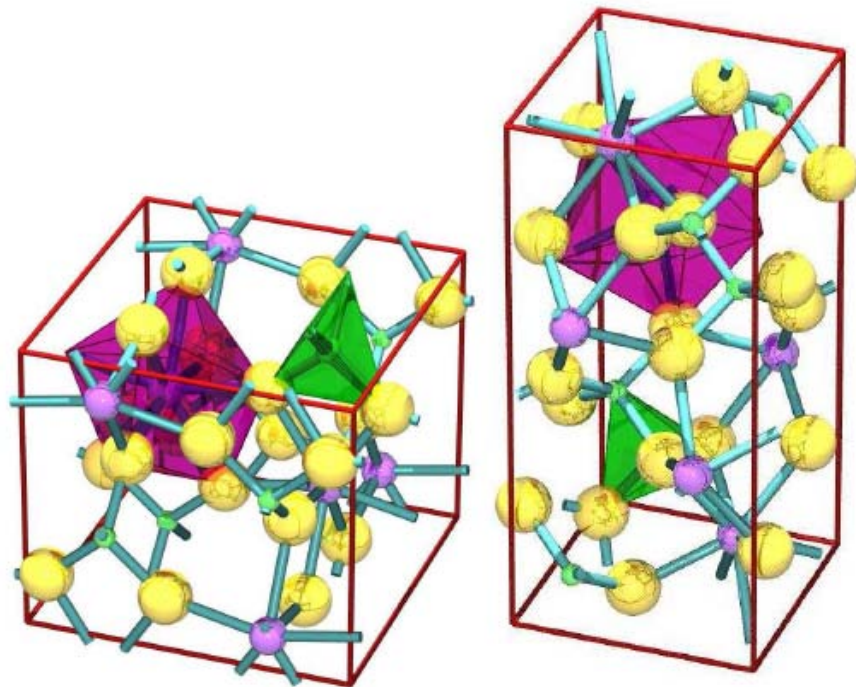


57 GPa
(ELF ≈ 0.95)
oP8 phase of K.

Chalcogenide
position

Mecanismo ortorrómbico para la transición B3-B1 en BeO





ZrSiO_4 es un material de mucho interés tecnológico que sufre una transición de fase inducida por presión entre dos estructuras tetragonales (zircon y reidita) que tienen una relación grupo-subgrupo

Los entornos locales de ambas estructuras son muy similares. Zr está rodeado por 8 oxígenos: dos tetraedros O_4 , con dos distancias Zr-O distintas. Si está rodeado por 4 oxígenos: un tetraedro O_4 , una distancia Si-O

Los cálculos generan resultados en buen acuerdo con los experimentos para la estructura, la EOS, el colapso del volumen y la presión de transición.

La transición muestra histéresis grande

Camino triclinico ($P-1$) o monoclinico ($C2/m$)

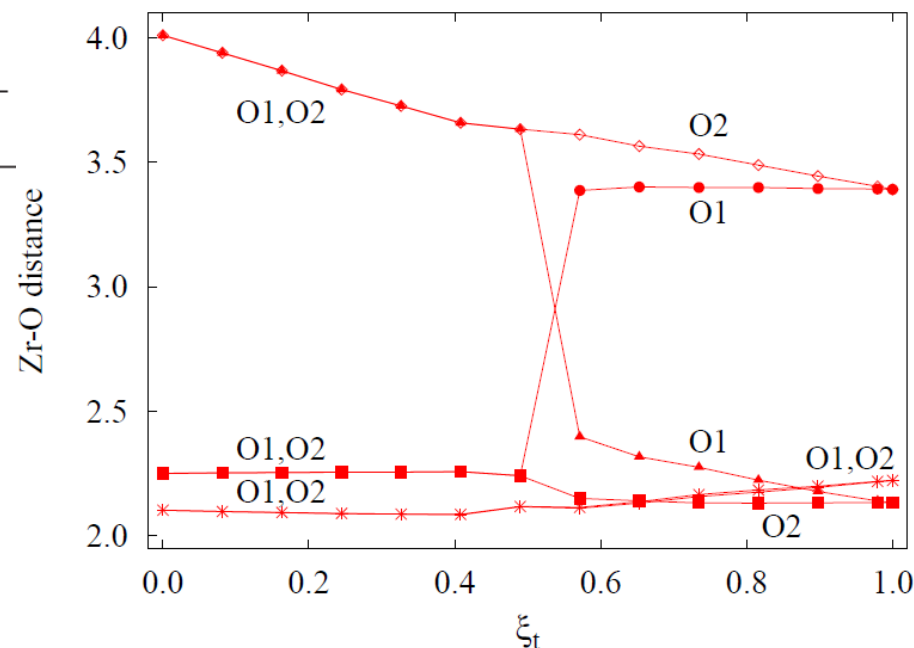
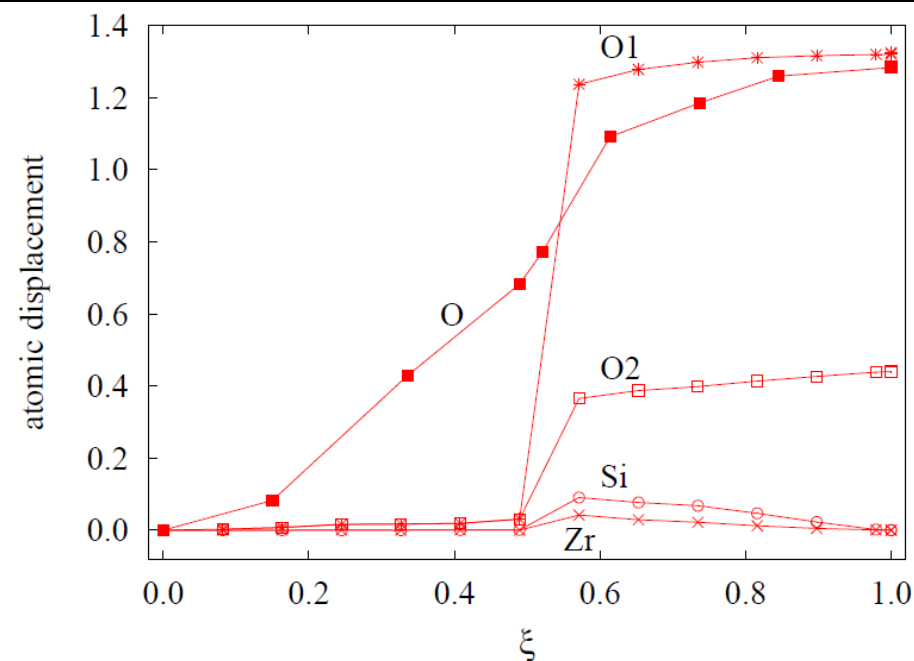
β coordenada de transformación

Barrera de activación en torno a 80 kJ/mol

Los desplazamientos atómicos muestran que los átomos O1 sufren mayores desplazamientos que los átomos O2

Se rompen dos enlaces Zr-O y se crean dos enlaces Zr-O

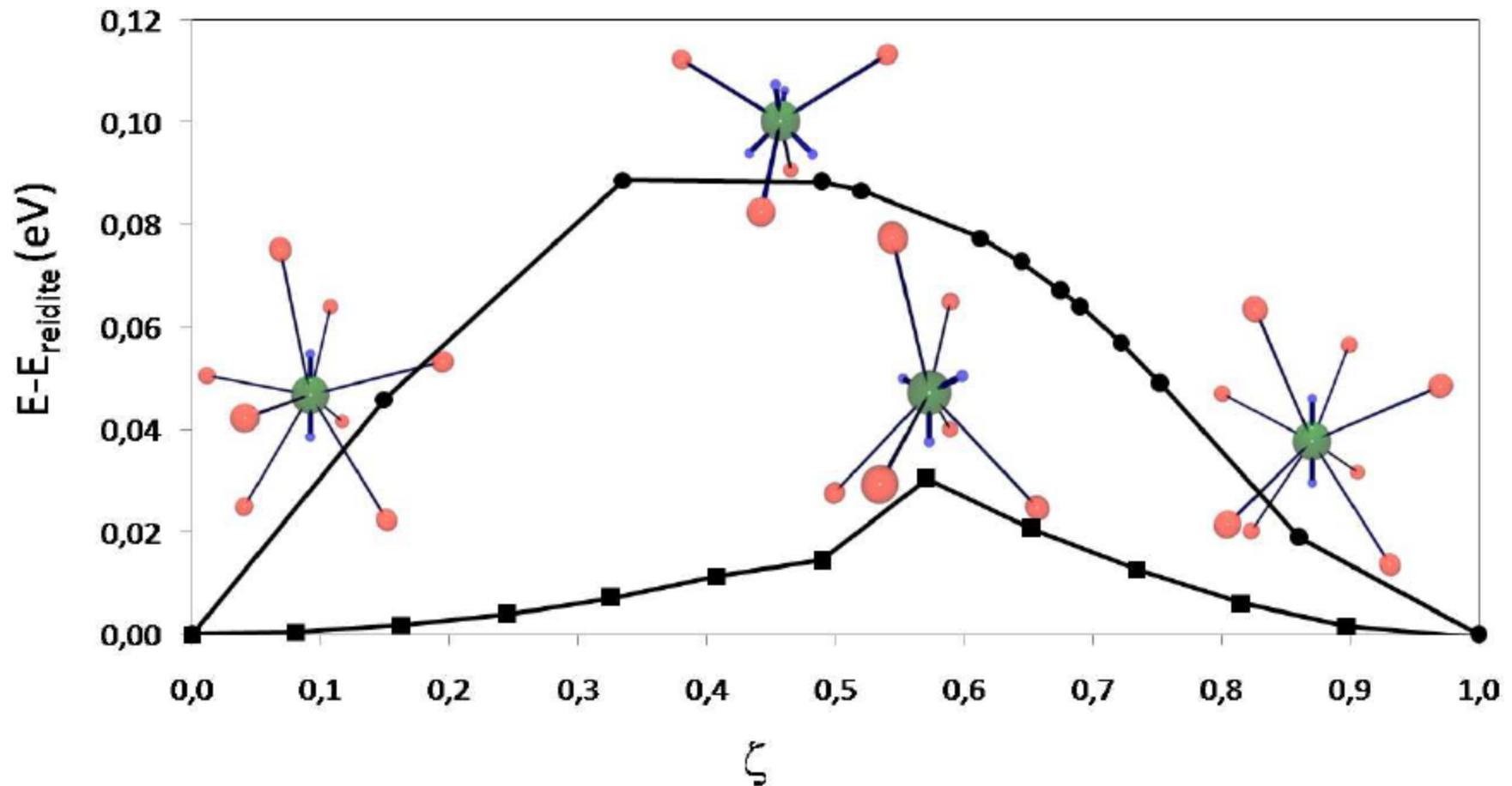
Transición no displaciva, es reconstructiva



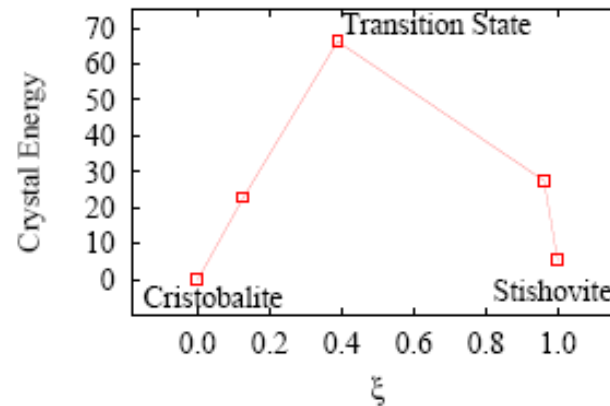
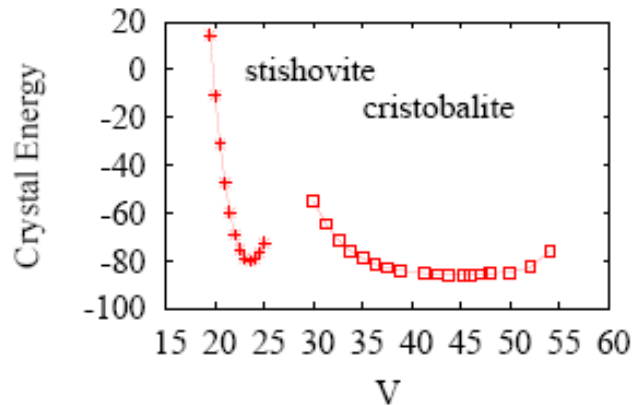
	$I4_1/a$		$P\bar{1}$	
	Reidite	$\beta_t = 102^\circ$	TS	Reidite
η_{11}	-0.2426	0.0012	-0.0804	-0.0601
η_{22}	-0.2426	0.0038	0.1177	0.1271
η_{33}	1.0162	0.0012	-0.0804	-0.0601
η_{13}	0	-0.1042	-0.1015	-0.1825
S	0.3575	0.0491	0.0726	0.1000
$\delta_0(\text{Zr-Zr})$	0	0.0001	0.0419	0
$\delta_0(\text{Si-Si})$	0	0.0008	0.0906	0
$\delta_0(\text{O}_1\text{-O}_1)$	1.2866	0.0309	1.2370	1.3246
$\delta_0(\text{O}_2\text{-O}_2)$		0.0307	0.3654	0.4381

Mecanismos tetragonal y monoclónico para la transición zircón-scheelita

Seguimiento del proceso de reconstrucción de enlaces en torno al Zr. El camino con menor reconstrucción es el más favorable energéticamente. Tiene menor *strain* y menos desplazamientos atómicos.



SiO₂ α -cristobalite $\rightarrow$ stishovite



α -cristobalite space group ($P4_12_12$) is a subgroup of stishovite space group

Figure . Calculated total energy ($+1.15 \times 10^6$, kJ/mol) *versus* volume curves for α -cristobalite and stishovite phases (left), and calculated energy profile (relative to the cristobalite structure) across the transition (right). Energy in kJ/mol, volume in Å³.

Tetragonal unit cell: normalized c/a ratio appropriate transformation coordinate.

Change in coordination: Si from four to six, O from two to three.

O-Si-O angle closes to 90.

Small increase of Si-O distance.

Oxygen lone pairs play an important role in the creation of new bonds across the transition path.

Attractors of Si L-shell point toward vertices of a tetrahedra and a cube, respectively, in α -cristobalite and stishovite.

LOCCC should be revisited.

Física y Química bajo alta presión desde cálculos ab initio

**Grupo: Estructura electrónica y simulación
de sólidos y materiales**

Alfonso Muñoz

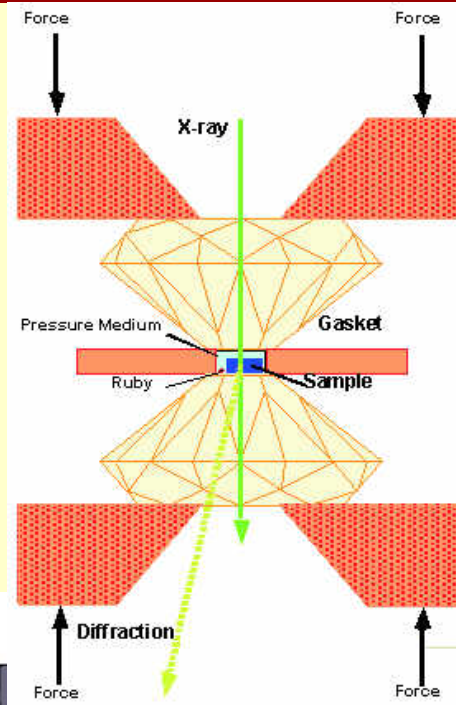
**Dpto. de Física Fundamental II
Universidad de La Laguna. Tenerife**



Universidad
de La Laguna



High Pressure experiments: Diamond Anv. Cell

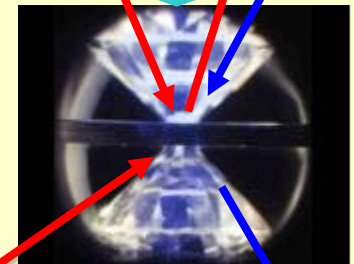


DAC

Vol. $< 0.002 \text{ mm}^3$

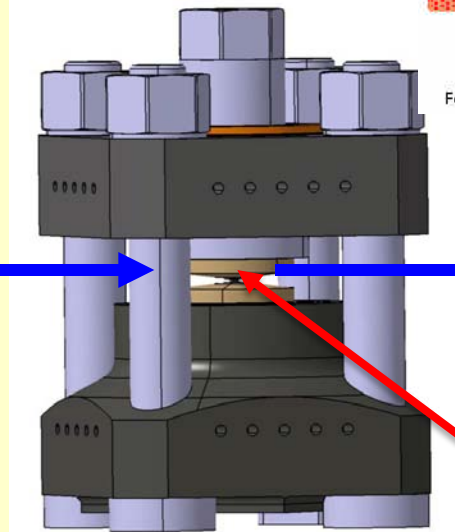
Raman

DRX



EXAF, INS etc...

Laser heating



Neutrons

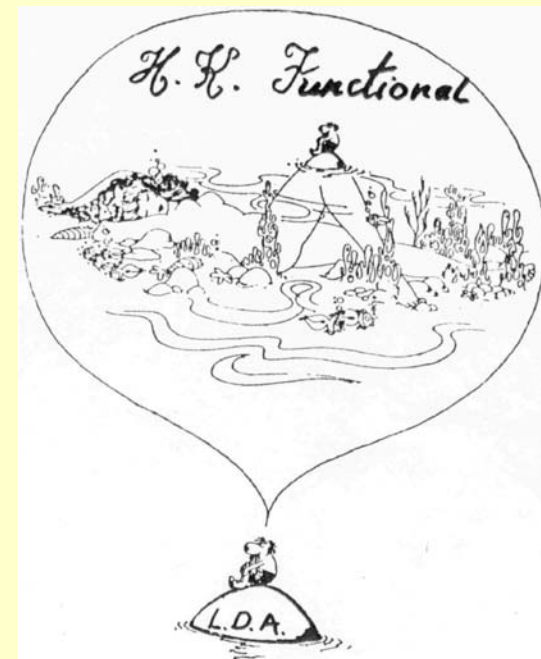
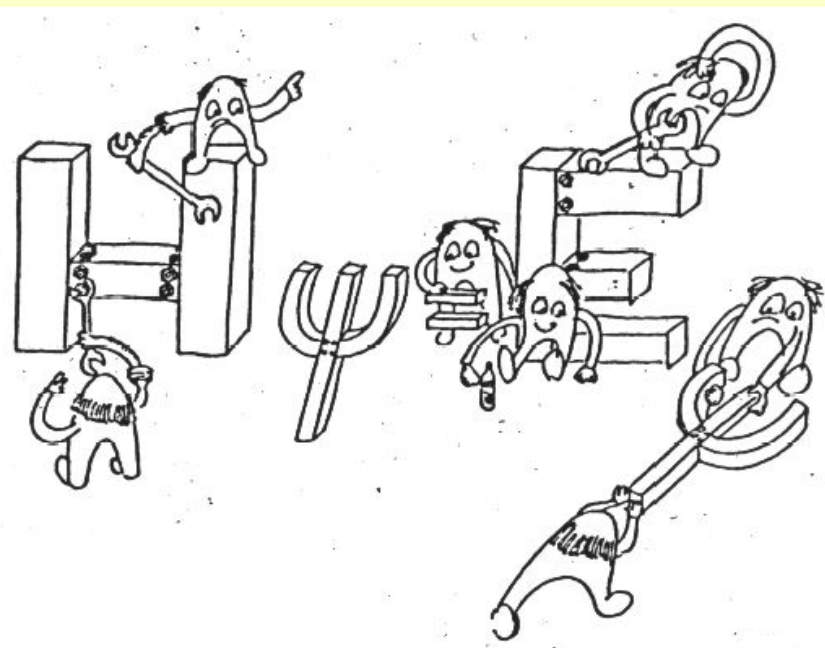
Vol. $30-60 \text{ mm}^3$

Paris-Edimburg (PE)

Simulación ab initio

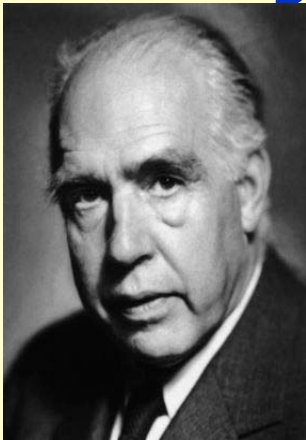
La simulación de materiales a escala atómica basada en "first principles quantum mechanics", tiene ya un importante papel en el estudio de la materiales bajo condiciones extremas.

¡Toda teoría exacta está basada en la idea de APROXIMAR ! DFT



“An expert is a person who has made all the mistakes that can be made in a very narrow field”.

“Prediction is very difficult, especially about the future”.



Niels Bohr

High-pressure phase of gallium nitride

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(Received 13 May 1991; revised manuscript received 22 July 1991)

The recently found high-pressure phase of GaN is studied theoretically, using the density-functional theory. The $E(V)$ phase diagram set up from the calculated total energies shows that the crystal structure of this phase is rocksalt or NiAs, and the calculated energy bands indicate that both modifications are semiconducting.

RAPID COMMUNICATIONS

44

HIGH-PRESSURE PHASE OF GALLIUM NITRIDE

10 373

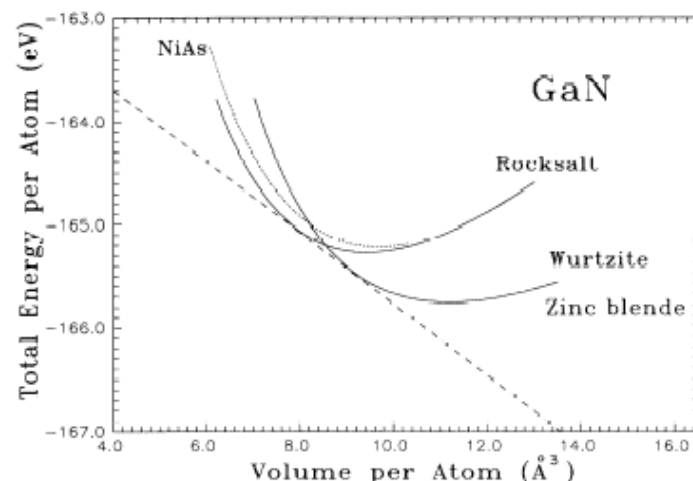


FIG. 1. The $E(V)$ equations of state for the energetically most favorable modifications of GaN. Solid lines represent the density-functional pseudopotential calculations with plane-wave

and 30 GPa (downstroke).

The calculated data in Fig. 1 provide further quantities of interest: The transition volumes turn out to be $V_t(\text{wurtzite})/V_0=0.82$ and $V_t(\text{NaCl})/V_0=0.71$, where $V_0=11.18 \text{ \AA}^3$ is the calculated equilibrium volume per atom in the wurtzite structure. The calculated equilibrium volume in the rocksalt structure is $V_0(\text{NaCl})/V_0=0.84$, in other words the transition wurtzite $\rightarrow$ rocksalt makes the volume per atom (at ambient pressure) smaller by $\Delta V_0 \equiv V_0(\text{NaCl}) - V_0(\text{wurtzite}) = 1.77 \text{ \AA}^3$; the corresponding increase in energy, between the two minima of $E(V)$, is $\Delta E_0=484 \text{ meV/atom}$.

The static data on GaN in the rocksalt phase can be predicted as $a_0=4.22 \text{ \AA}$, and the bulk modulus $B_0=244 \text{ GPa}$; the structure is semiconducting, with the (density-functional-)indirect gap $\Gamma-X$ of 0.5 eV; for the direct gap at Γ one obtains 2.5 eV. The alternative high-pressure modification, the NiAs structure, is semiconducting as well, with a direct gap of 1.2 eV at Γ ; this structure is hex-

Ab initio methods provide an alternative and complementary technique to the experiments under extreme conditions.

Well tested:

REVIEWS OF MODERN PHYSICS, VOLUME 75, JULY 2003

High-pressure phases of group-IV, III–V, and II–VI compounds

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R. J. Needs[§]

TCM Group, Cavendish Laboratory, Cambridge CB3 0HE, United Kingdom

T= 0 K calculations

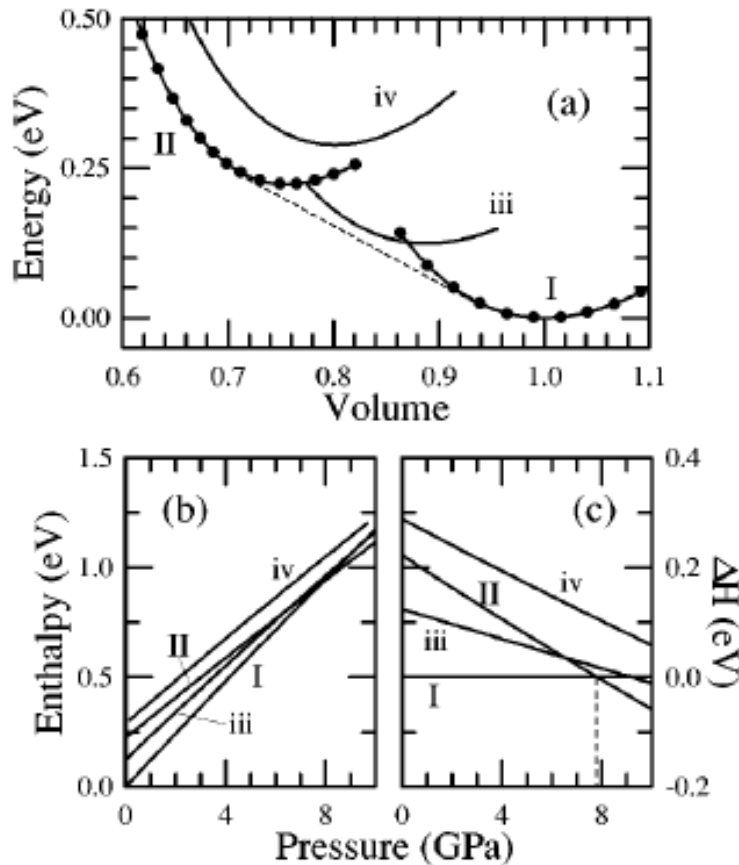


FIG. 3. Typical output data from a series of total-energy calculations: (a) Schematic diagram of the energy-volume curves for four phases of a material. For phases I and II we have indicated by filled circles the discrete set of calculated $E(V)$ points. The curves correspond to fitting of the calculated points [in the present case, using a Murnaghan-type expression (Mur

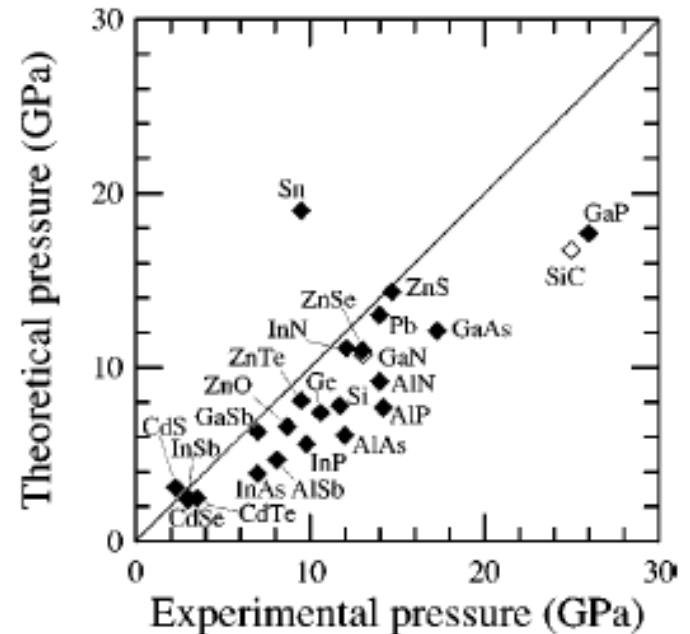
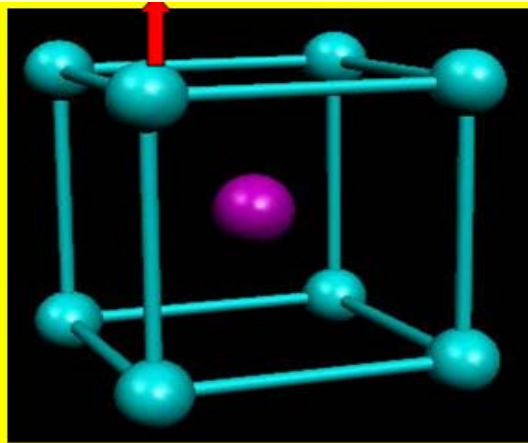


FIG. 11. Theoretical LDA coexistence pressures vs experimental transition pressures for the first phase transition in group-IVA elements and IIIA–VA and IIB–VIA compounds. The data are those in Tables I–III. The values of the pressures for SiC and GaN ($\diamond$) have been divided by 4 in order to represent them on the scale shown.

Dynamical properties under pressure..

The construction of the dynamical matrix at gamma point is very simple:

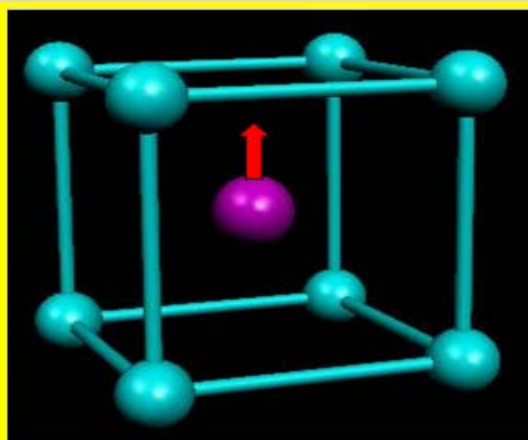


Potential: $V = \frac{1}{2} \sum_{n,m} \Phi(n, m) u(n) u(m)$

Force: $F(n) = - \sum_m \Phi(n, m) u(m)$

Dynamical matrix:

$$D(k) = 1/M \sum_m \Phi(0, m) \exp[-ik(R(0)-R(m))]$$



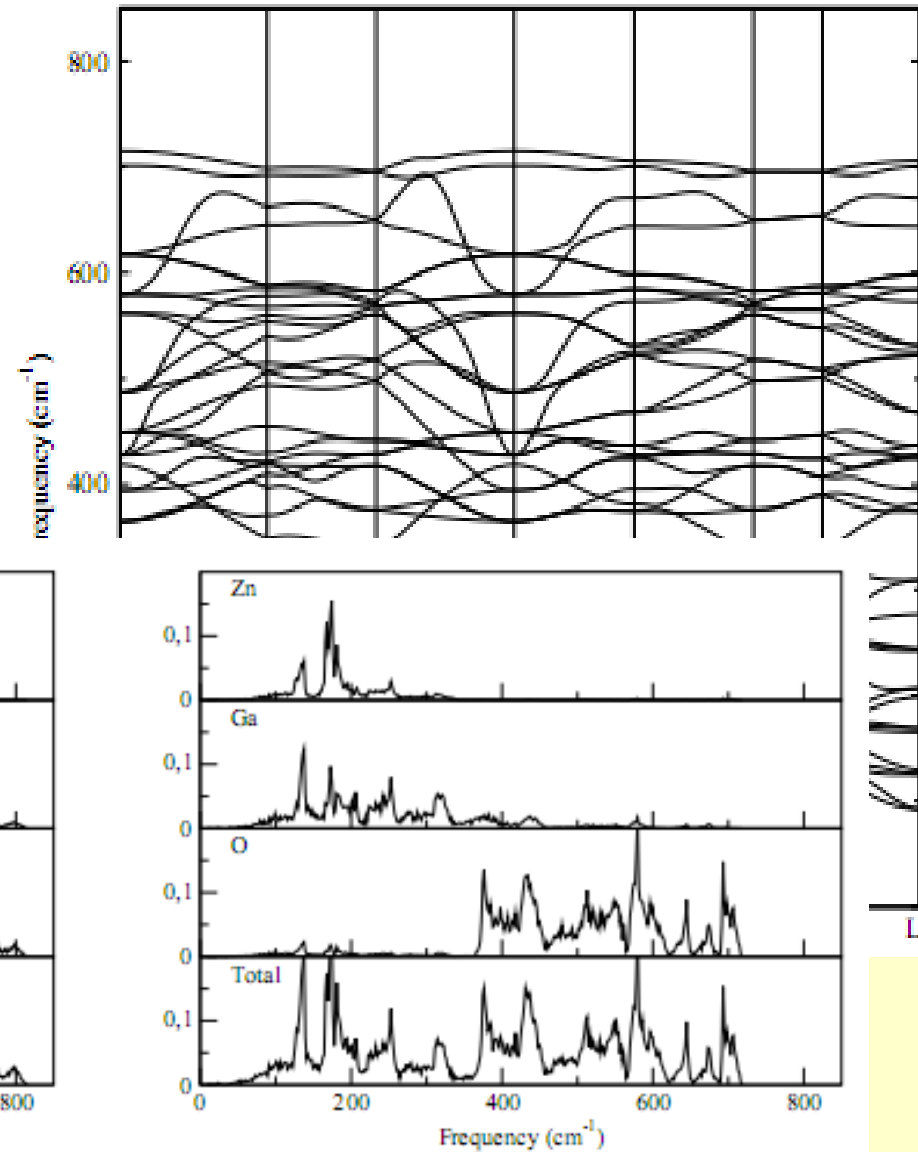
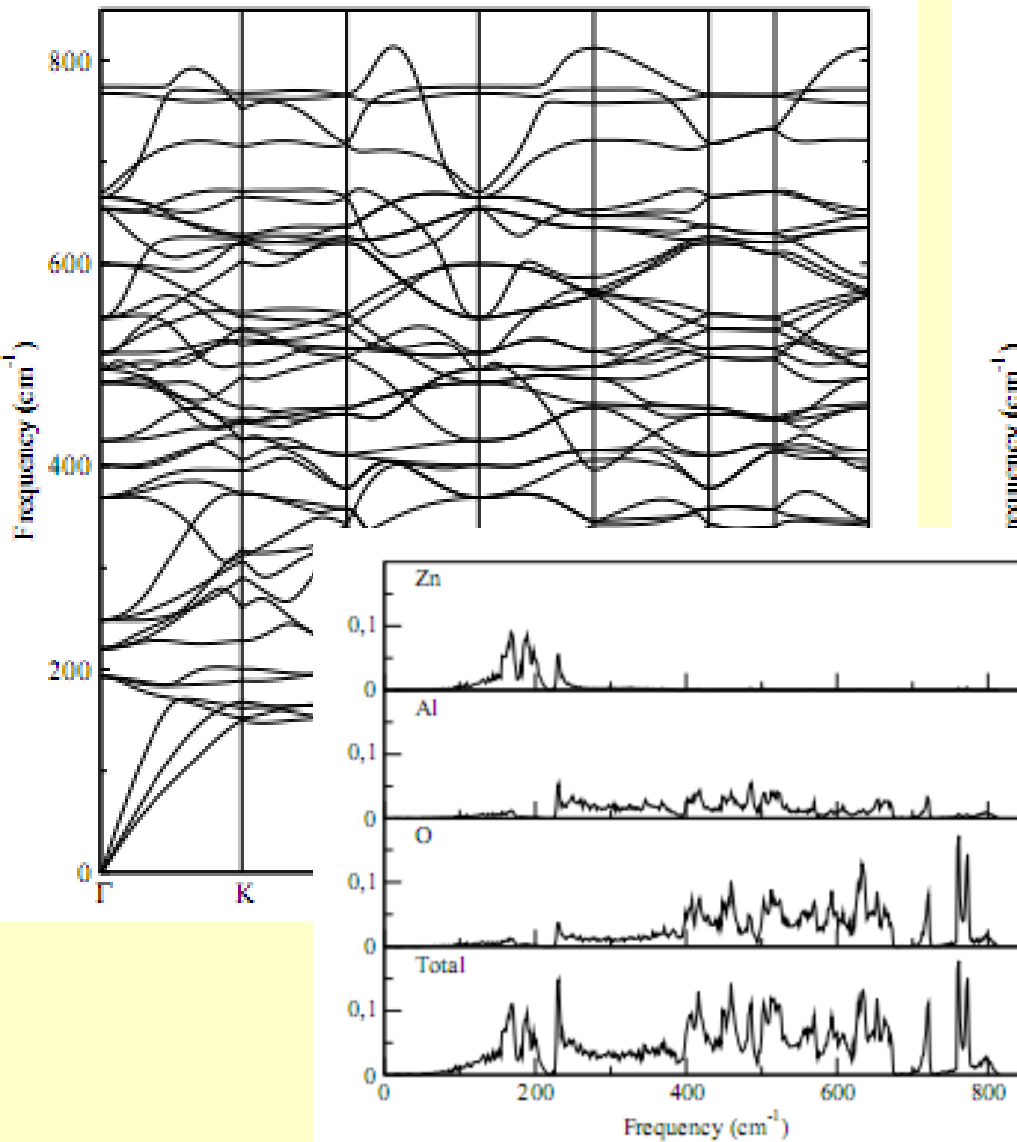
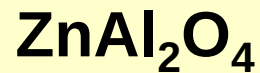
Phonons: $\omega^2(k) e(k) = D(k) e(k)$

Hellmann-Feynman forces $F(n)$ arise due to displacements of an atom in supercell

$$F(n) \longrightarrow \Phi(n, m) \longrightarrow \omega(k)$$

Potential: $V = \frac{1}{2} \sum_k \omega^2(k) |Q(k)|^2$

Phonon dispersion at equilibrium volumes.



Spin-orbit, phonon dispersión, temperature effects, etc....

DFPT

CARDONA *et al.*

PHYSICAL REVIEW B 80, 195204 (2009)

TABLE I. Values at $k=0$ of the spin-orbit splitting Δ_0 , the negative p - s gap E_0 (in eV) and the lattice constant a_0 (in Å) as calculated with various codes and experimentally determined. Notice the negative value of Δ_0 calculated by our three methods for HgS. It is due to an admixture of p wave functions of the cation with $5d$ of Hg (the latter have a negative contribution similar to results found for CuCl, ZnO, and CuGaS₂). The differences of Δ_0 for the different computational methods are due to minor differences in the compensating p and d contributions. The negative Δ_0 of β -HgS has already been mentioned recently (Refs. 22 and 23).

		HgS	HgSe	HgTe
Δ_0 (eV)	VASP-LDA	-0.111	+0.23	+0.783
	ABINIT-LDA	-0.18	+0.34	+0.81
	VASP-GGA	-0.091	+0.25	+0.751
	Overhof		+0.48	+1.13
	Experimental	-0.25 ^a	+0.38 ^b	0.9 ^b

Inverted s-o interaction.
Contribution of the negative splitting of 5d Γ_{15} states of Hg wich overcompesate the positive splitting of the S 3p.

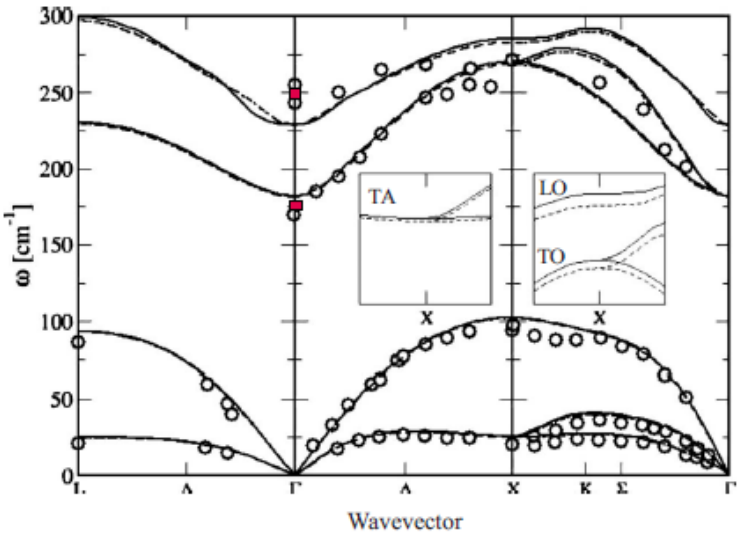


FIG. 4. (Color online) Phonon dispersion relations of β -HgS calculated with the ABINIT-LDA code with (solid line) and without (dashed line) s - o coupling. The circles were obtained with INS (Ref. 50). The LO and TO phonons at $k \sim 0$ (red) squares were obtained by Raman scattering (Ref. 14). The frequency scales in the insets have been expanded to show the effect of the s - o around X.

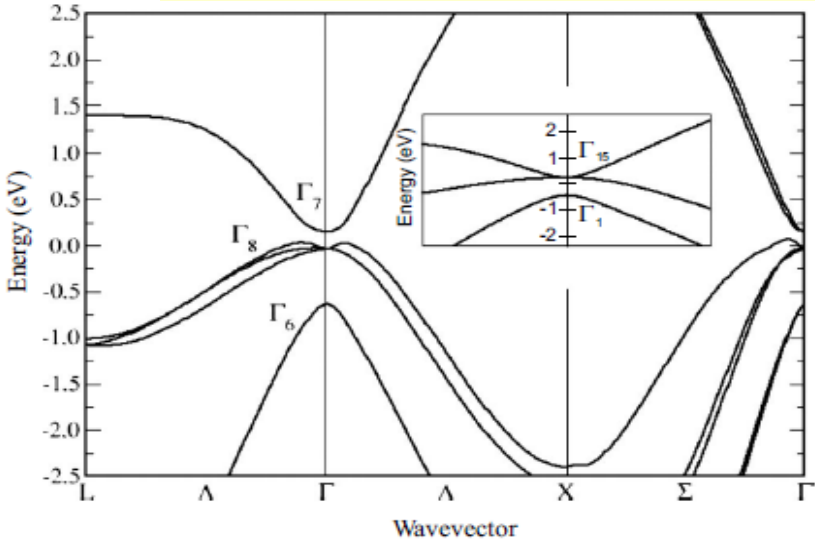


FIG. 2. Electronic band structure of β -HgS calculated with the ABINIT code in the LDA approximation (see Sec. II) using the lattice parameter $a_0=5.80$ Å obtained by total energy minimization as in Fig. 1, but with the energy scale enlarged so as to display the details of the top valence bands, including s - o splitting, and the lowest conduction band around Γ . The Γ_8 - Γ_7 separation corresponds to the negative s - o splitting Δ_0 . Γ_6 - Γ_8 is the E_0 gap. The inset represents the band structure without s - o splitting near the Γ point.

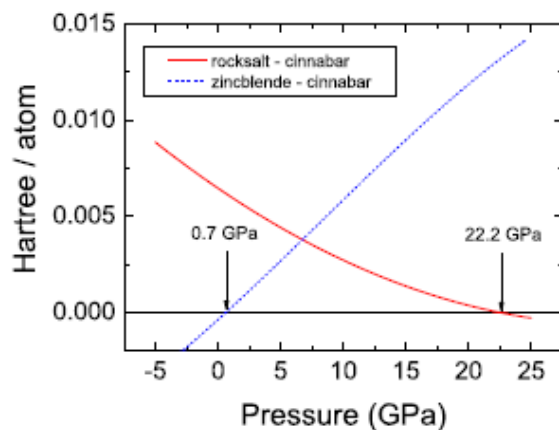


FIG. 9. (Color online) Enthalpy of the three phases of HgS calculated with the ABINIT-LDA code with s - o interaction. Cinnabar and rock-salt phases are basically degenerate (within any reasonable error estimates) at $p=0$, although formally, their enthalpies cross at ~ 0.7 GPa. The cinnabar $\rightarrow$ rock salt transition is predicted to occur at ~ 22 GPa. Experimental data place it at 20.5 GPa (Ref. 64).

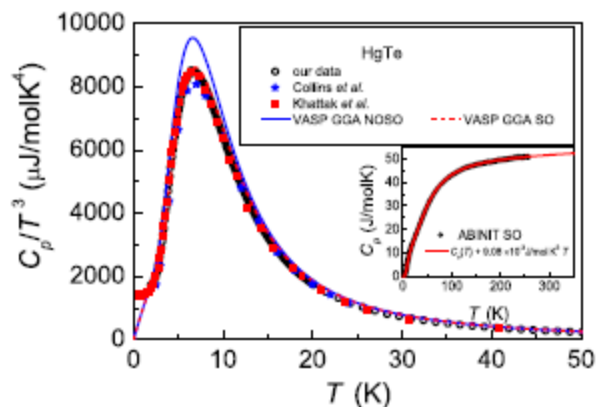


FIG. 15. (Color online) C_v/T^3 vs T for HgTe calculated with both, ABINIT-LDA and VASP-GGA codes including and not including s - o interaction compared with our experimental data. The inset depicts $C_v \approx C_p$ obtained by ABINIT with s - o interaction included. A contribution linear in temperature, $9.08 \times 10^{-3} \text{ J/mol K}^2 T$ (Ref. 25), due to thermal expansion has been added to the calculated data.

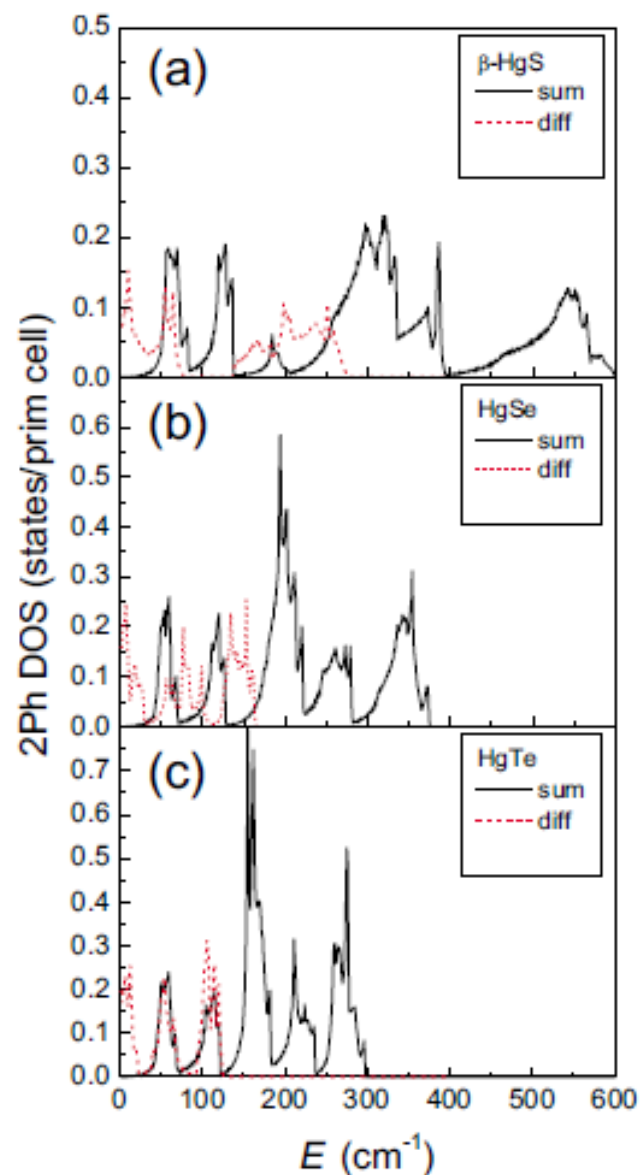


FIG. 8. (Color online) Sum [(black) solid line] and difference [(red) dashed line] of the two-phonon DOS of β -HgS, HgSe and HgTe. The wave vectors of the two phonons are taken to be equal (but opposite), as required by optical spectroscopies.

ZnS, Phys. Rev B **81** 075207 (2010)
Cardona, ...Muñoz . et al.

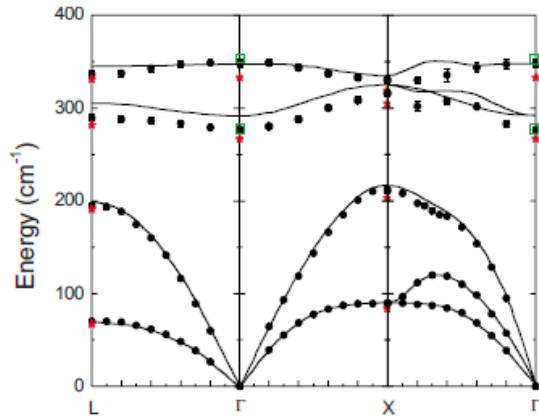


FIG. 3. (Color online) Phonon-dispersion relations of zb-ZnS, calculated with the ABINIT-LDA code, compared with the results of INS (dots, Ref. 55). The (green) squares represent the Raman frequencies measured at low temperatures. The stars display *ab initio* calculations performed with the CASTEP-GGA code (Ref. 24).

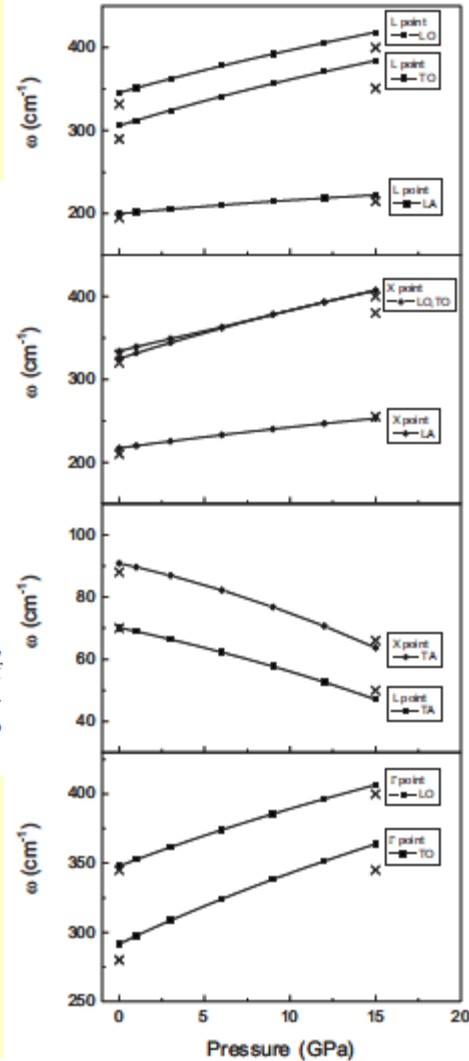


FIG. 16. (Solid lines) Pressure dependence of the phonons of natural ZnS as calculated with the *ab initio* ABINIT-LDA code at the indicated high-symmetry points in the Brillouin zone. Experimental data taken from Ref. 77 are represented by $\times$.

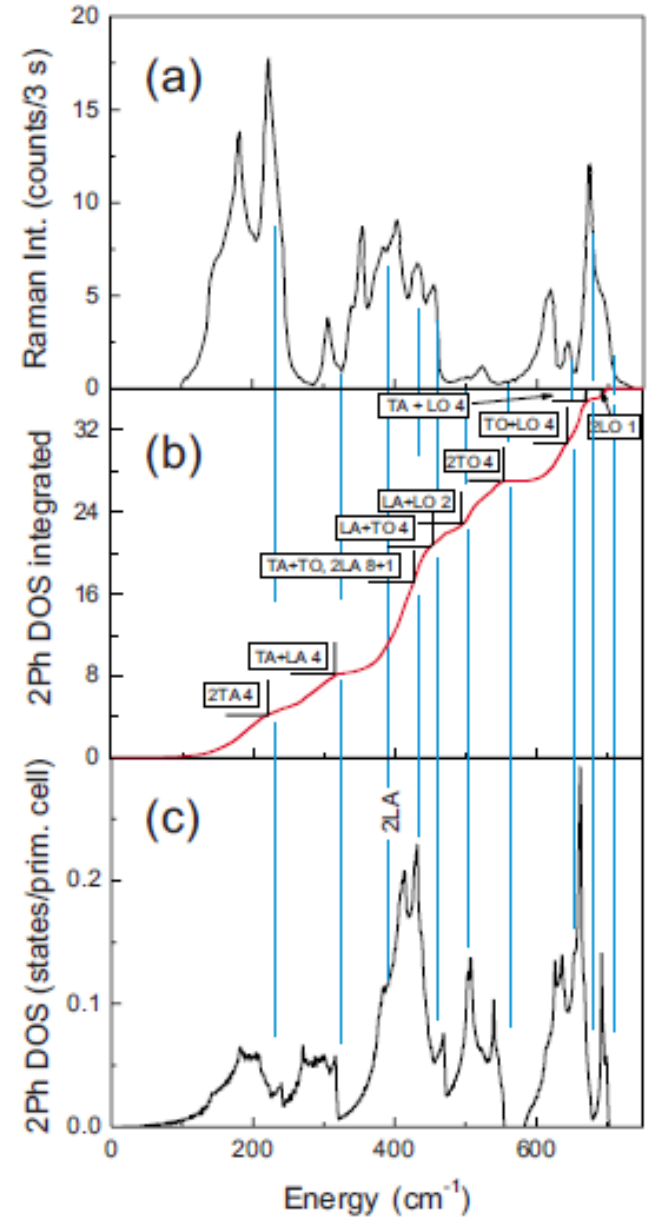


FIG. 5. (Color online) The lower vignette (c) displays the density of states which corresponds to the sum of two phonons with equal but opposite wave vector (2Ph DOS). The middle vignette (b) represents the integral of that 2Ph DOS (see text) whereas the upper vignette (a) shows the corresponding 2Ph Raman spectrum (Ref. 9). The 2Ph DOS is normalized to 36 states per primitive cell.



High-pressure x-ray diffraction and *ab initio* study of $\text{Ni}_2\text{Mo}_3\text{N}$, $\text{Pd}_2\text{Mo}_3\text{N}$, $\text{Pt}_2\text{Mo}_3\text{N}$, $\text{Co}_3\text{Mo}_3\text{N}$, and $\text{Fe}_3\text{Mo}_3\text{N}$: Two families of ultra-incompressible bimetallic interstitial nitrides

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⁴*Departamento de Química, Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, S3000A OM Santa Fe, Argentina*

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(Received 15 September 2010; published 8 November 2010)

We have studied by means of high-pressure x-ray diffraction the structural stability of $\text{Ni}_2\text{Mo}_3\text{N}$, $\text{Co}_3\text{Mo}_3\text{N}$, and $\text{Fe}_3\text{Mo}_3\text{N}$. We also report *ab initio* computing modeling of the high-pressure properties of these compounds, $\text{Pd}_2\text{Mo}_3\text{N}$ and $\text{Pt}_2\text{Mo}_3\text{N}$. We have found that the nitrides remain stable in the ambient-pressure cubic structure at least up to 50 GPa and determined their equation of state. All of them have a bulk modulus larger

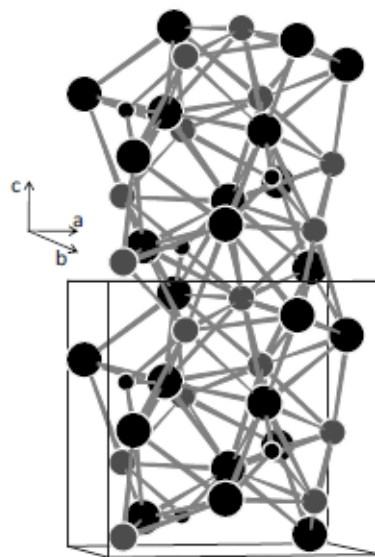
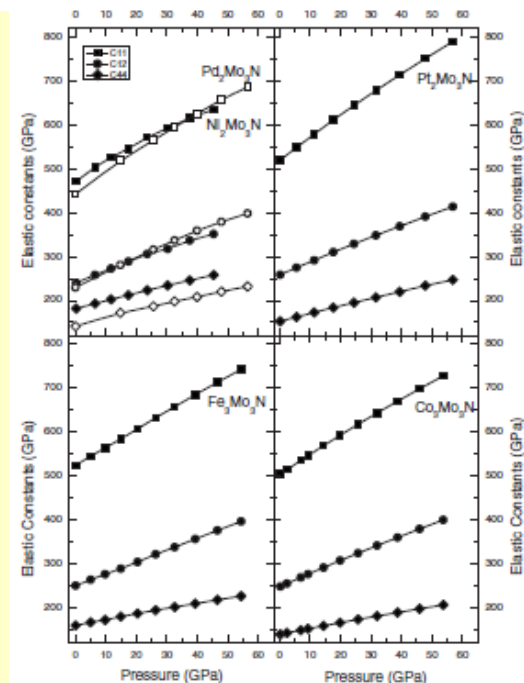


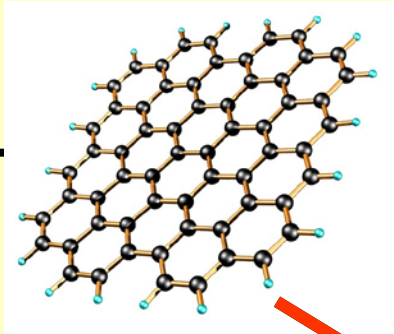
FIG. 1. Schematic representation of the structure of $\text{Ni}_2\text{Mo}_3\text{N}$. The unit-cell and atomic bonds are shown. Large black circles: Mo, small black circles: N, and gray circles: Ni.



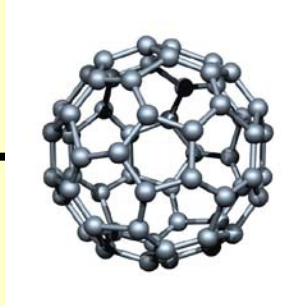
Carbon Clatrathes

Carbon

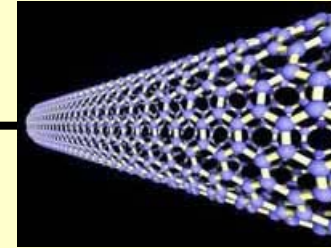
graphite (sp^2)



C_{60}



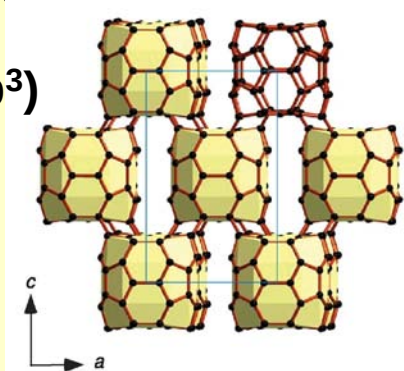
Nanotube



P, T

C_{60} polym.-3D
(15 GPa / 600 °C)

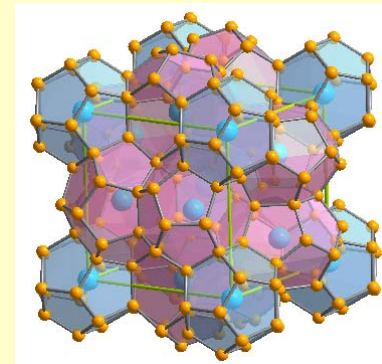
(sp^2 - sp^3)



Diamant
(sp^3)

+

CARBON Clathrates ?



sp^3

Properties of C-clathrate

Hypothetical ! but...

Promising → *ab initio* calculations

- Interesting Mechanical Properties

Bulk modulus 85 % of diamond

The minimum strength of Carbon clathrates should be larger than that of diamond

- Electronic Properties

High Temperature superconductors ?

- $T_c \sim 90$ K

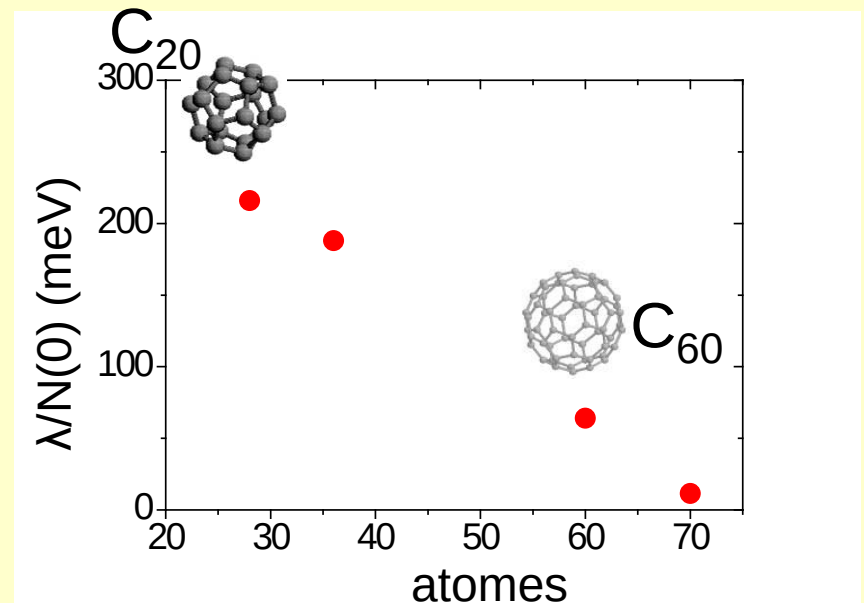
With **F** (type p) or **Li** (type n)

→ Metallic character

It is interesting to search a possible synthesis

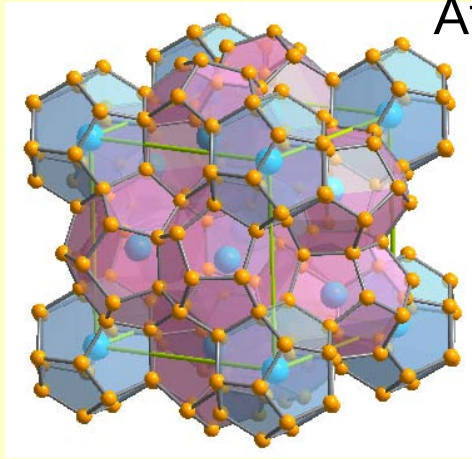
[1] Breda et al, PRB, **62**,130,(2000)

Potentiel d'interaction e-phonon [1]



Carbon Clathrates type-I C_{46} et Li_8C_{46}

ab initio (GGA-DFT) → Energy (Volume , Pressure)
à T=0 K



Atoms interc

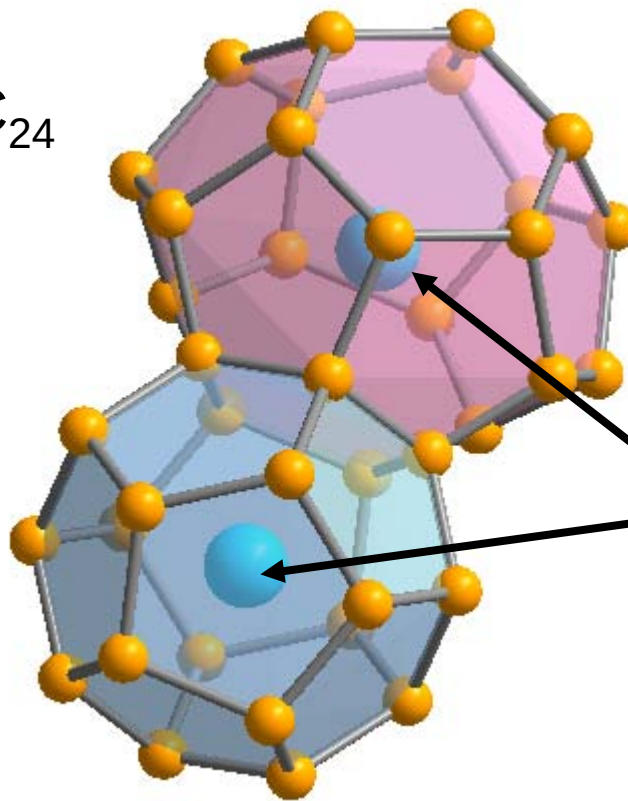


Avoid the conversion (sp^2) → (sp^3)



nano-cage
material

C_{24}



lithium atoms

$Pm\bar{3}m$

C_{46} : $a=6.696 \text{ \AA}$

Li_8C_{46} : $a=6.833 \text{ \AA}$

C_{20}

Carbon clathrates ?

Similar to Si clathrate

$8 BaSi_2 + 30 Si \rightarrow$

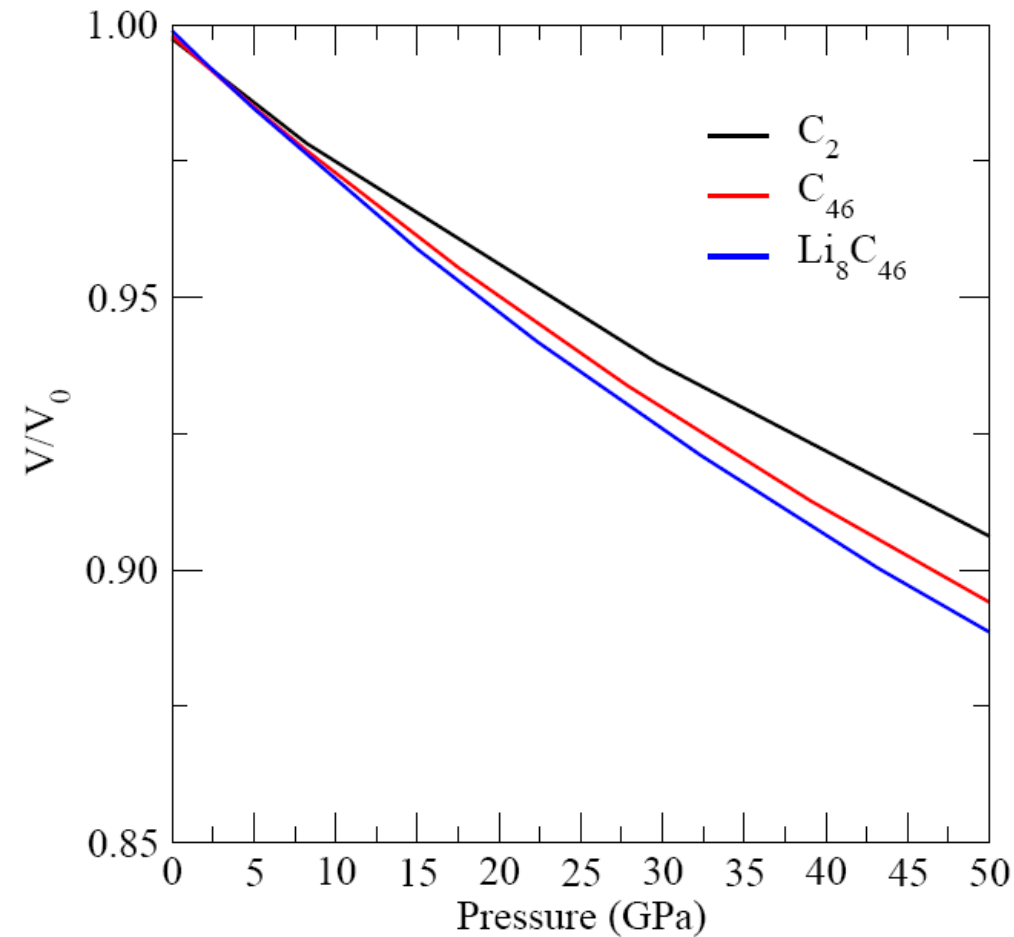
Ba_8Si_{46} (3 GPa/ 800°C)

Ba_8Si_{46} Studied by

Experiments + *ab initio* calculations

0-50 GPa

Diamant (C_2) , C_{46} et Li_8C_{46}



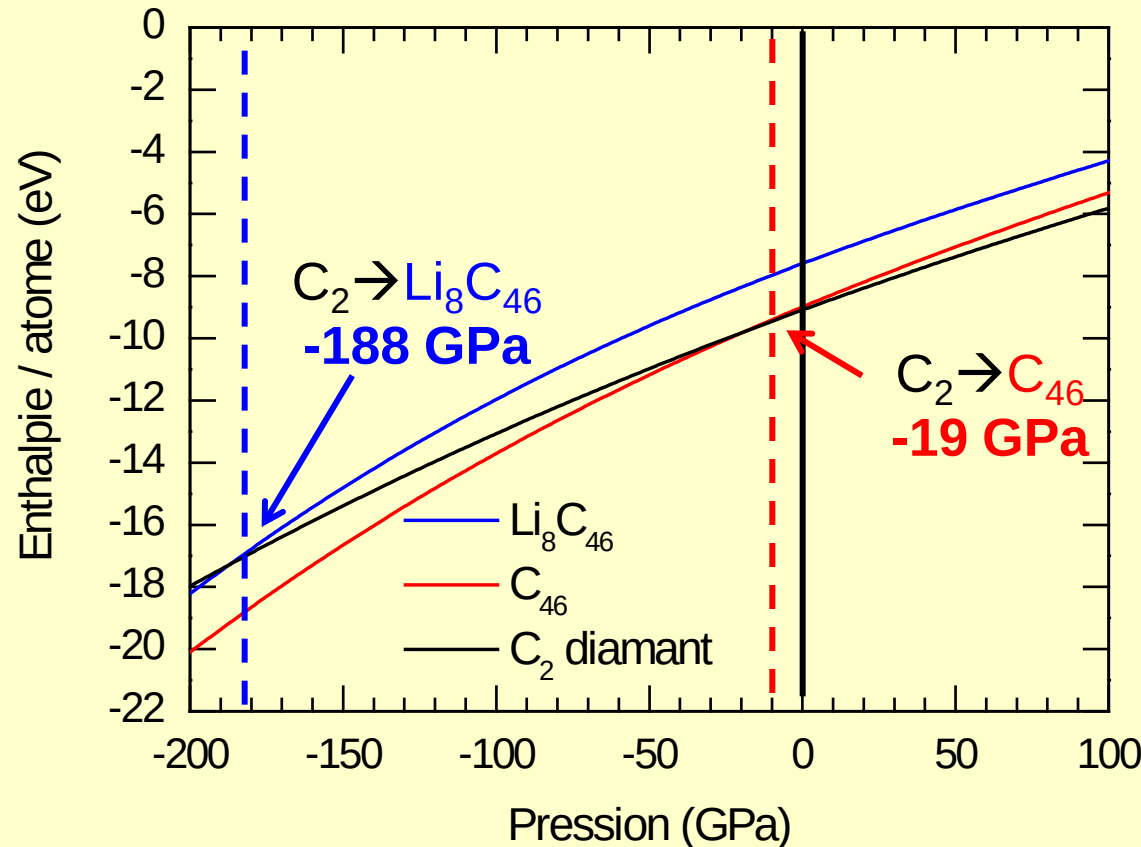
Bulk modulus:

C_2 $B_0 = 437$ GPa (*Exp 442 GPa*)

C_{46} $B_0 = 371$ GPa

Li_8C_{46} $B_0 = 356$ GPa

Stability $H(P) = E + p V$



Clathrates-I (group 14)
 P_t calculated

$Si_2 \rightarrow Si_{46}$ $P_t = -5.9$ GPa [1]

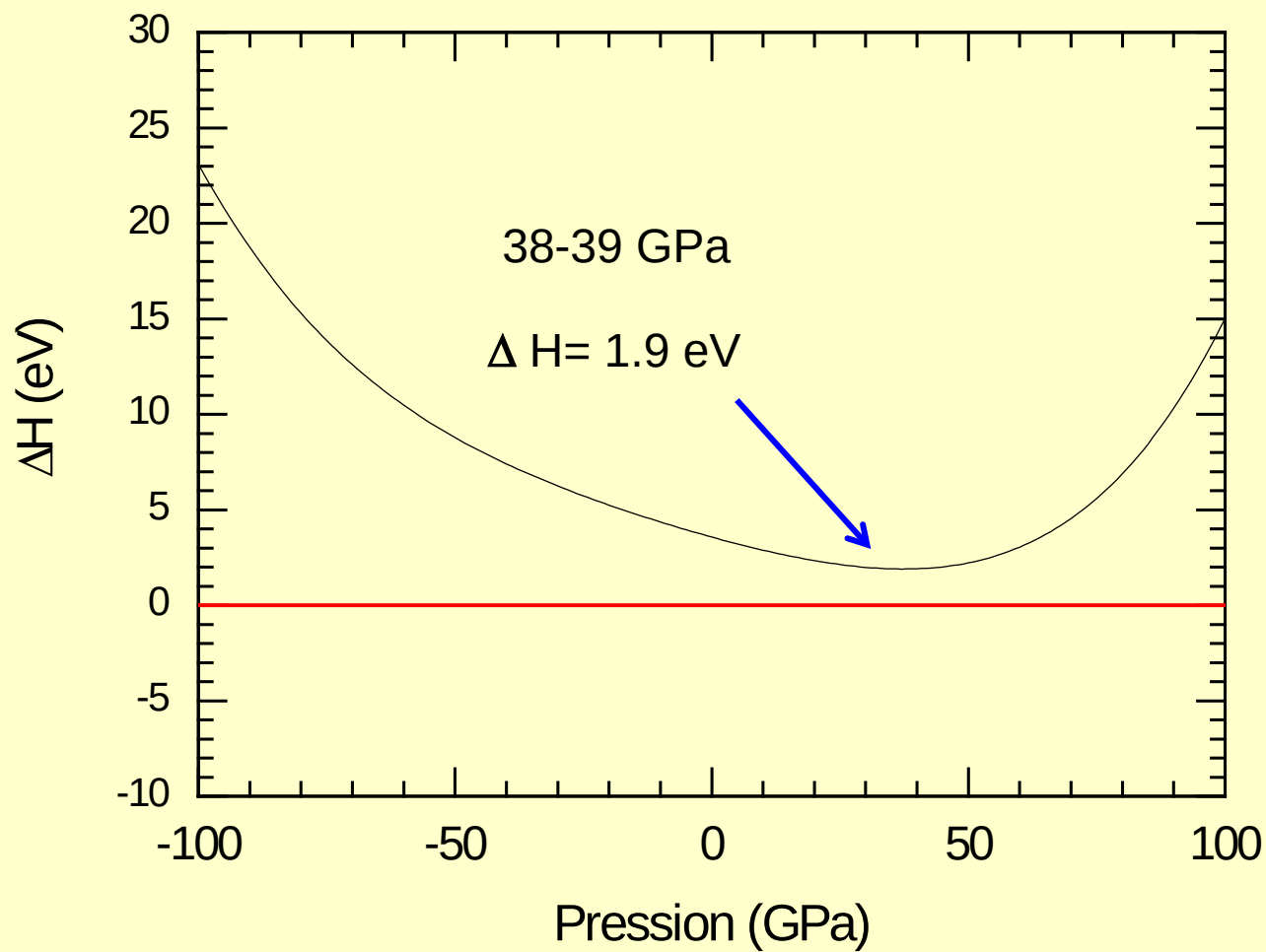
$Ge_2 \rightarrow Ge_{46}$ $P_t = -2.4$ GPa [2]

→ Negative transition Pressures !

[1] Perottoni et Da Jordana, J.Phys.Cond.Mat, 2001

[2] Dong et Sankey, J.Phys.Cond.Mat, 1999

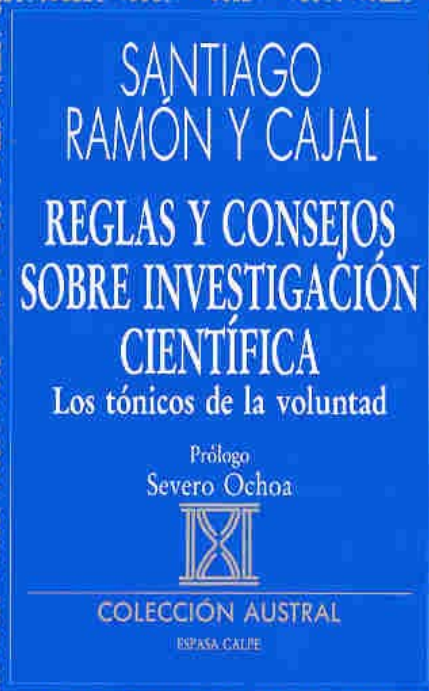
$$\Delta H(\text{Li}_8\text{C}_{46}) = H(\text{Li}_8\text{C}_{46}) - 8H(\text{Li}) - 23H(\text{C}_2)$$



CONCLUSIONS:

- *Ab initio methods can provide interesting and useful information of the physics and chemistry of materials properties under high pressure.*
- *Temperature, S-O etc... effects can be included.*
- *These techniques can help to design and to understand problems in the synthesis process.*

Tengamos la sinceridad de confesarlo: en la mayoría de los casos, frases desalentadoras como las siguientes: "Carezco de laboratorio; ejerzo una profesión incompatible con el vagar indispensable de la labor científica; las obligaciones de familia me roban el tiempo y el dinero exigidos por el trabajo de investigación" etc., etc, representan los alegatos del *dolce far niente* o disculpas de un pratriotismo desmayado.



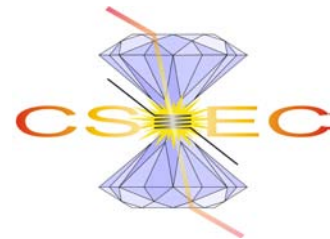
Fácil será reducir a su cabal valor tales lamentaciones e insistir de pasada en esta verdad capital : *para la obra científica los medios son casi nada y el hombre lo es casi todo*"

S. Ramón y Cajal

Electride behaviour of the alkali metals under pressure



Miriam Marqués Arias
Centre for Science at Extreme Conditions
University of Edinburgh

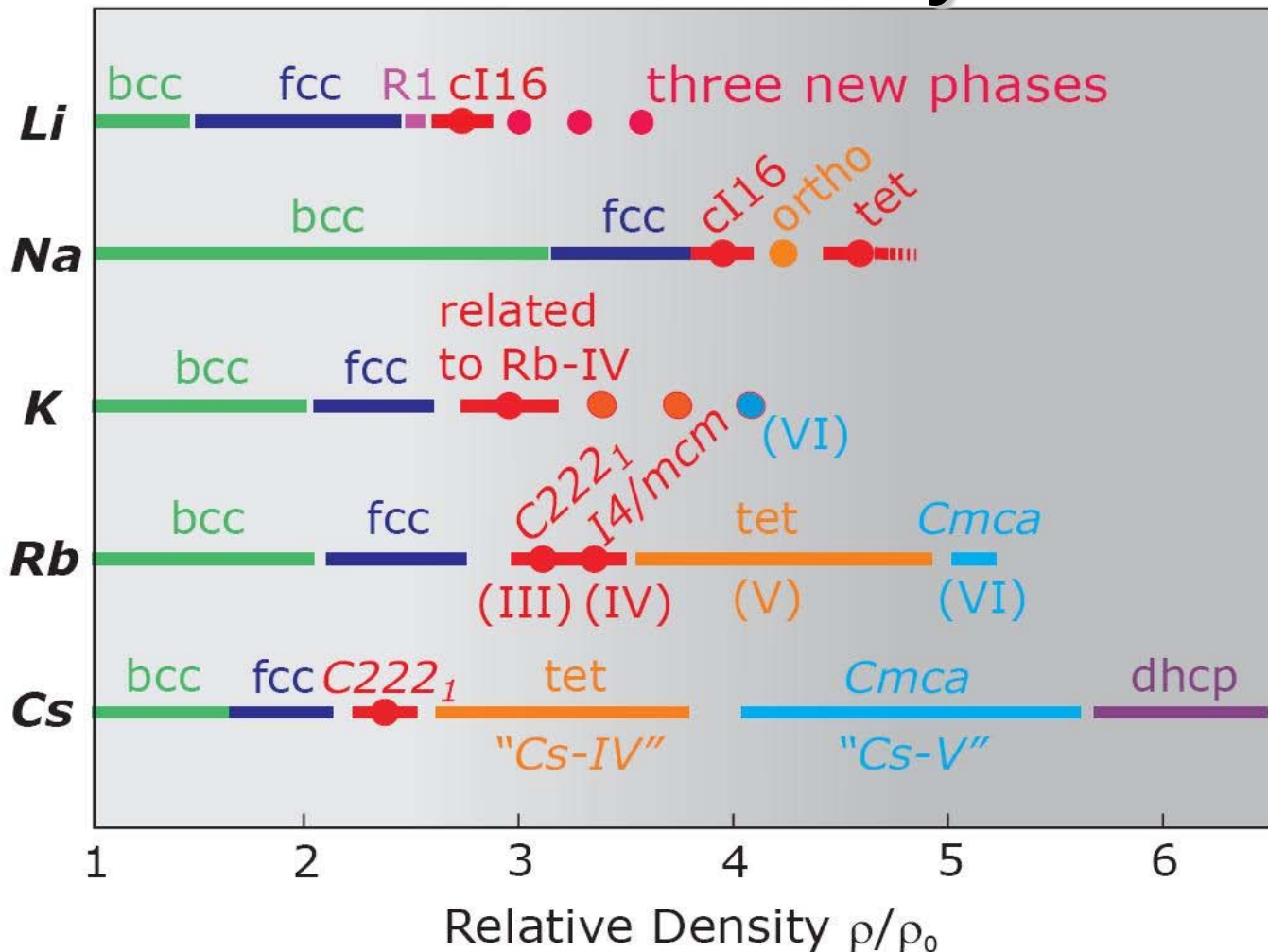




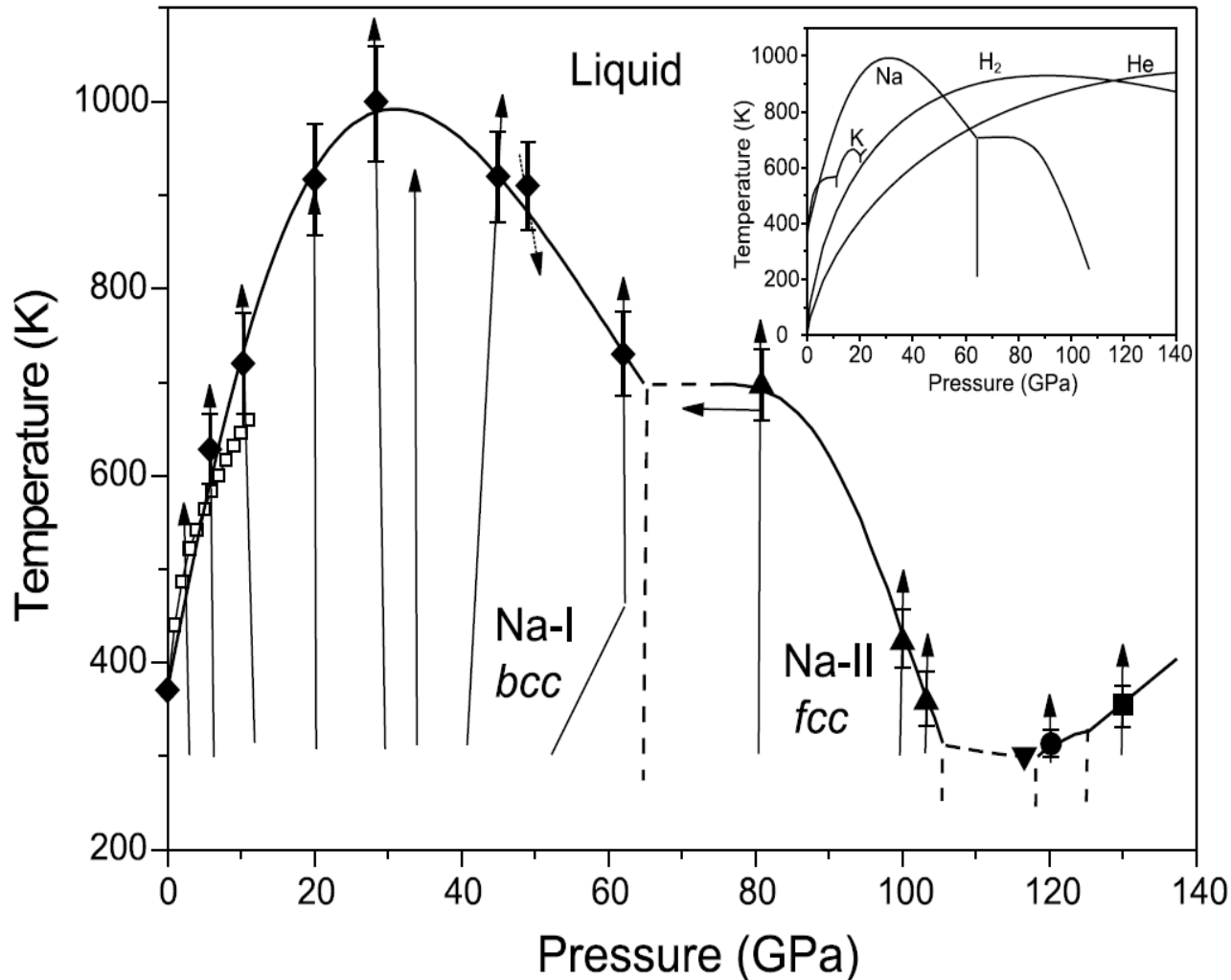
2. Alkali metals at HP

- It is becoming strikingly clear that the free-electron model of simple metals is not applicable when metals are compressed at intermediate pressures.
- New structures appear: open, incommensurate structures
- Unusual properties: decreased conductivity and melting points, superconductivity
- This challenging state of matter has been explained in terms of $s \rightarrow p$ or $s \rightarrow d$ electronic transitions, and more recently related to an **increase of valence electron density in interstitial regions**.
- A new model is required (work in progress)

2. Alkali metals: phases versus relative density

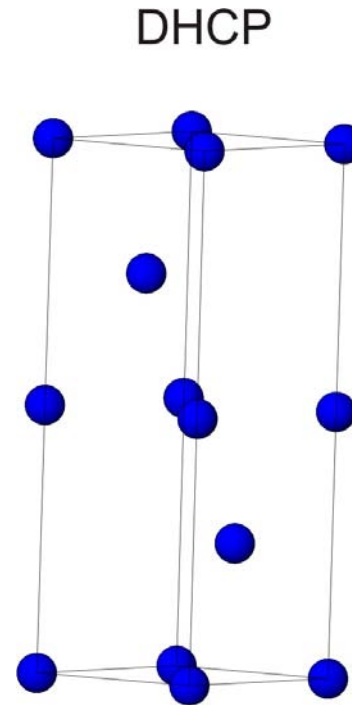
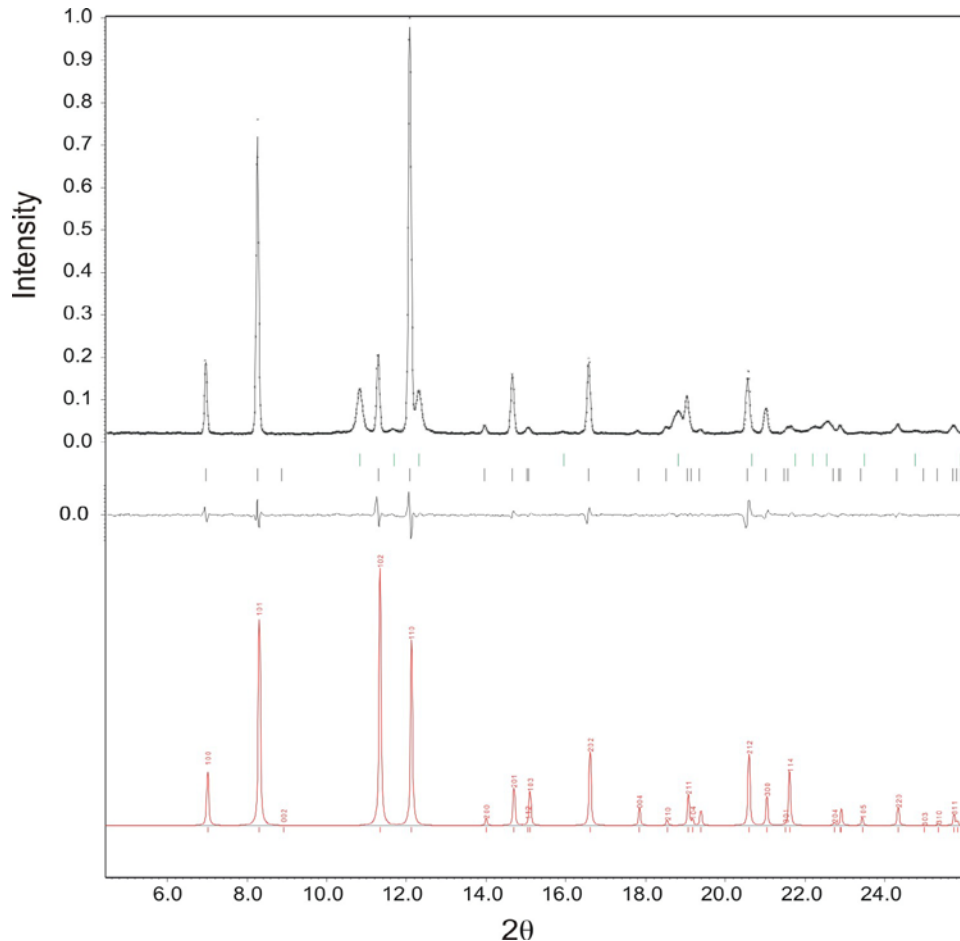


2. Melting curve of Na

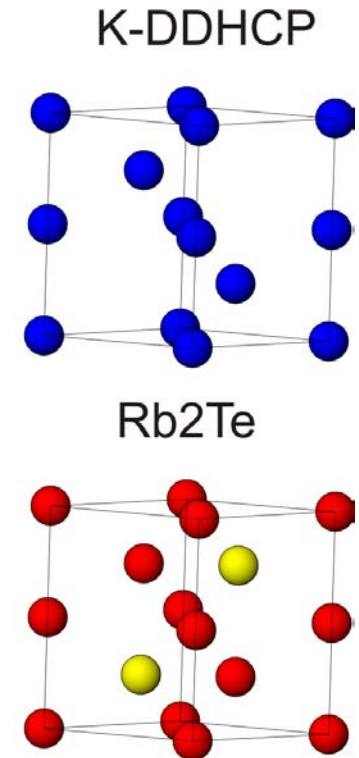


PRL (2005) Gregoryanz, Degtyareva, Somayazulu *et. al.*

3. K: hP4 phase



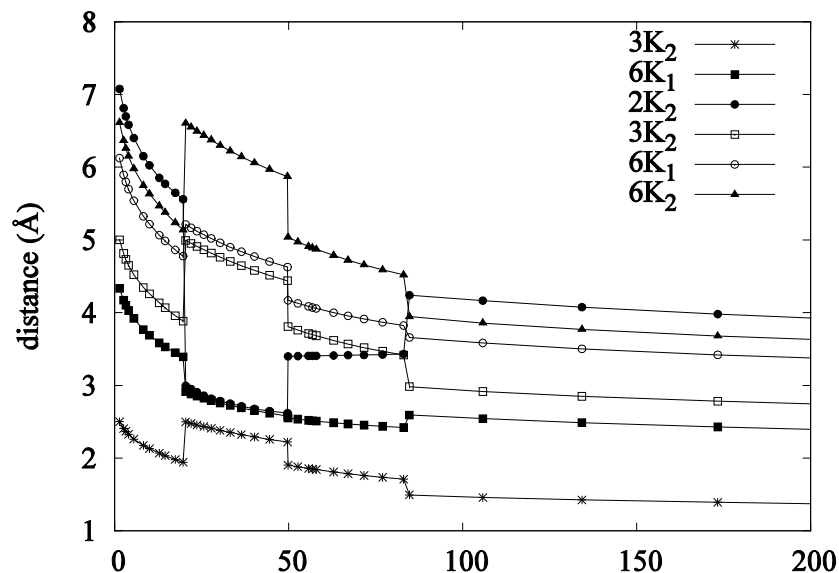
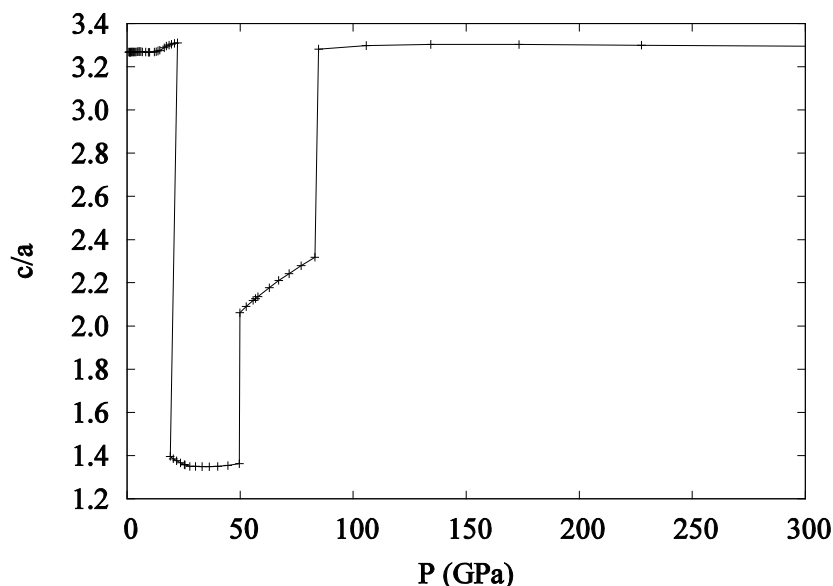
$$c/a=3.266$$



$$c/a=1.36$$

Crystal structure: hexagonal, SG $P6_3/mmc$, two different sites (Wyckoff 2a (0,0,0) and 2c (1/3,2/3,1/4))

3. K: hP4 phase



ATOMIC ARRANGEMENT

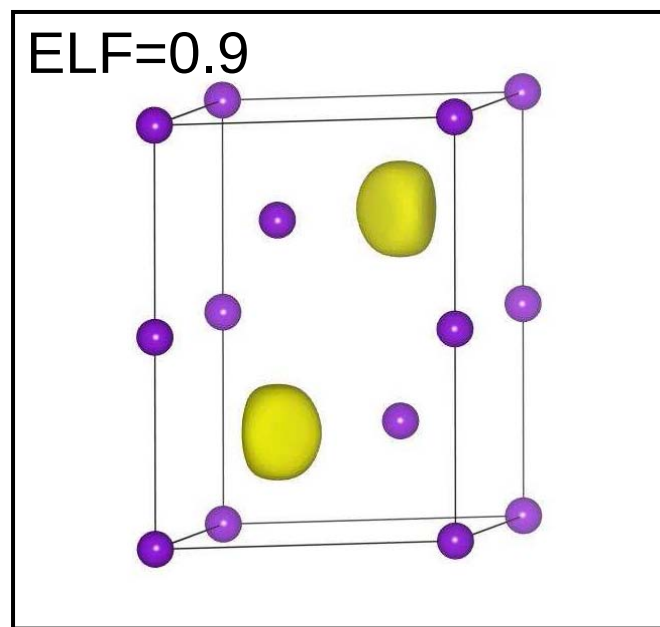
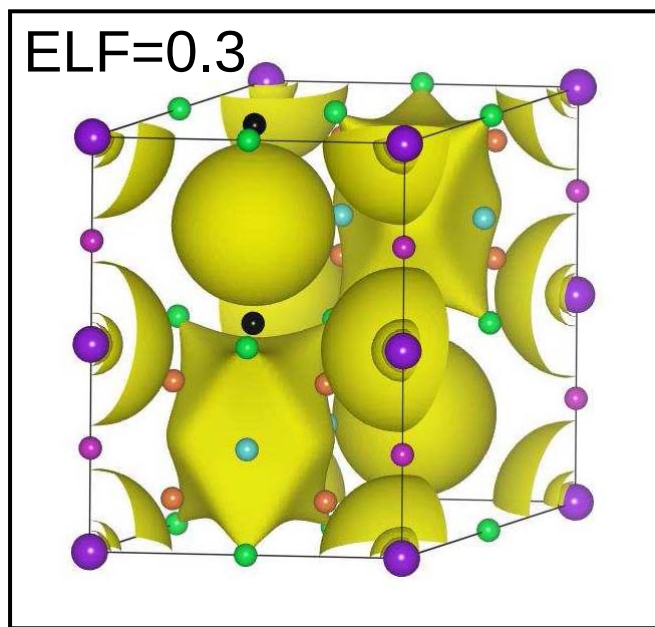
- 20-50 GPa: cation sublattice of Ni₂In-type structures of Na₂S ($c/a=1.31$), Rb₂Te ($c/a=1.29$), Na₂SO₄ ($c/a=1.34$), K₂SO₄ ($c/a=1.37$)
- 50-85 GPa: cation sublattice of Li₂O₂ ($c/a=2.42$), Na₂Se₂ ($c/a=2.25$), K₂Te₂ ($c/a=2.18$)
- striking changes in interatomic distances

3. K: hP4 phase

Localization regions in interstitial voids
 Core-like topology
 Same structure as A_2X compounds!
 Electrons in same position as anions!
 Close packing preserved if are considered!

COMPOUND → IONIC-LIKE

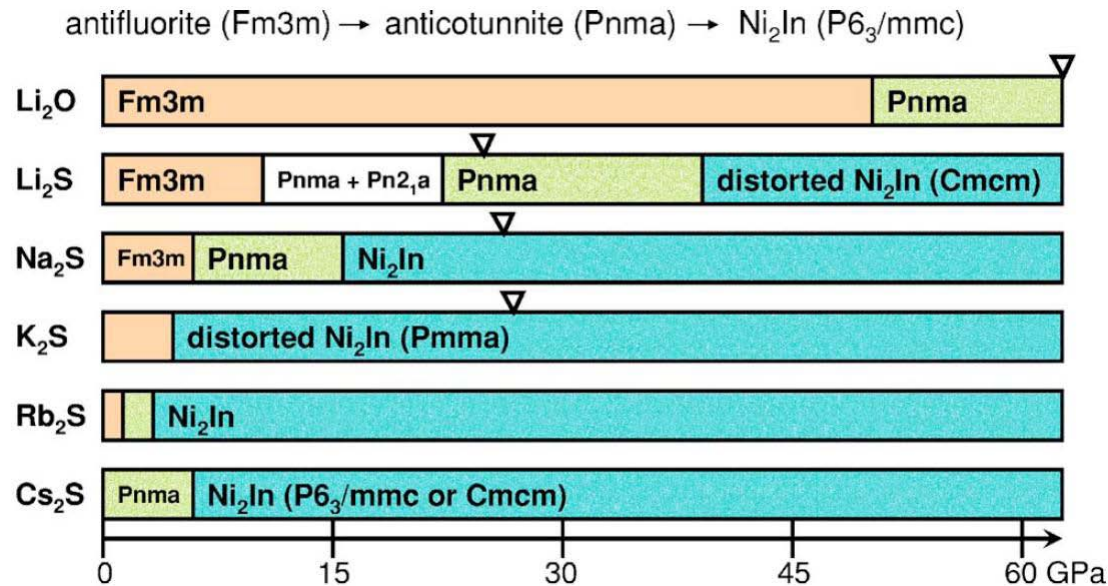
ELECTRONS → PSEUDOANIONS



Experimental potassium at $P=27$ GPa

3. K at 58 GPa?

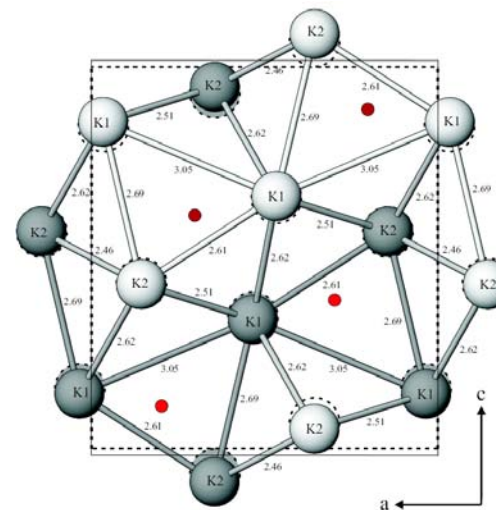
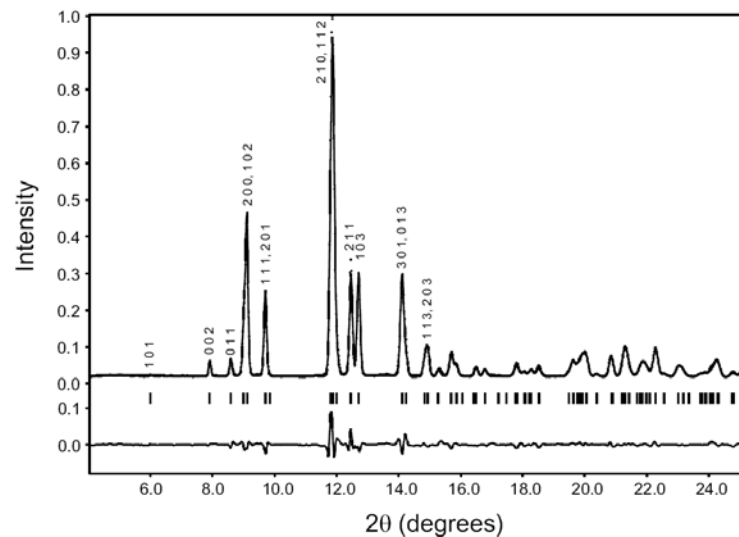
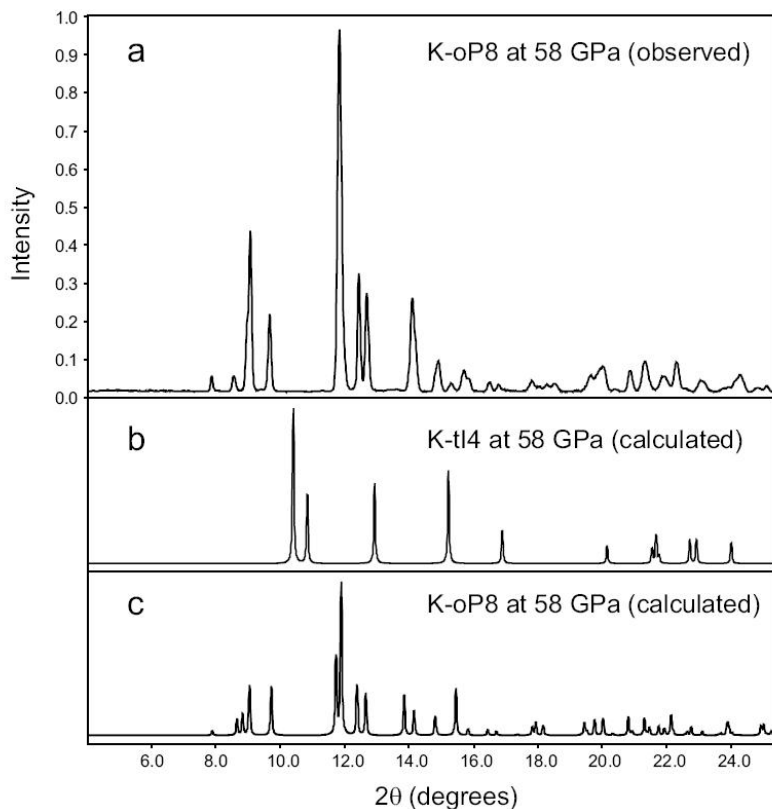
- tl4 structure predicted by variable-cell simulations
- behaviour of alkali-metal chalcogenides?



- cation sublattice of anticotunnite structure:

SG: *Pnma*, Pearson oP8, K1 and K2 atoms locate on 4c sites .
subgroup of the Ni₂In-type structure

3. K: oP8 phase

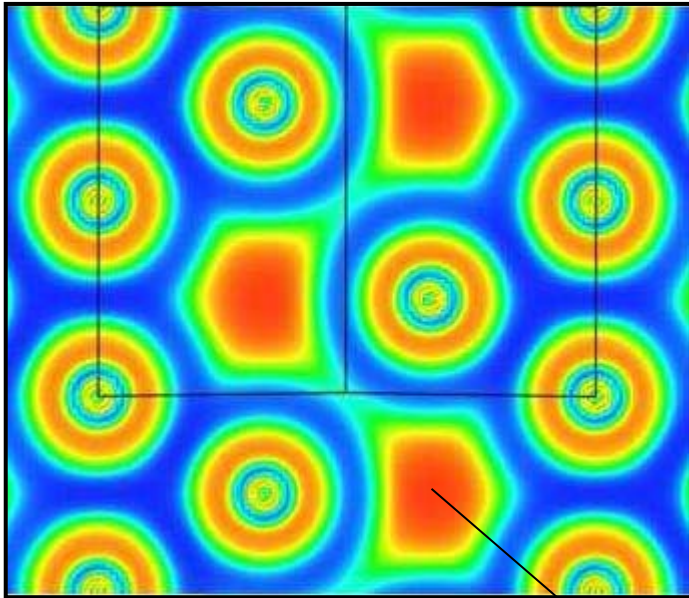


- Similar calculated oP8 and experimental diffraction pattern. Excellent Rietveld refinement.

3. K: electrider phases

K→Alkali chalcogenide

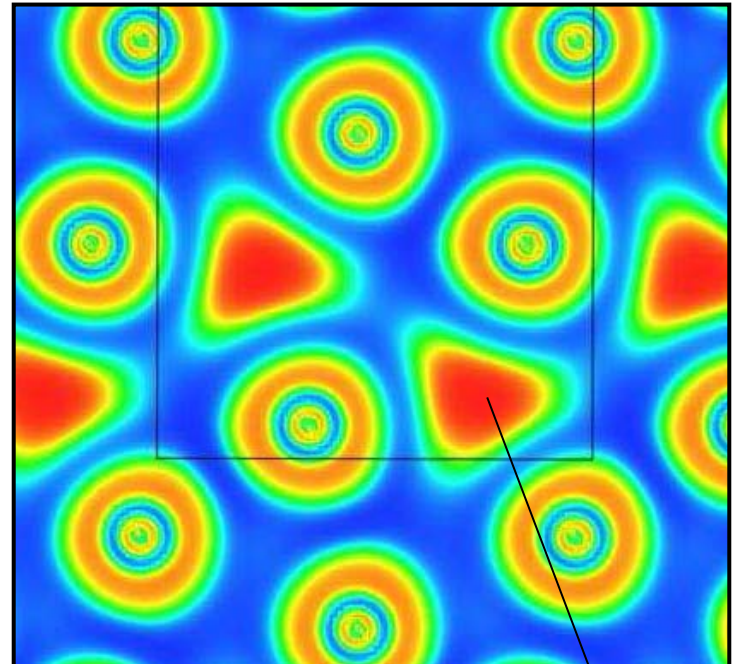
Same structure as A_2X
(Ni_2In)



25 GPa
(ELF ≈ 0.95)
hP4 phase of K.

Chalcogenide
position

Same structure as A_2X
(antidotunnite)



57 GPa
(ELF ≈ 0.95)
oP8 phase of K.

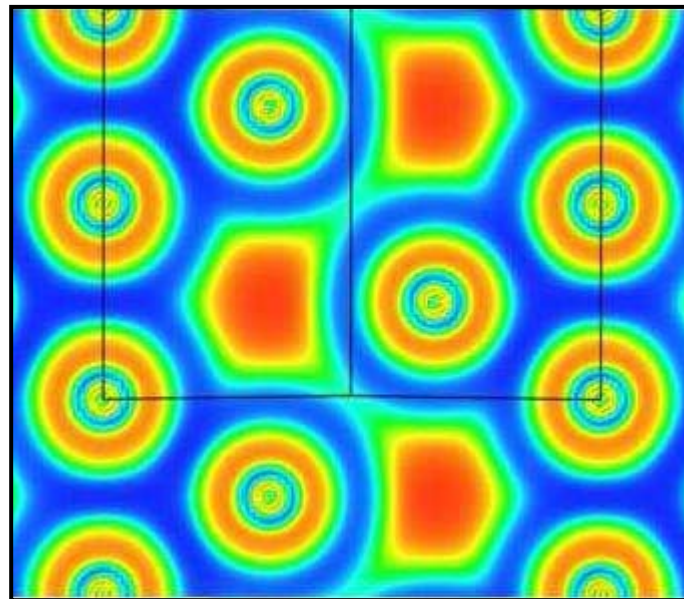
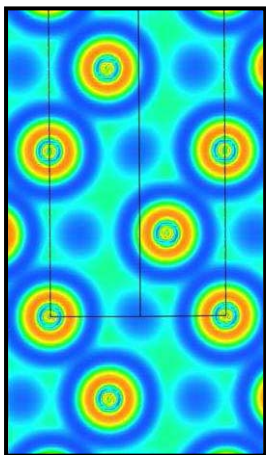
Chalcogenide
position

3. K: origin of phase transitions

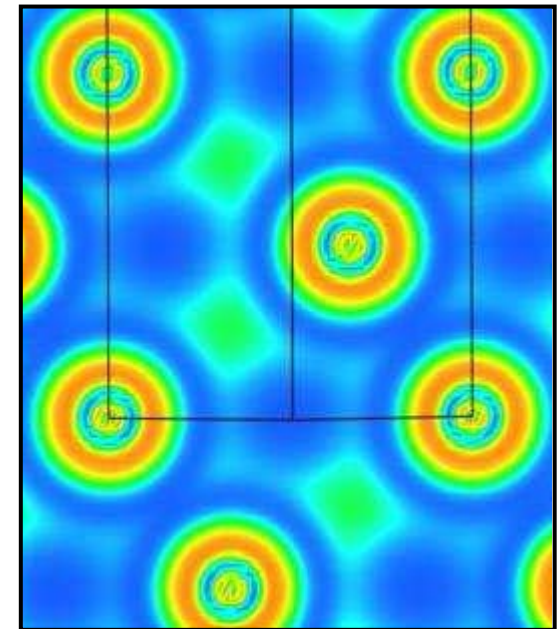
DRIVING FORCE OF DISTORTIONS AT INTERMEDIATE PRESSURES?
GREATER LOCALIZATION

c/a collapse
3.2→1.35

10 GPa:
Normal
metal.

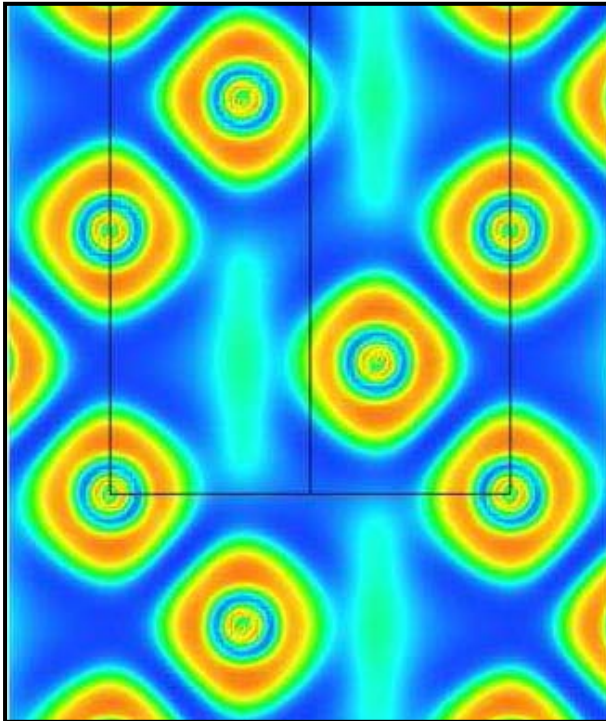


25 GPa: phase transition
towards strong interstitial
localization (ELF=0.95)



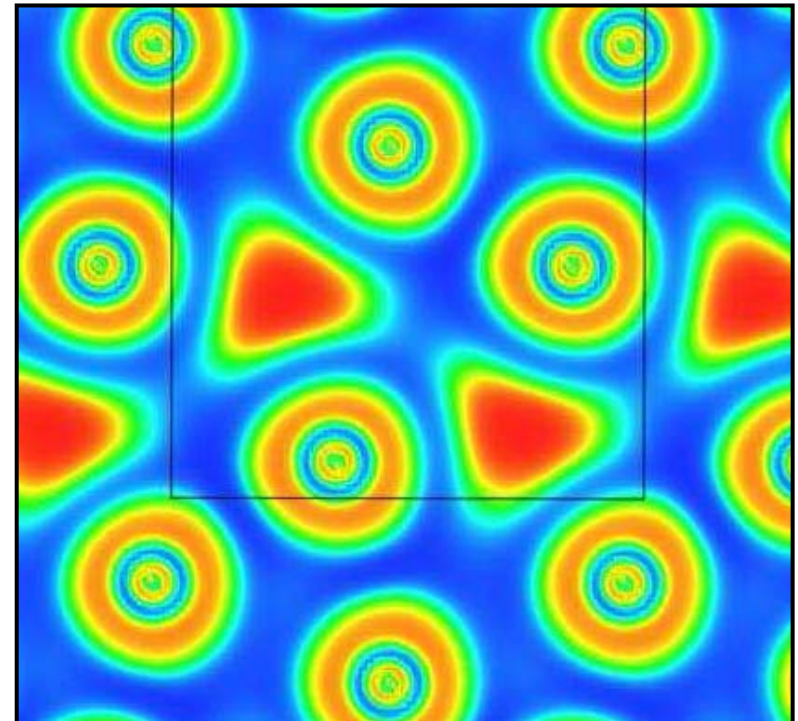
25 GPa. If no transition
took place, localization
would be a lot weaker

3. K: origin of phase transitions



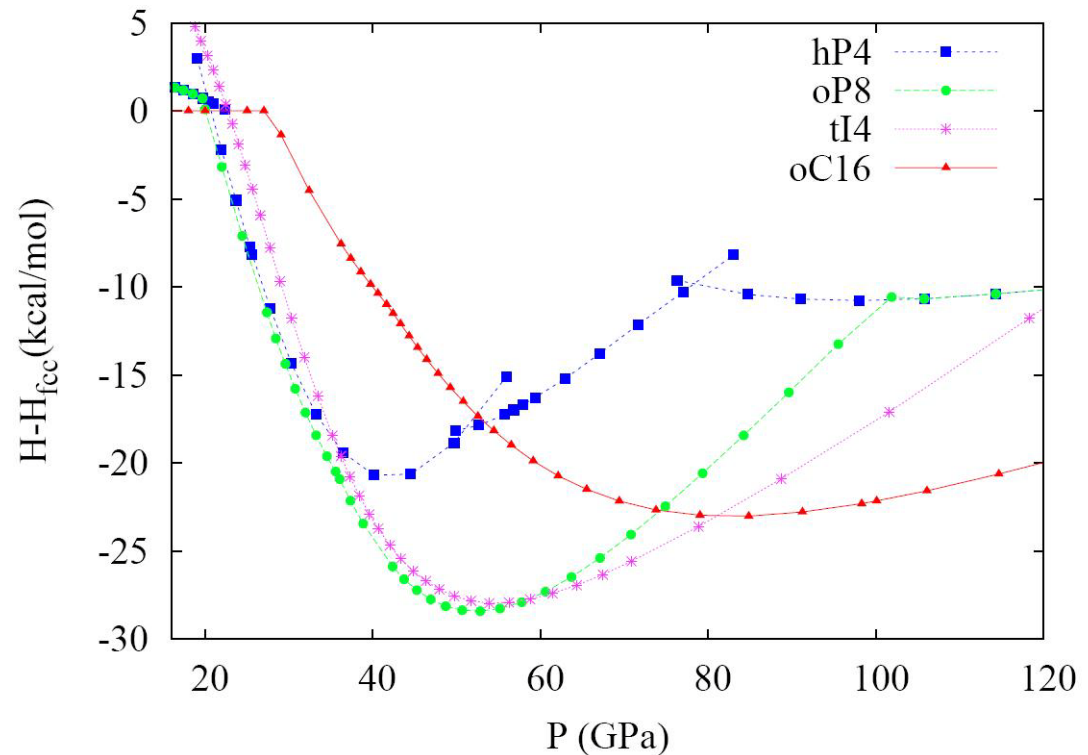
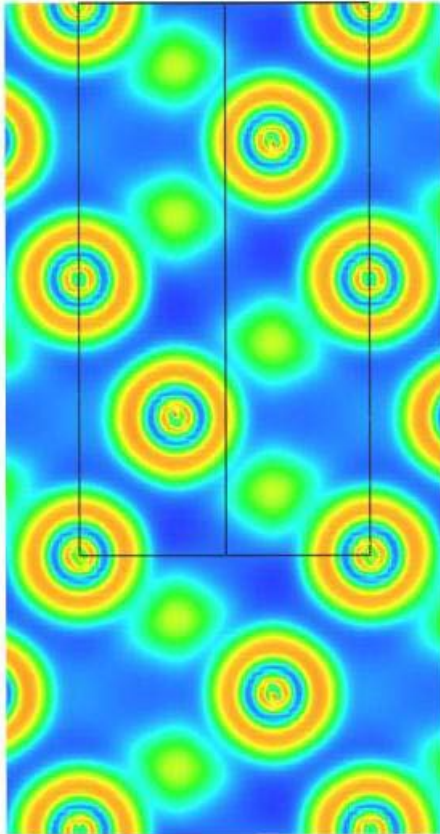
57 GPa: Elongated basins appear showing a flow of electronic localization towards other sites and instability of the phase vs distortion

oP8 distortion



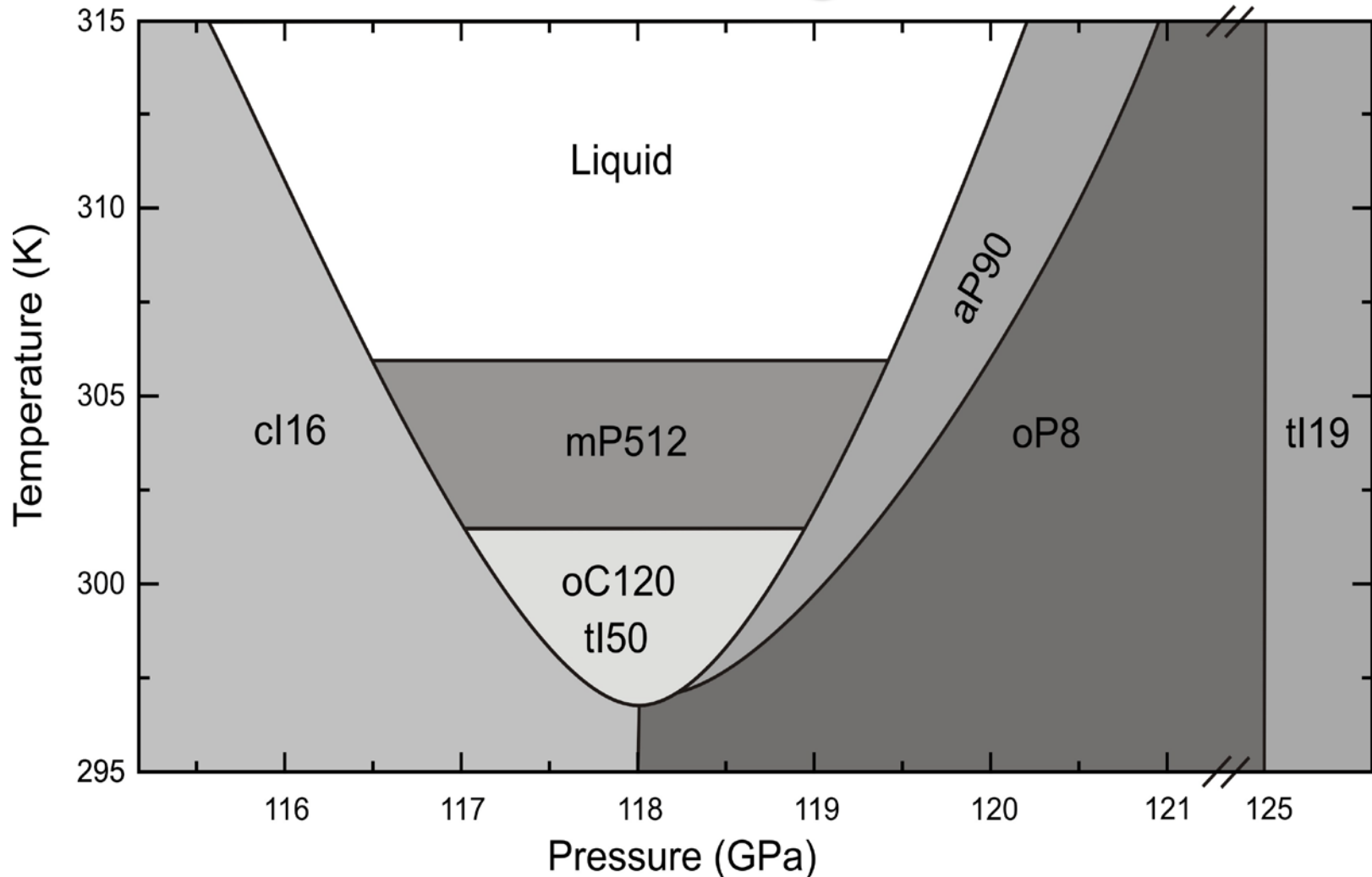
57 GPa with oP8 distortion. Distorted phase favors strong localization (ELF value close to 0.95)

3. K at higher pressures?



- Above 85 GPa, the electronic flow completes, metallic ELF maxima.
- Predicted transitions to tI4 and oC16 structures.
- Recovery of the dhcp arrangement above 250 GPa.

4. Na: melting curve

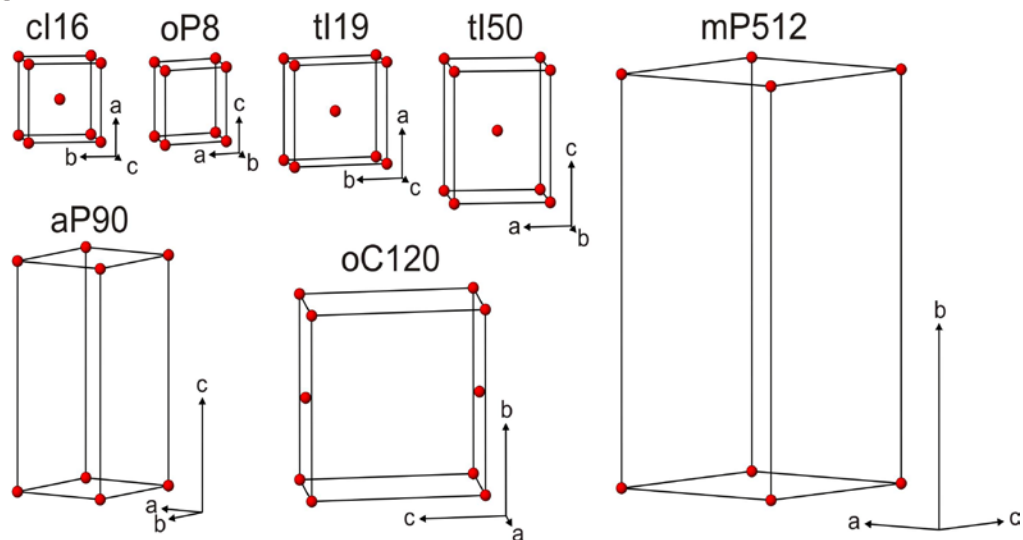


SCIENCE (2008) Gregoryanz, Lundegaard, McMahon *et al.*

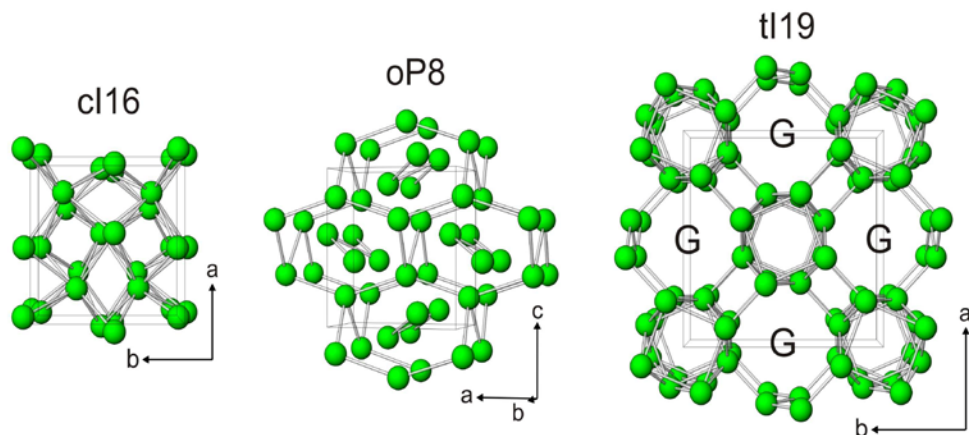
Miraflores, 26th Jan 2011 —

4. Na: structural diversity

A



B



SCIENCE (2008) Gregoryanz, Lundegaard, McMahon *et al.*

Miraflores, 26th Jan 2011 —

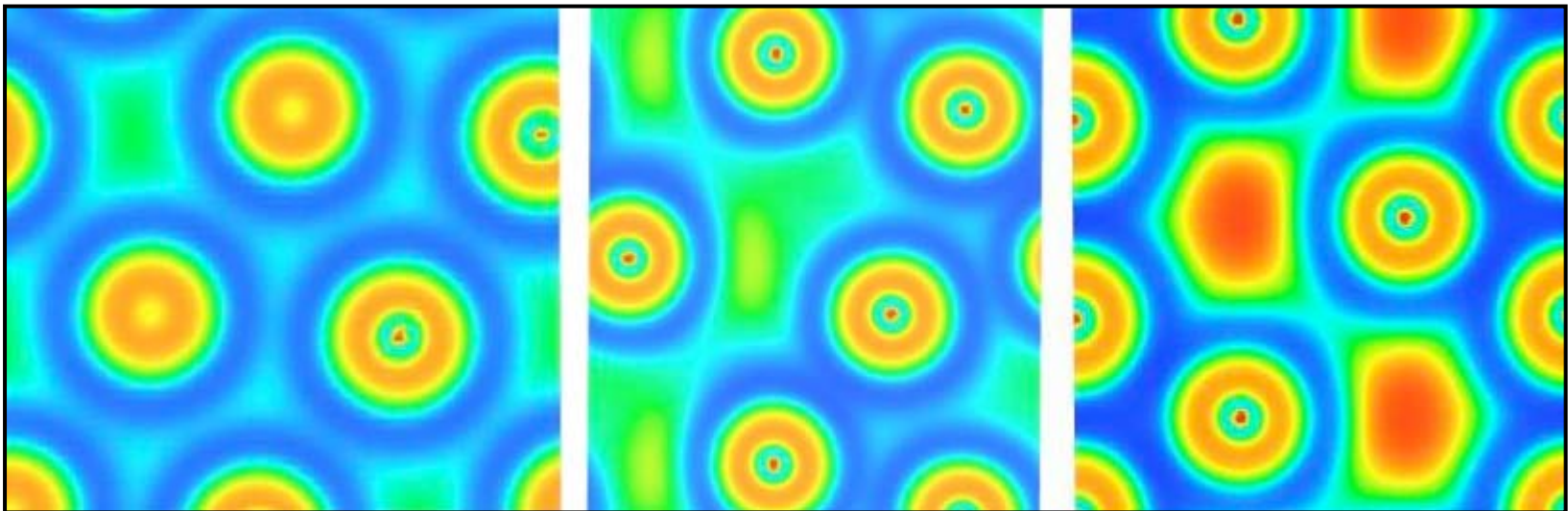
4. Na under pressure

Localization of valence electrons is observed under pressure

cl16

oP8

hP4



pressure

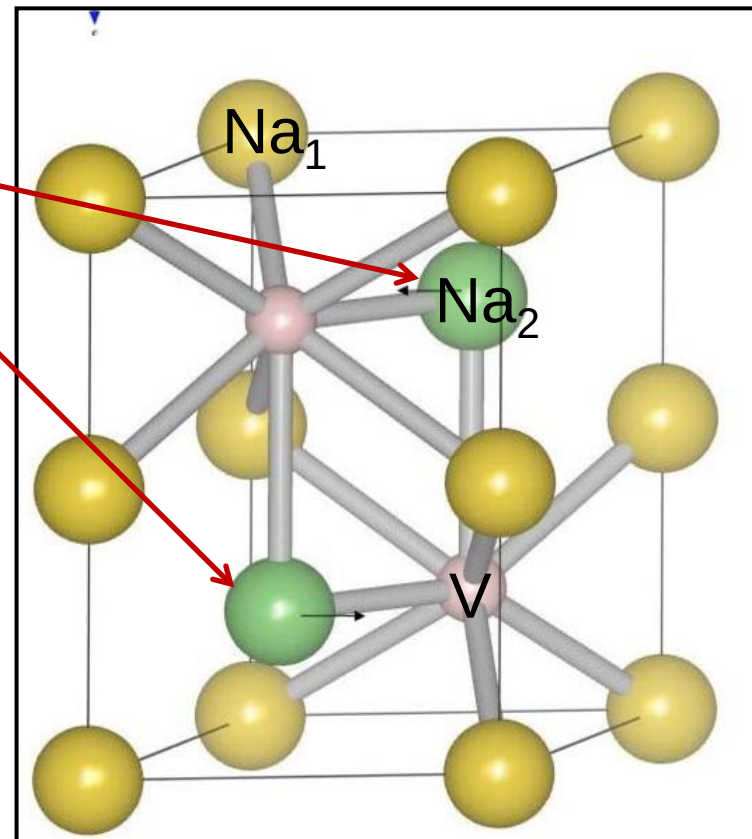
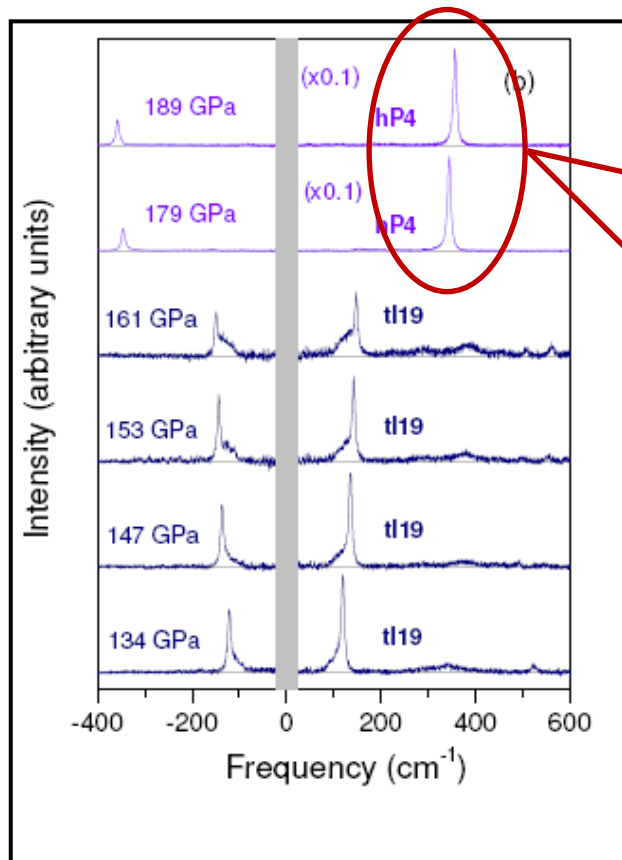
New properties appear

- Incompatible with common metals
- Associated to the new pseudoanions

- Anomalous melting curve
- Raman activity
- Band gap

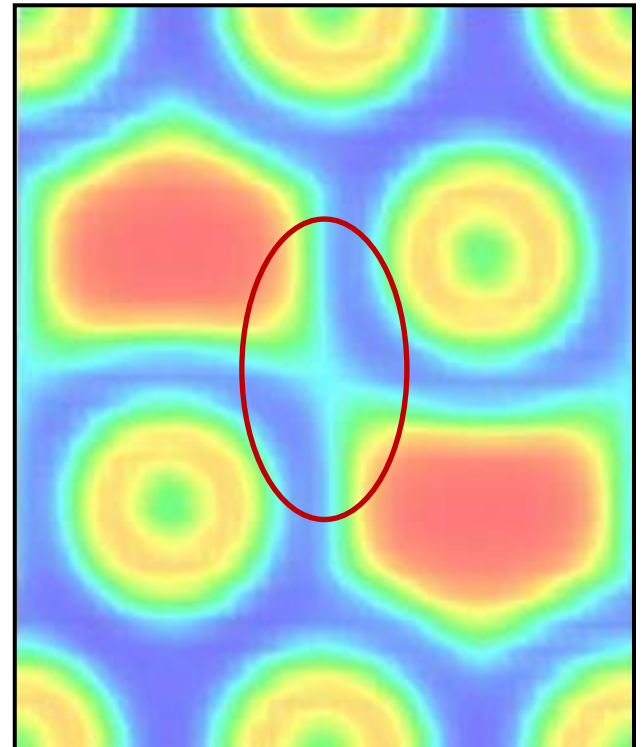
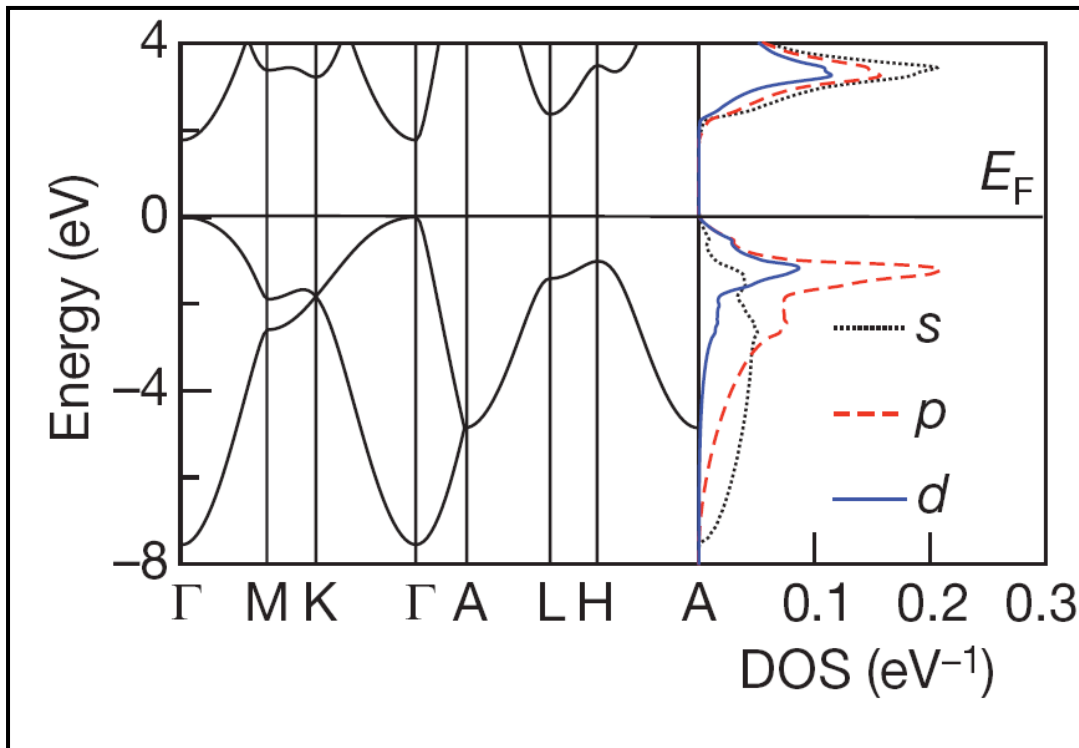
4. Na: Raman activity

- Annihilation of polarizability does not hold in oP8 and hP4 (localized phases): intense active Raman modes are found.
- The most intense modes can be associated with movements of the sodium atoms with respect to the valence attractors.



4. Na: hP4 phase

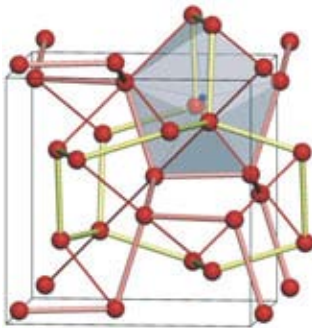
- hP4 phase: direct band gap insulator ($E_g=2.1$ eV)
- Localized units give no connection between ELF basins. Can this help us understand the nature of conductivity?
(W. Kohn, Phys Rev A **133**,171: Theory of the insulating state")
- What is a metal?



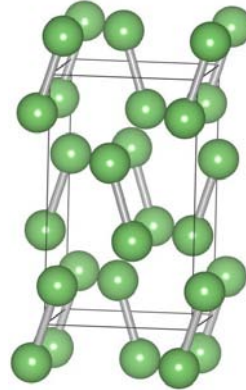
5. Li at high pressures

Previously:

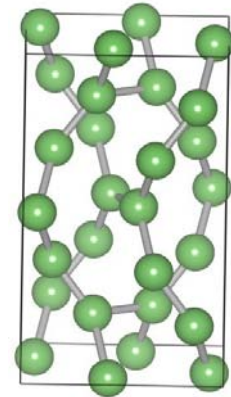
- Neaton & Ashcroft predicted a low-symmetry “paired-atom” phase (oC8) with near-insulating properties.
- Diffraction studies: bcc $\xrightarrow{7.5 \text{ GPa}}$ fcc $\xrightarrow{42 \text{ GPa}}$ cl16
- cl16 is predicted to transform to an oC24 structure at 88 GPa or 100 GPa.



Li-cl16



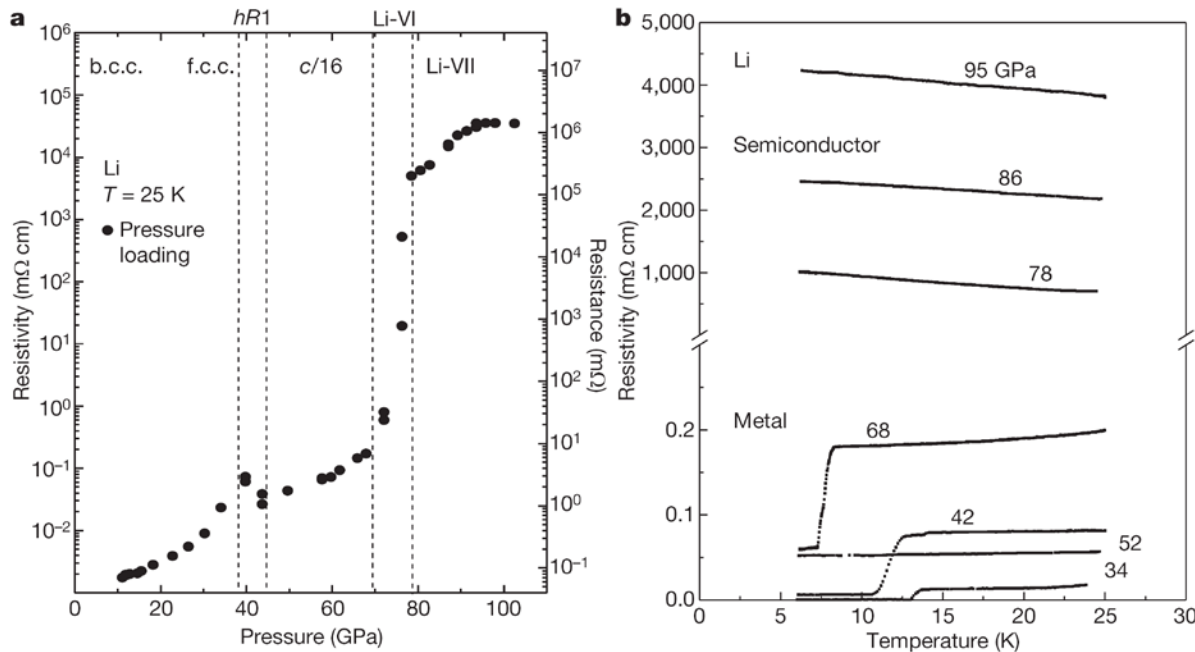
Li-oC8



Li-oC24

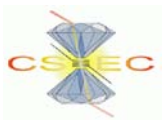
5. Li at high pressures

More recently:



Matsuoka *et al* (2009)

- Yao *et al.*: cI16 $\xrightarrow{74 \text{ GPa}}$ C2-24 $\xrightarrow{91 \text{ GPa}}$ C2cb-24
- Pickard *et al.*: cI16 $\xrightarrow{86 \text{ GPa}}$ Pbca-24 $\xrightarrow{98 \text{ GPa}}$ C2cb-24 $\xrightarrow{106 \text{ GPa}}$ Cmca-24



5. Li at high pressures

Our experiments:

- x-ray diffraction studies ($P = 5\text{--}130\text{ GPa}$, $T = 77\text{--}300\text{ K}$)
 - Extremely difficult: chemical reaction/Li penetration into diamonds



- Structures of Li-VI, Li-VII and Li-VIII (**first time observed**)?
 - Proposed as oC88, oC40 and oC24.

After refinement:

- oC24 has the Cmca-24 structure proposed previously.
- oC40: cell parameters and Cmca space group



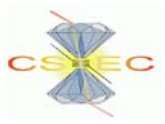
5. oC40 Li

Our calculations:

- AIRSS approach (random structure searching + DFT calculations)
- ❖ CASTEP code, PBE PP, cutoff energy: 350 eV.....
- ❖ Stringent reoptimization of the lowest-enthalpy structures

oC40 structure:

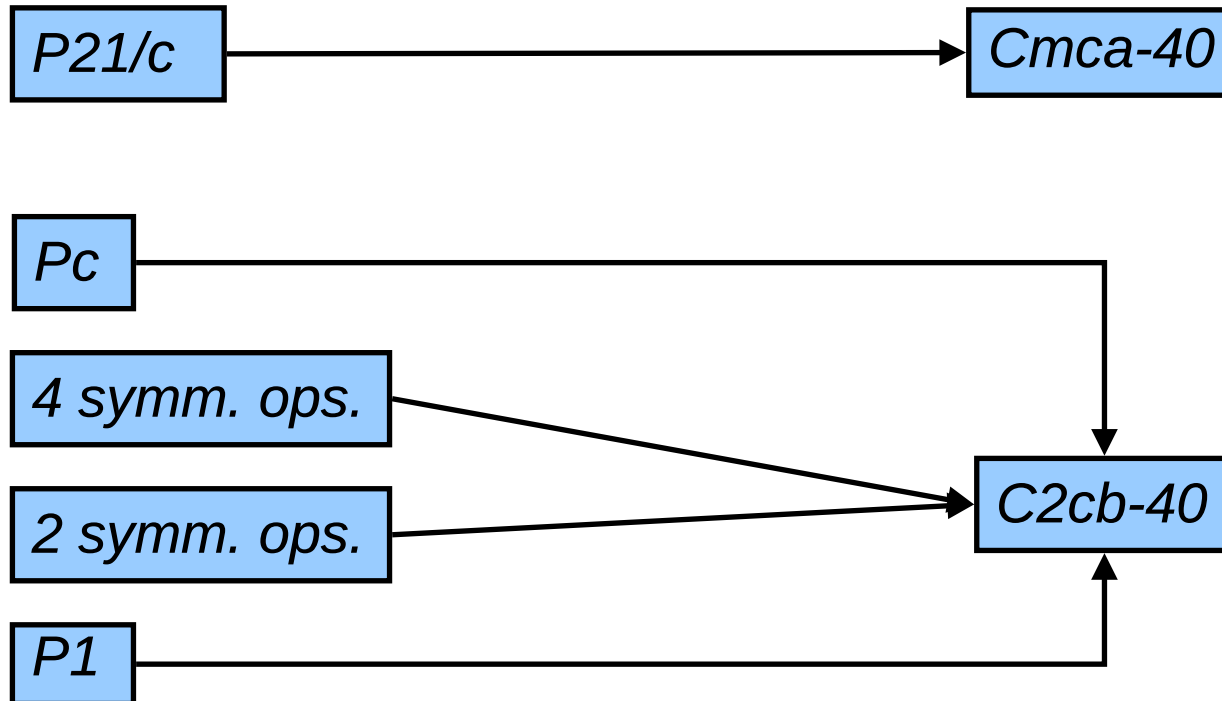
- ❖ 20-atom primitive cells, initial expt. lattice parameters
- ❖ Using the experimental symmetry as a constraint
- ❖ Searches within *P21/c* (subgroup of *Cmca*), *Pc*, randomly-selected space groups with 4 and 2 symmetry operations and no symmetry (*P1*).



5. oC40 Li

Initial structures

Lowest enthalpy structure

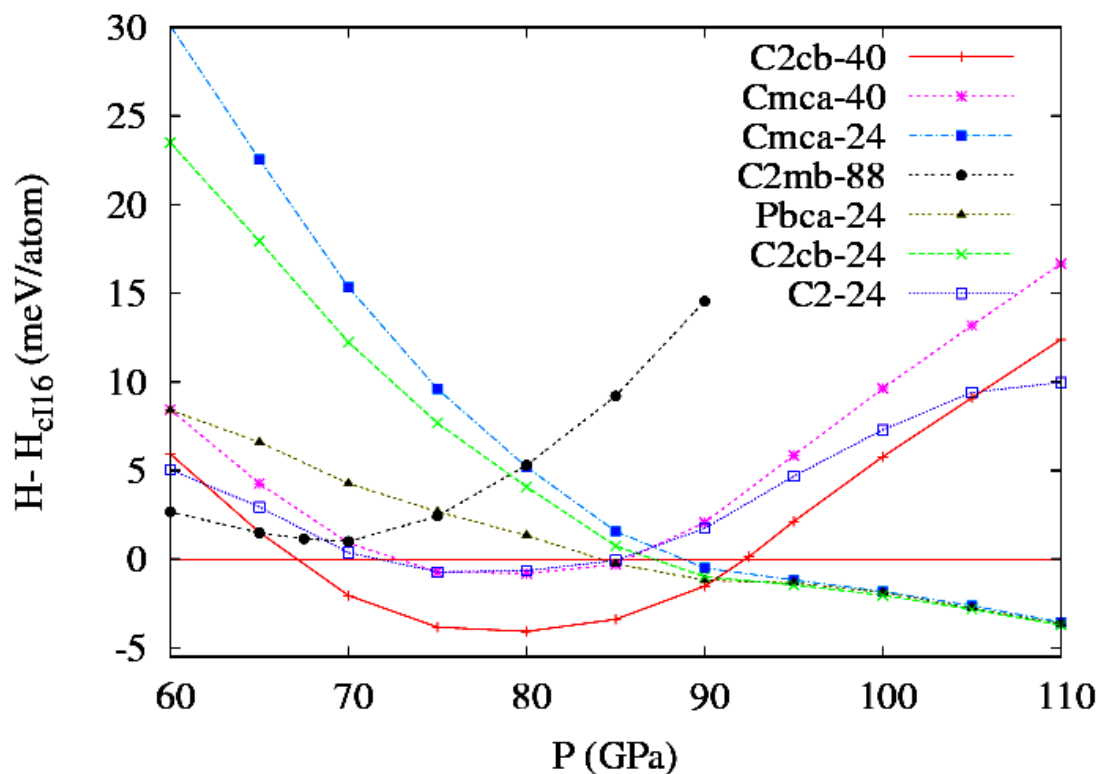


- *C2cb-40* struct. is a subgroup of *Cmca-40* struct.



5. oC40 Li

From H-P curves:



C2cb-40 is the most stable phase between 67-90.5 GPa.

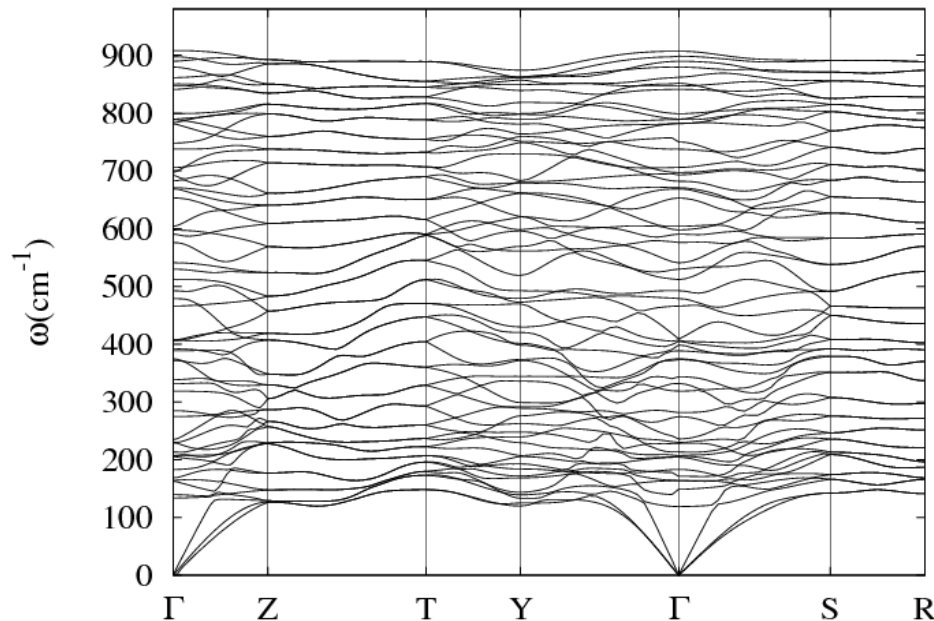
Hypothetically:



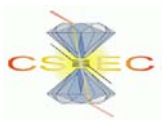
Li at high pressures

Dynamical stability?

- Phonon calculations with the Quantum-ESPRESSO code.
- Imaginary frequency for a B_{3u} mode of the $Cmca$ -40 struct.



Phonon dispersion curves of the $C2cb$ -40 structure:
dynamically stable



Li at high pressures

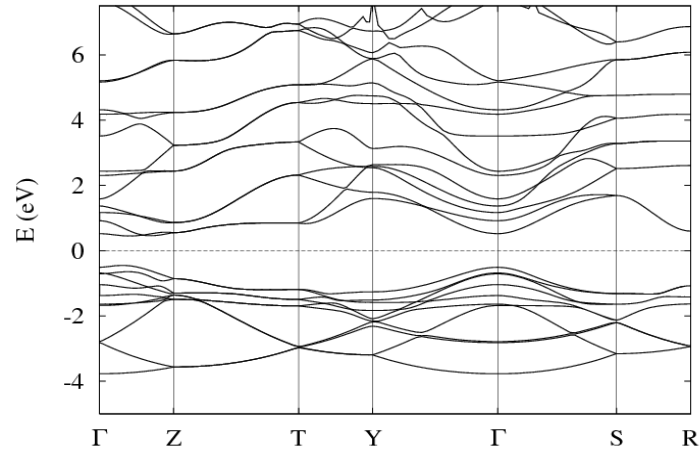
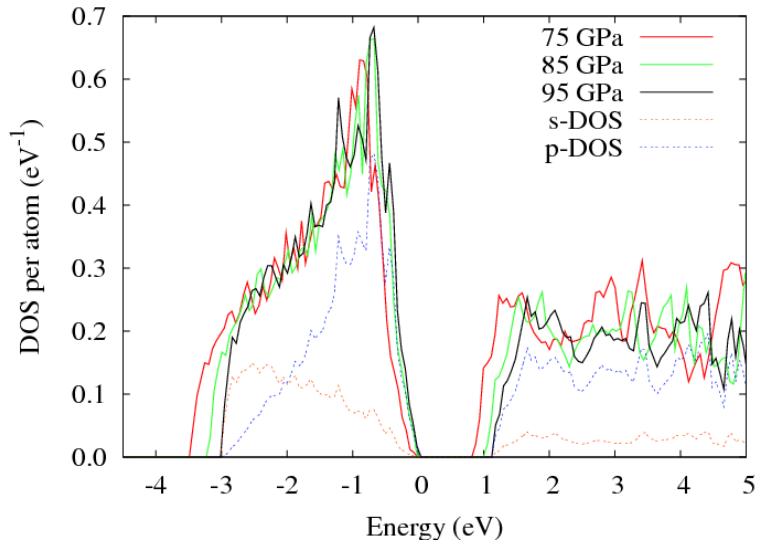
Comparison with experimental data:

- Single crystals of poorer quality than those for oC24.
- Intensities estimated as strong, medium, weak or unobserved
- Cmca is the highest space group consistent with the data, but C2cb is also compatible.
- Excellent agreement between the calculated intensities of the C2cb-40 structure and those obtained experimentally.
- Poorer agreement with the Cmca-40 structure.

SOLUTION: C2cb-40 structure

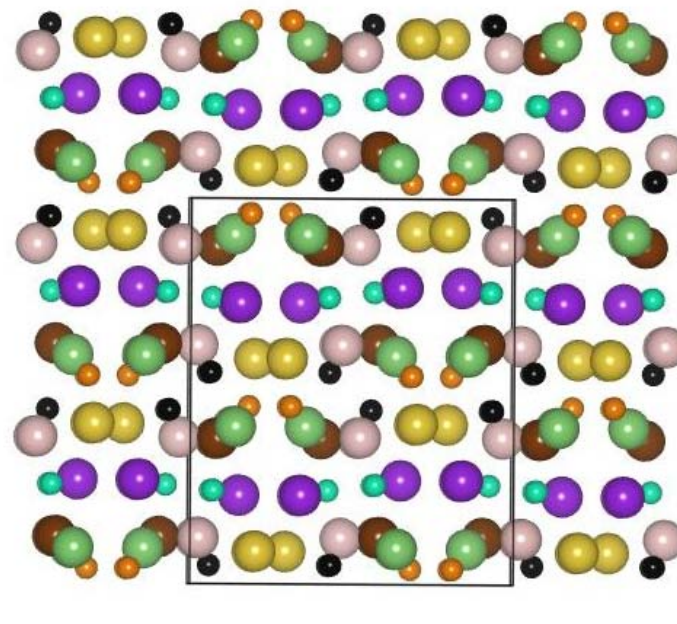
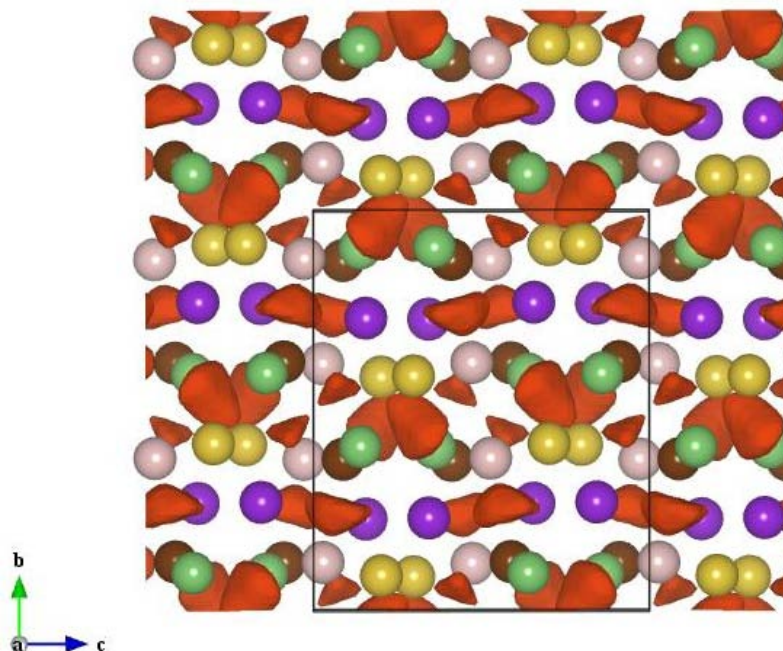
5. oC40 Li

Semiconductor?



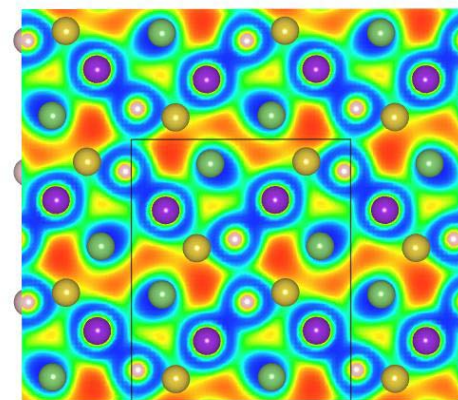
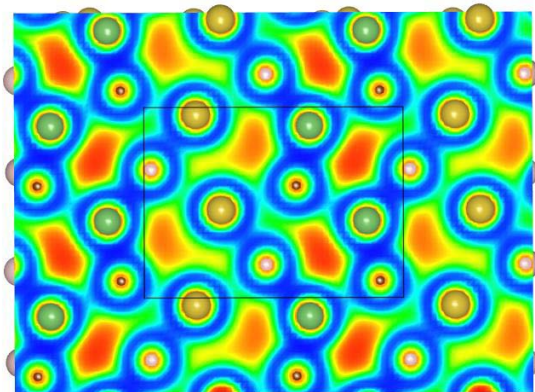
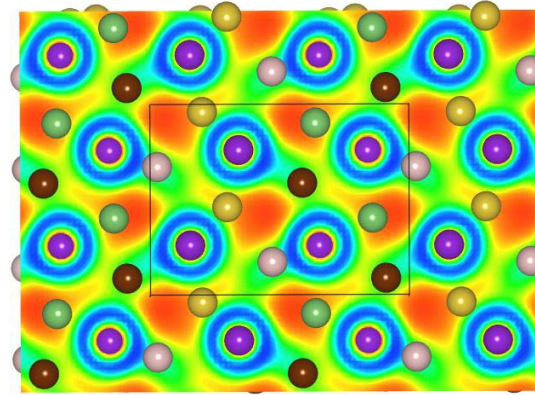
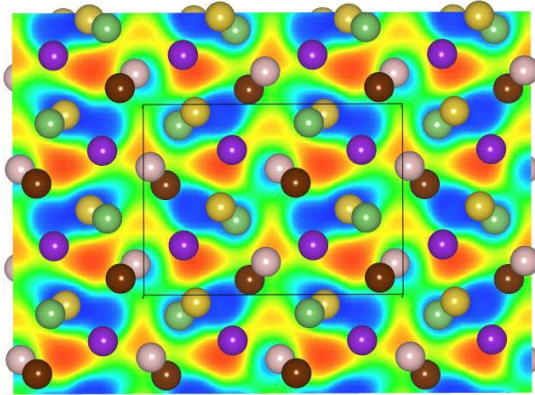
- Indirect band gap along Γ Z similar to the Γ -direct band gap
- Gap increases with pressure, 1.15 eV at 95 GPa
- Larger gap than the other structures (0.276 eV for the C2-24)

5. oC40 Li



- Modulated layers. 5 neq. Li atoms, 3 ELF attractors.
- M1: $2 e^-_s$, M2: $2 e^-_s$, M3: $1 e^-$ → Li_5ABC .
- New elemental structure, not found previously.

5. oC40 Li



Summary

- Relationships between localized metallic structures and ionic compounds are found to hold at intermediate and high pressures.
- The greater interstitial localization helps to stabilize these phases.
- Unusual properties (Raman activity, decreased melting and conductivity) explained by this pseudoionic character.
- Problems of current DFT functionals to deal with these localized structures.

Acknowledgements

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Graham Stinton

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Cristophe Guillaume

__University of Florence__

Mario Santoro
Federico Gorelli

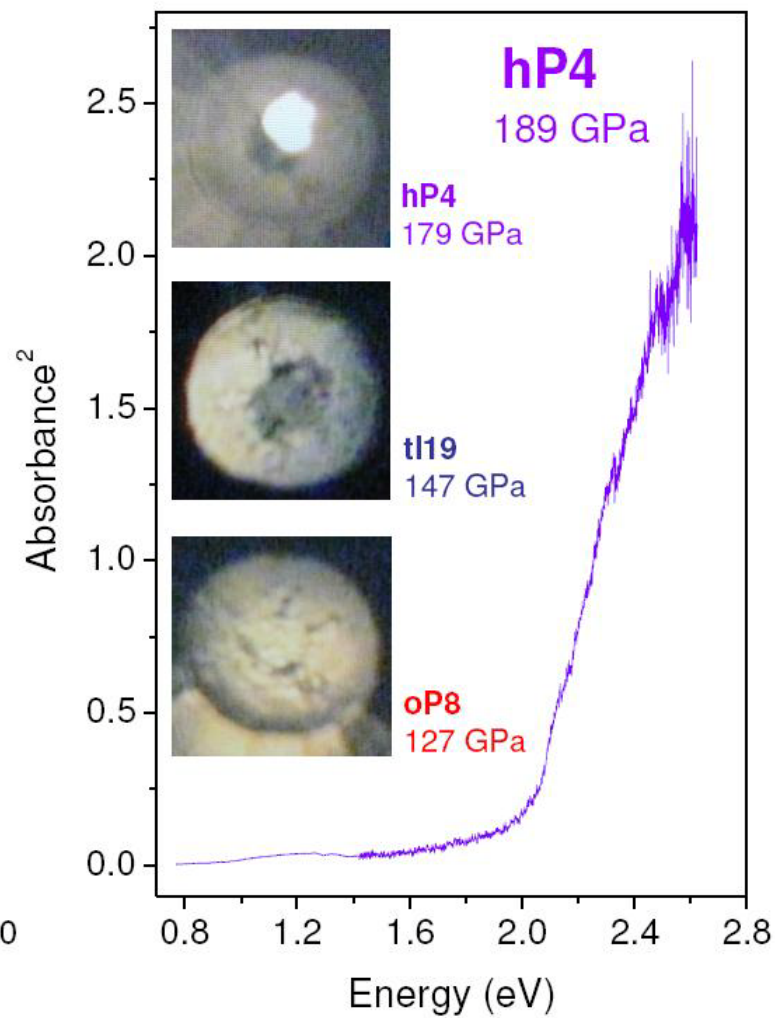
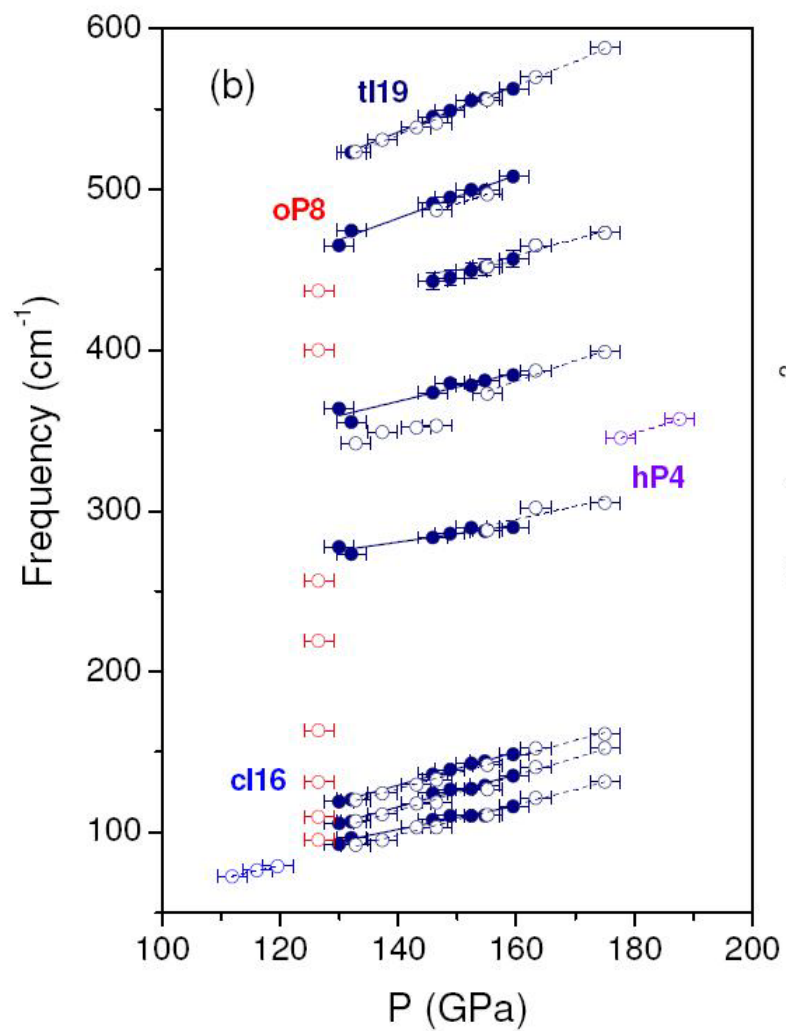
__Universidad de Oviedo__

Julia Contreras-Garcia



MALTA Consolider

Thank you for listening!



5. Alkali metals at HP: problems

- **Wrong transition pressures** (cannot be associated to hysteresis)
- K: transition from localized oP8 to delocalized tI4
 - Experimental ≈ 90 GPa
 - Theoretical ≈ 58 GPa
- Na: transition to localized hP4
 - Experimental ≈ 178 GPa
 - Theoretical ≈ 250 GPa
- **LDA/GGA functionals tend to over-delocalize electrons: greater stability range of delocalized phases**
- **Not able to correctly stabilize the pseudo-ionic state (localized)**
- **New functionals?**

High Pressure Study on Rb₂S.

*Structural Comparison between
Alkali-metal Sulfides and their Corresponding Oxides*

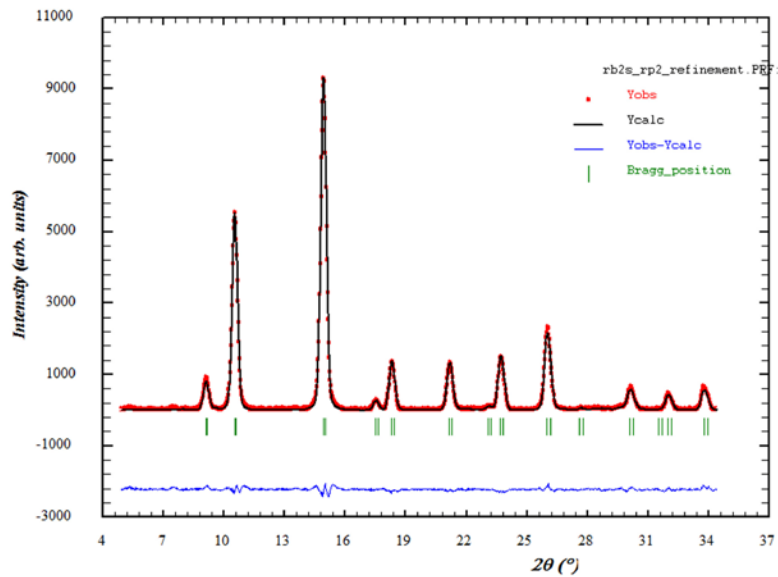
David Santamaría-Pérez

Universidad Complutense de Madrid



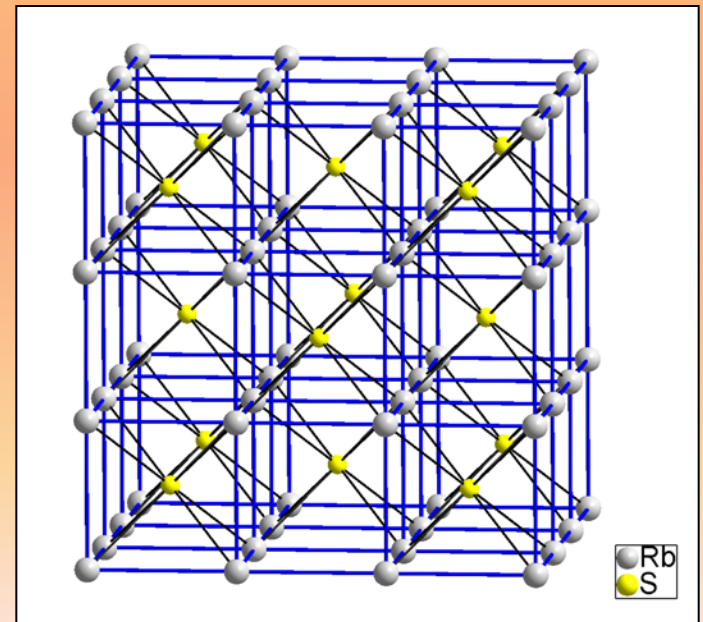
Rb₂S at ambient pressure

WDICVOL04 solution (Automatic generated PCR file) CELL: 7.72610

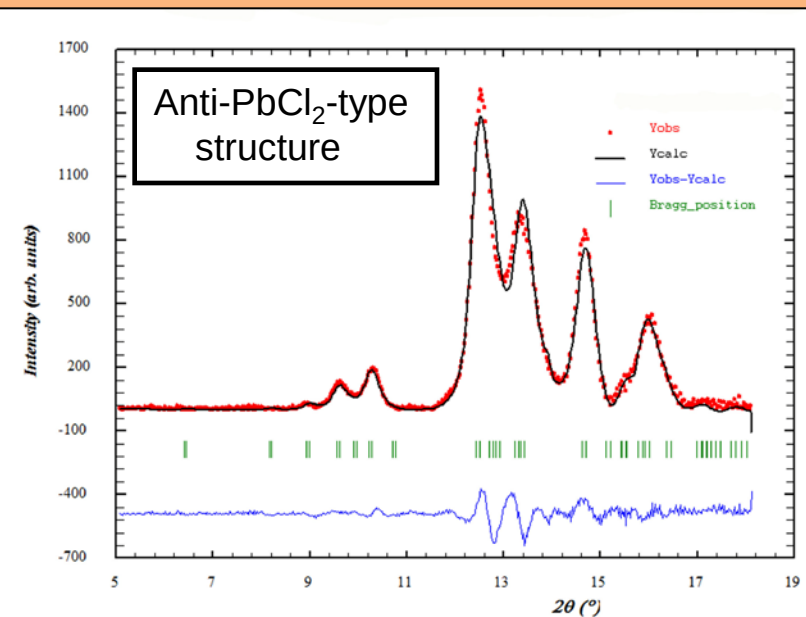
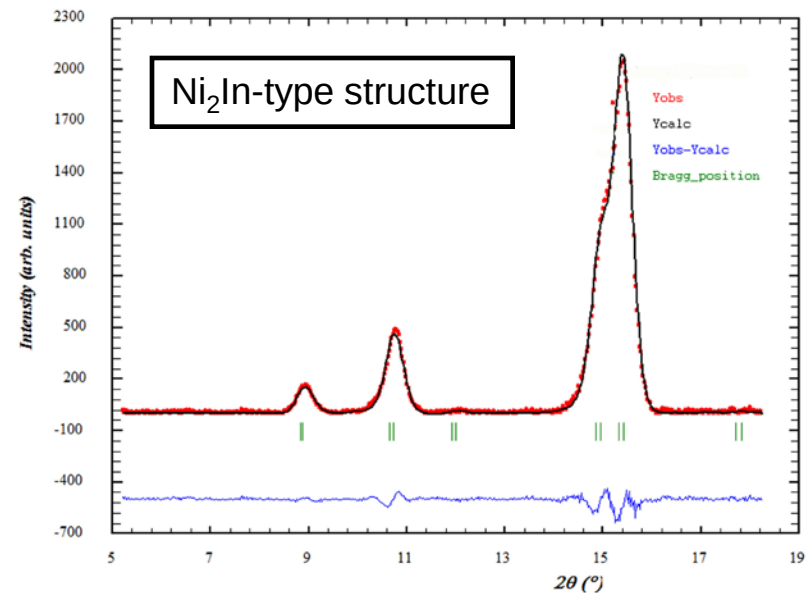
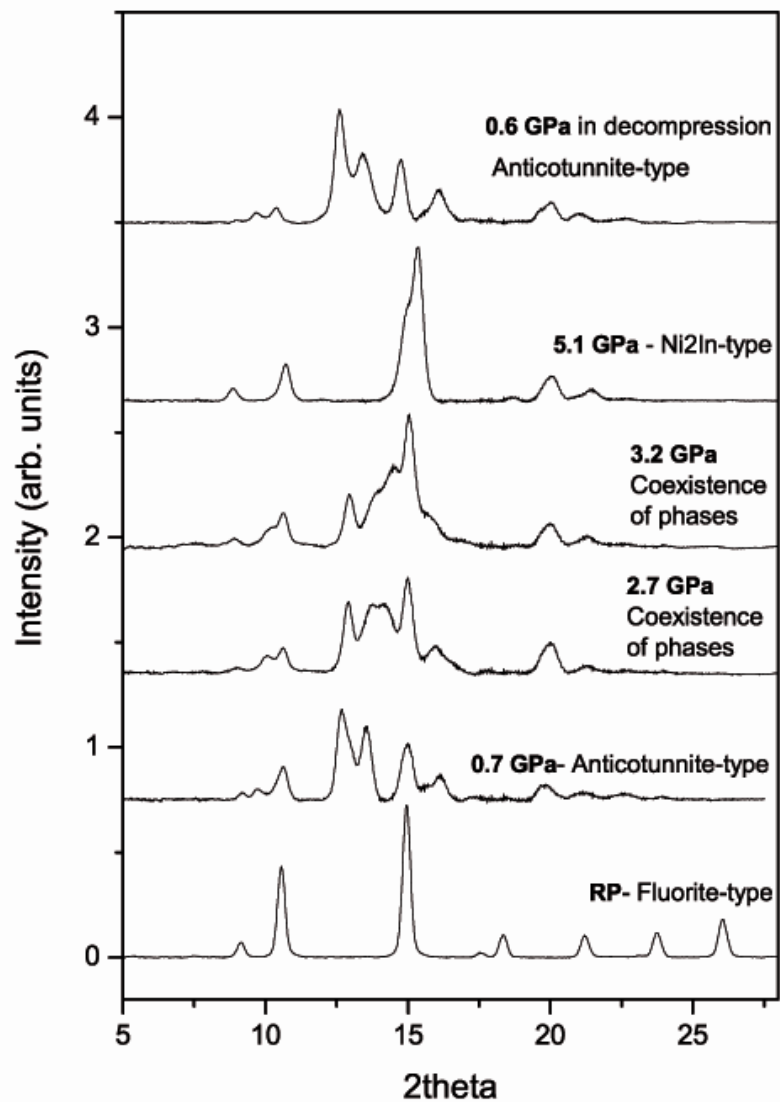


Anti-CaF₂-type structure

- C.N (S atoms) = 8 ($8 \times 3.346 \text{ \AA}$)
- C.N (Rb atoms) = 4

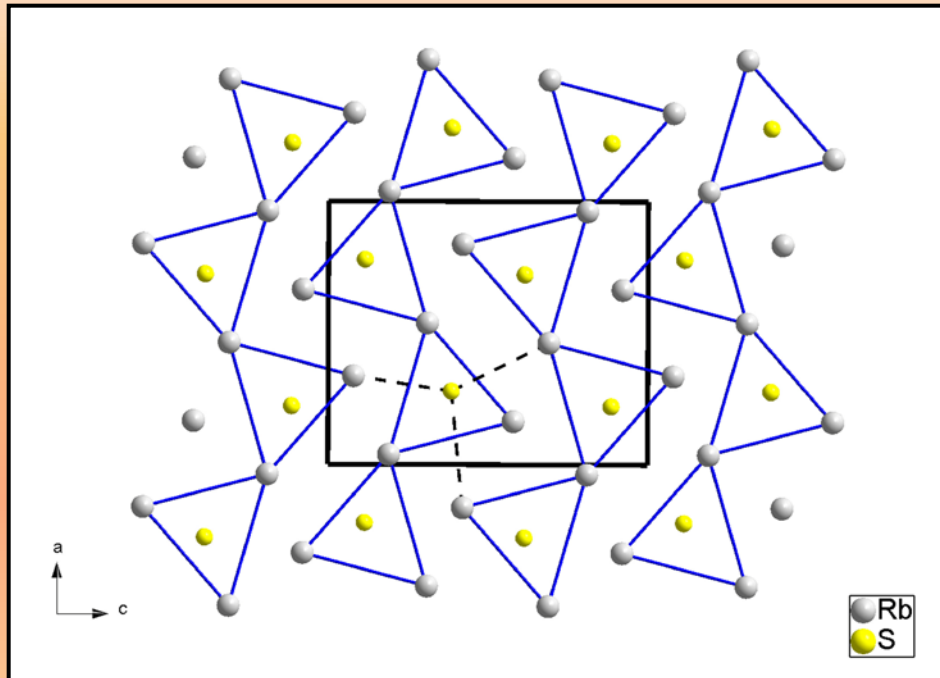


Rb₂S at high pressure



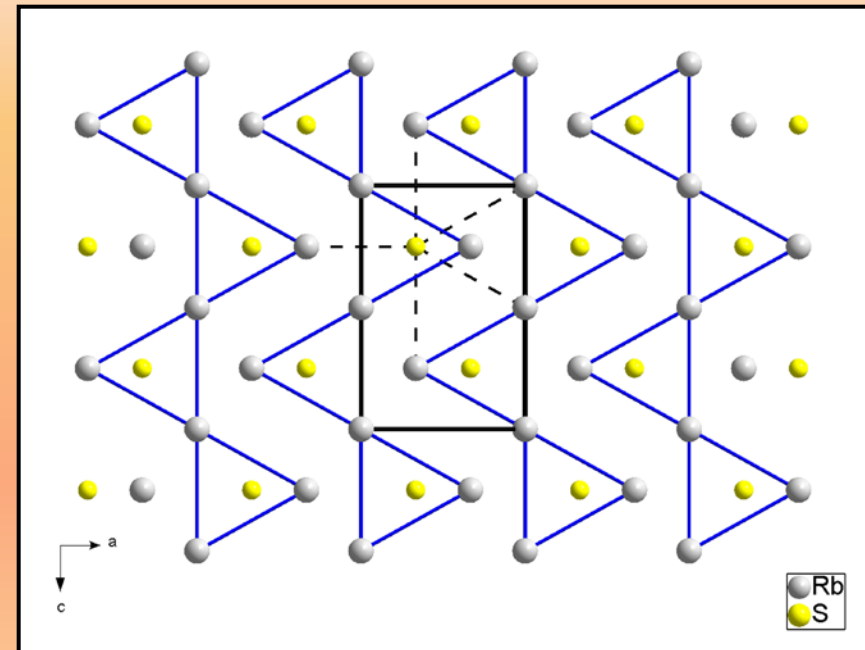
Structures of the high pressure phases of Rb_2S

Anti- PbCl_2 -type structure (at 0.7 GPa)



- C.N (Rb atoms) = 9
 $(1 \times 3.137 \text{ \AA}, 2 \times 3.296 \text{ \AA}, 1 \times 3.349 \text{ \AA},$
 $2 \times 3.424 \text{ \AA}, 1 \times 3.62 \text{ \AA}, 2 \times 3.771 \text{ \AA})$

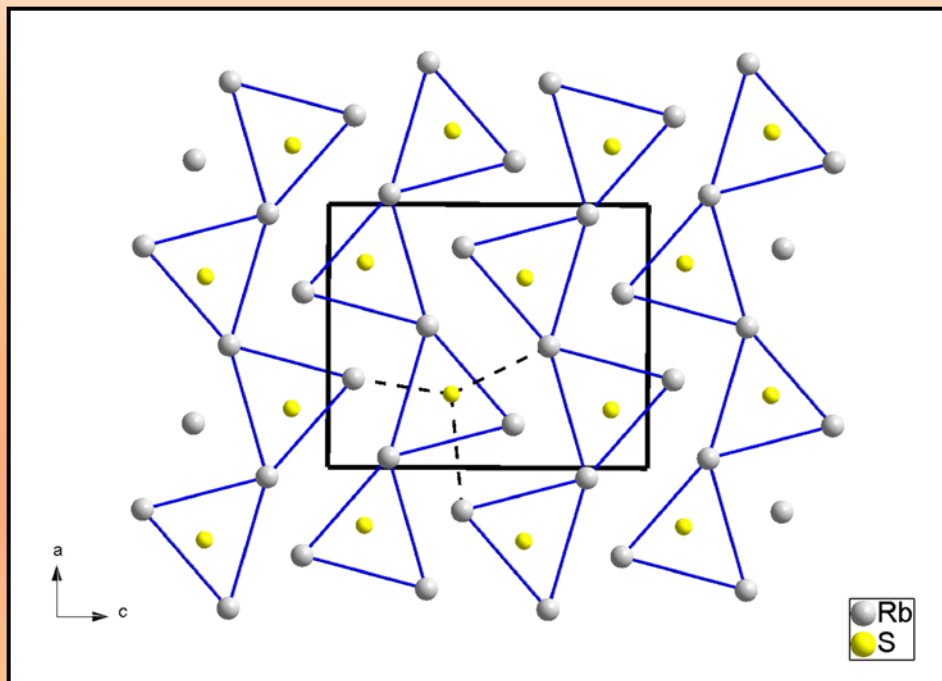
Ni_2In -type structure (at 5.1 GPa)



- C.N (Rb atoms) = 11
 $(3 \times 3.067 \text{ \AA}, 2 \times 3.405 \text{ \AA}, 6 \times 3.507 \text{ \AA})$

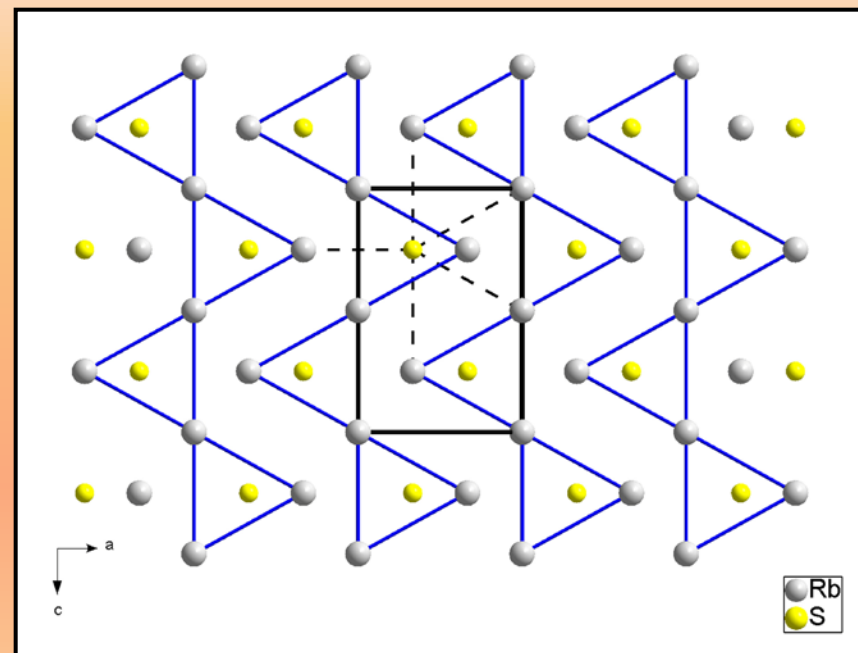
Structures of the high pressure phases of Rb_2S

Anti- PbCl_2 -type structure (at 0.7 GPa)



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 $(1 \times 3.137 \text{ \AA}, 2 \times 3.296 \text{ \AA}, 1 \times 3.349 \text{ \AA},$
 $2 \times 3.424 \text{ \AA}, 1 \times 3.62 \text{ \AA}, 2 \times 3.771 \text{ \AA})$

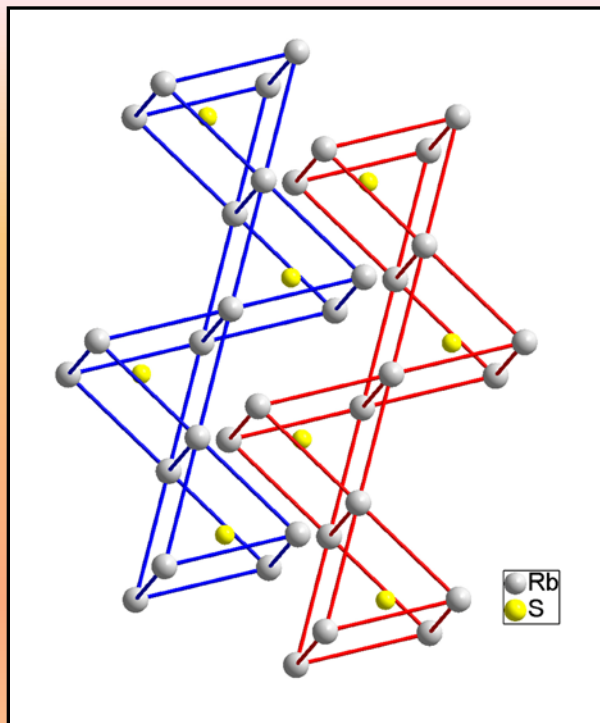
Ni_2In -type structure (at 5.1 GPa)



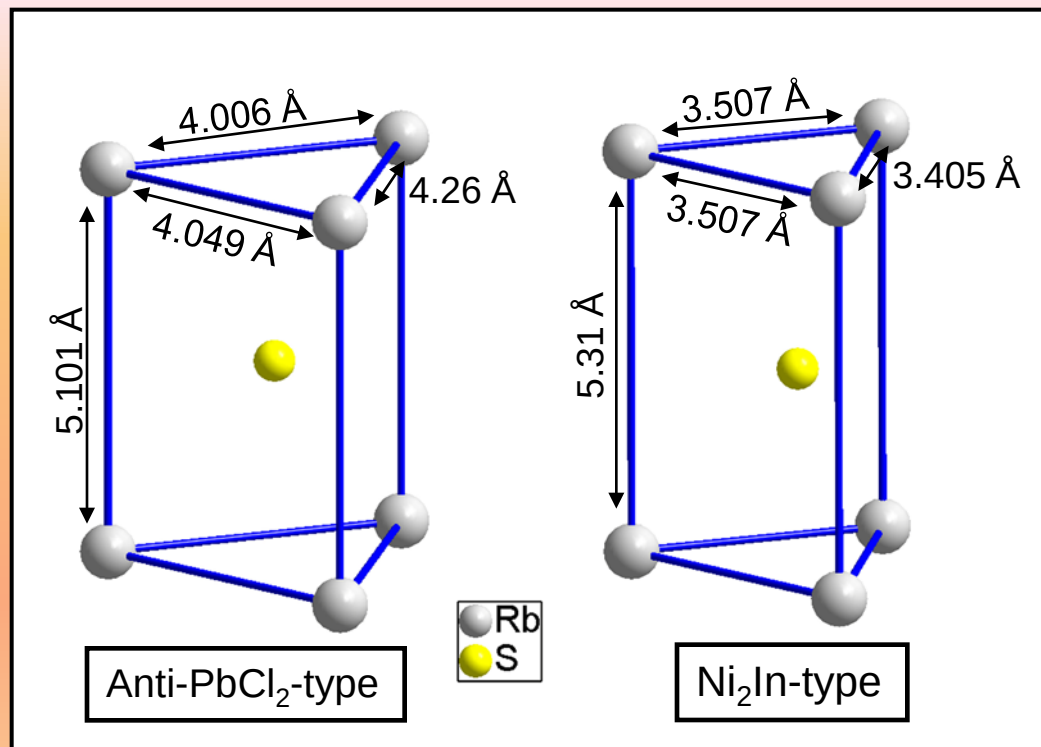
- C.N (Rb atoms) = 11
 $(3 \times 3.067 \text{ \AA}, 2 \times 3.405 \text{ \AA}, 6 \times 3.507 \text{ \AA})$

The mean distance Rb-S in the trigonal prisms does not change!!

Analysis of the bondlengths in the anti-PbCl₂- to Ni₂In-type phase transition

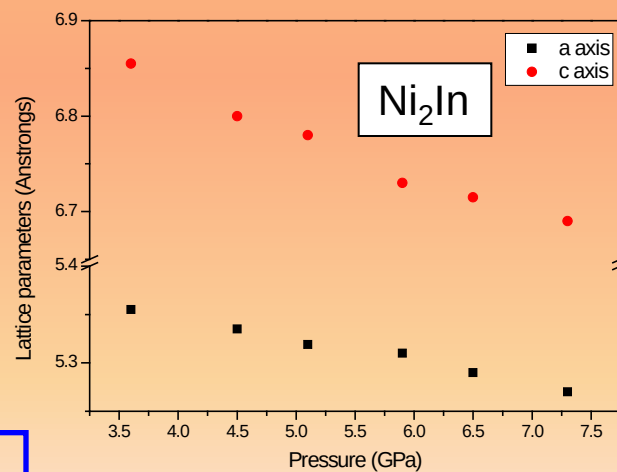
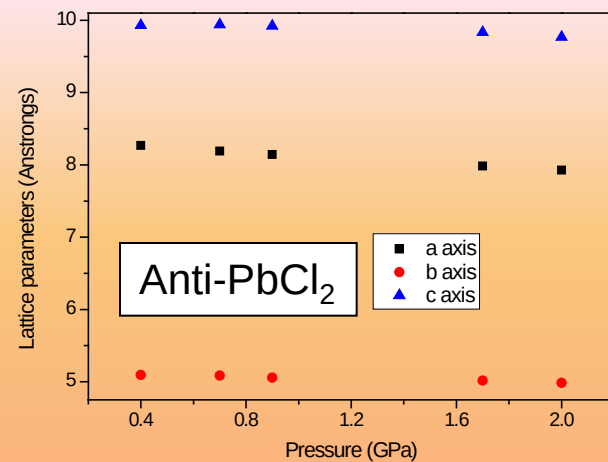
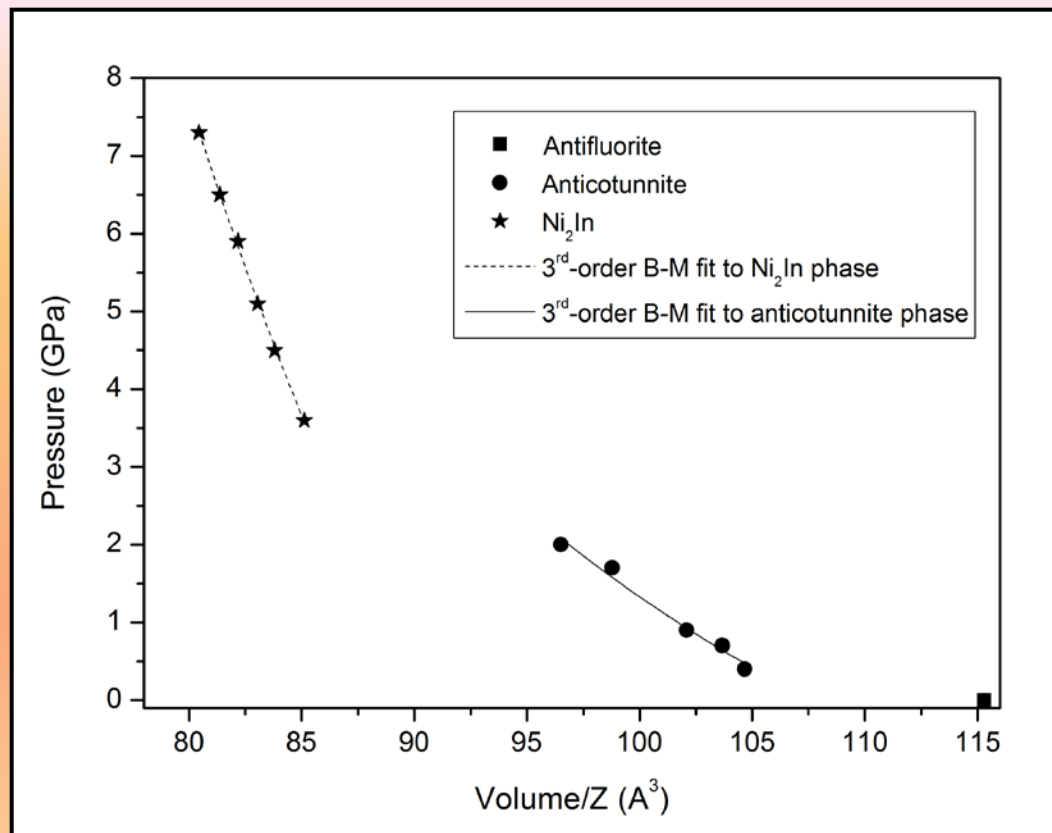


Ni₂In-type



The decrease of the area of the trigonal face makes possible that, in the Ni₂In-phase, the S atoms could interact with a larger number of Rb atoms capping the lateral faces. CN from 9 to 11.

Equations of state



- Anti- PbCl_2 : $B_0 = 14 \pm 1$ GPa, $B_0' = 4$, $V_0 = 430 \pm 2$ $\text{\AA}^3$, $Z = 4$
- Ni_2In : $B_0 = 33 \pm 1$ GPa, $B_0' = 4$, $V_0 = 181.5 \pm 0.3$ $\text{\AA}^3$, $Z = 2$

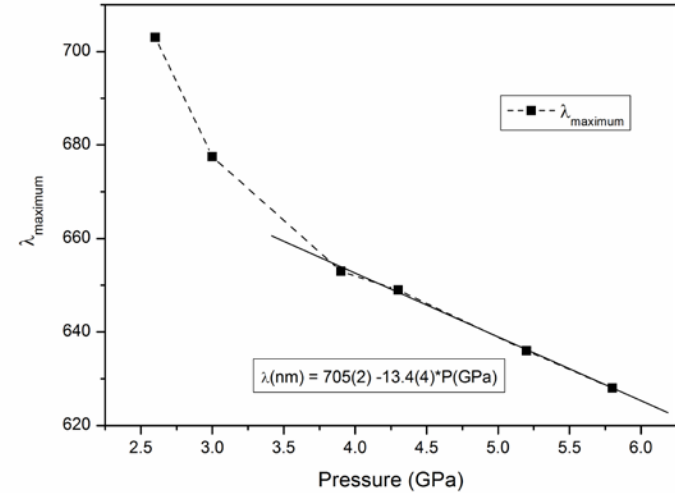
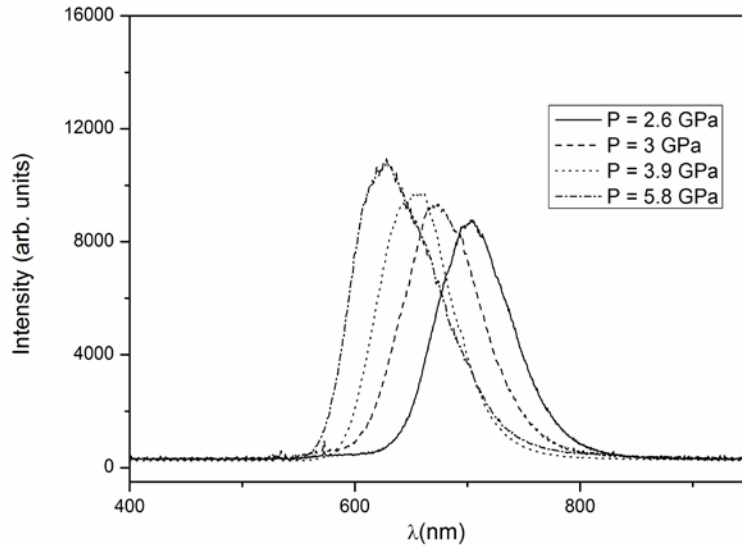
Correspondence between the structures of:

- alkali-metal sulfides
- and
- the cation arrays of their corresponding oxides

Antifluorite (anti- CaF_2)	Anticotunnite (anti- PbCl_2)	Ni_2In	Anti- TiSi_2
Li_2S (RP-RT) Li_2SO_4 (RP-HT)	Li_2S (HP-RT)	$\text{d-Li}_2\text{SO}_4$ (HP-RT)	
Na_2S (RP-RT)	Na_2S (HP-RT)	Na_2S (HP-RT) $\text{d-Na}_2\text{SO}_3$ (RP-RT) Na_2SO_4 (RP-HT)	Na_2SO_4 (RP-RT)
K_2S (RP-RT)	K_2SO_4 (RP-RT)	K_2S (HP-RT) $\text{d-K}_2\text{SO}_3$ (RP-RT) K_2SO_4 (RP-HT)	
Rb_2S (RP-RT)	Rb_2S (HP-RT) Rb_2SO_4 (RP-RT)	Rb_2S (HP-RT) Rb_2SO_4 (RP-HT)	
	Cs_2S (RP-RT) Cs_2SO_4 (RP-RT)	Cs_2SO_4 (RP-HT)	

$\text{P} \uparrow, \text{O content} \uparrow$

Luminiscence at high pressure



- Strong luminescence above 2.6 GPa (directly related with the Ni_2In -phase).
- Band maxima show a non-linear blue shift with pressure (linear when transition is completed).
- Constant shift of 13.5 nm/GPa.
- The shape of the emitted peak deviates from Gaussian profile with pressure (anisotropic broadening).

That's all!

Thank you for your attention

Aplicación de la absorción de rayos X al estudio de las delafositas bajo presión



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A. Muñoz^e, P. Rodríguez-Hernández^e, L. Nataf^d, O. Gomis^f, E. Martínez^g, D. Kim^h,
N. Guignot^b and G. Aquilanti^b.**

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^e*MALTA Consolidider Team, Universidad de La Laguna, Tenerife (Spain)*

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^g*ICMUV, Universidad de Valencia, Valencia (Spain)*

^h*Pukyong National University, Busan (Korea)*

Outline:

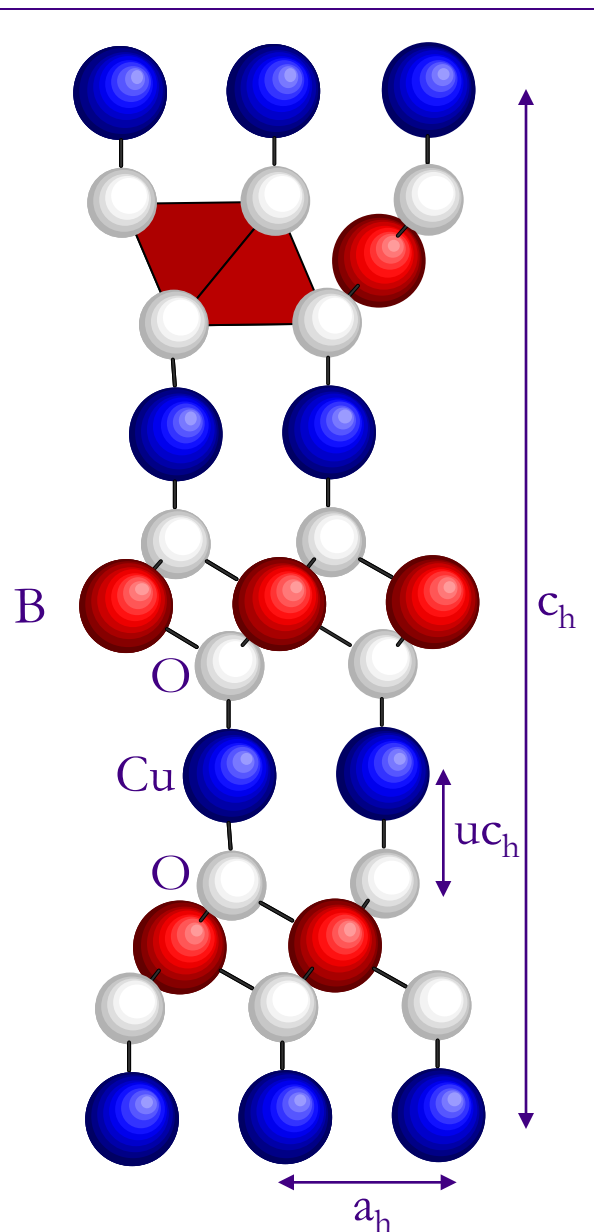
- **Introduction: delafossites.**
- **Experimental.**
- **Results.**
- **Discusion.**
- **Conclusions.**

Delafossites

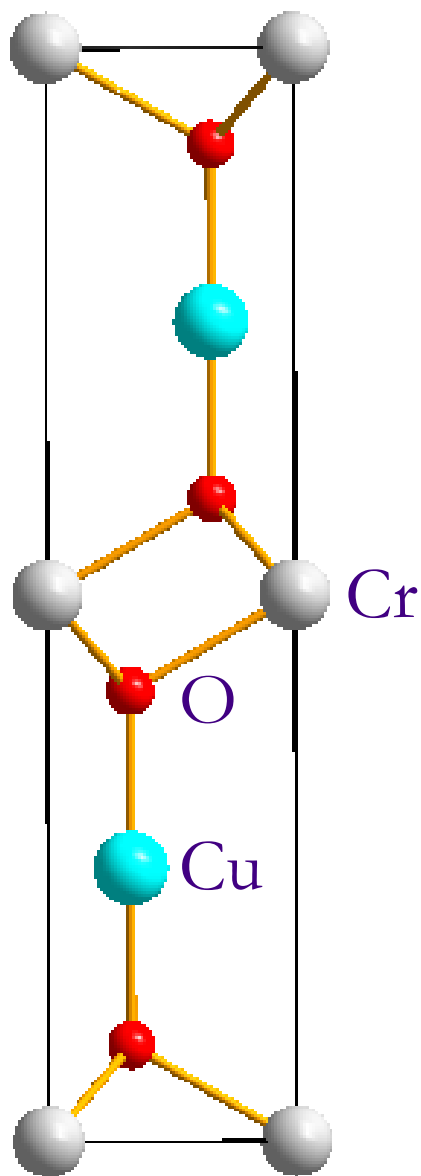
- Mineral: CuFeO_2 (G. Delafosse)
- Family: ABO_2 (~ 40 simple compounds)
- CuBO_2 or AgBO_2 : TCO.
- CuAlO_2 , CuGaO_2 and CuCrO_2 : p-type semicond.

Structure

$$S.G : R\bar{3}m$$



CuGaO_2	CuAlO_2
$a_h = 2.977 \text{ \AA}$	$a_h = 2.858 \text{ \AA}$
$c_h = 17.171 \text{ \AA}$	$c_h = 16.958 \text{ \AA}$
Cu 3(a) (0,0,0)	Cu 3(a) (0,0,0)
Ga 3(b) (0,0,1/2)	Al 3(b) (0,0,1/2)
O 6(c) (0,0,u)	O 6(c) (0,0,u)
$u = 0.1076$	$u = 0.1099$



S.G : $P63/mmc$



Outline:

- Introduction: delafossites.
- **Experimental.**
- Results.
- Discussion.
- Conclusions.

CuGaO₂

Energy dispersive

XRD:

- DW11 wiggler station of DCI in LURE
- $2\theta = 14.97^\circ$
- Membrane diamond anvil cell
- Silicon oil
- Powder

Ambient temperature:

High temperature $T = 510\text{K}$:

- Inconel gasket
- Ruby

- External heating
- Rhenium gasket
- $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$

XAFS:

- D11 station of DCI in LURE (Dispersive EXAFS)
- Membrane diamond anvil cell
- Silicon oil
- **Powder**
- **Cu and Ga K-edges** (8979 and 10367 eV, respectively)
- Inconel (Cu K-edge) and rhenium (Ga K-edge) gaskets
- Ruby

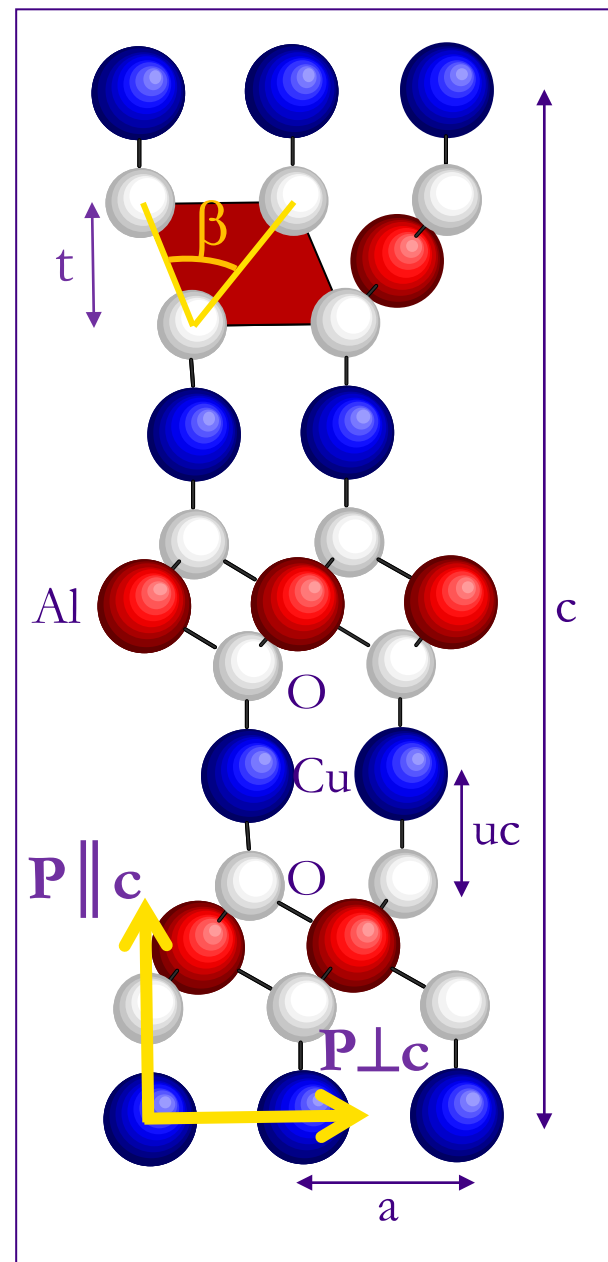
CuAlO₂

Angle dispersive XRD:

- ID30 at the ESRF.
- MAR3450 image plate
- $\lambda=0.3738 \text{ \AA}$
- Membrane diamond anvil cell
- Silicon oil
- Powder
- Inconel gasket

XAFS:

- ID24 at the ESRF (Dispersive EXAFS)
- Membrane diamond anvil cell
- Silicon oil
- **Single crystal, two orientations.**
- **Cu K-edge** (8979 eV)
- Inconel gasket
- Ruby



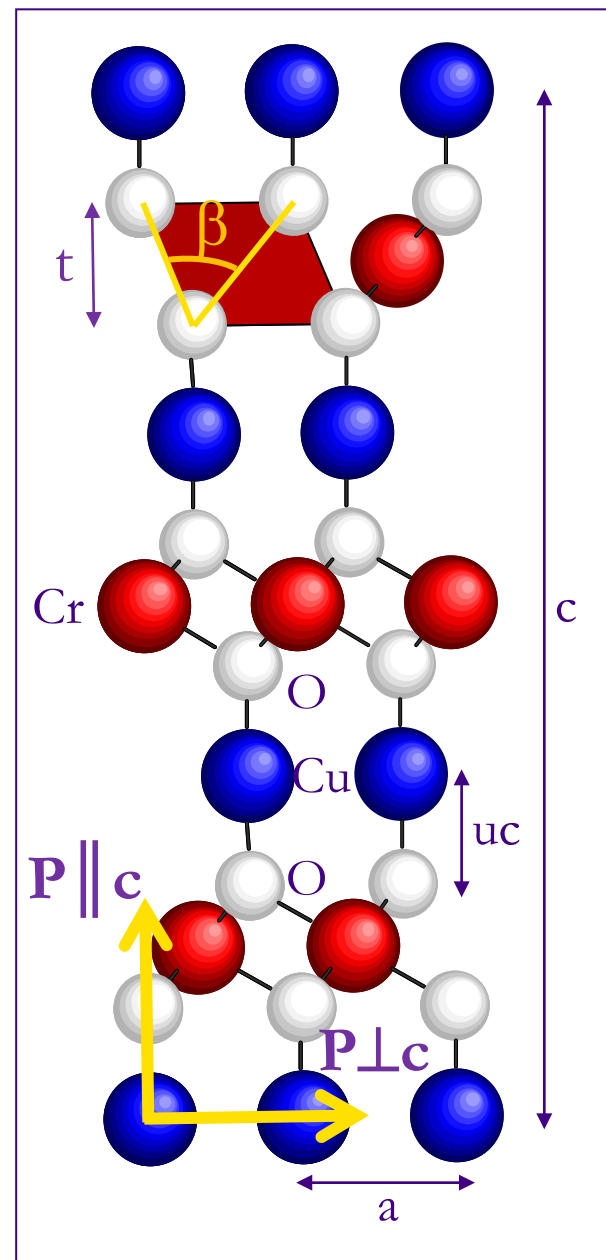
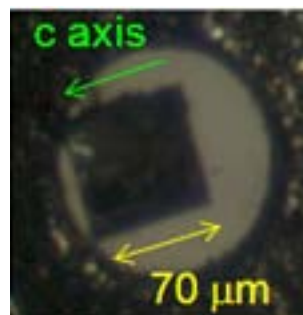
CuCrO₂

Angle dispersive XRD:

- I15 at DIAMOND.
- MAR3450 image plate
- $\lambda=0.4133 \text{ \AA}$
- Membrane diamond anvil cell
- Methanol-ethanol-water
- Powder
- Inconel gasket

XAFS:

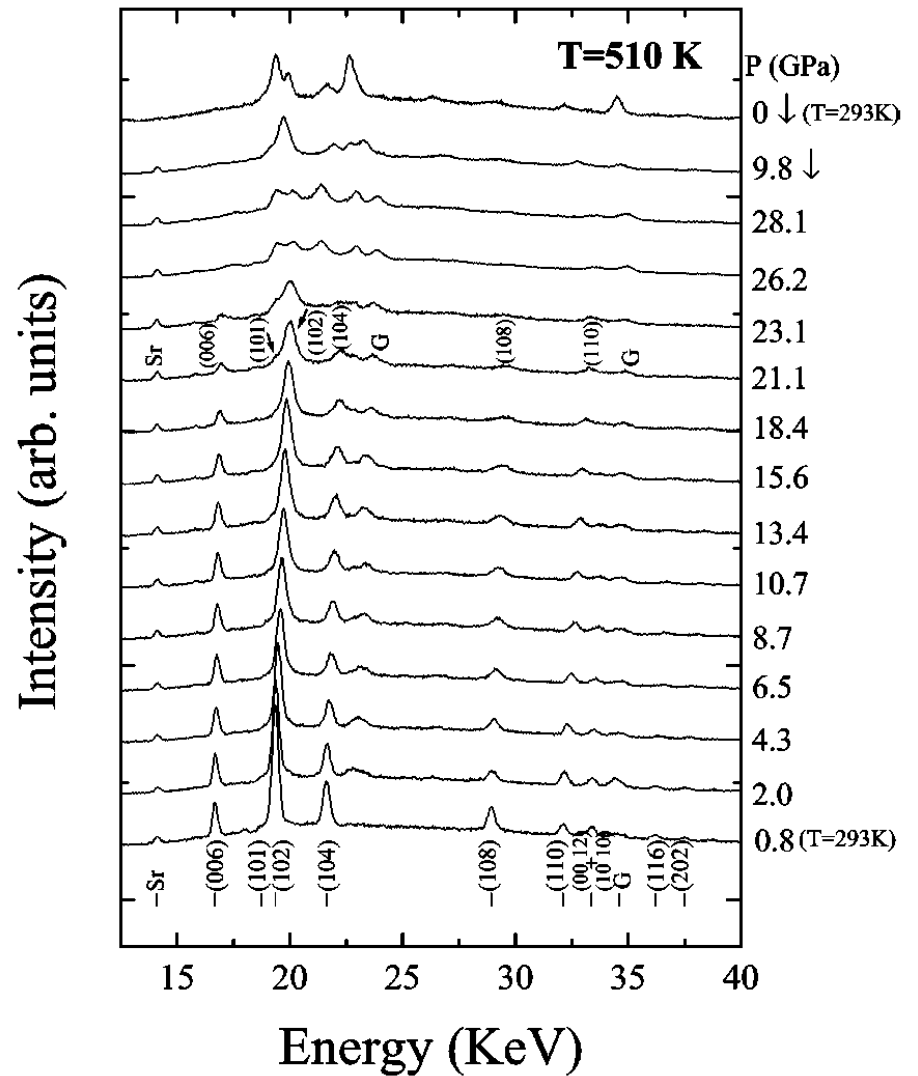
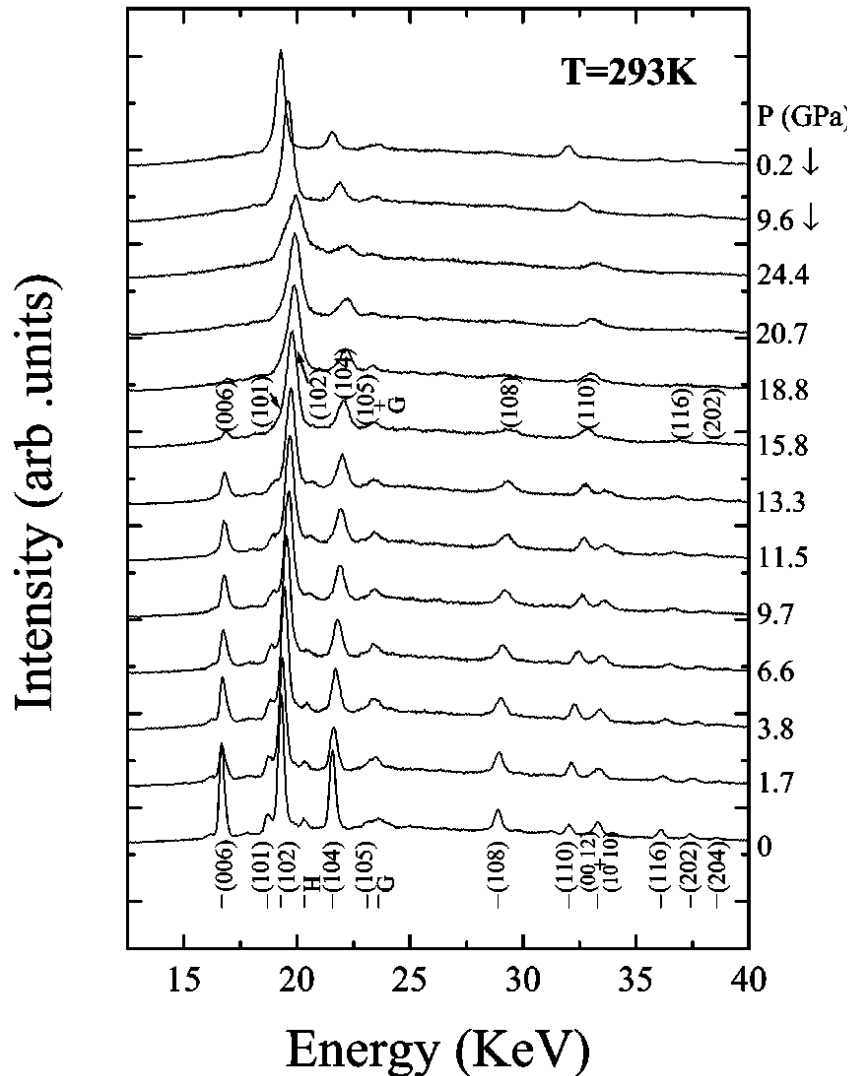
- ODE at SOLEIL (Dispersive EXAFS)
- Membrane diamond anvil cell
- Silicon oil
- **Single crystal, two orientations.**
- **Powder**
- **Cu K-edge** (8979 eV)
- Inconel gasket
- Ruby



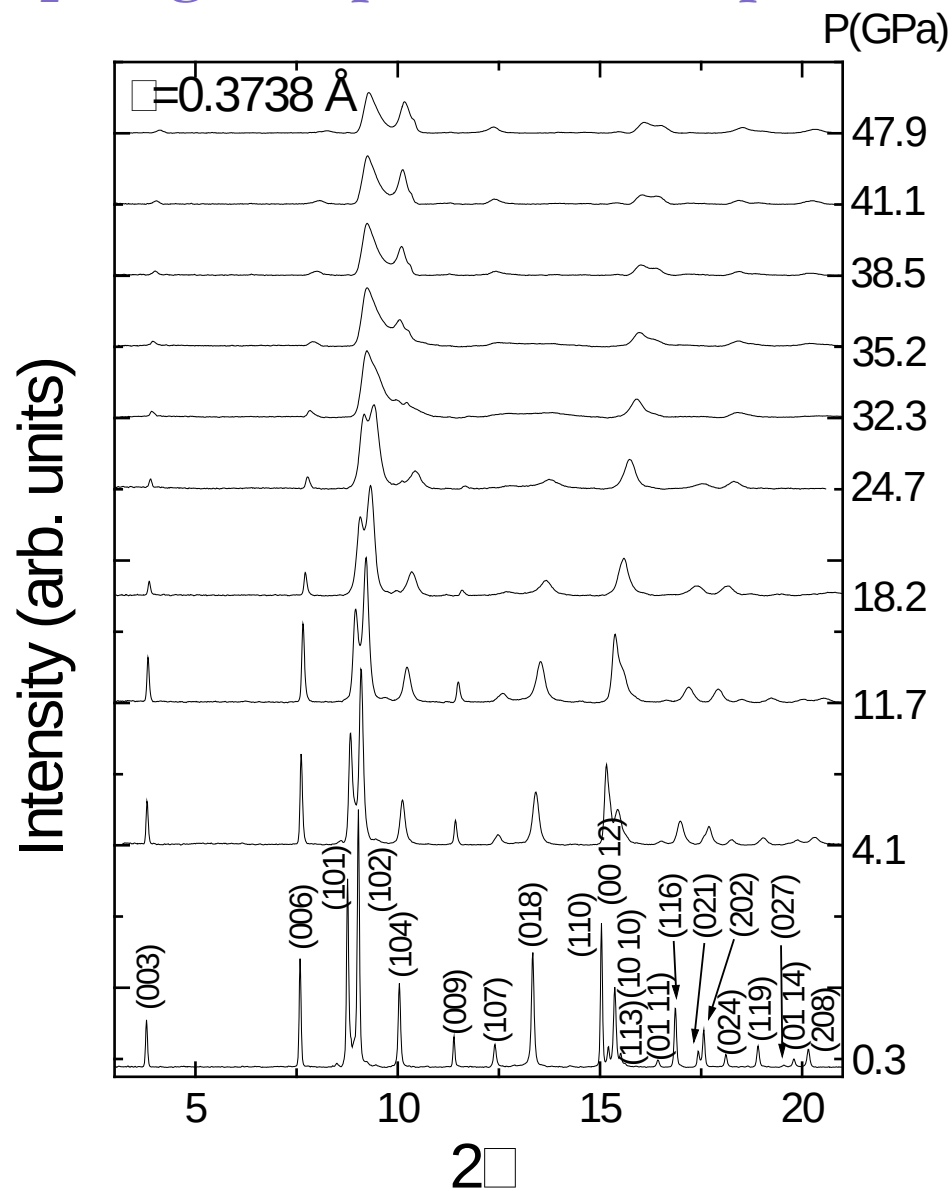
Outline:

- Introduction: delafossites.
- Experimental.
- Results.
 - XRD.
 - XAFS
- Discussion.
- Conclusions.

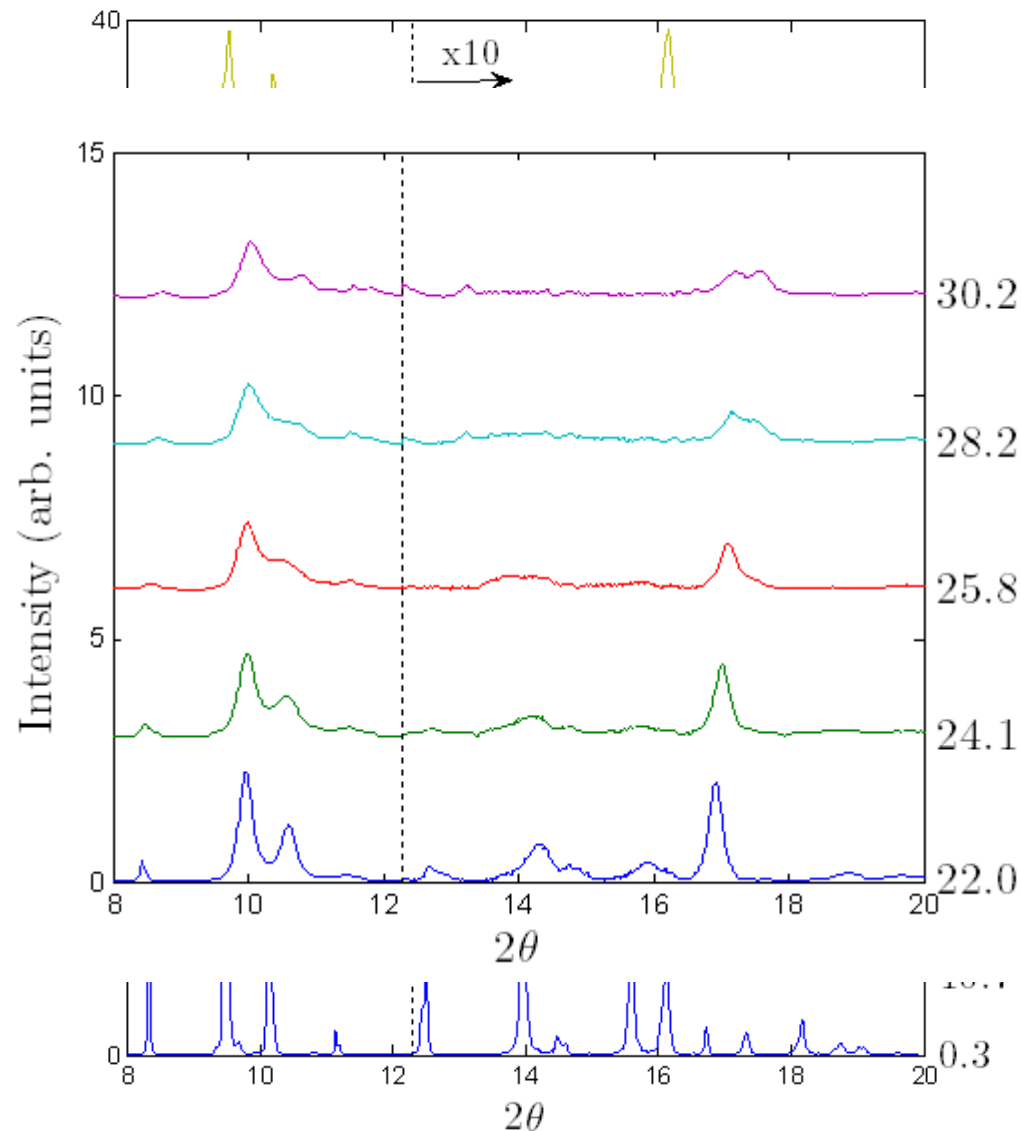
CuGaO₂: Energy-dispersive XRD spectra



CuAlO₂: Angle-dispersive XRD spectra

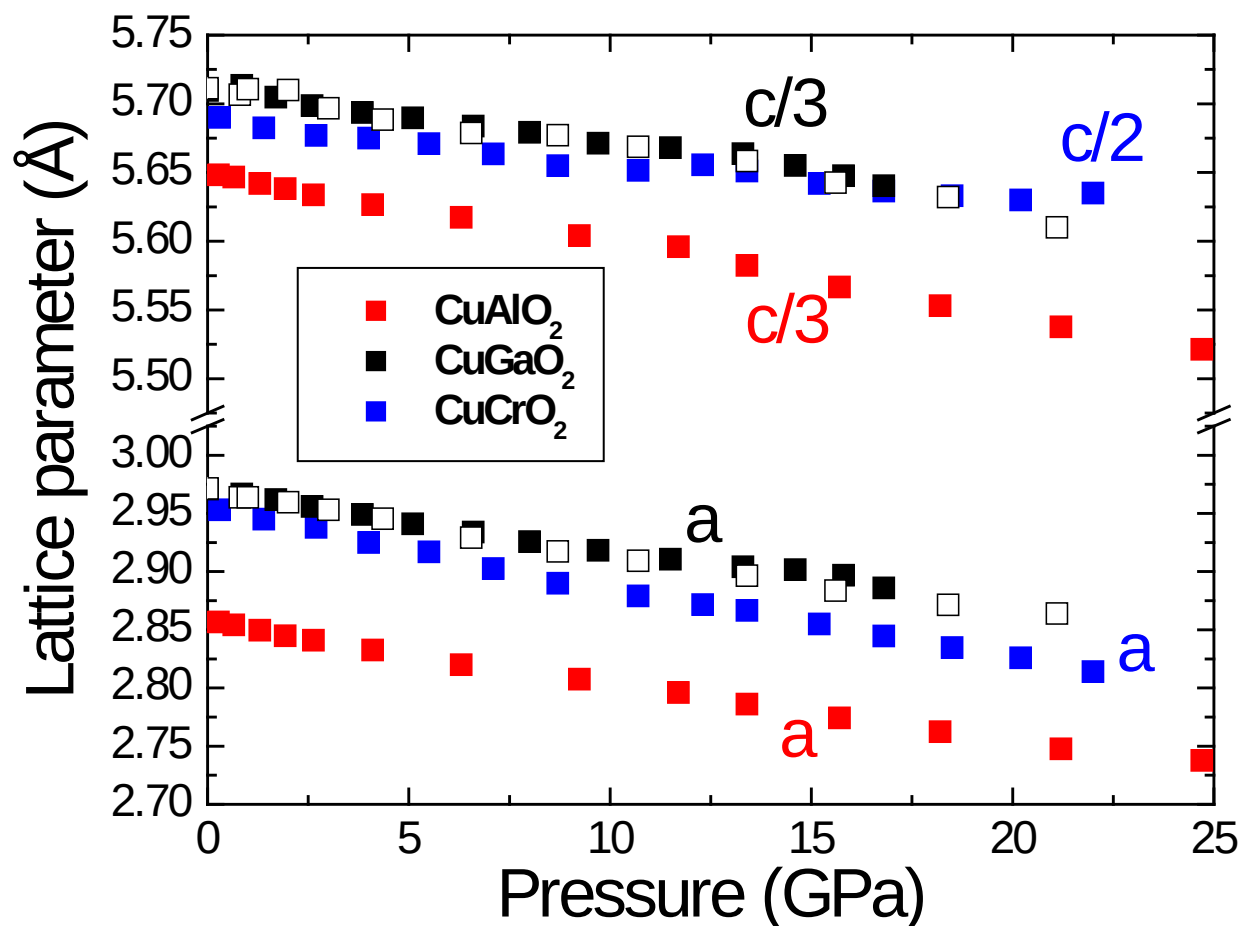


CuCrO₂: Angle-dispersive XRD spectra



Phase
transition at
 25 ± 1 GPa

Lattice parameters



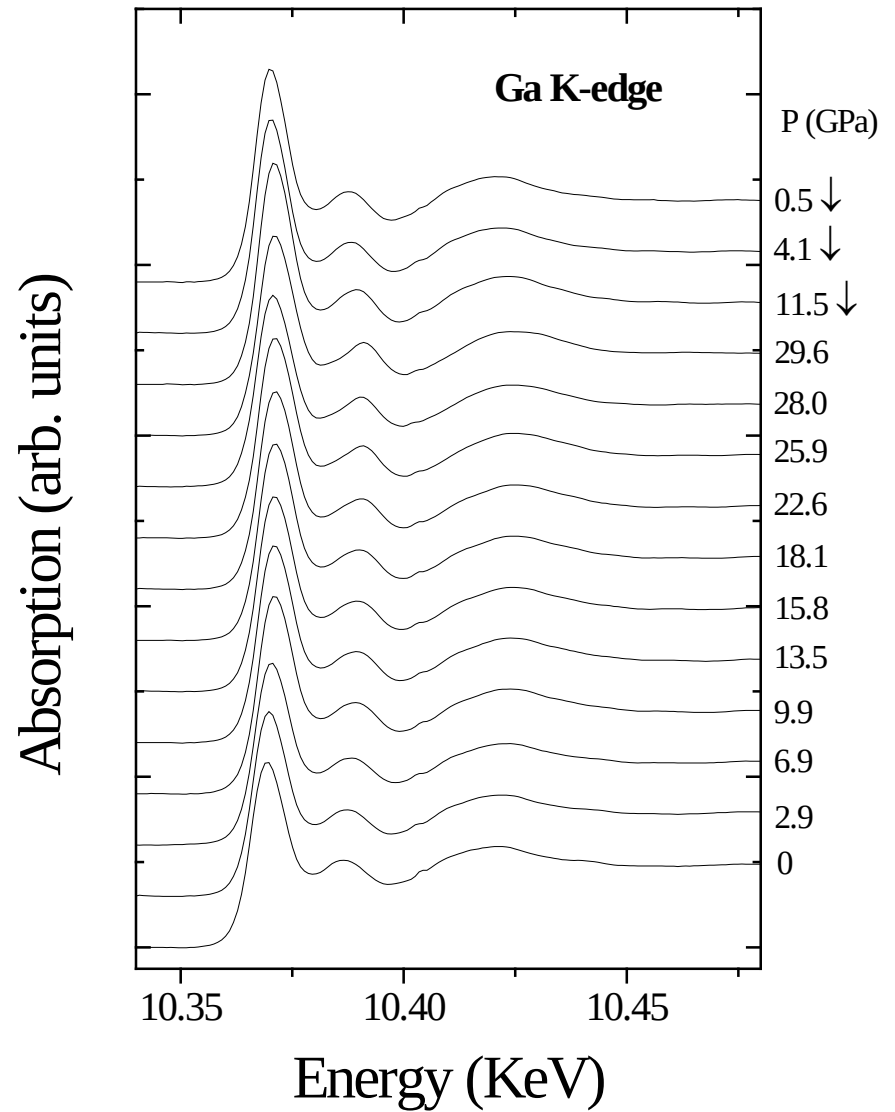
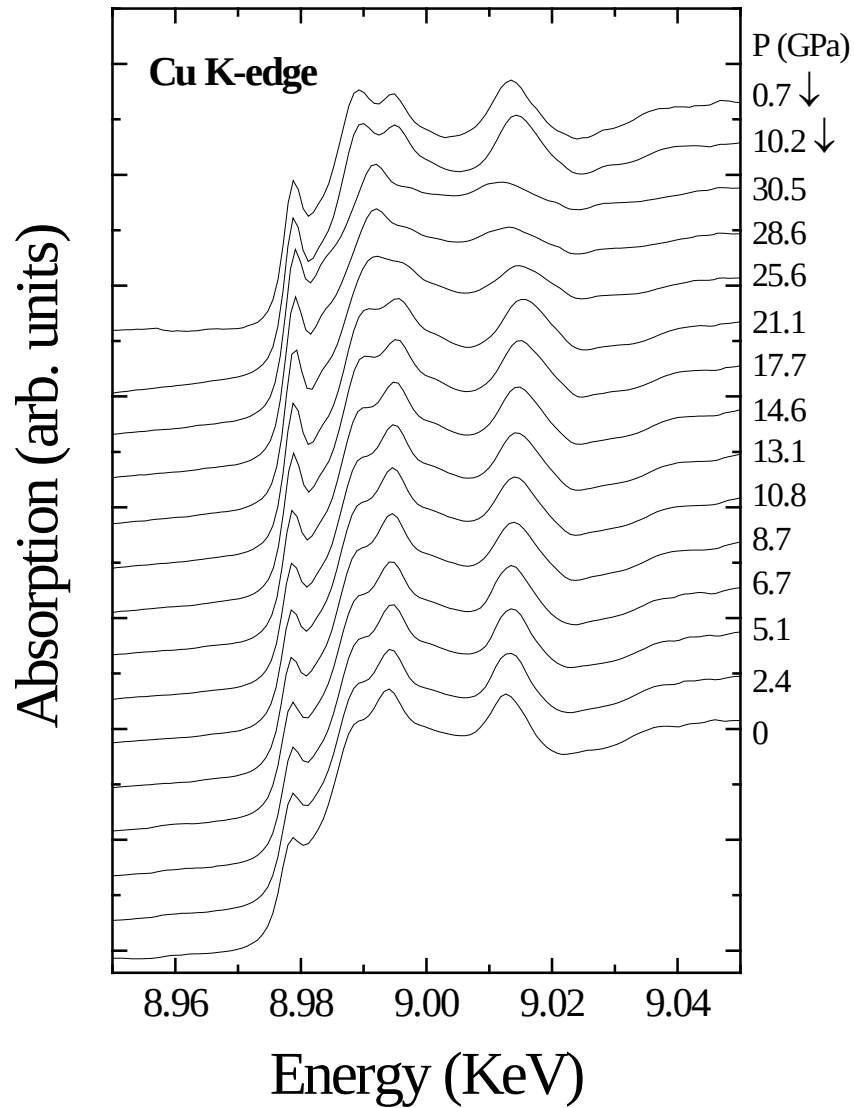
Compressibility:

	CuGaO_2	CuAlO_2	CuCrO_2
χ_a (10^{-4}GPa^{-1})	19.6(5)	20.6(5)	22.0(5)
χ_c (10^{-4}GPa^{-1})	7.5(4)	8.3(4)	6.8(6)

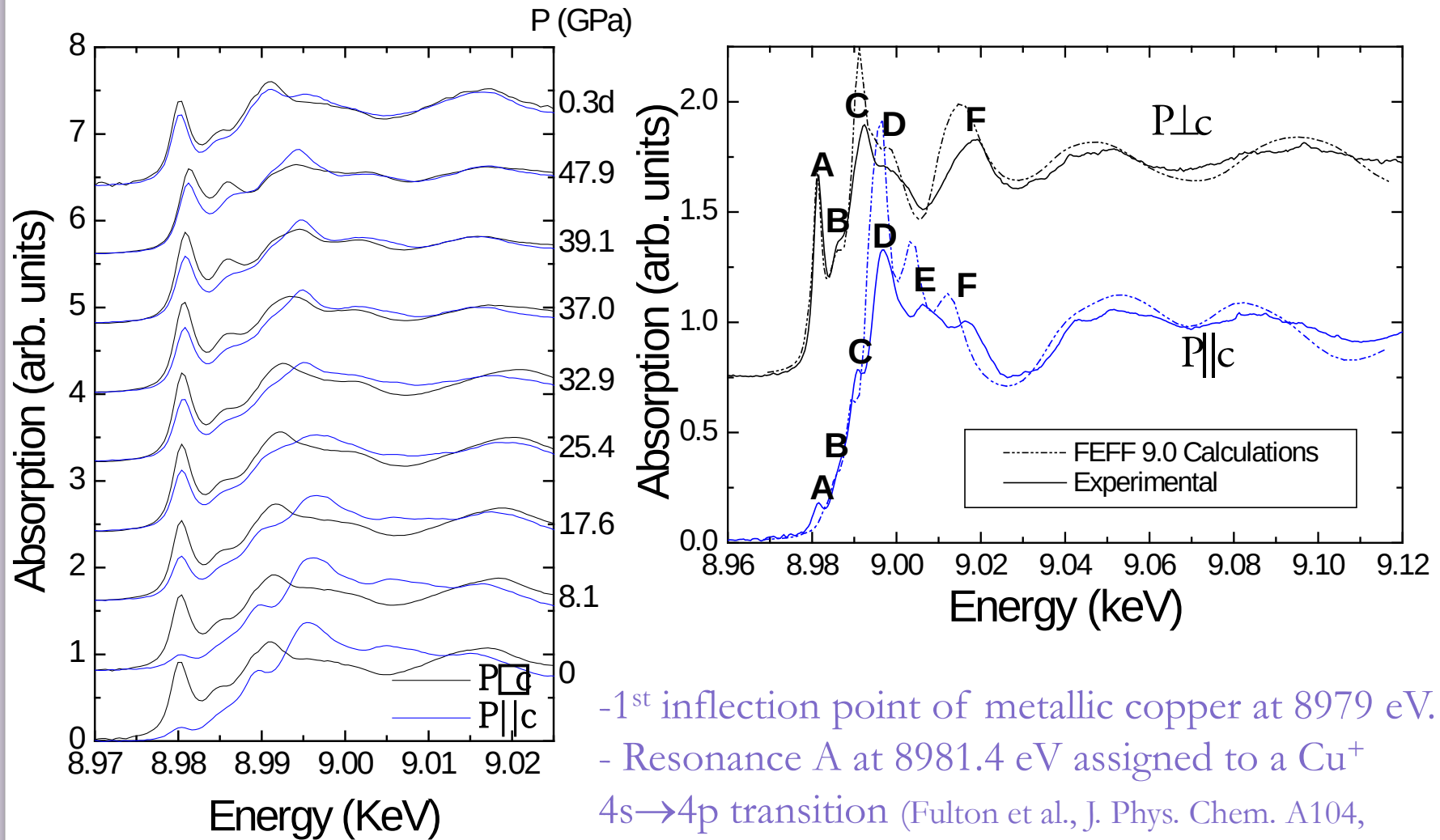
Outline:

- Introduction: delafossites.
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 - XRD.
 - XAFS
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- Conclusions.

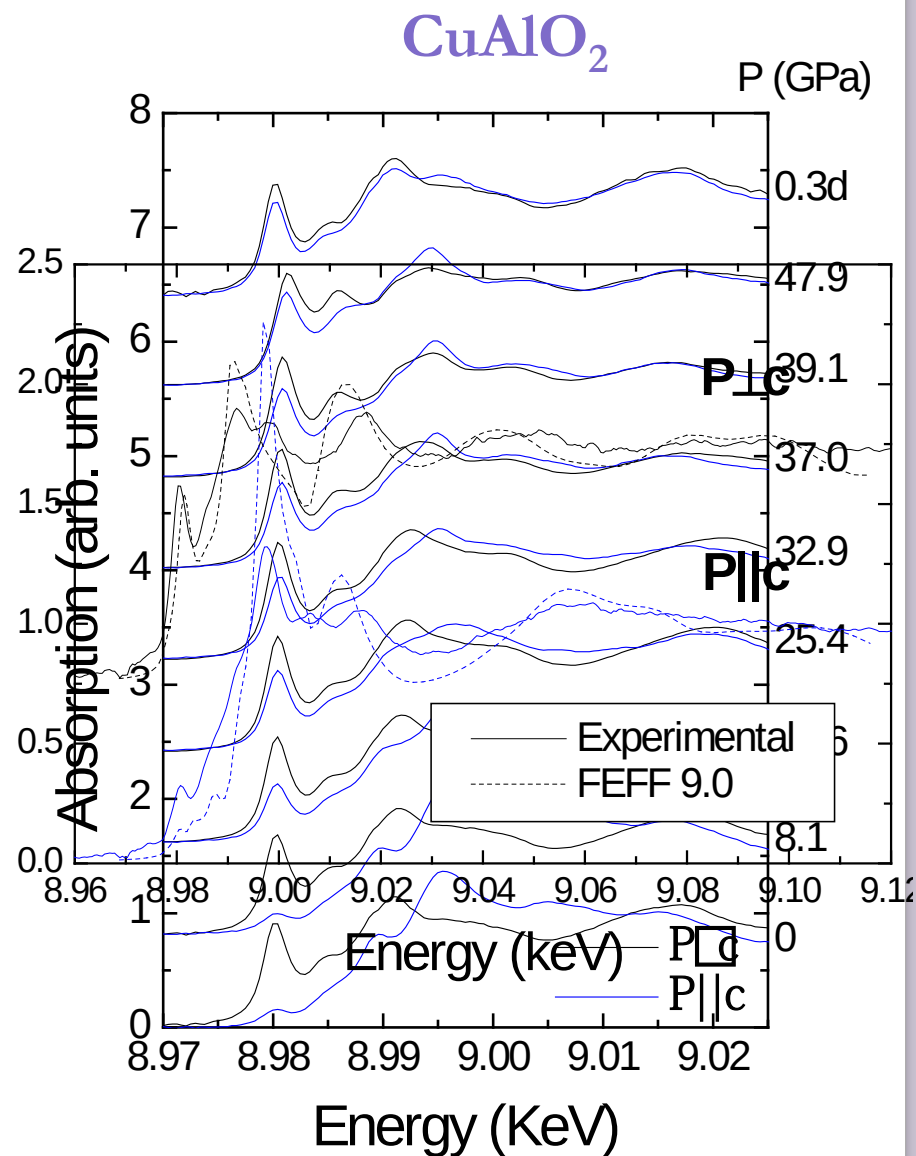
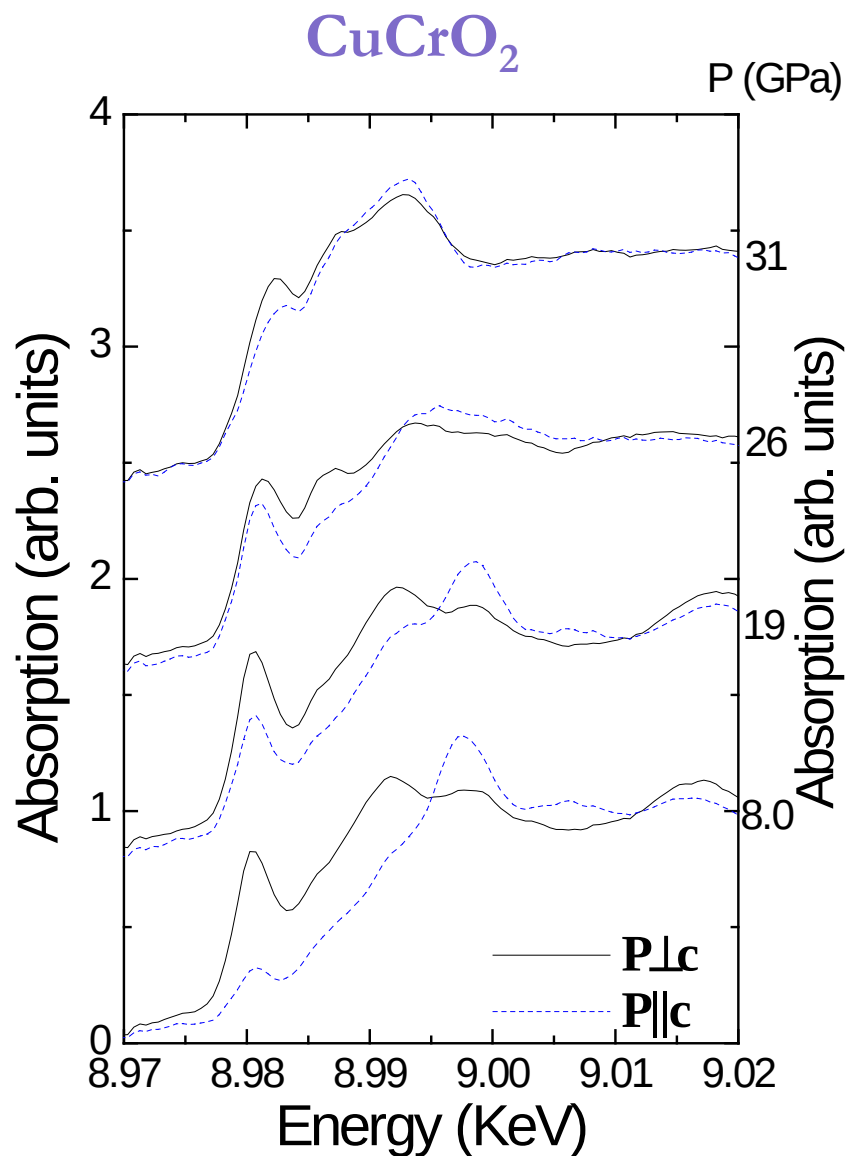
CuGaO_2 : XANES



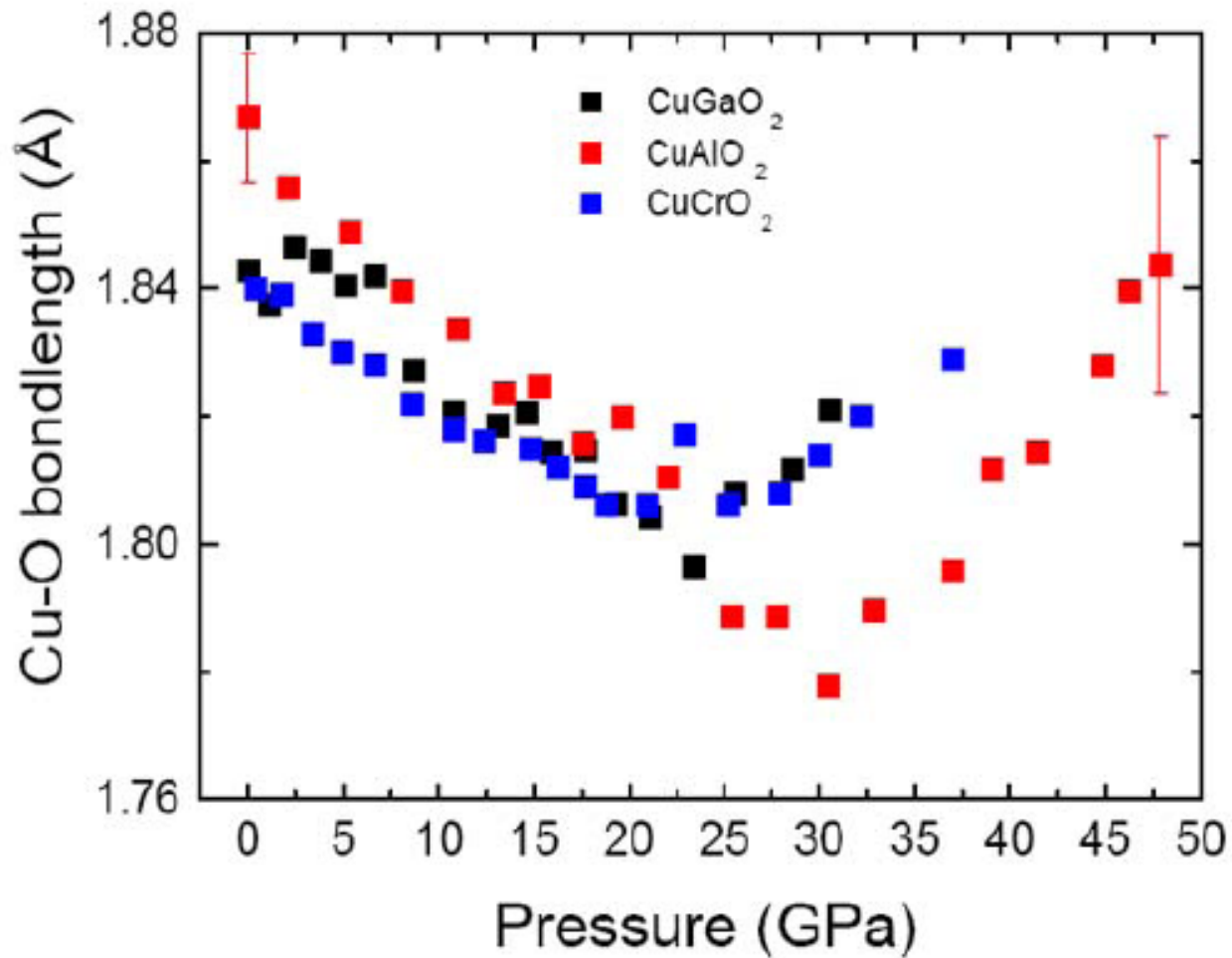
CuAlO₂: XANES



- 1st inflection point of metallic copper at 8979 eV.
- Resonance A at 8981.4 eV assigned to a Cu⁺ 4s→4p transition (Fulton et al., J. Phys. Chem. A104, 11651 (2000))

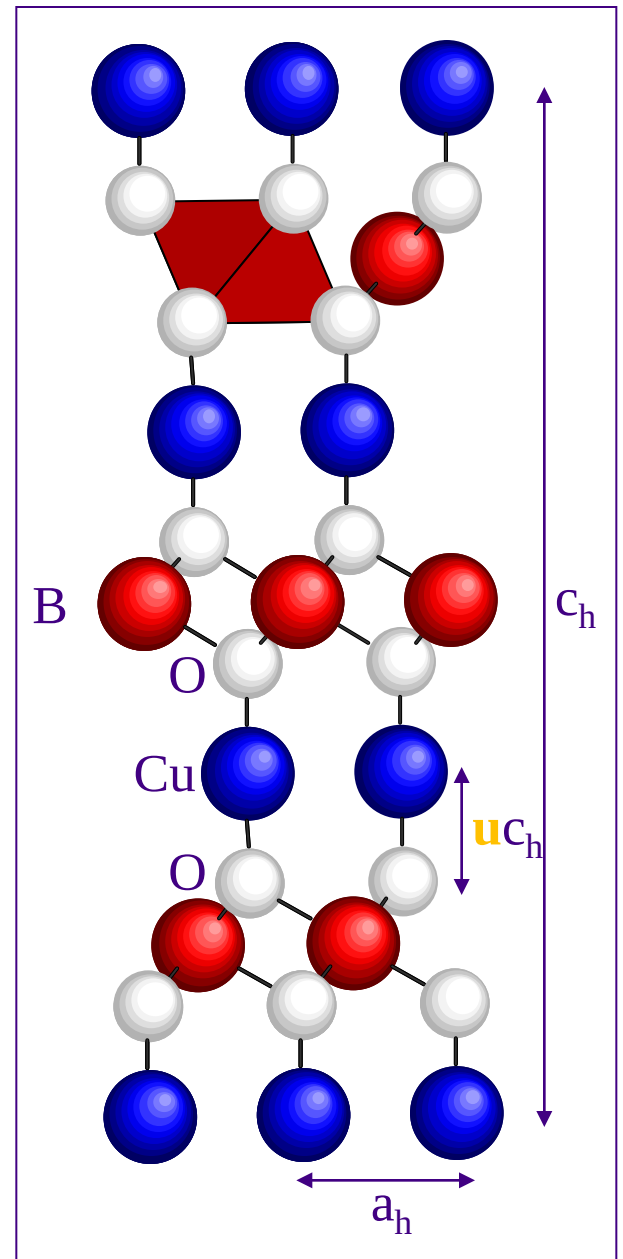
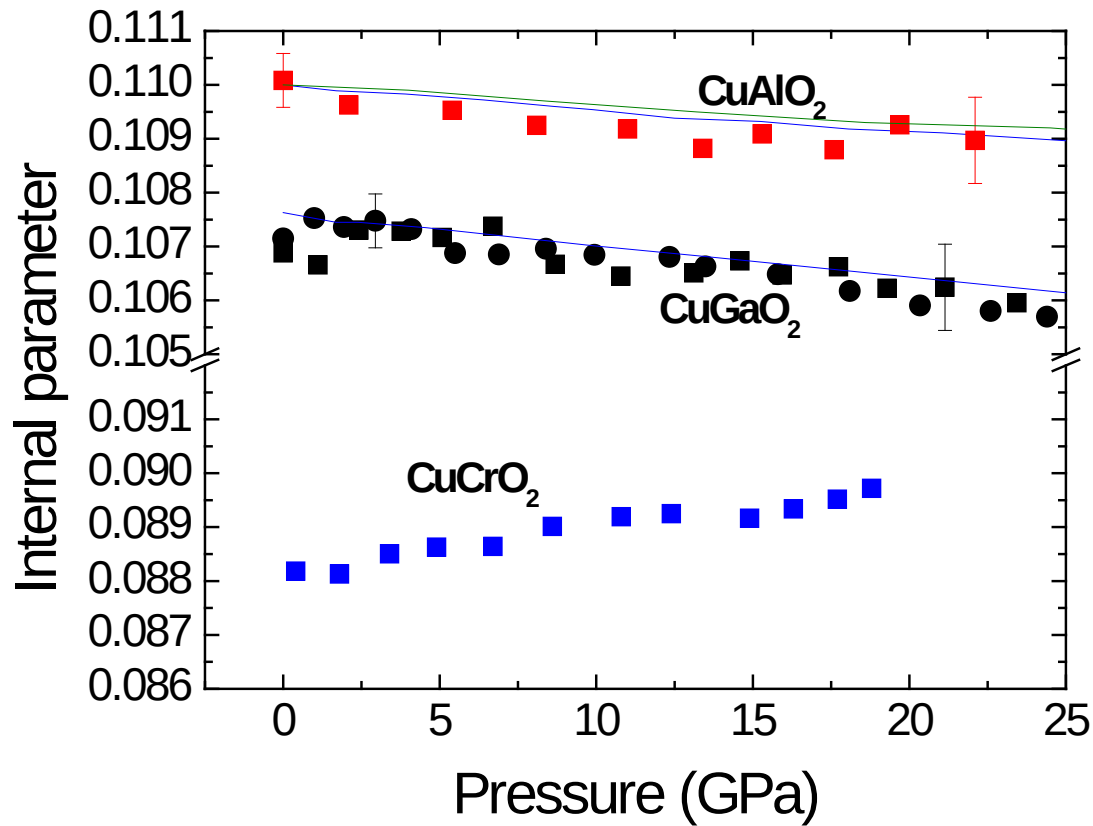


Cu-O bondlength from EXAFS fit



Outline:

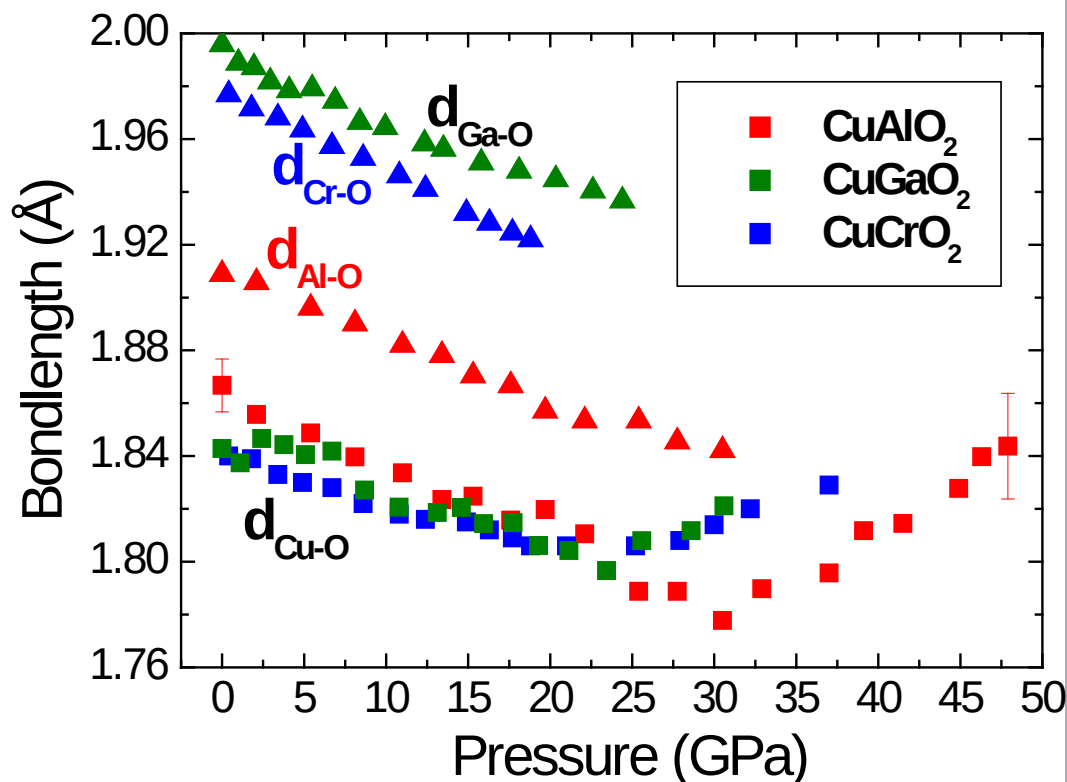
- Introduction: delafossites.
- Experimental.
- Results.
- Discussion.
 - Structural changes in the low pressure phase.
 - High pressure phase and precursor effects.
- Conclusions.

Internal parameter u 

Bond compressibility

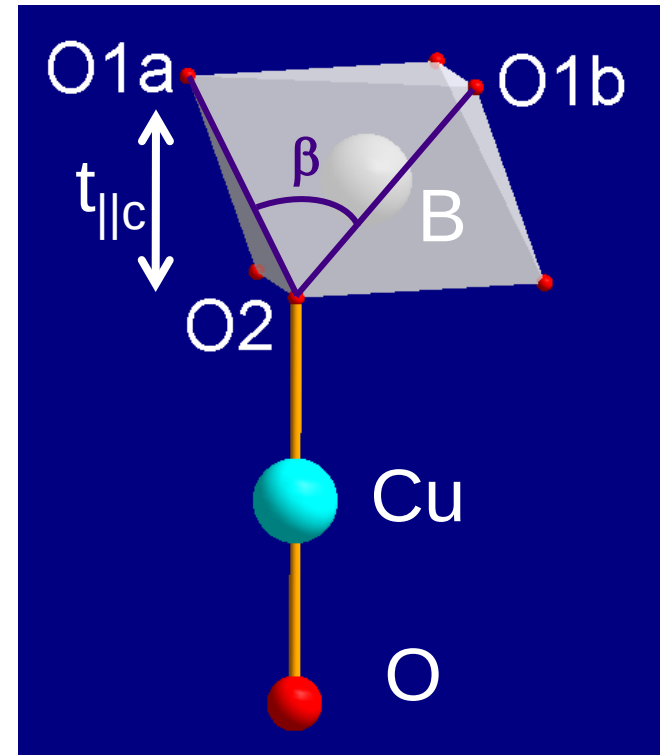
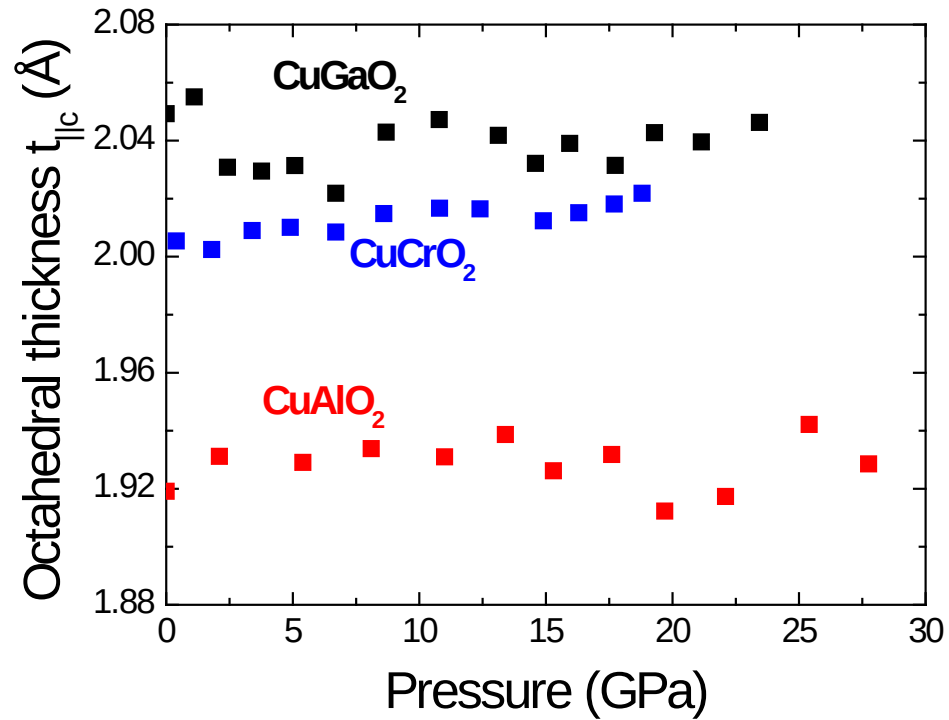
-The monovalent (Cu) and trivalent (Al, Ga) bond lengths show similar compressibility in CuAlO_2 and CuGaO_2

-On the opposite, in CuCrO_2 the Cu-O bond is harder and the Cr-O bond softer.

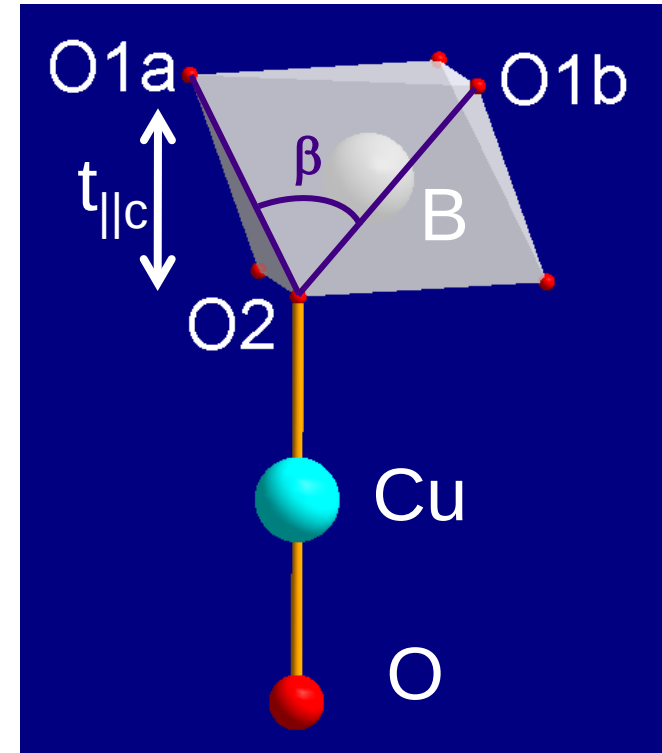
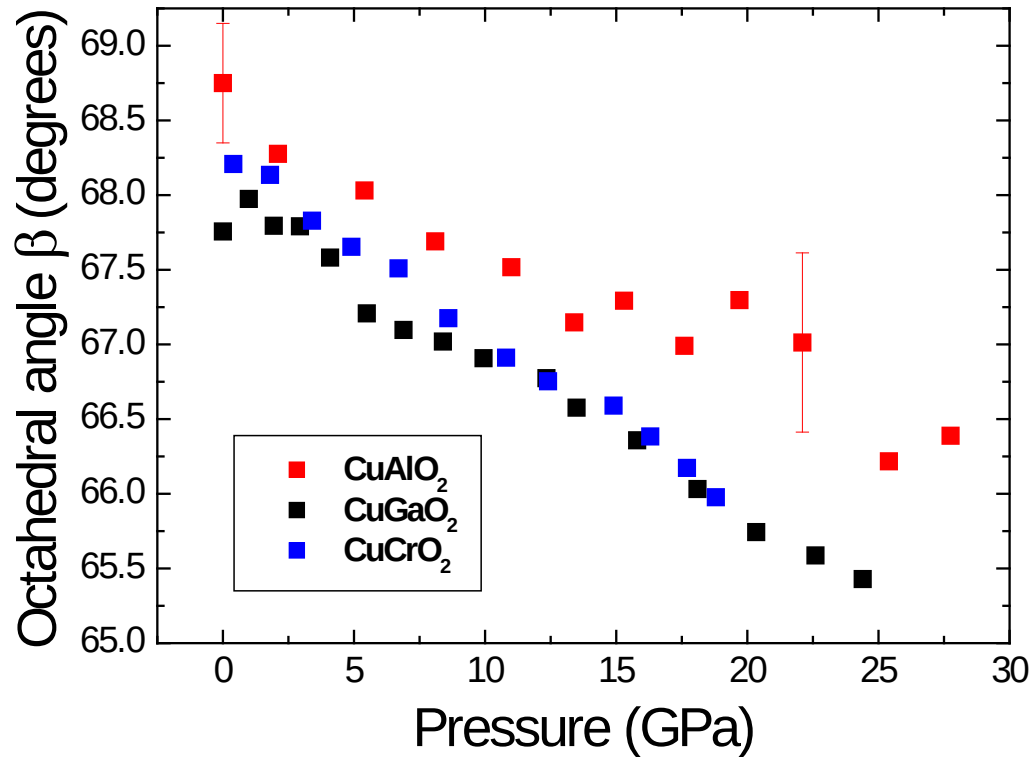


	CuGaO_2	CuAlO_2	CuCrO_2
χ_a (10^{-4}GPa^{-1})	19.6(5)	20.6(5)	22.0(5)
χ_c (10^{-4}GPa^{-1})	7.5(4)	8.3(4)	6.8(6)
$\chi_{\text{Cu-O}}$ (10^{-4}GPa^{-1})	12.5(8)	14.6(7)	9.7(4)
$\chi_{\text{B-O}}$ (10^{-4}GPa^{-1})	11.6(9)	12.0(5)	15.2(2)

Octahedral thickness



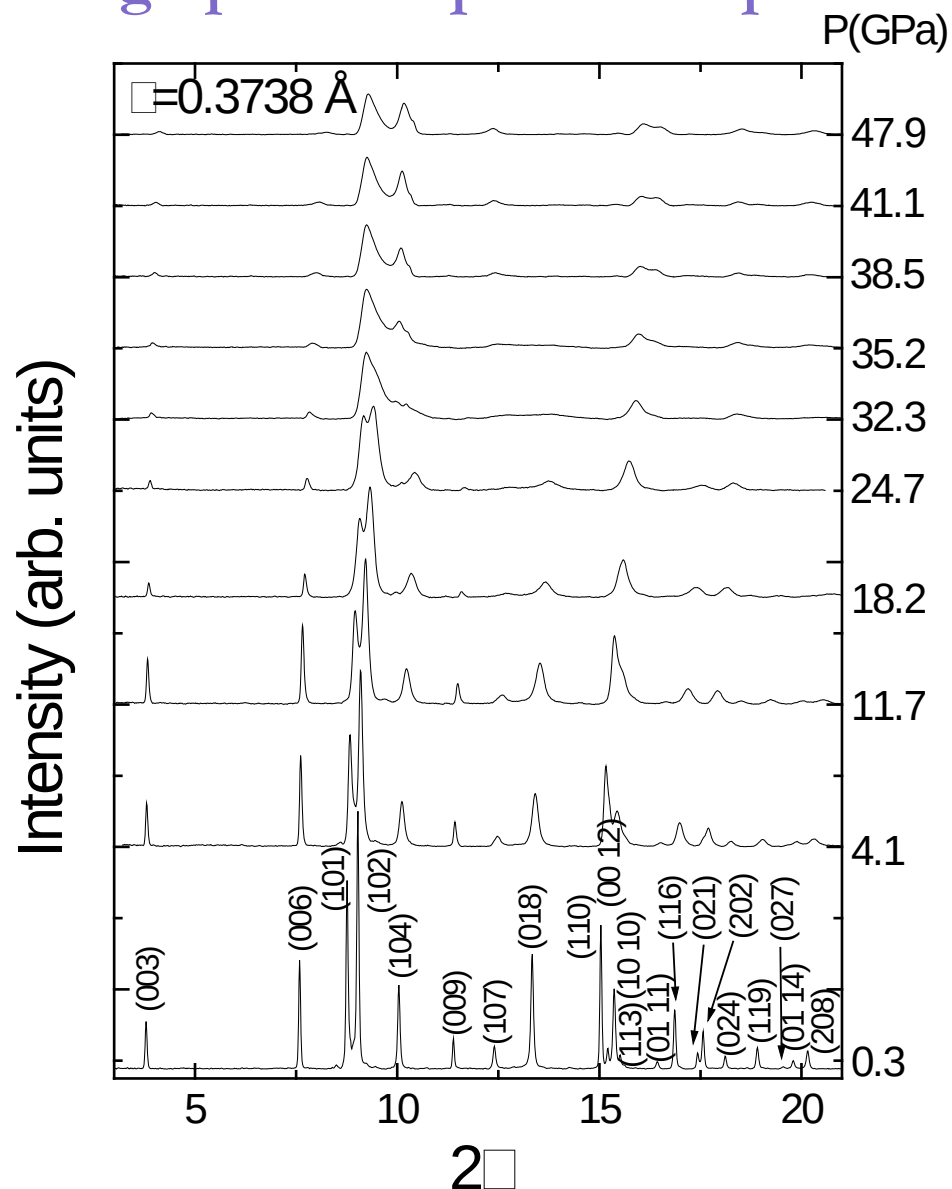
Octahedral angle



Outline:

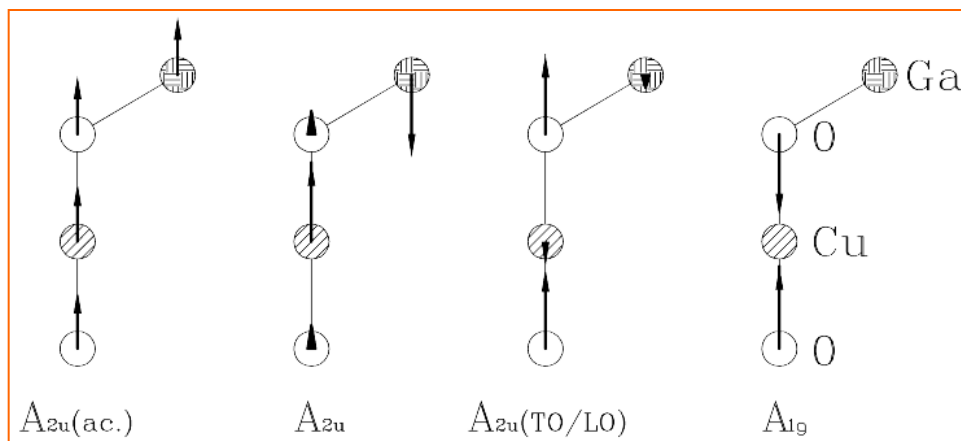
- Introduction: delafossites.
- Experimental.
- Results.
- Discussion.
 - Structural changes in the low pressure phase.
 - High pressure phase and precursor effects.
- Conclusions.

High pressure phase and precursor effects.



- We do not know the structure of the high pressure polymorph.

Raman modes



$$\Gamma = A_{1g} + E_g + 3A_{2u} + 3E_u$$

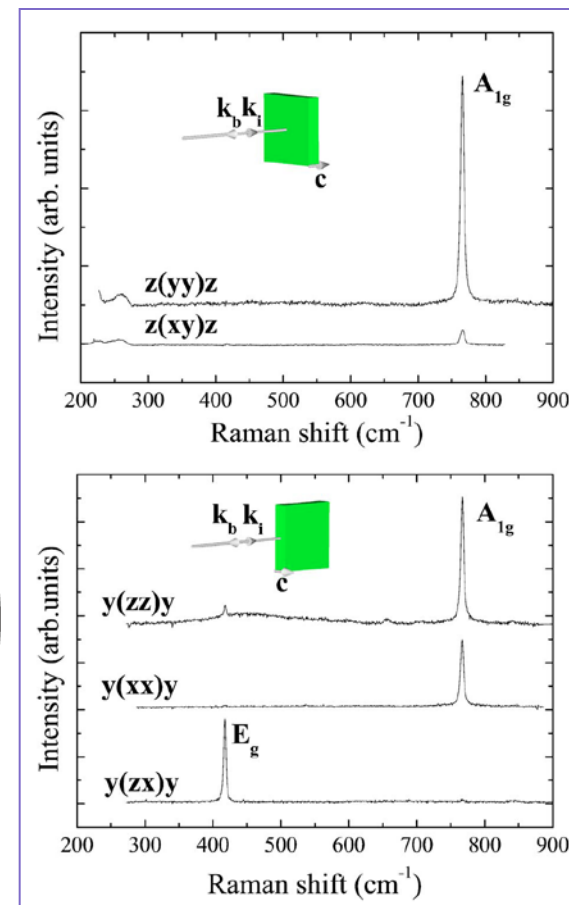
$$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \quad E_g(y) = \begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix} \quad E_g(x) = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}$$

PRB 72, 064301 (2005)

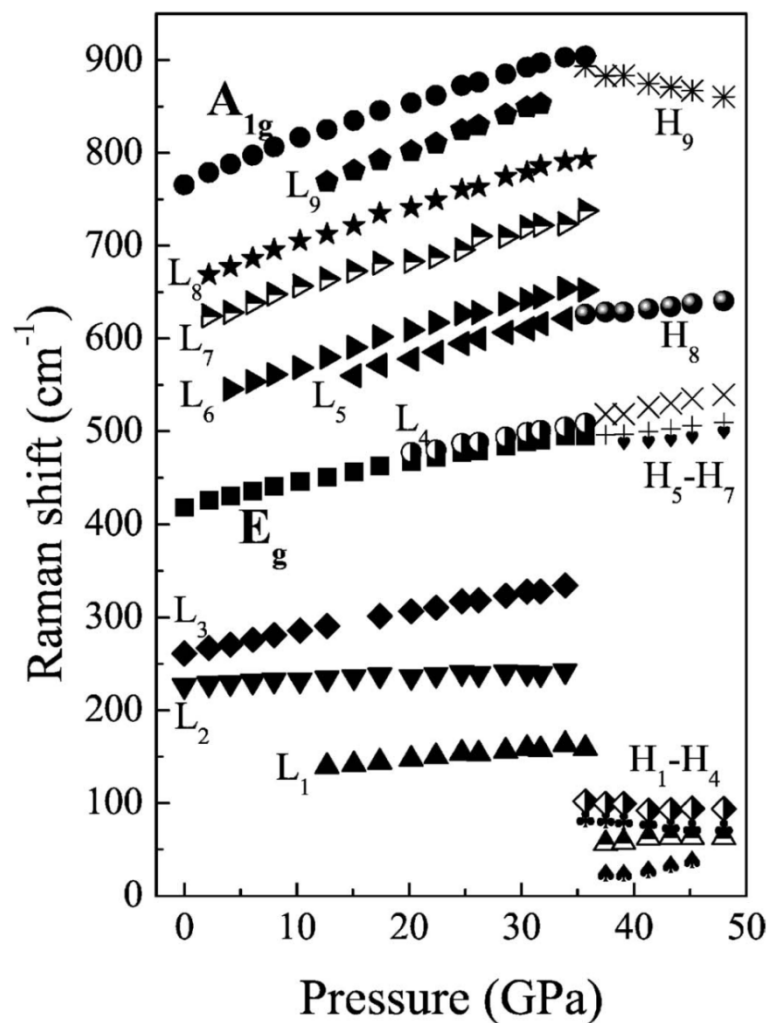
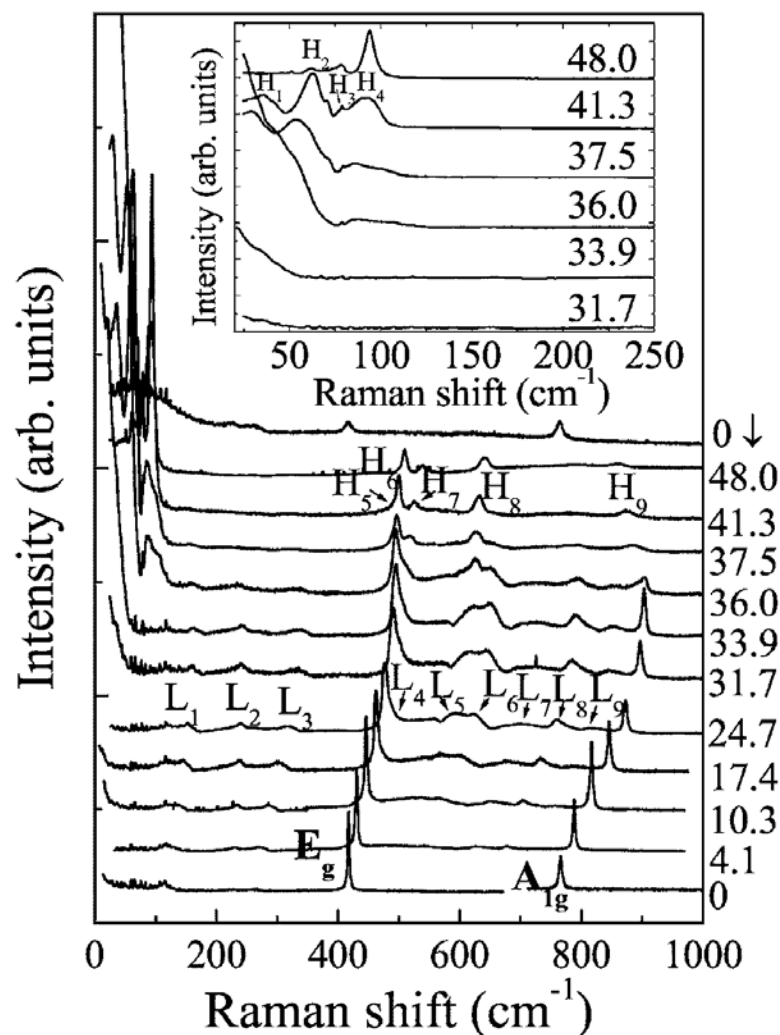
PRB 74, 184301 (2006)

Phys. Stat. Sol. b)244, 342 (2007)

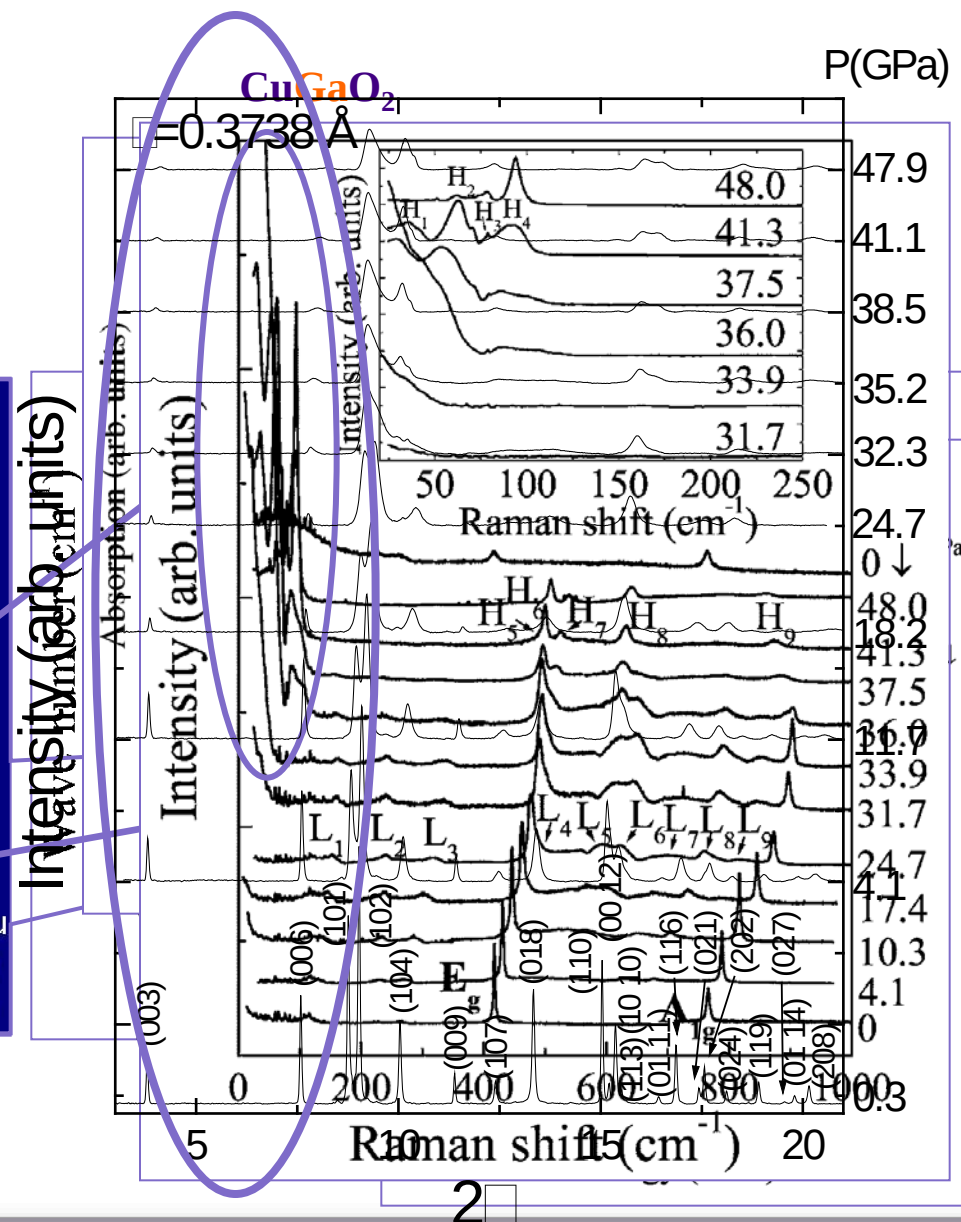
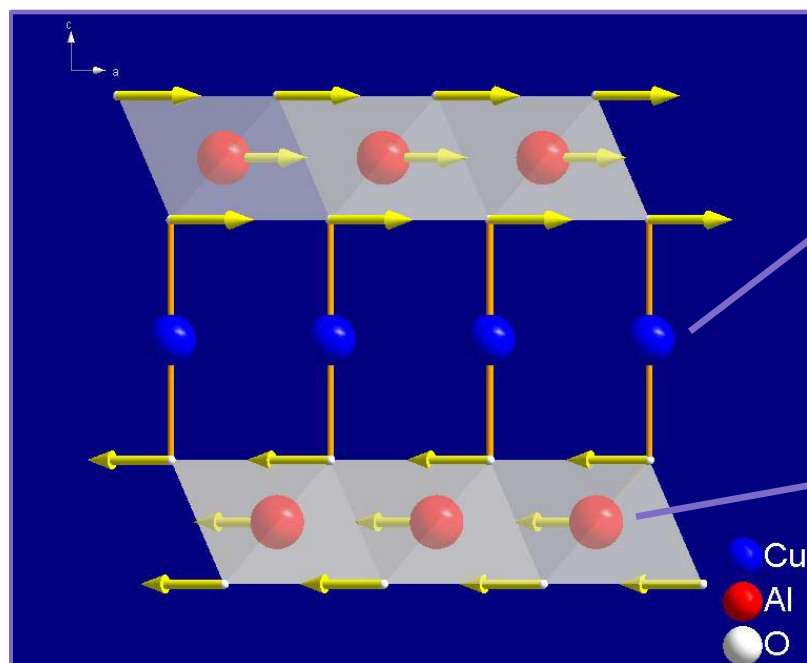
CuAlO_2



High pressure Raman experiment in CuAlO_2



Softening of the transversal acoustic branch along ΓT



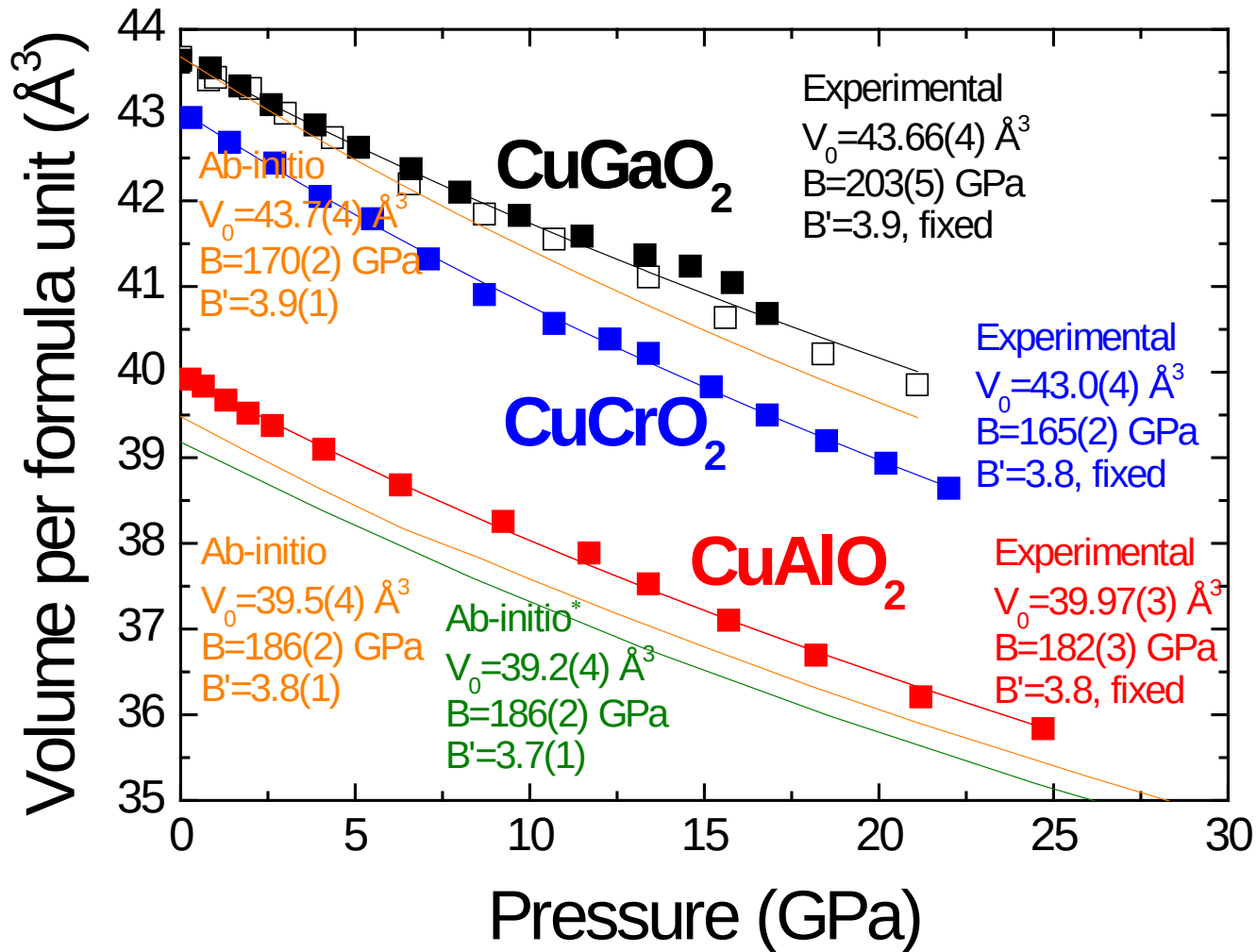
Outline:

- Introduction: de la fosforescencia.
- Experimental.
- Results.
- Discussion.
- **Conclusions.**

Conclusions

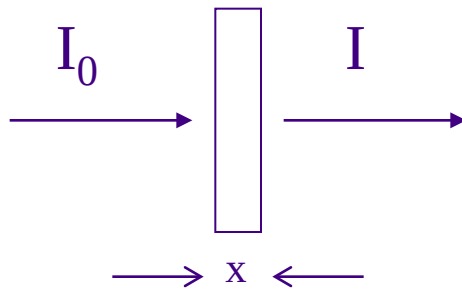
- XRD evidence anisotropic compression, the a-axis being more compressible than the c-axis.
- EXAFS yields the cation-oxygen bondlengths, from which the internal parameter u can be deduced. Results from different edges and available ab-initio calculations are in perfect agreement.
- The combination of anisotropic compression and internal parameter variation results in a regularization of the BO_2 octahedra.
- There is an irreversible phase transition that clearly manifests at 25 GPa in CuGaO_2 and CuCrO_2 and at 33 GPa in CuAlO_2 , with precursor effects observable from lower pressures.
- In CuGaO_2 and CuAlO_2 the phase transition affect the Cu environment but not that of the trivalent cation (Ga or Al). The phase transition is related to the softening of the acoustic branch.

Equations of state

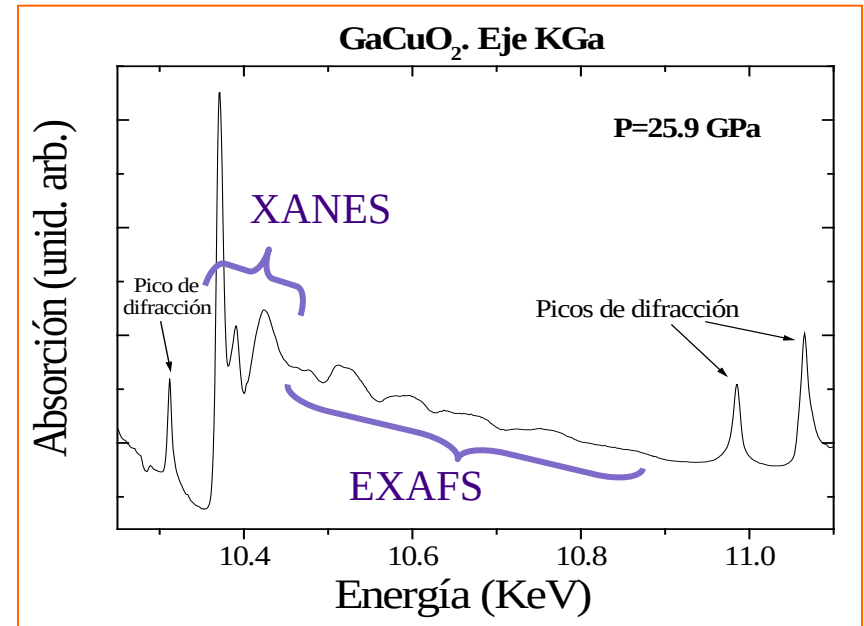


ABSORCIÓN DE RAYOS X (XAS)

- Experiencia de transmisión:



$$I = I_0 e^{-\mu x}$$



XANES: X-ray Absorption Near Edge Structure

EXAFS: Extended X-ray Absorption Fine Structure

- Ventajas:



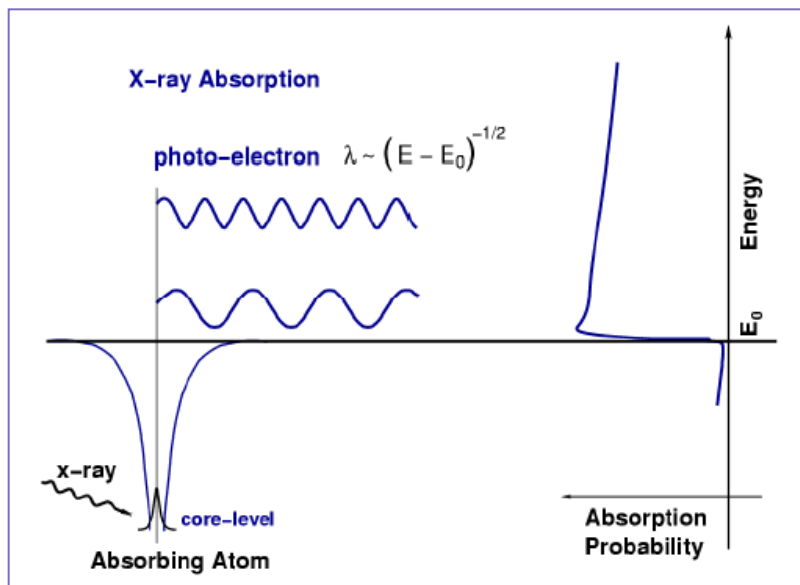
No se requiere orden de largo alcance. Se pueden estudiar del mismo modo sólidos cristalinos y no cristalinos



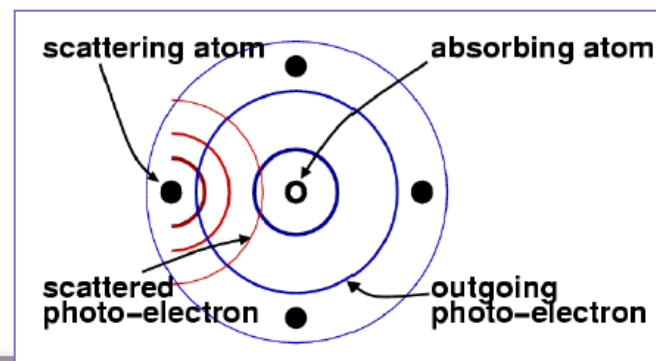
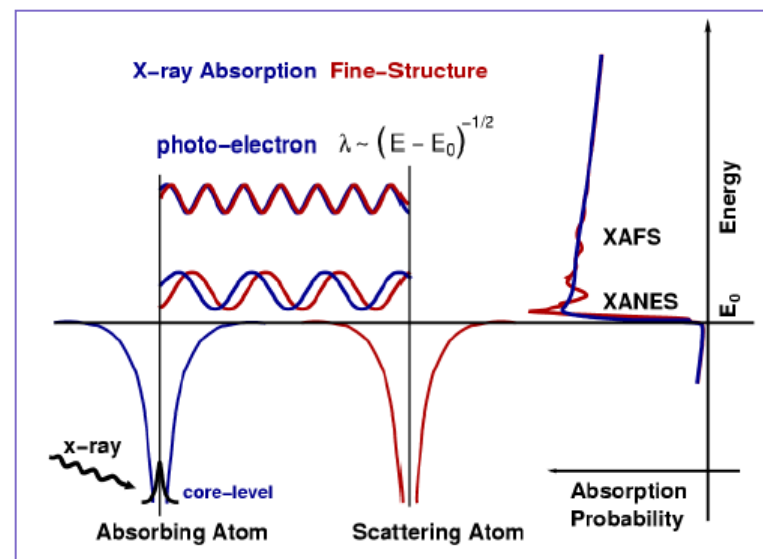
Es posible estudiar el entorno de cada átomo por separado. Es una técnica local.

Efecto del entorno sobre la absorción

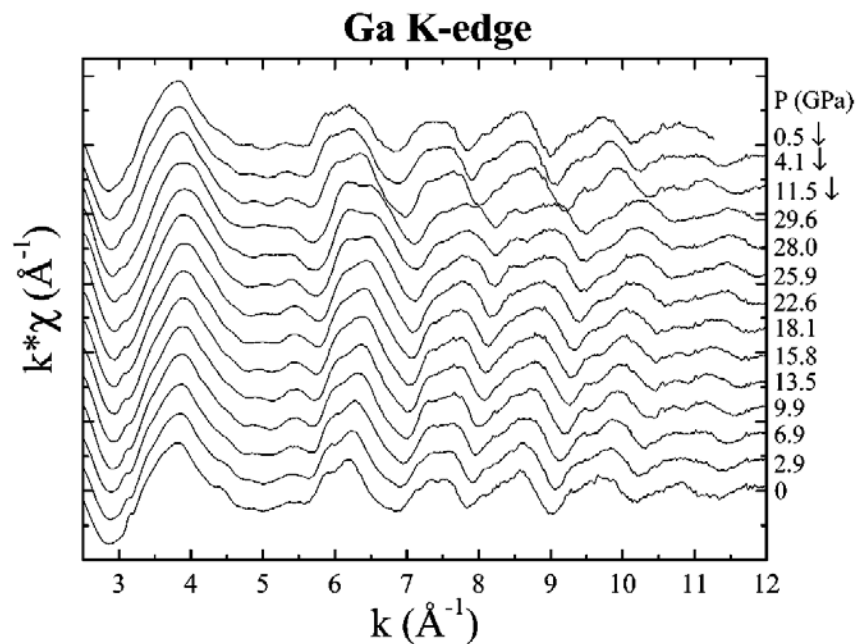
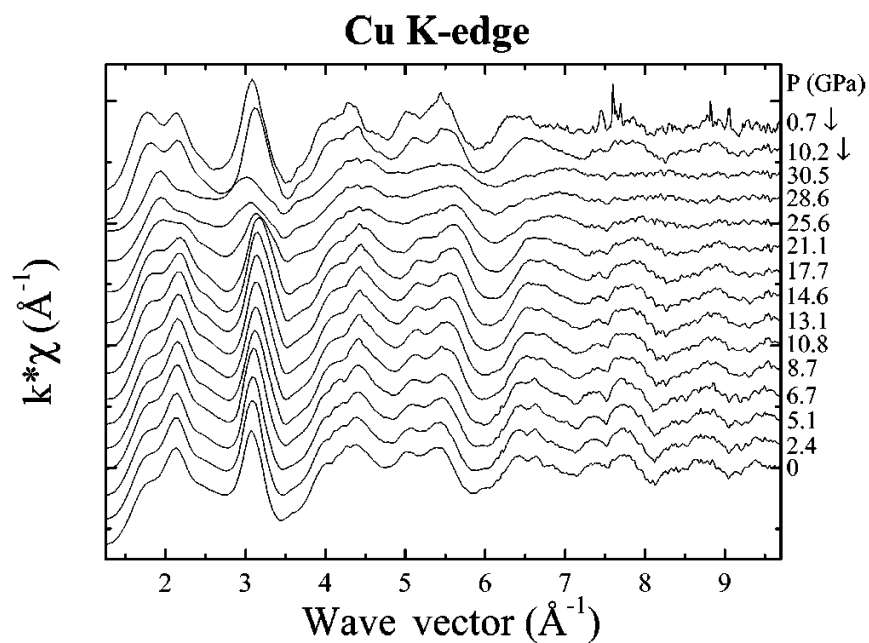
Átomo aislado



Átomo absorbente+vecinos

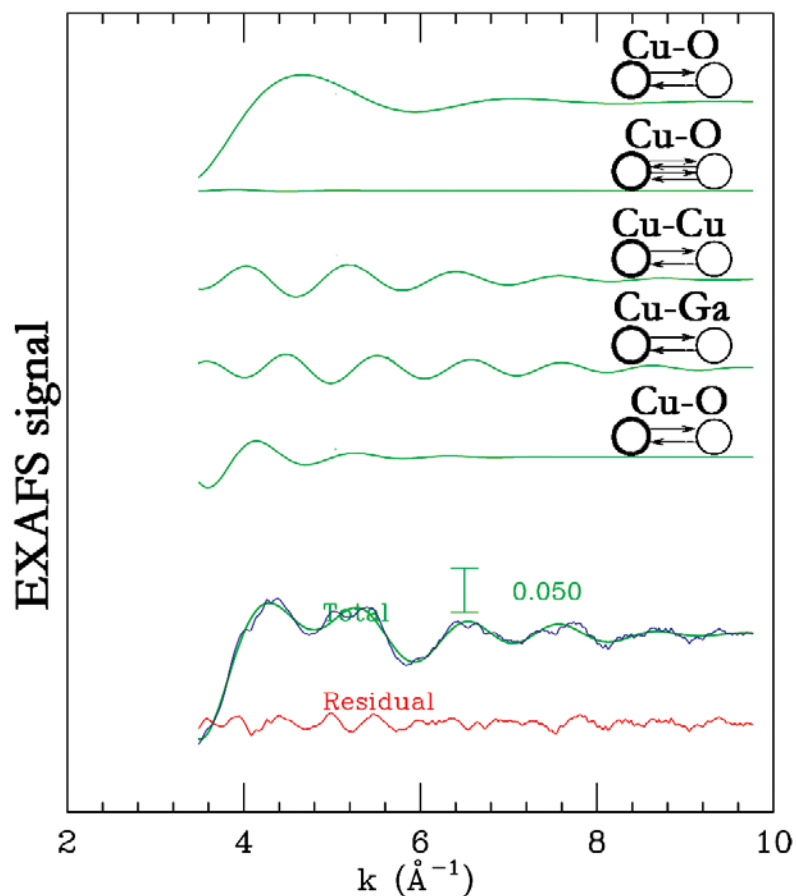


CuGaO₂: EXAFS signal

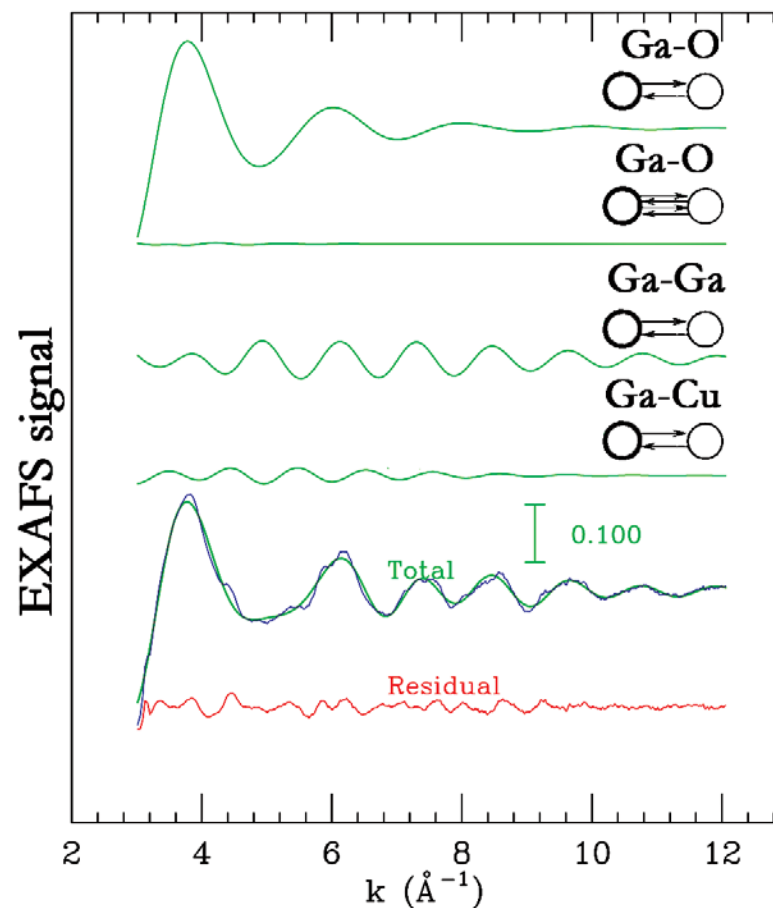


CuGaO₂: EXAFS fit (GNXAS package)

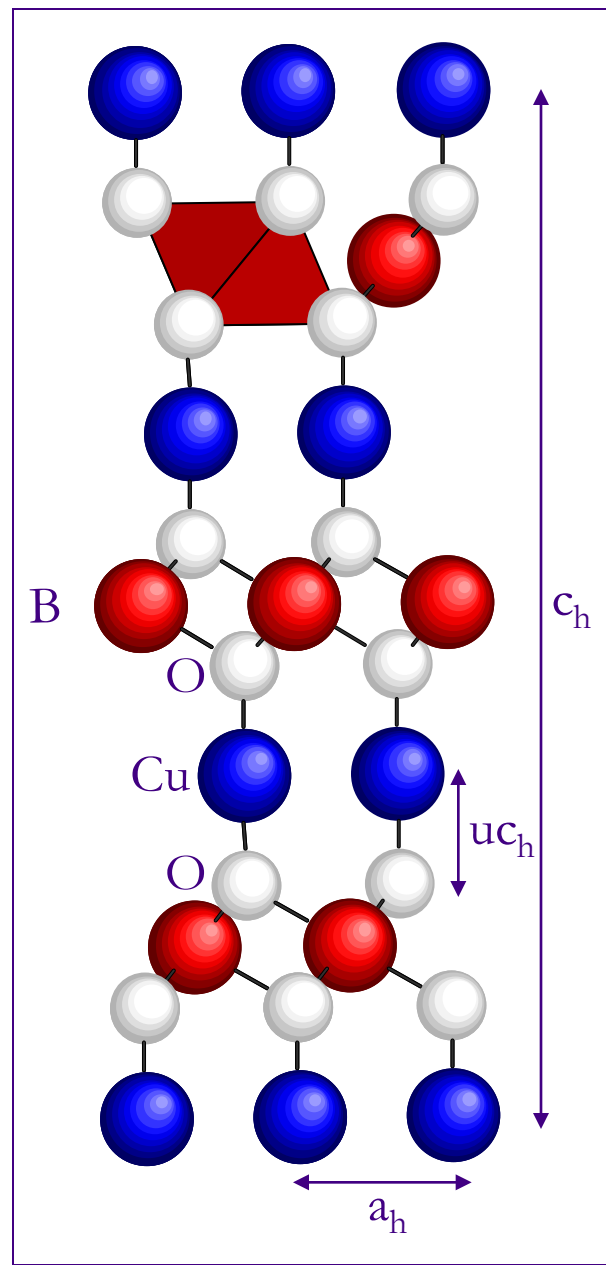
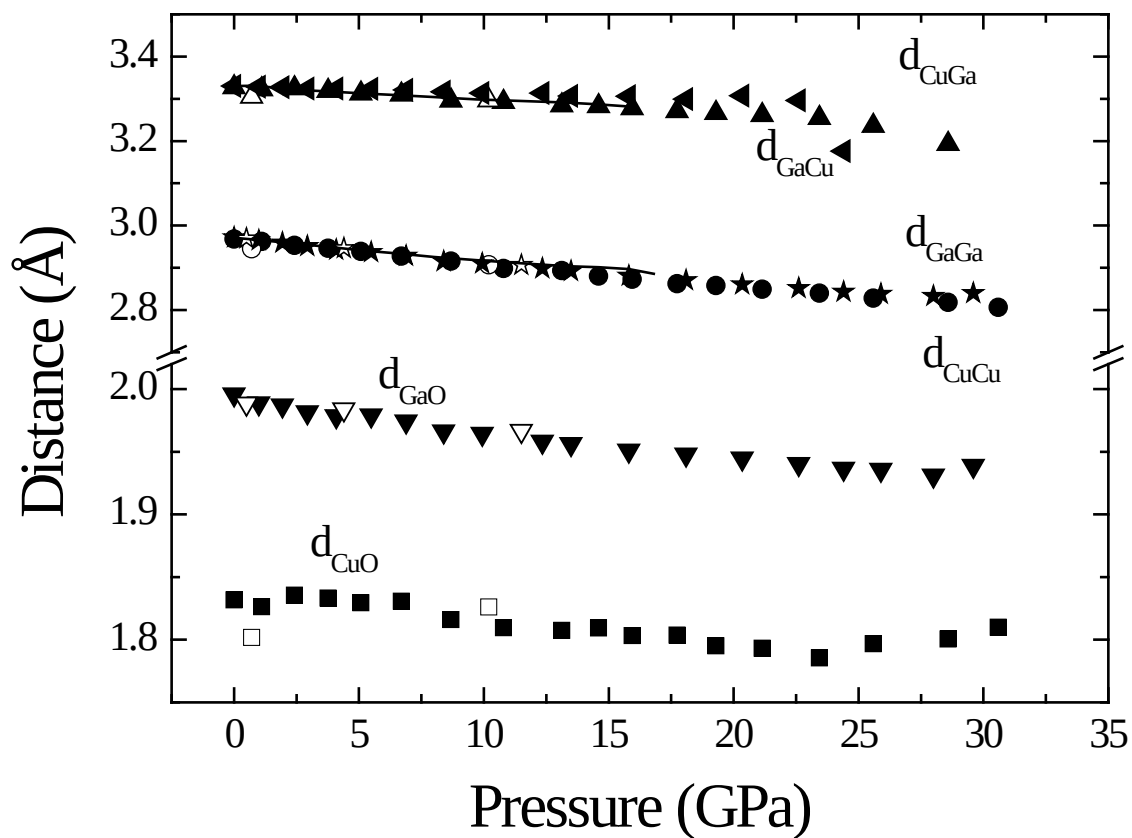
Cu K-edge



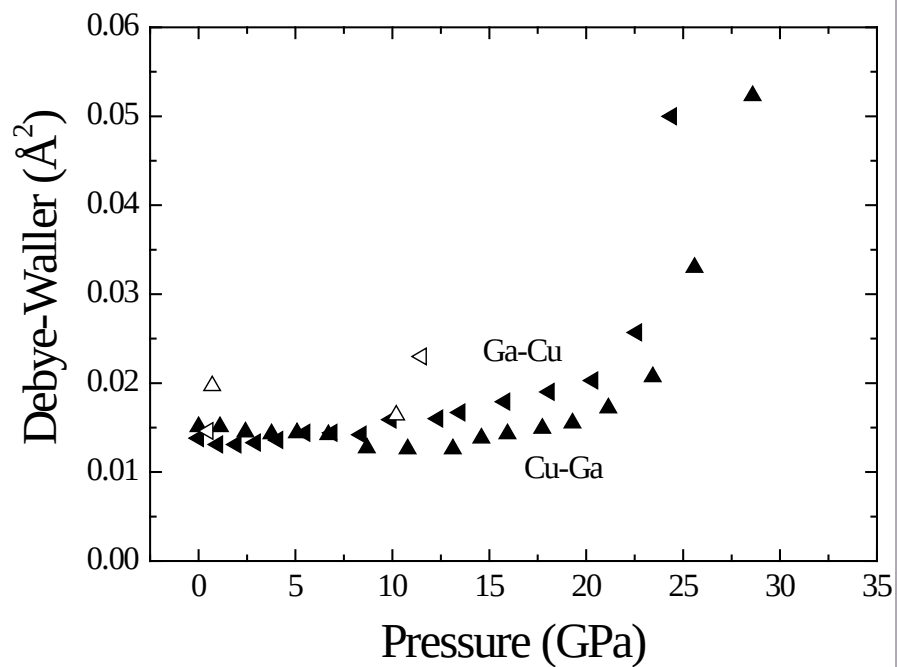
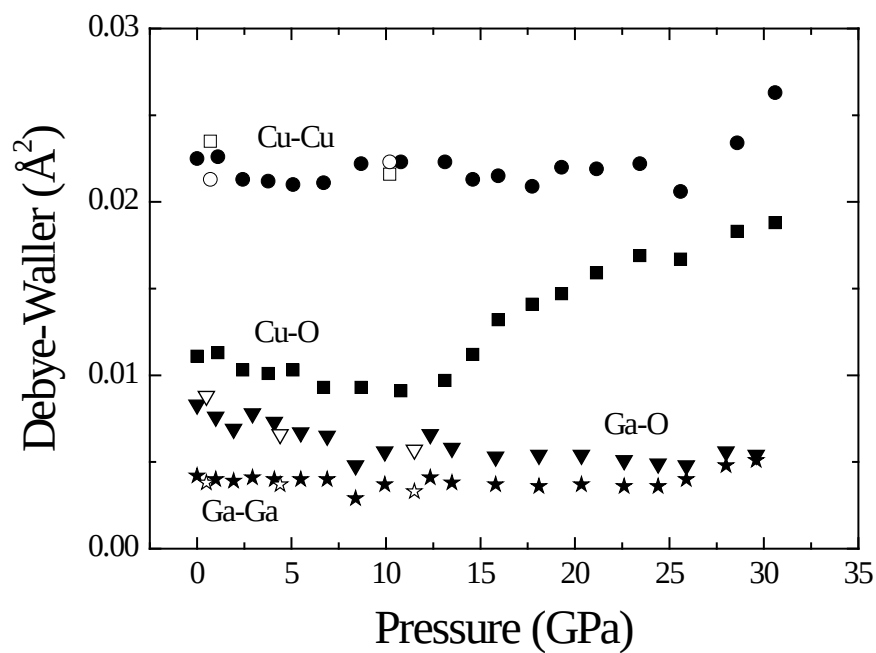
Ga K-edge



CuGaO₂: Bonding lengths

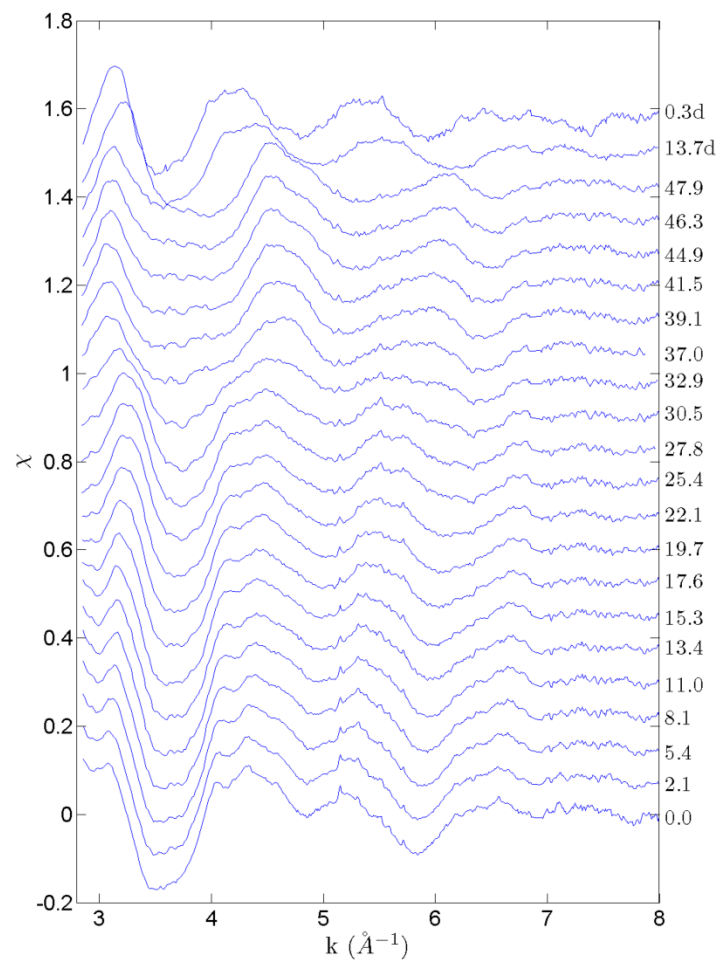


CuGaO₂: Debye-Waller

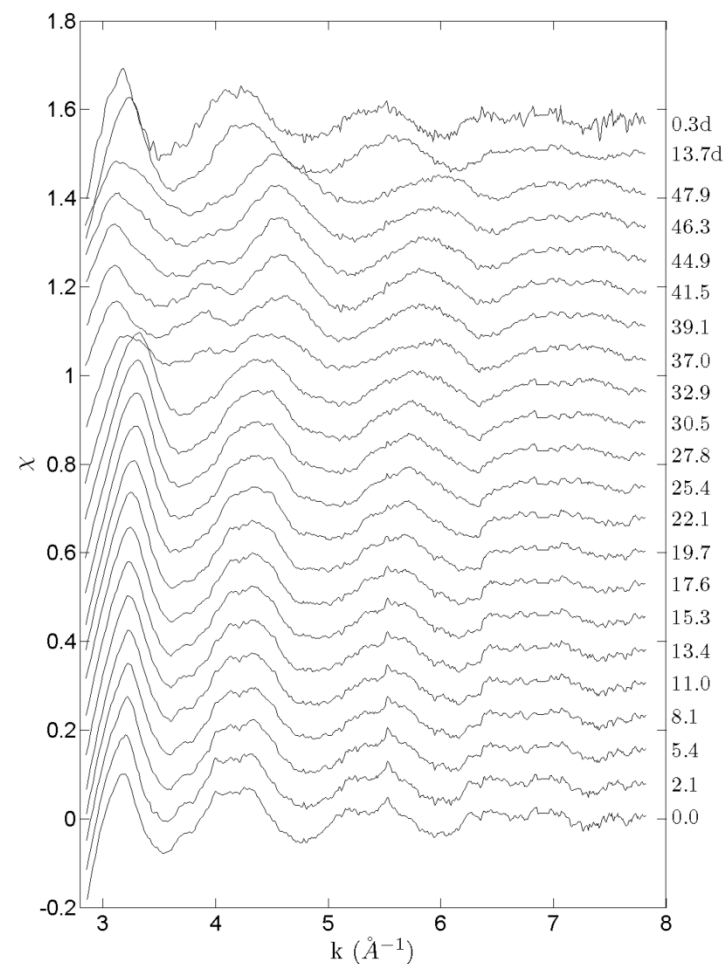


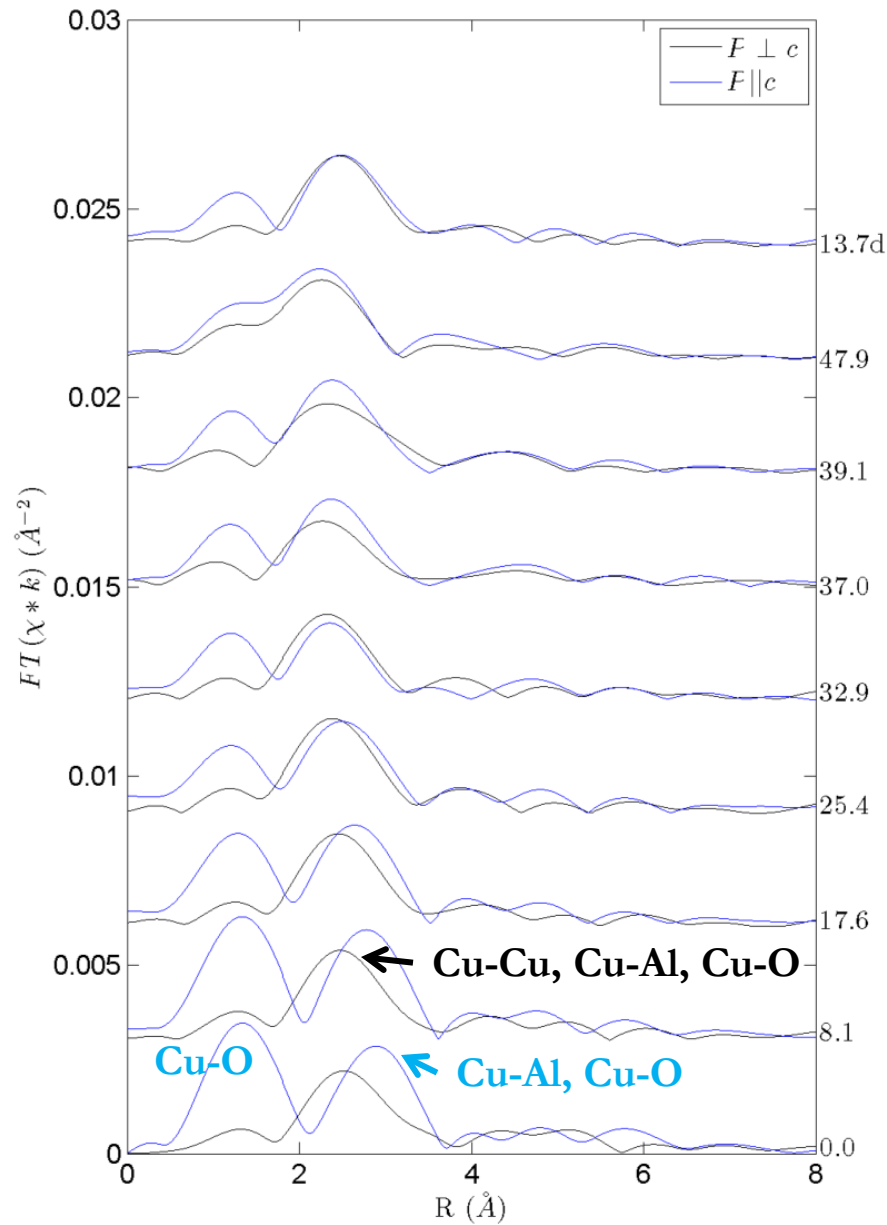
CuAlO_2 : EXAFS signal

$P || c$



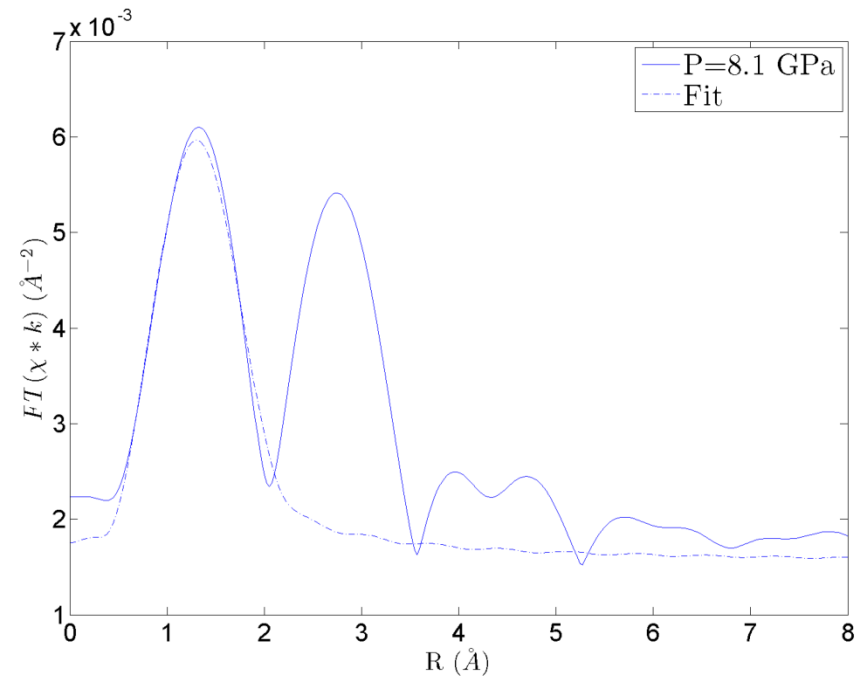
$P \perp c$



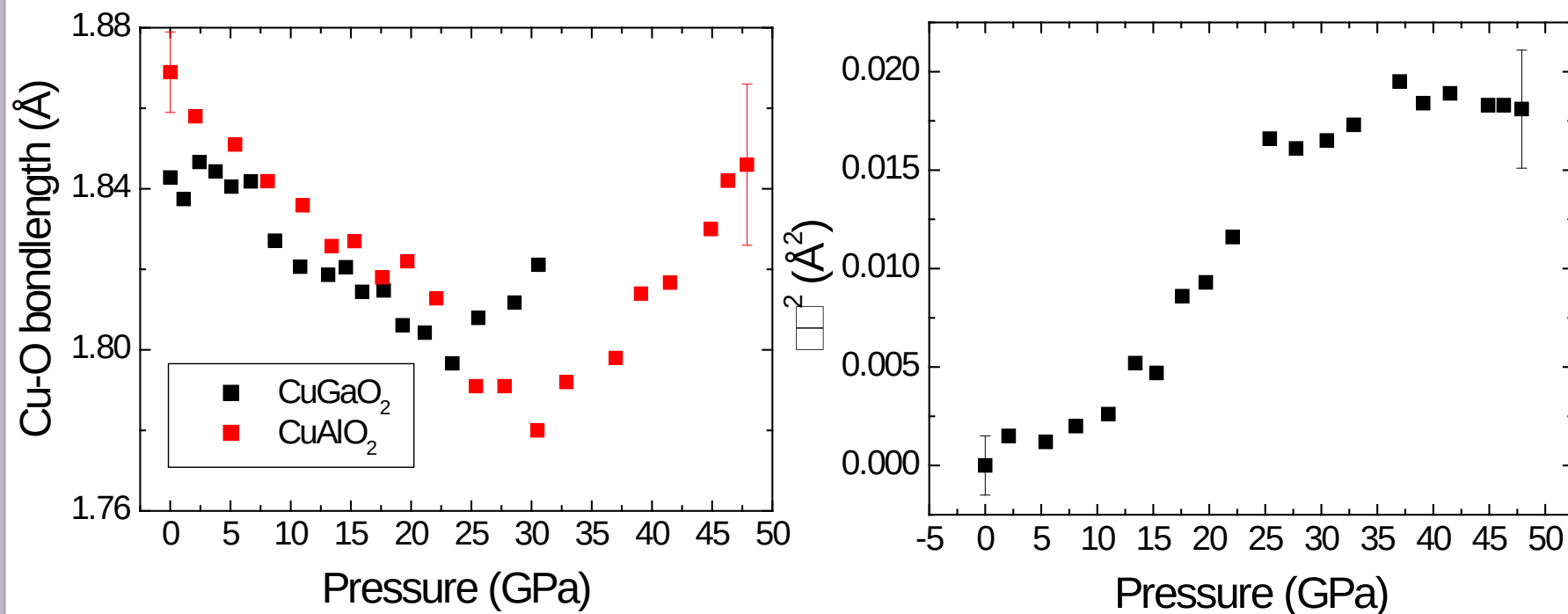


CuAlO_2 : EXAFS fit (WinXAS)

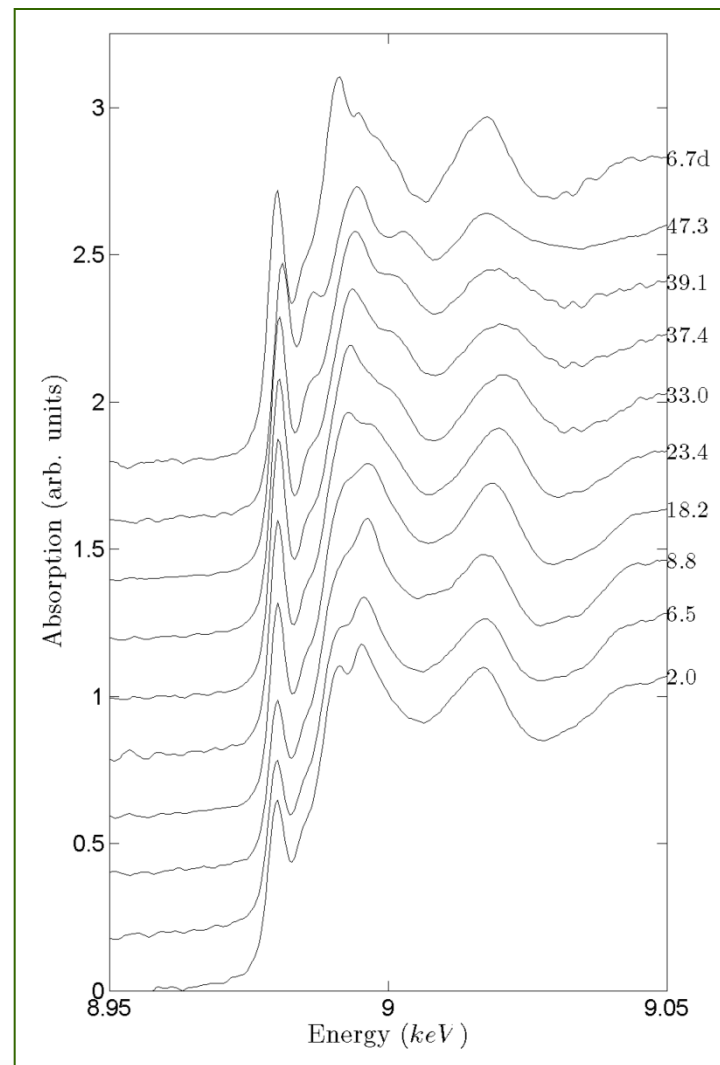
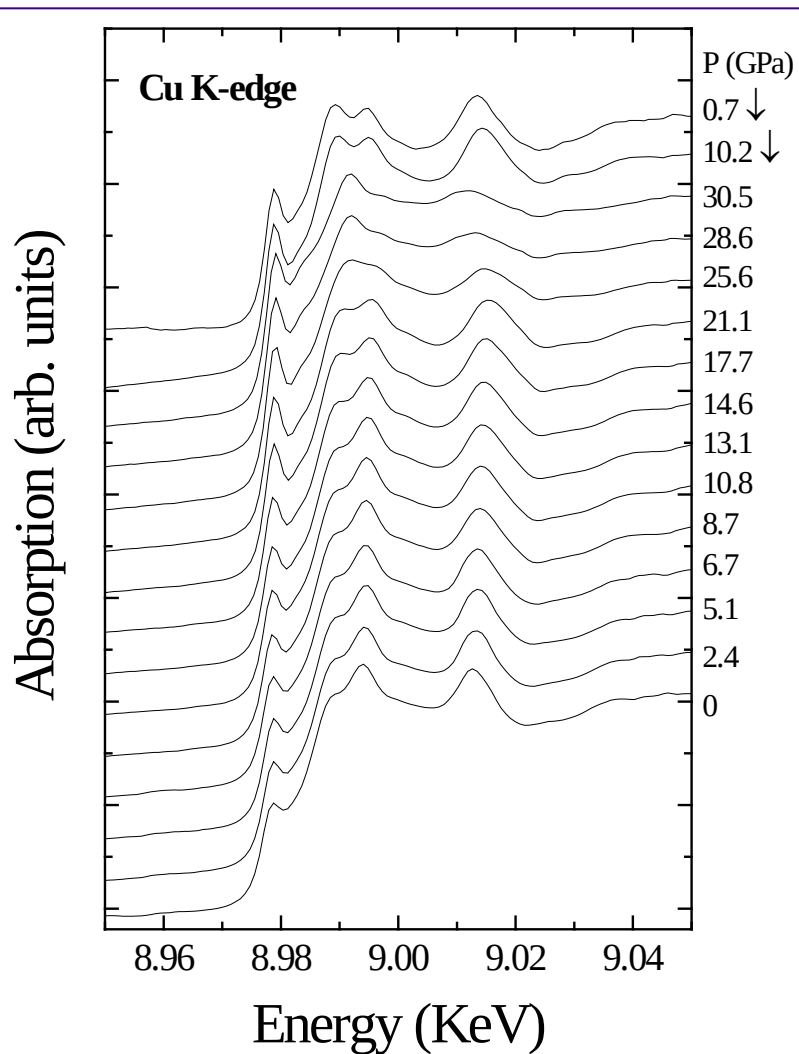
- FT range $[3.3, 7.7] \text{ \AA}^{-1}$, Hanning apodization, $\beta=0.2$.
- We employed **experimental phases and amplitudes** deduced from ambient pressure spectra.



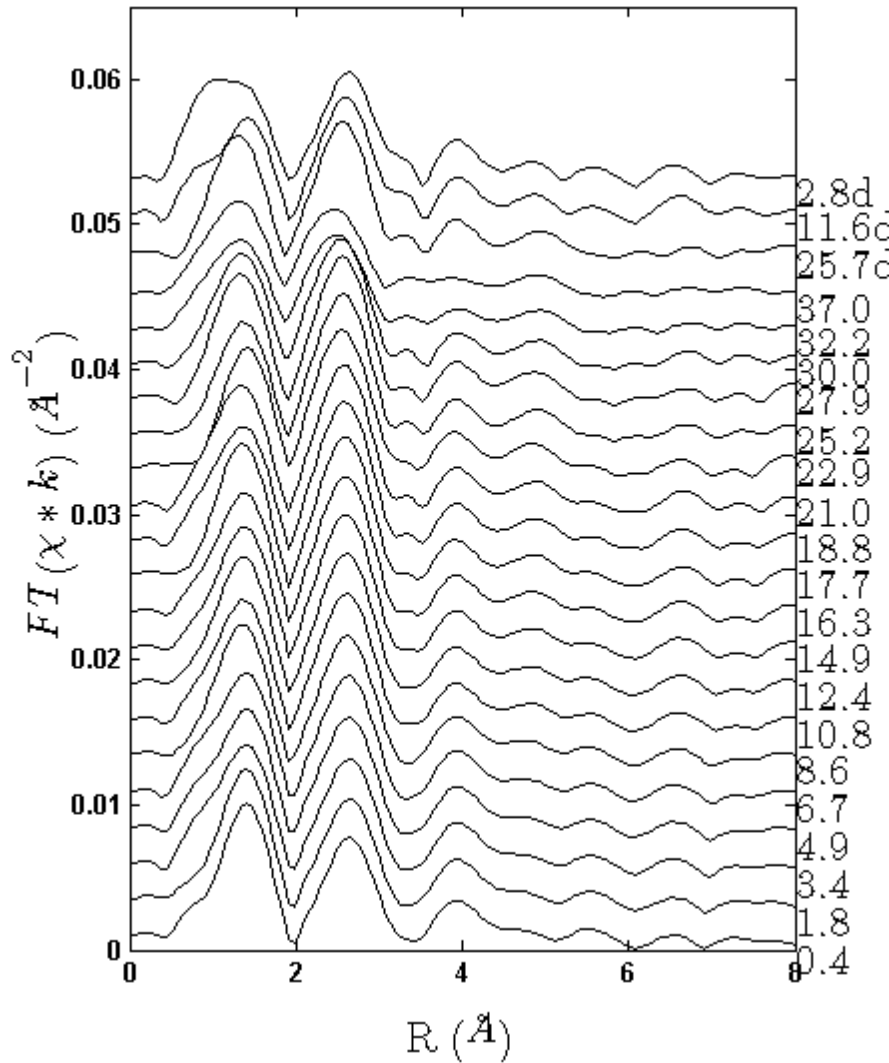
CuAlO₂: EXAFS fit (WinXAS)



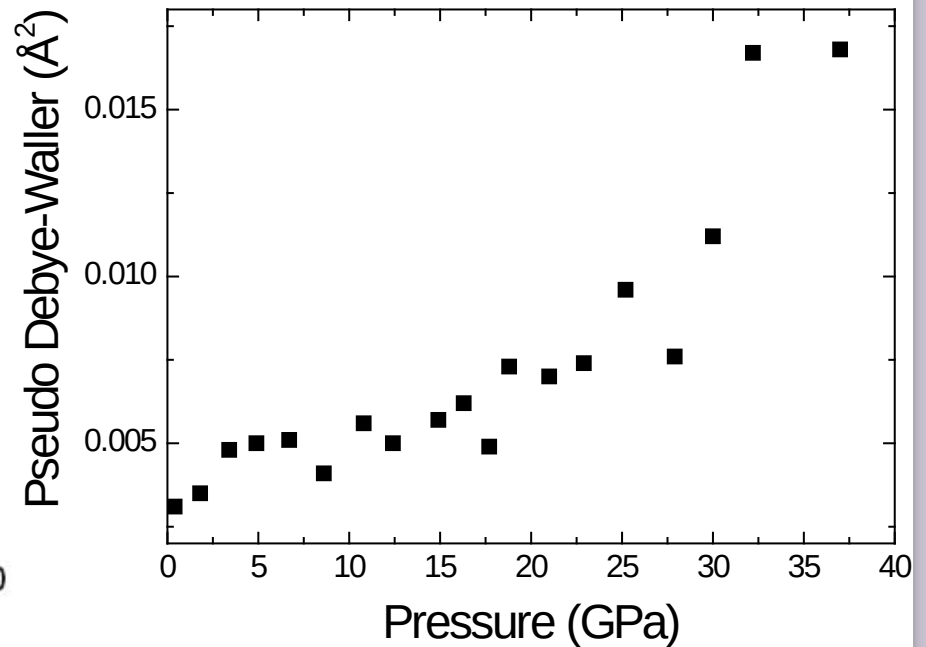
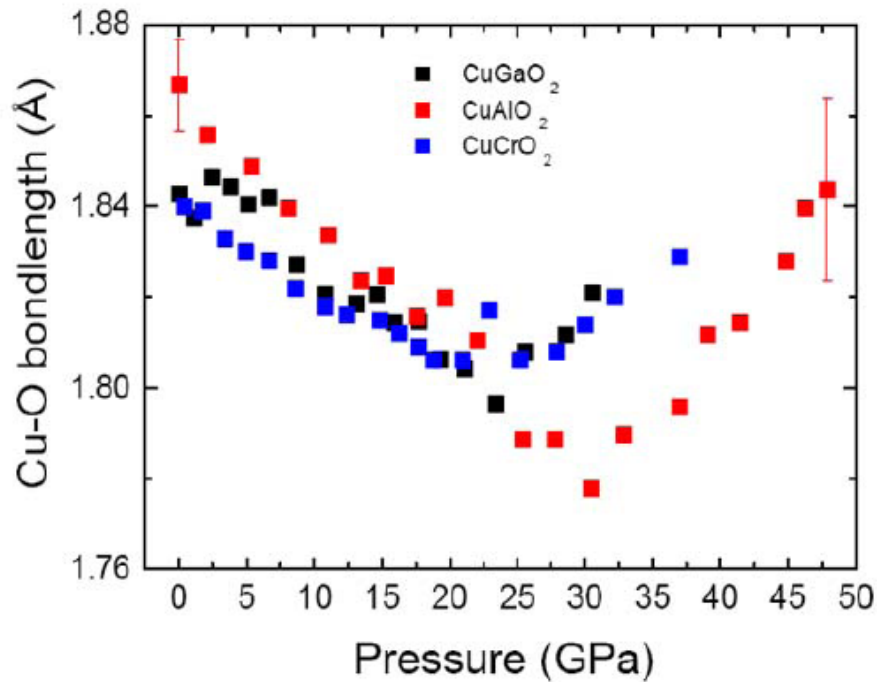
XANES of powder samples



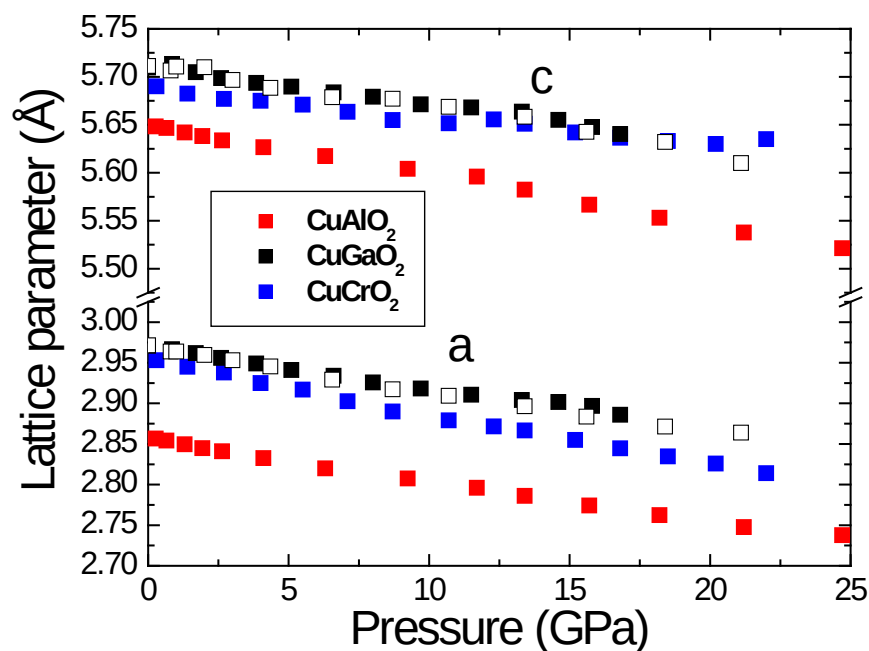
CuCrO₂: EXAFS fit (Matlab)



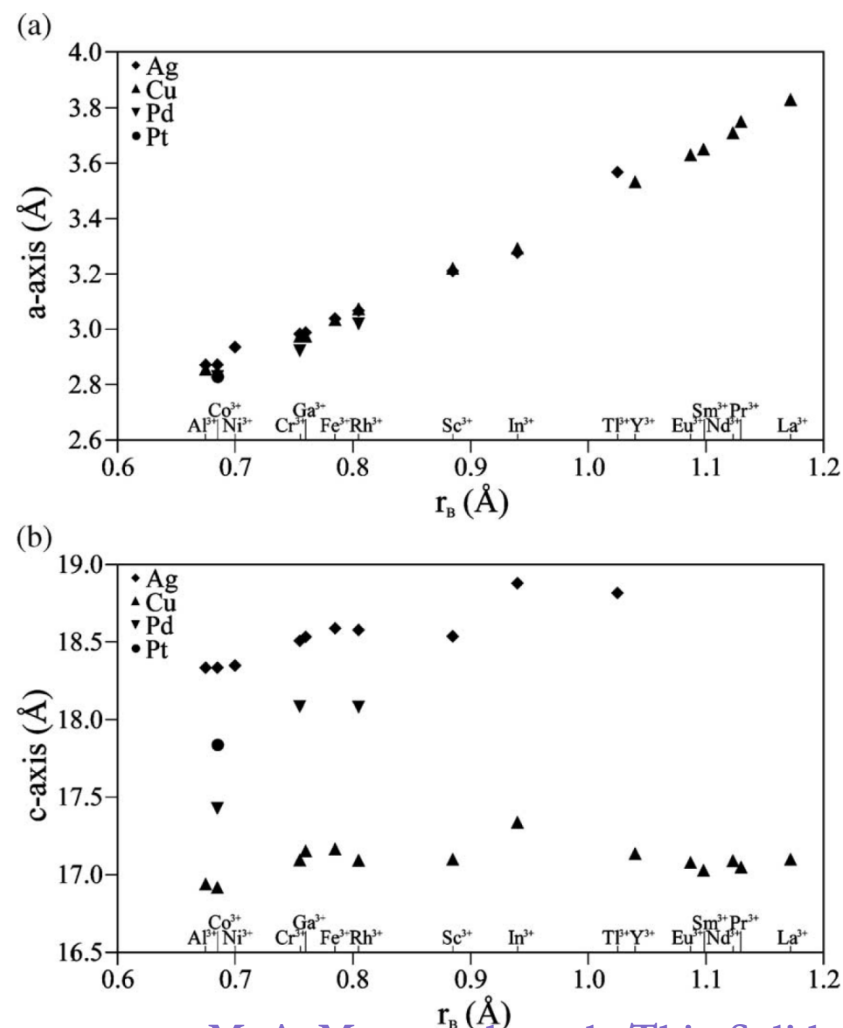
CuCrO_2 : EXAFS fit (Matlab)



Chemical pressure

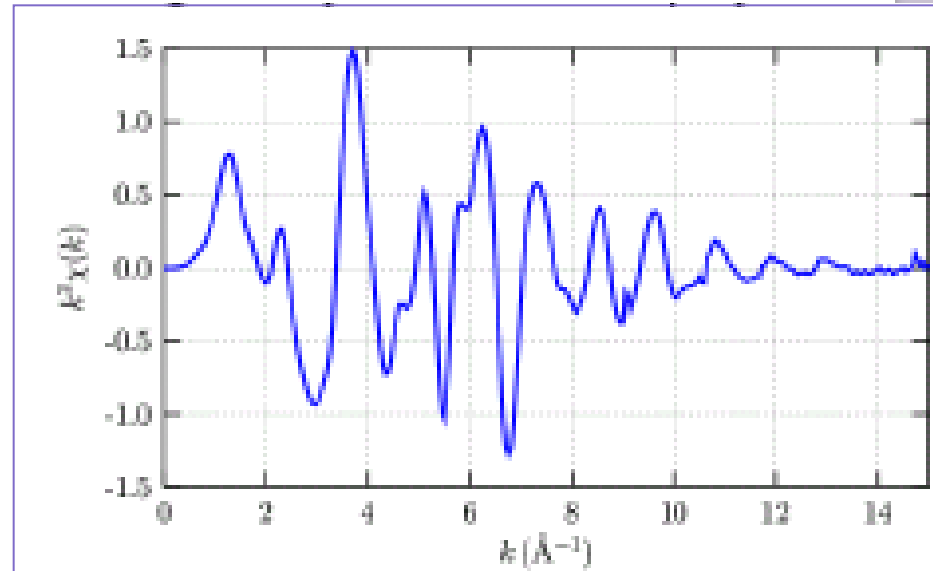
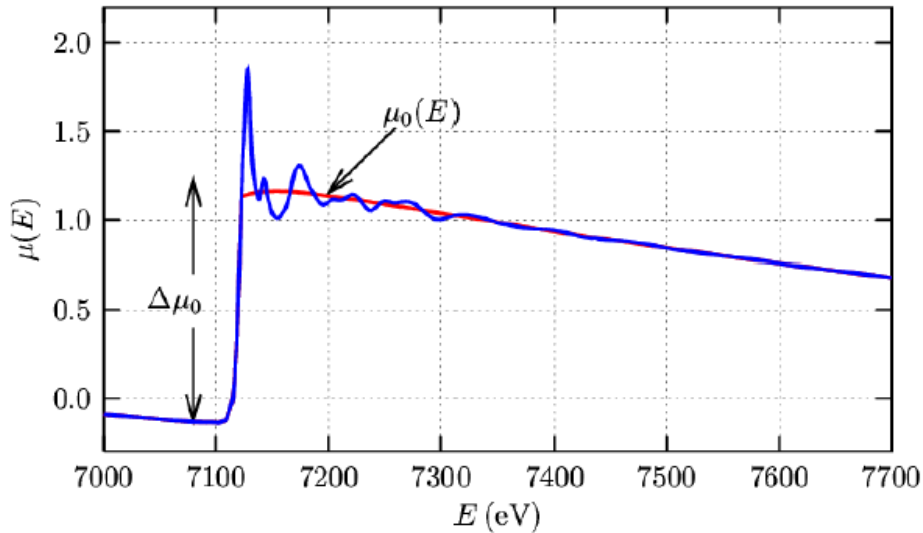


	CuGaO_2	CuAlO_2	CuCrO_2
χ_a (10^{-4}GPa^{-1})	19.6(5)	20.6(5)	22.0(5)
χ_c (10^{-4}GPa^{-1})	7.5(4)	8.3(4)	6.8(6)



M. A. Marquardt et al., Thin Solid Films 496, 146 (2006)

Señal EXAFS



$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}$$

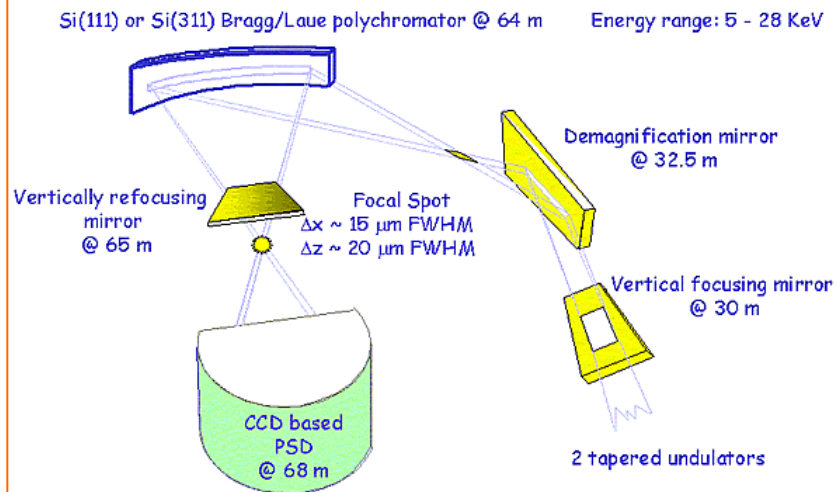
$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

Fórmula EXAFS:

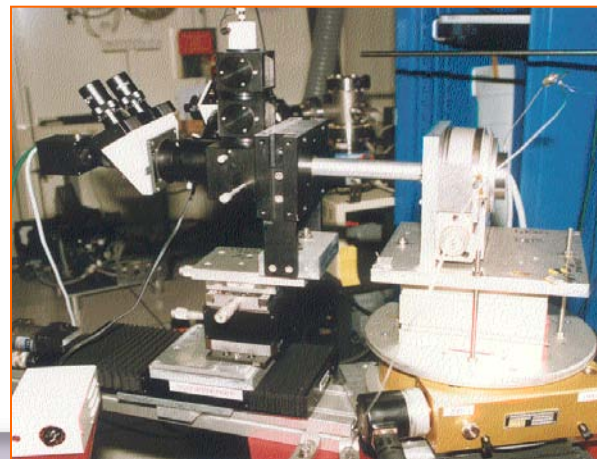
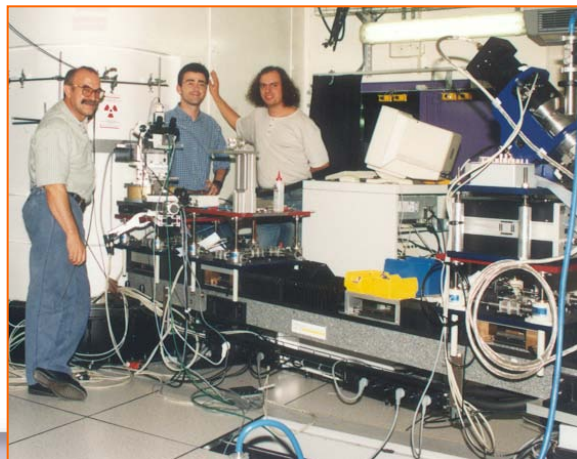
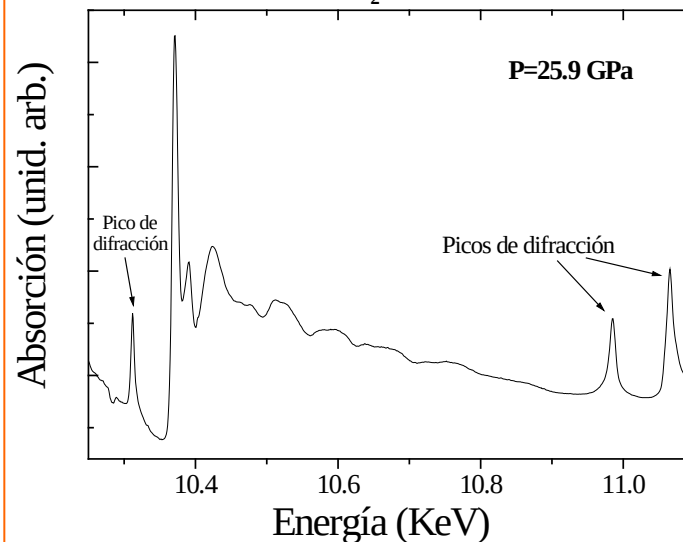
$$\chi(k) = S_0^2 \sum_j \frac{N_j F_j(k)}{k R_j^2} e^{-2k^2 \sigma_j^2} e^{-\frac{2R_j}{\lambda}} \sin[2kR_j + \delta_j(k)]$$

EXAFS DISPERSIVO

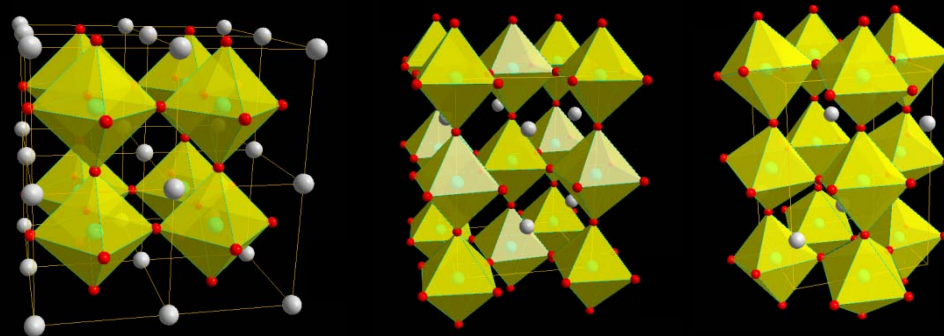
Beamline ID24



GaCuO₂, Eje KGa



Comportamiento estructural de perovskitas sometidas a condiciones extremas



Fernando Aguado Ménendez
Universidad de Cantabria

Índice

1.- Introducción: perovskitas

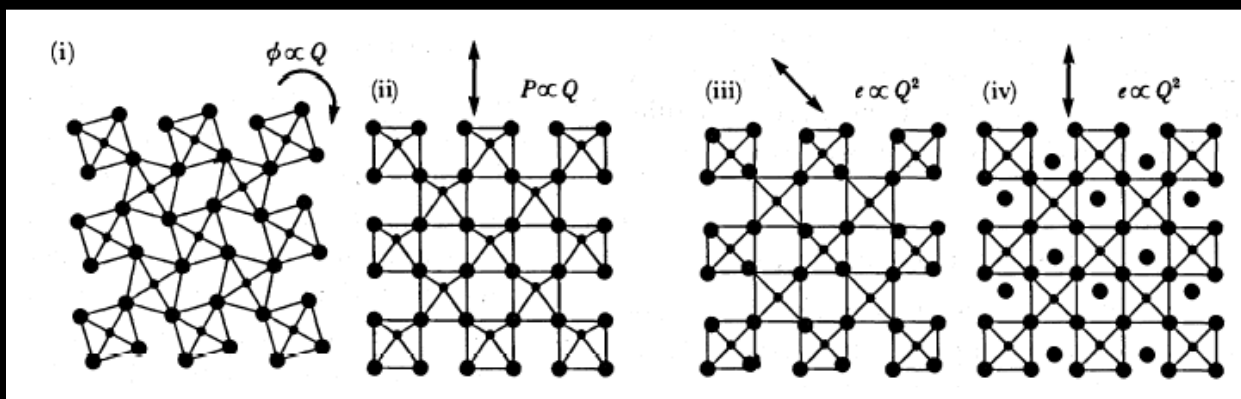
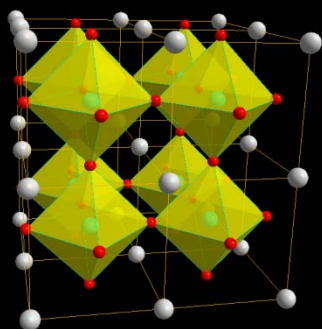
2.- Proyecto: planteamiento y sistemas

3.- Algunos resultados bajo condiciones extremas

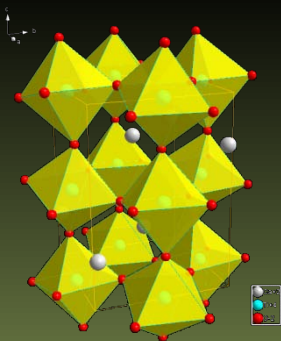
4.- Modelos y Cálculos (colaboraciones)

5.- Trabajo Futuro

Estructura perovskita y sus aplicaciones

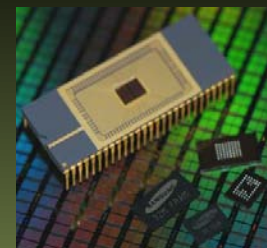


Geofísica:
(Mg, Fe)SiO₃, CaSiO₃, análogos...



Materiales
Ferroicos:

BST, PZT,
BiFeO₃
RMnO₃ ...

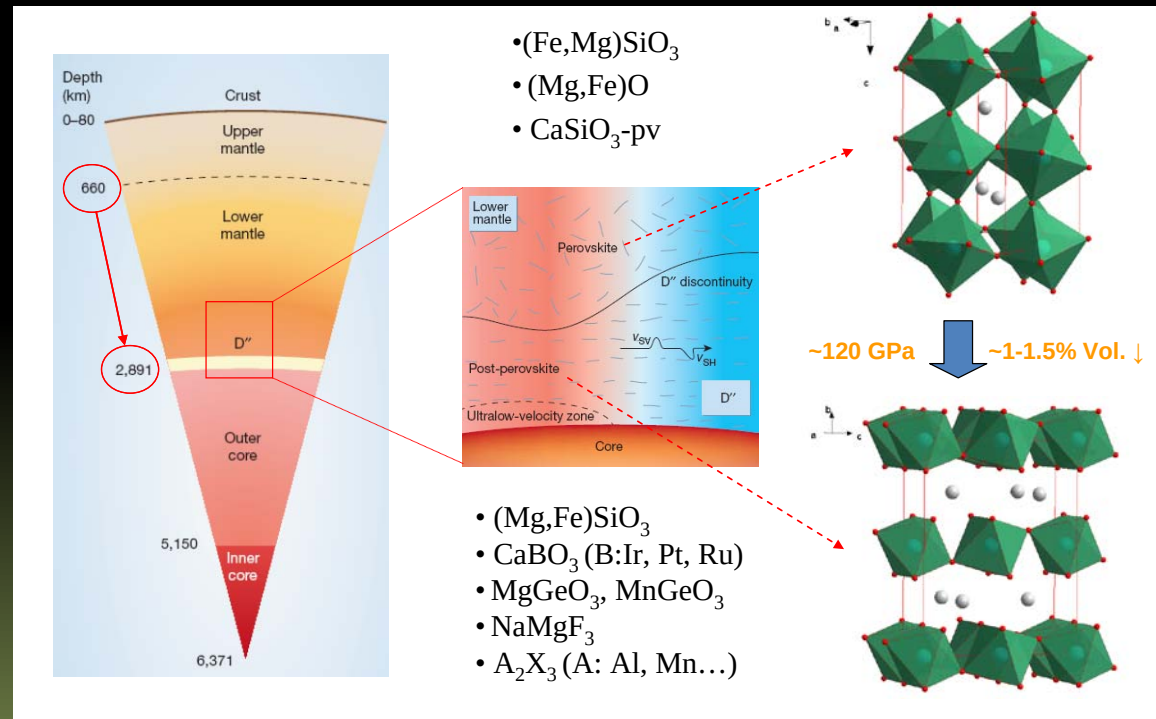
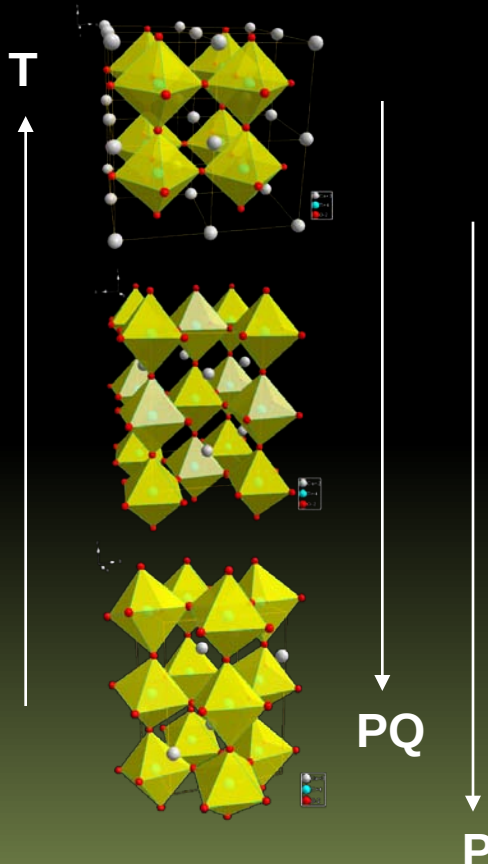


Estructuras tipo perovskita

* Estructura ideal

* Estructuras distorsionadas mediante giro (tilting)

Presión Química
Temperatura
Presión hidrostática
Presión/ alta temperatura



Sistemas

Análogos "blandos": ABF_3 y $\text{ABCl}_3 \rightarrow \text{KMF}_3$ (Mg, Co, Zn, Ni,...)

Óxidos: ABO_3 , tanto pv (BMO_3 , M: Ir, Mn, Sn) como ppv (CaIrO_3)

Cuestiones abiertas (objetivos)

1.- Distorsión de la estructura cúbica: ¿factible? Mecanismos

Vías de distorsión de la perovskita: Presión/temperatura

2.- Estructuras distorsionadas: Evolución bajo presión

Modelos para predecir el comportamiento estructural

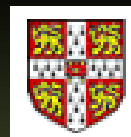
3.- Límite de estabilidad estructural

Implicaciones geofísicas

Distribución del proyecto



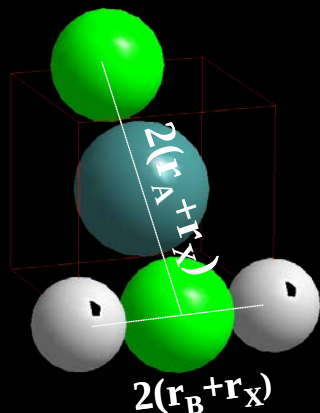
Difracción rayos x
Polvo
Monocrystal



Difracción de neutrones



Racionalización de las estructuras



Tolerance Factor (Goldschmidt, 1926)

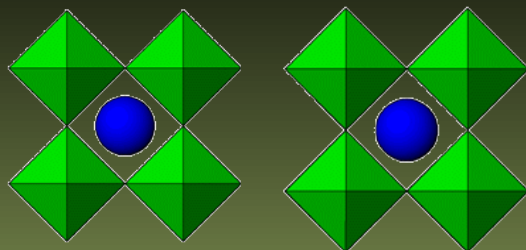
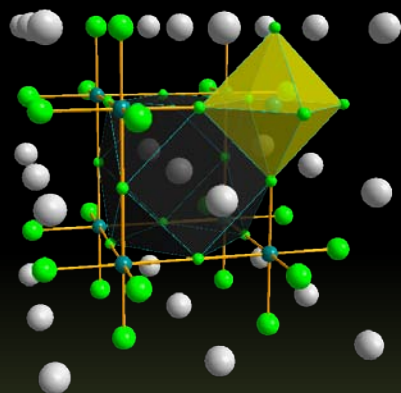
$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

Polyhedral ratio

$$r = \frac{V_{AX_{12}}}{V_{BX_6}}$$

Formación, Propensión a la distorsión (?), Evolución

Ejemplo: KMnF_3 vs. KMgF_3



Site Parameter

$$M_i = \frac{N_i R_i}{B} \exp\left(\frac{R_0 - R_i}{B}\right)$$

* J. Zhao et al. Acta Crystallogr. B60, 263 (2004)

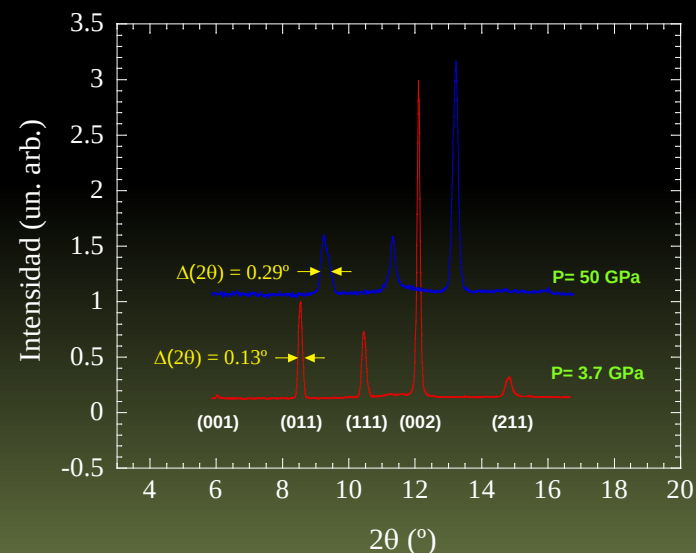
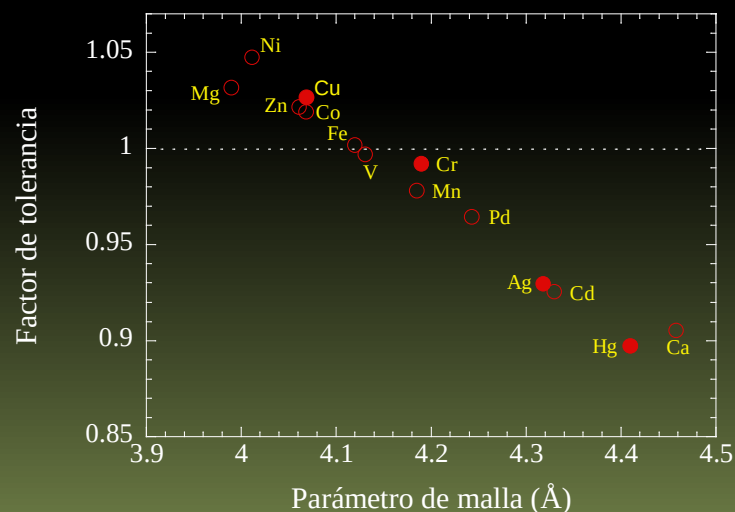
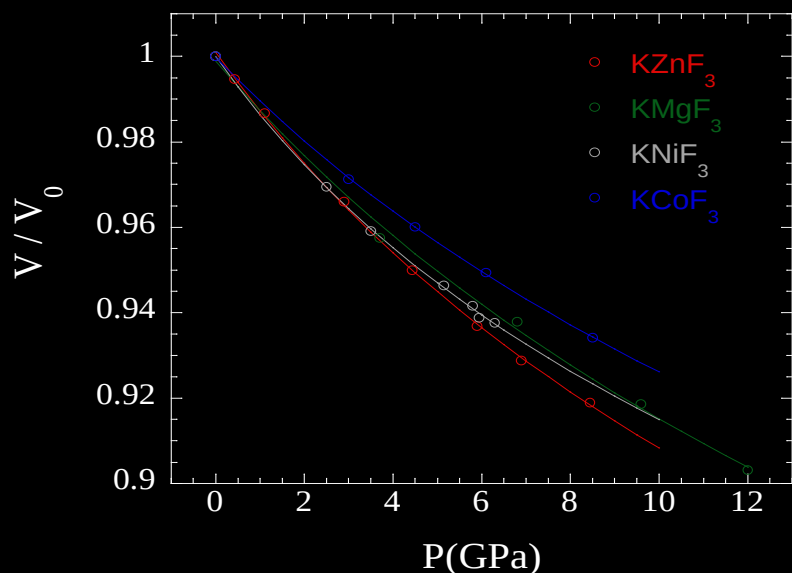
* Good for high pressure evolution (Tilting)

$$\frac{\beta_B}{\beta_A} = \frac{M_A}{M_B}$$

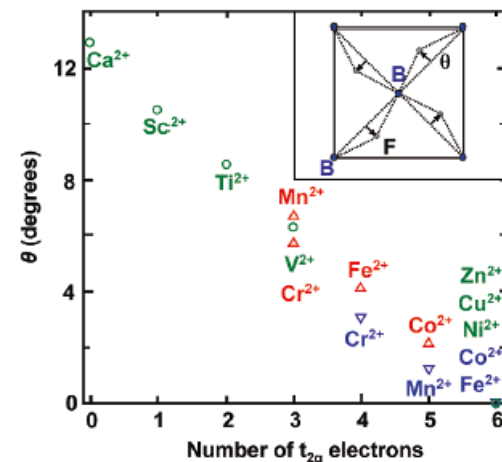
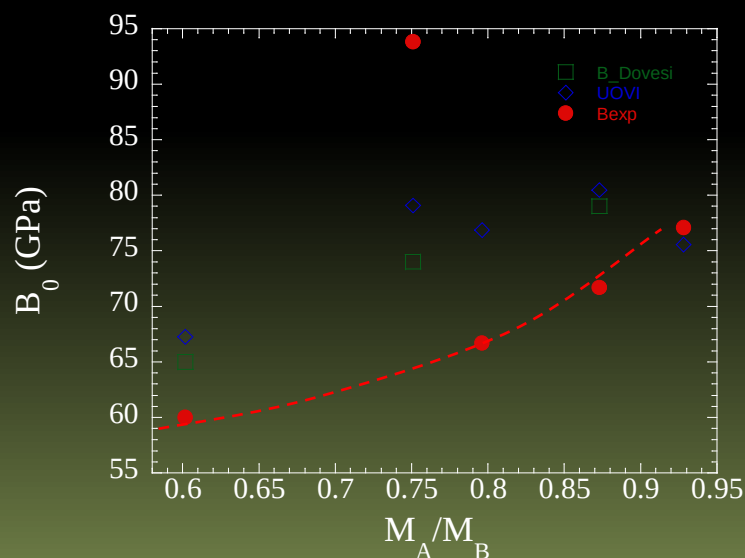
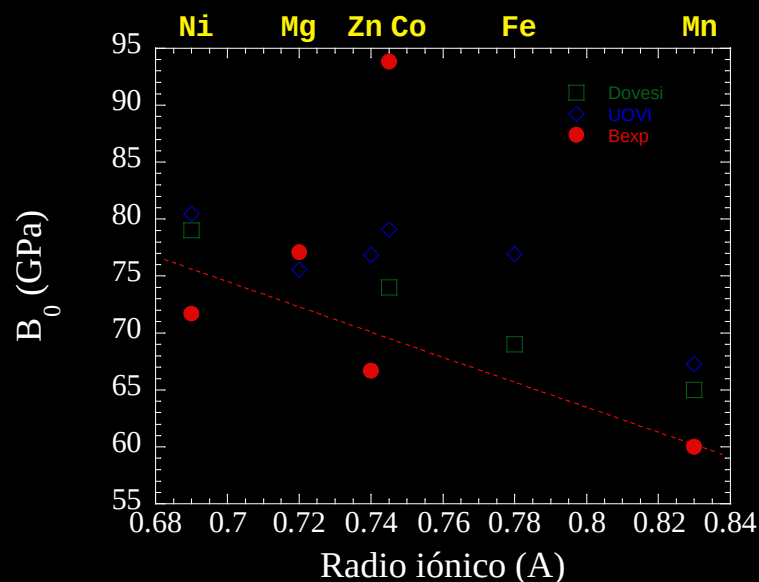
**Evolución de la distorsión en perovskitas ABO_3
a partir de modelos BV**

Algunos resultados en KMF_3

- Todos los sistemas analizados (a diferencia del KMnF_3) son estables en el rango 0-10 GPa.
- En algunos casos la estabilidad se extiende a rangos mucho más altos de P (como KMgF_3 o KCoF_3)
- Compresibilidades similares (excepto Co)



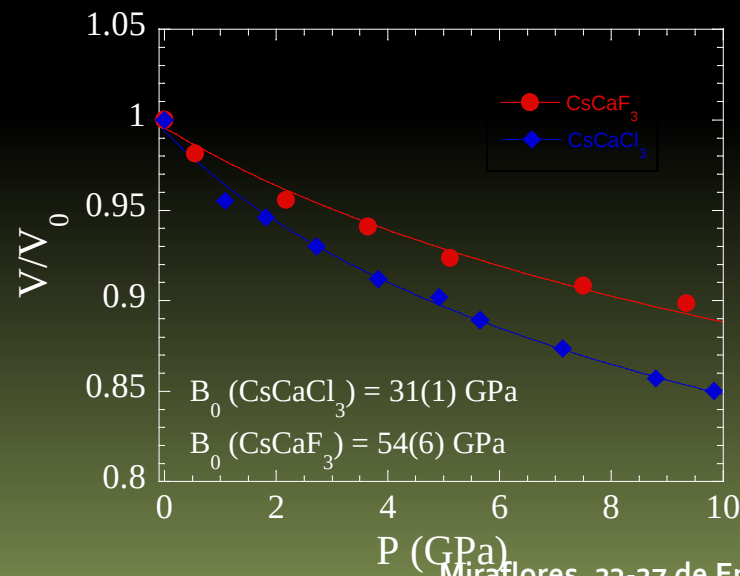
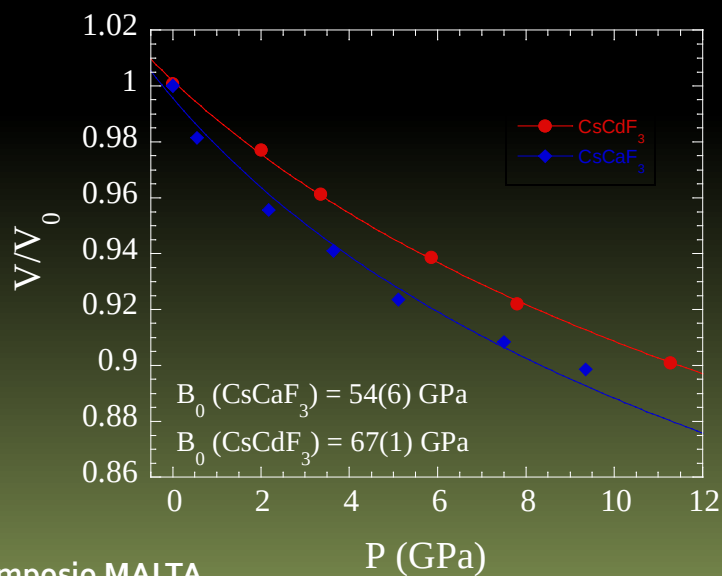
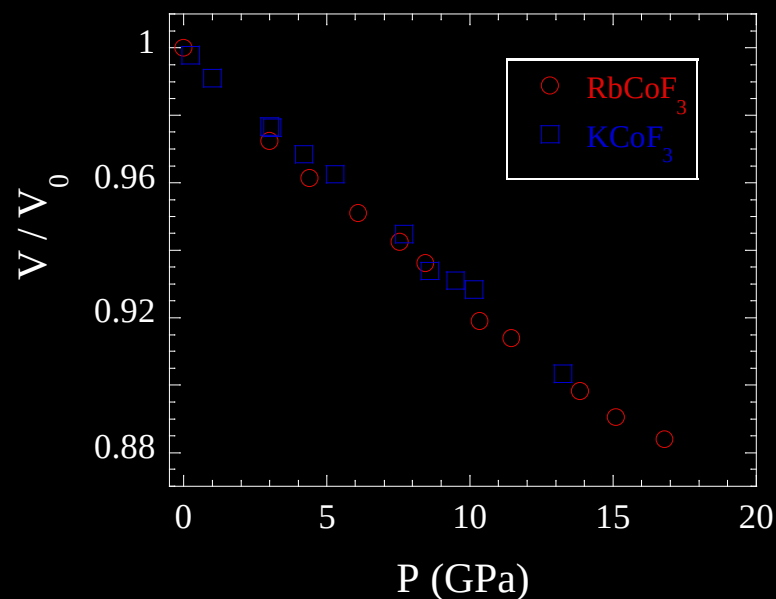
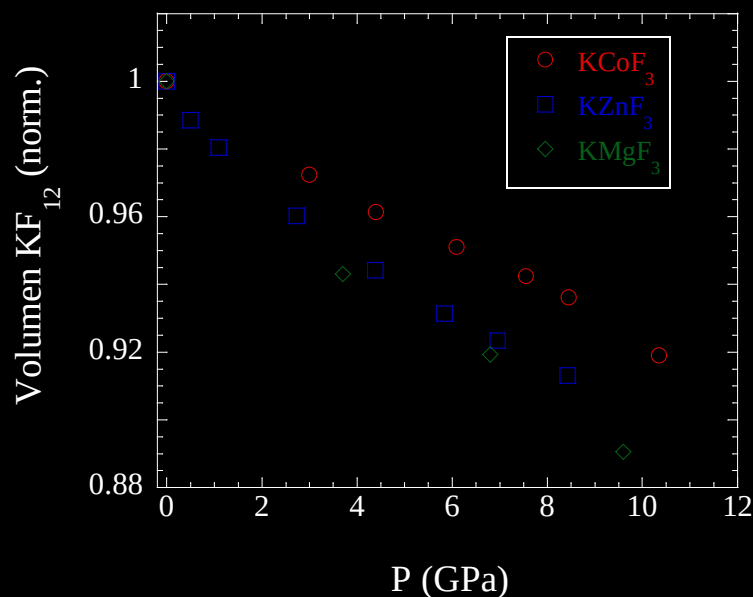
Cálculos en KMF_3 : Sistematización



P. Garcia *et al.* J.Phys. Chem. Lett. 1, 647(2010)

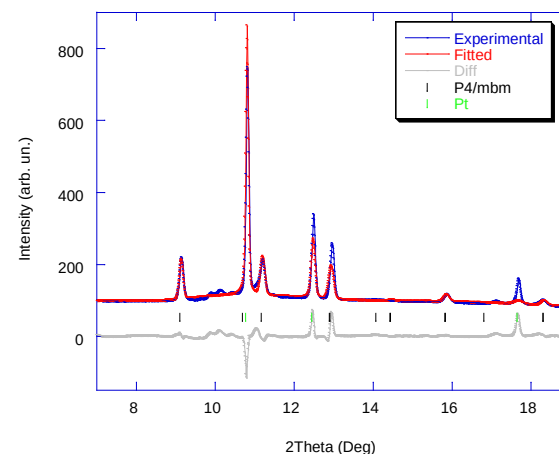
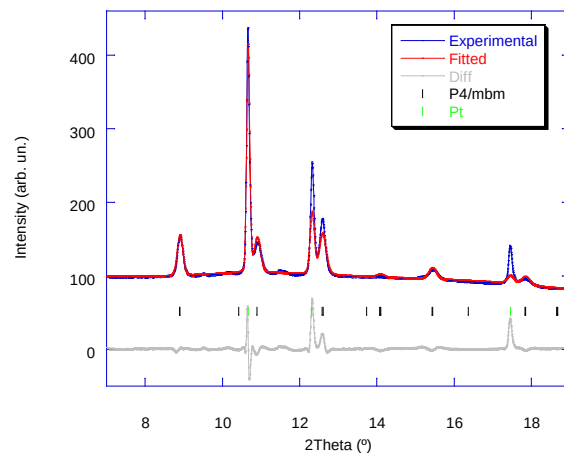
- La parametrización de la compresibilidad a partir factores puramente geométricos es complicada.
- La utilización de la teoría BV bajo presión parece ofrecer mejores resultados. Otra posible vía $\rightarrow$ electrones t_{2g} ?
- Anomalías en los sistemas no distorsionados de Co (KCoF_3 y RbCoF_3)

Otros sistemas ABX_3 (X:F,Cl)



Efecto de P/T en la estabilidad de perovskitas KMgF_3

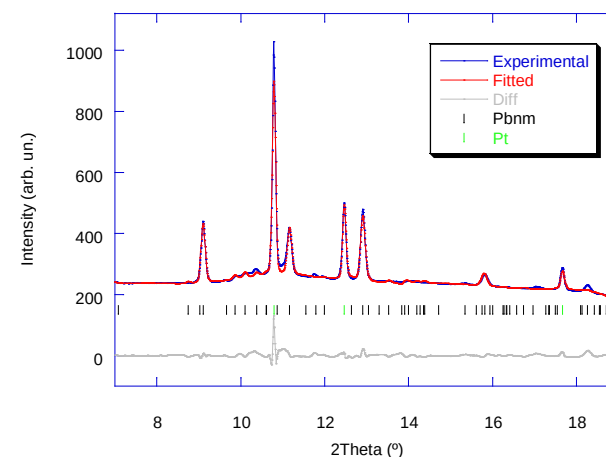
KMgF_3 at 33GPa and 2000K



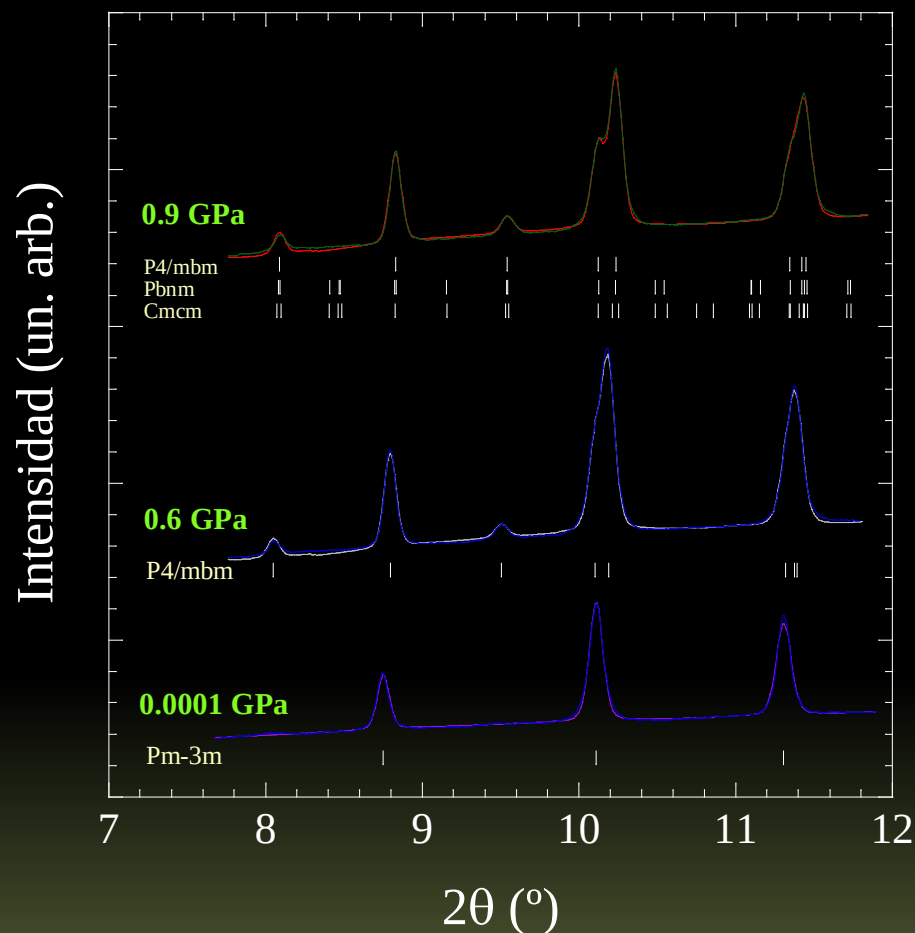
- (1) Initially (immediately after laser heating) sample remains in the cubic structure. Attempts of fitting the pattern with a distorted perovskite structure lead to an undistorted structure.

- (2) New features in the diffraction pattern appear after a few seconds. Undistorted (Pm-3m) or even tetragonally distorted (P₄/mbm) structures can't reproduce the new peaks

- (3) An orthorhombic S.G. (Pbnm) is necessary in order to account for all the new peaks → **TILTED STRUCTURE !!!**



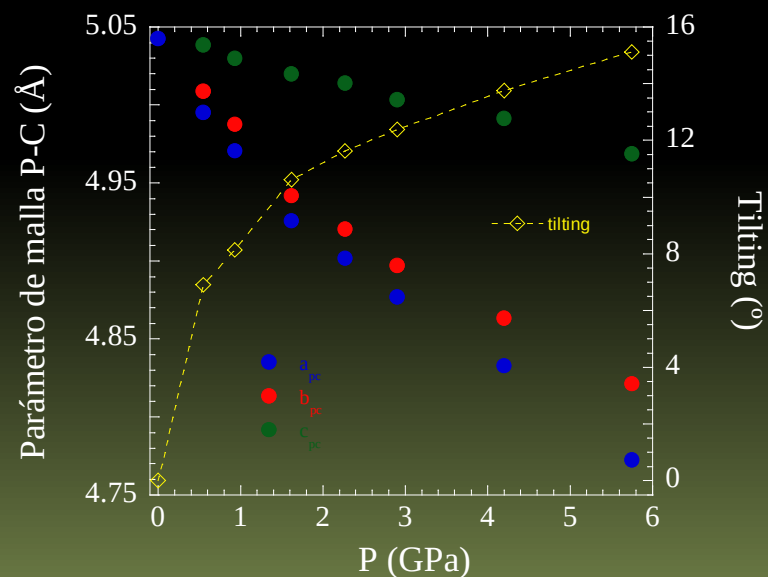
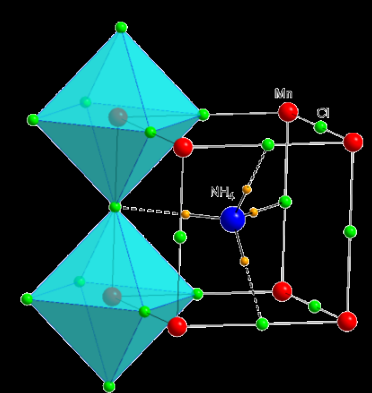
Evolución bajo presión de perovskitas distorsionadas



Pm-3m

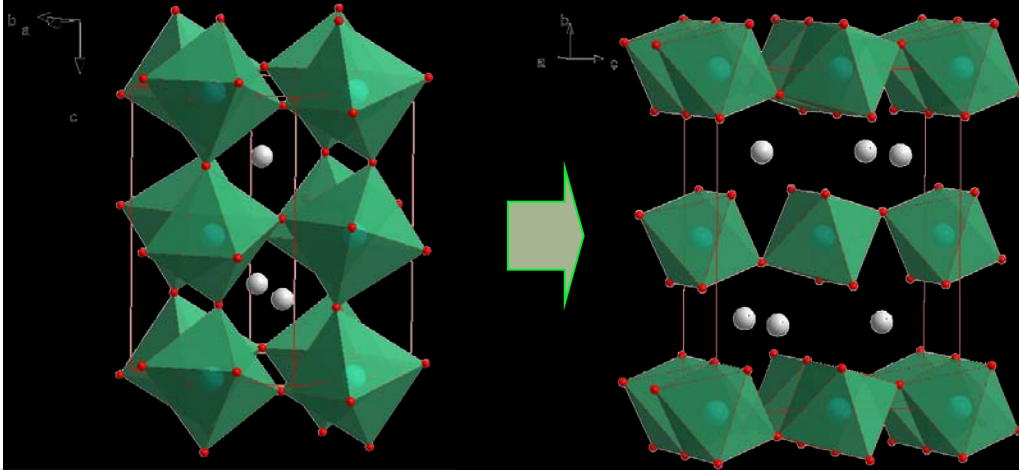


¿?



Rietveld bajo presión?
Tilting + M-X

Límite de estabilidad y estructuras más densas



-Transición de fase fundamental para entender la interfase manto-núcleo.

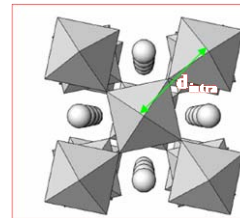
- Dificultades técnicas asociadas.

- Exploración de posibles fases más densas (pppv)?

-Estudios en estructuras ppv derivadas en óxidos (CaIrO_3) o fluoruros (NaMgF_3)

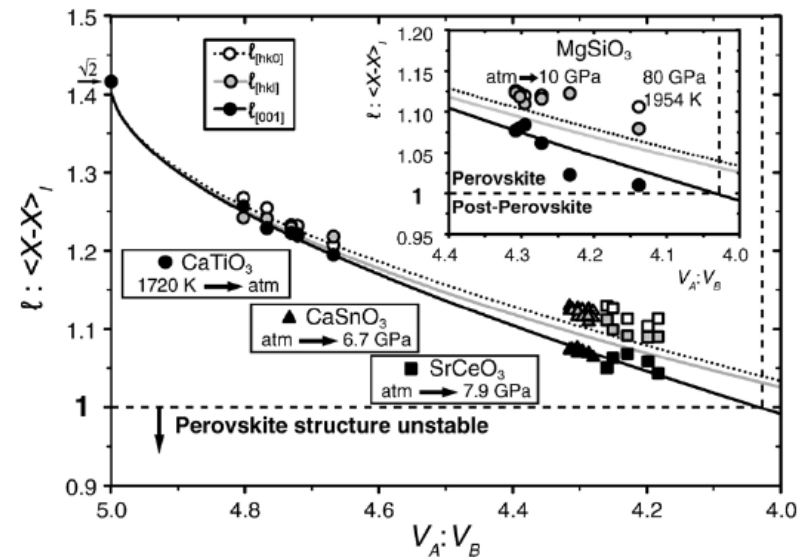
- Estudio sistemático en familias de análogos (P/T)

-Modelos universales para la estabilidad de perovskitas



Inestabilidad

- $d_{\text{inter}} = d_{\text{intra}}$
- $V_A/V_B \approx 4$



C.D. Martin et al. Earth and Planet. Science Lett. 265 , 630 (2008)

Participantes en el proyecto

- S.A.T. Redfern, University of Cambridge
- S. Hirai, University of Edinburgh
- C. Wang, Chinese Academy of Sciences
- F. Rodríguez, J. González, R. Valiente, S. Gómez, Universidad de Cantabria

Colaboraciones MALTA



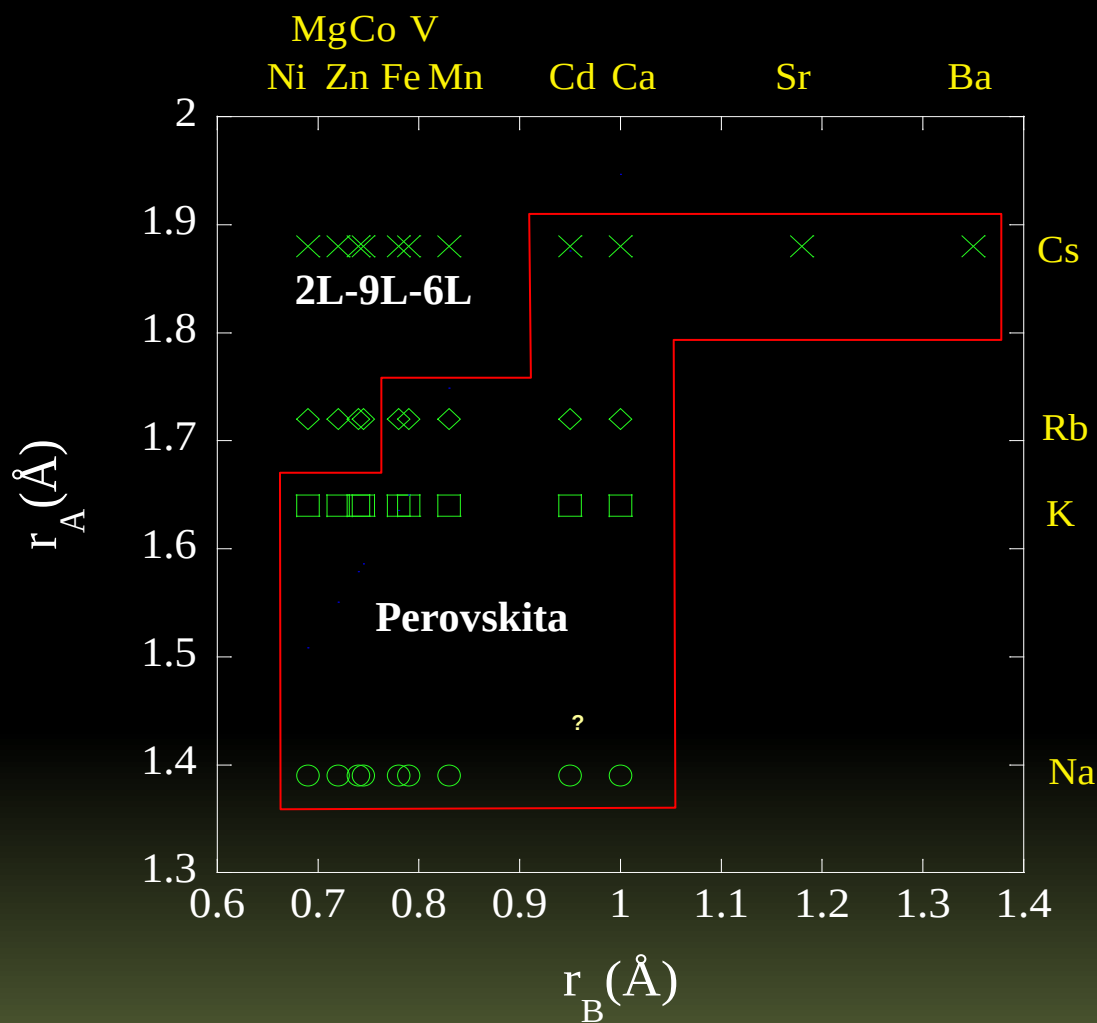
José Manuel Menéndez, UOVI

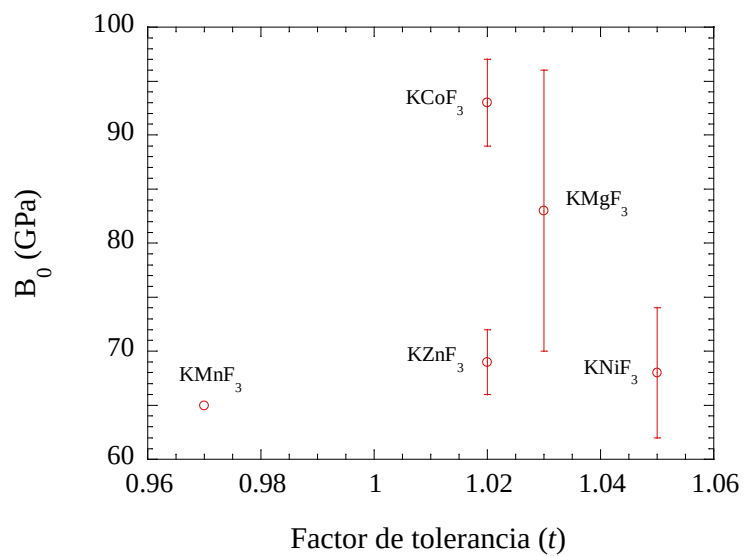
José Manuel Recio, UOVI

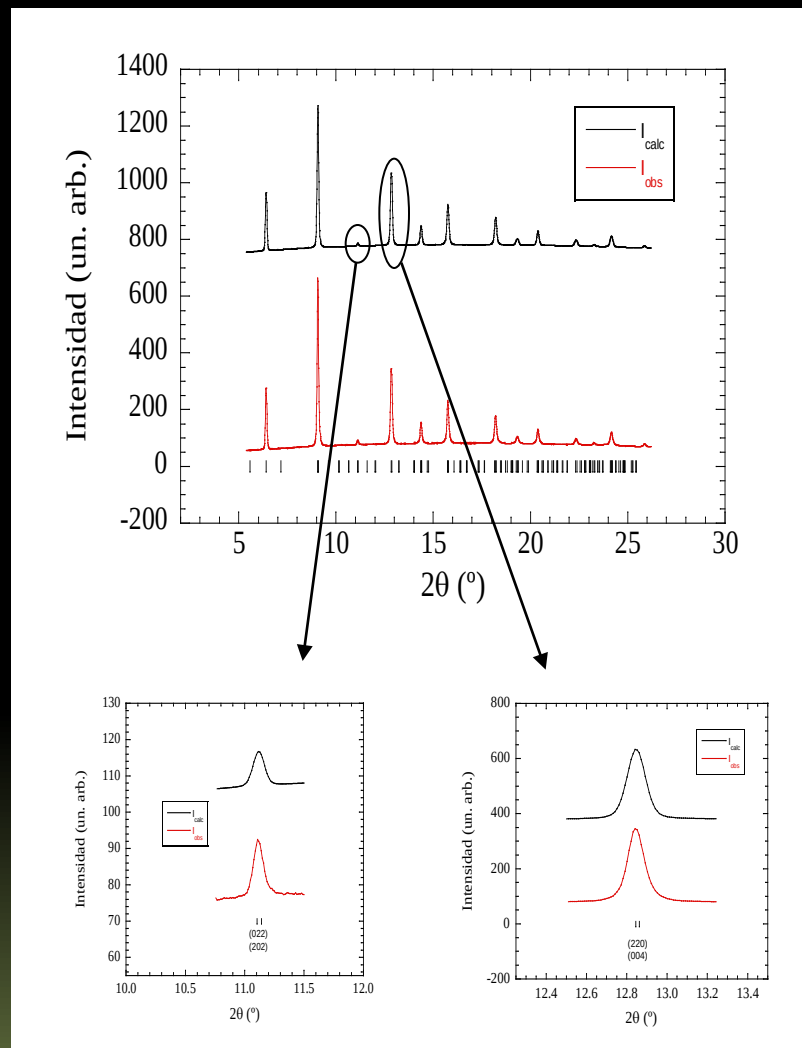
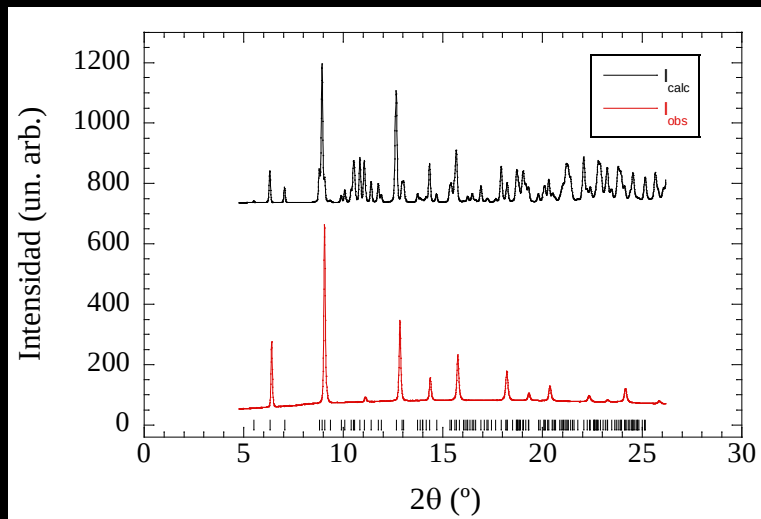
Lourdes Gracia, UJI

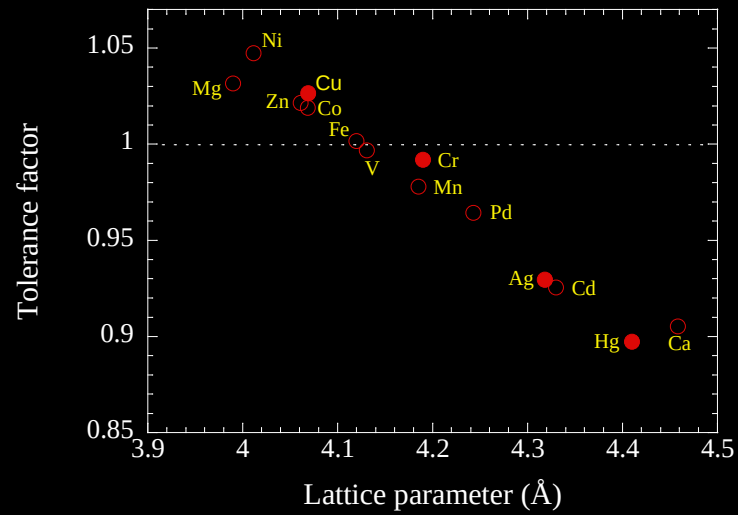
Armando Beltrán, UJI

David Santamaria, UCM



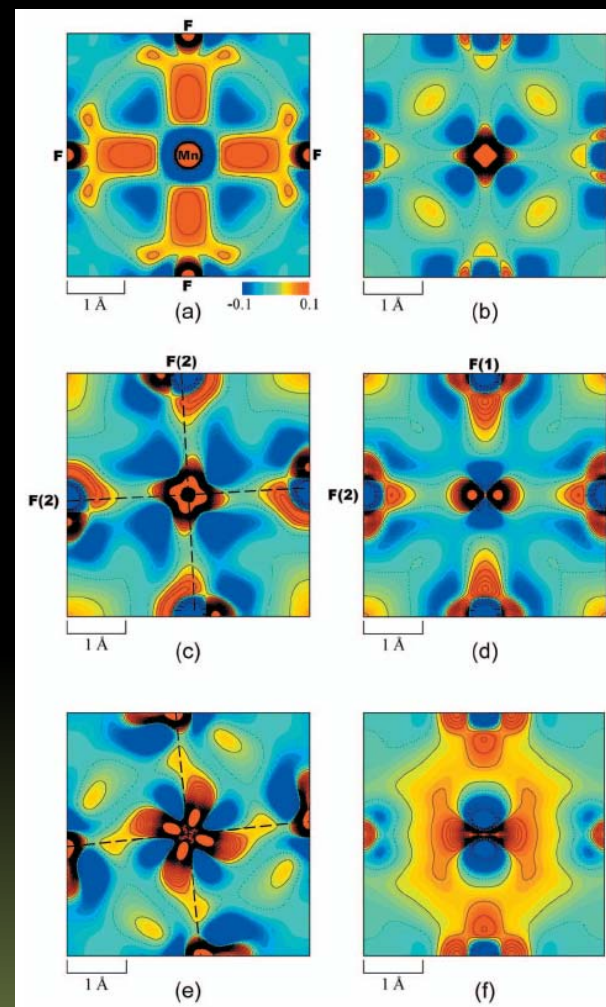
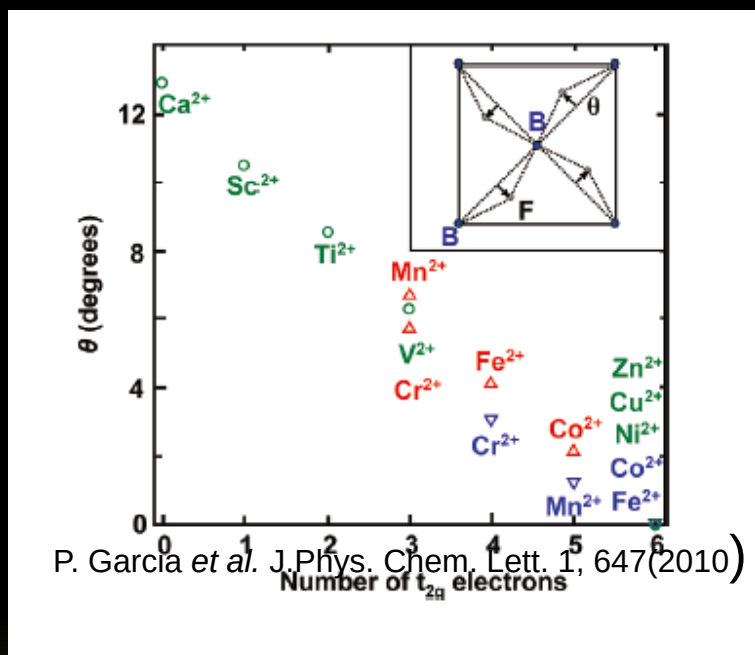


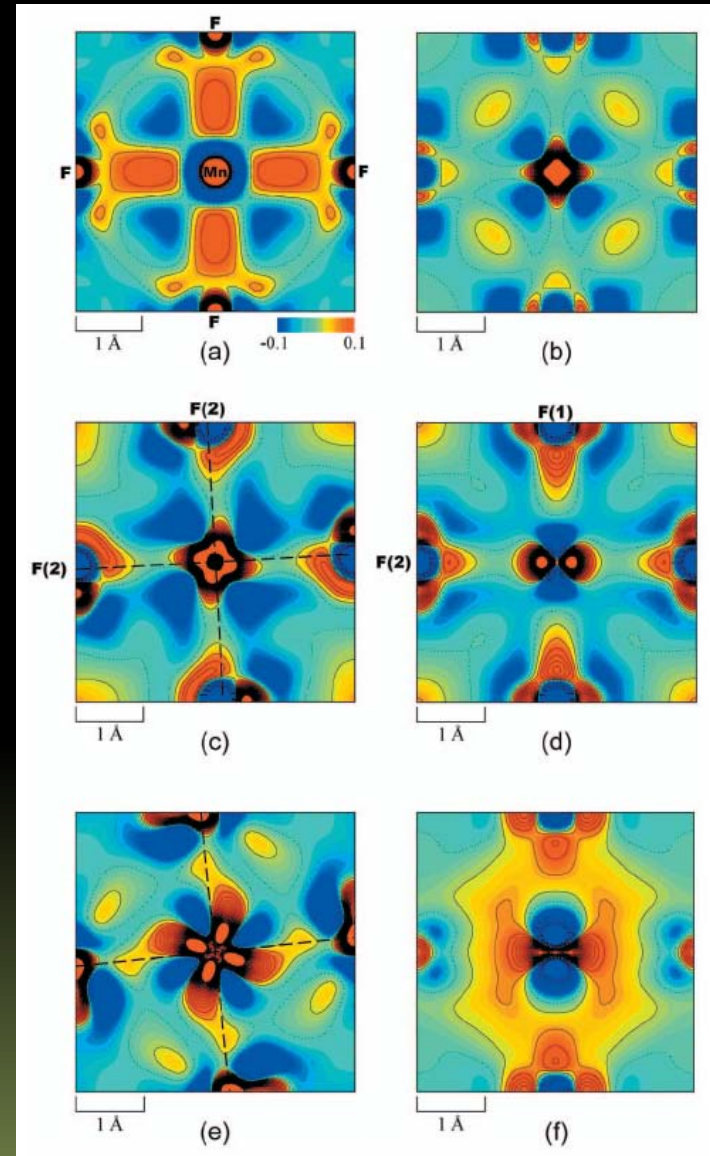
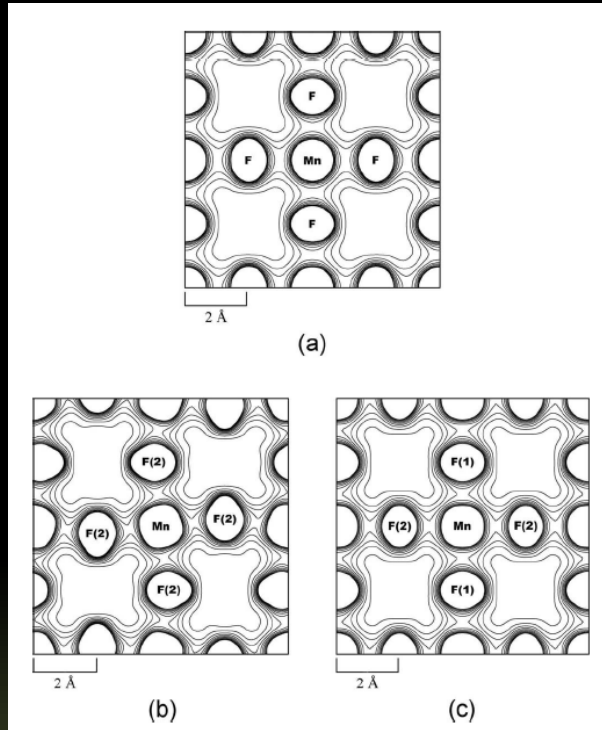




Correlaciones estructurales

Magnitud del giro en simetría tetragonal (T)





In Memoriam

Miguel Álvarez Blanco
1969-2010



Miguel como persona

Miguel nació en Oviedo en 1969.



Miguel como persona

Estudió en el Colegio de los Jesuitas EGB, BUP, y COU.



Miguel como persona



Miguel como persona

- Comienza la licenciatura en Química en la Univ. de Oviedo en el curso 87-88.
- En cuarto y quinto obtiene becas de colaboración y del centro de cálculo, y se incorpora al grupo de Química Cuántica.
- Gran aficionado al baloncesto, ski, la literatura de ciencia ficción, y los beatles.



Miguel como persona



Miguel como persona



Miguel como persona

En 1997 se casa con Aurora.



Miguel como persona



Miguel como persona



Miguel como persona



Miguel como persona







Miguel como investigador

- En cuarto, 1991, Comienza a trabajar con V. Luaña y se incorpora al grupo.
- Primera máquina Linux y tiempos de Convex.
- Se licencia en junio de 1992. Premio fin de carrera y de licenciatura.
- En 1993 obtiene una beca FPU.
- En 1994 concluye su DEA, titulado *Métodos locales para el estudio de impurezas en cristales iónicos*, dirigido por Víctor.
- En 1997 lee su tesis doctoral, *Métodos cuánticos locales para la simulación de materiales iónicos*.

Miguel como investigador

- En 1999 obtiene una beca MEC-fullbright y en julio se va a Michigan, a trabajar bajo la supervisión de Ravindra Pandey, de la MTU.
- Allí estará hasta febrero de 2000, en que vuelve a Oviedo. En junio obtiene una plaza de Prof. Titular de Química Física.
- Desde 2001-2003 sigue con estancias postdoctorales en MTU.

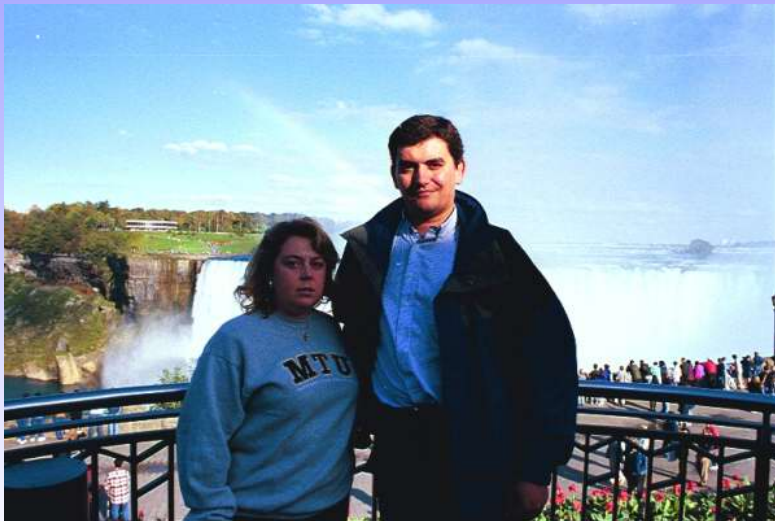
Miguel como investigador



Miguel como investigador



Miguel como investigador



Miguel como investigador



Miguel como investigador

Comienza su periplo por el circuito profesional..
En 2001 en el EHPRG celebrado en Santander.



Miguel como investigador

En 2001 en el Escorial.



Miguel como investigador

En 2003 en el VI Girona Seminar.



Miguel como investigador

En 2005 en Chennai (India), formando parte del comité científico.
En 2006 en la Sagamore Conference, en Inglaterra.
En julio de 2007 en la GRC celebrada en Boston.
En marzo de 2008 en Honolulu y después en Gravedona.



Miguel como investigador



Miguel como investigador



Miguel como investigador



Contribuciones científicas. Métodos locales

- En la TSE de McWeeny: $\Phi(1, \dots, N) = \hat{\mathcal{P}} \prod_R \Phi^R$
 - Fuerte Ortogonalidad: $\int \Phi^{R*}(1, i, j, \dots) \Phi^S(1, k, l, \dots) d1 = \delta_{RS}$
 - Energía Total: $E = \sum_R H^R + \sum_{R>S} [J^{RS} - K^{RS}]$.
 - Energía Efectiva de Grupo: $E_{\text{eff}}^R = H^R + \sum_{S \neq R} [J^{RS} - K^{RS}]$ está sometida a Principio Variacional restringido, $\delta_R E_{\text{eff}}^R = 0$
 - Las Condiciones de FO se introducen mediante Operadores de Proyección (Huzinaga)
 - Para Φ^R monodeterminantal, $\hat{F}^R |\psi_i^R\rangle = \varepsilon_i^R |\psi_i^R\rangle$
 - $\hat{F}^R = \hat{F} + \sum_{S \neq R} \hat{P}^S,$
 - $\hat{P}^S = \sum_{j \in S} |\psi_j^S\rangle (-\alpha \varepsilon_j^S) \langle \psi_j^S|$
- $$\{\Psi^S\} \xrightarrow{\hat{F}^R} \{\Psi'^S\}$$

El método *aiPI*

Aproximaciones:

- Sistemas Iónicos
- Ψ^R monodeterminantal
- Capa cerrada
- Base Monocéntrica STO
- Simetría esférica
 $R_i(l, m) = R_i(l, m')$
- Resolución Espectral Truncada para $\hat{K}$ intergrupo
 $\hat{K}_{TMSR}^S = \hat{1}_S \hat{K} \hat{1}_S$
 Sólo se necesitan integrales de solapamiento bicéntricas
- $\langle \hat{P}^S \rangle$ se añade a E

Ventajas:

- Extraordinariamente rápido
- Permite examinar SEPs multidimensionales
- No depende de periodicidad
- Pie de igualdad cristales puros e impurificados
- E se escribe de forma químicamente intuitiva:
 $E = \sum_R E_{\text{self}}^R + \sum_{R>S} E_{\text{int}}^{RS}$
- Proporciona átomos (iones) adaptados a la estructura cristalina: Efectos de empaquetamiento cristalino

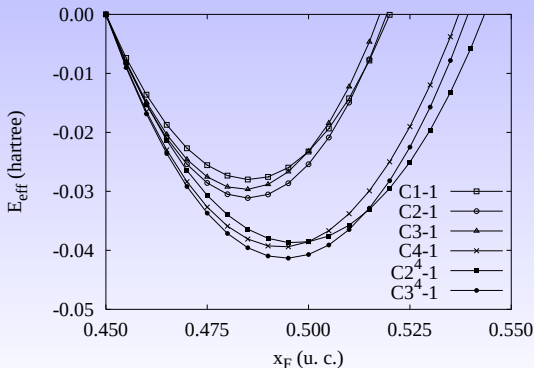
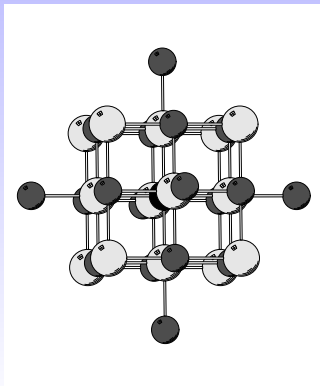
El método *aiPI*

Contribuciones:

- 1 Optimizaciones algorítmicas: vectorización y portabilidad
- 2 Construcción de Makefiles generales
- 3 Reescritura de los módulos de Ewald
- 4 Construcción de módulos de impureza (cluster, impurity)
- 5 Aplicaciones variadas.

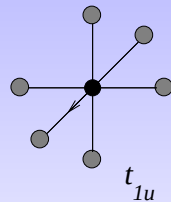
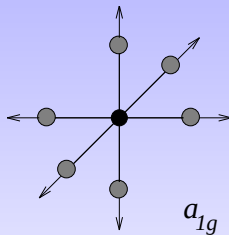
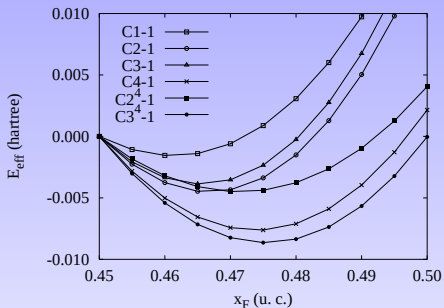
Aplicaciones de *aIP*

- Consistencia del modelo clúster-en-la-red.
 - Si se trata un cristal puro como una impureza, ¿se recupera la estructura electrónica y la geometría del cristal puro?
- Sistema=clúster (*C*) + red (*R*) $\Rightarrow$ grave problema en la frontera.
 - $C = C_1 + C_2 \Rightarrow$ modelos C_{n-m} .



Aplicaciones de *aIPi*

La impureza $\text{Cu}^+:\text{AX}$ y vibraciones locales



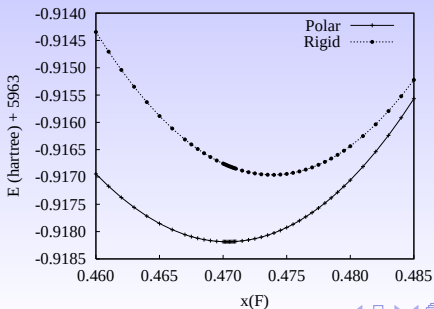
AX	LiF	LiCl	LiBr	NaF	NaCl	NaBr	KF	KCl	KBr
$\bar{k}_{11a_{1g}}$	8.30	6.68	6.95	4.97	4.15	4.41	2.45	2.26	2.40
$\bar{\omega}_{1a_{1g}}$	339.7	223.1	151.6	263.0	175.9	120.8	184.6	129.8	89.1

Correcciones de Polarización en *aIPi*

- Producto de la simetría esférica $\Rightarrow$ primer término corrector = μ :

$$E_e^{RS} = \frac{q^R q^S}{R} + q^S \frac{\vec{\mu}^R \cdot \vec{R}}{R^3} - q^R \frac{\vec{\mu}^S \cdot \vec{R}}{R^3} + \frac{\vec{\mu}^R \cdot \vec{\mu}^S}{R^3} - 3 \frac{\vec{\mu}^R \cdot \vec{R} \vec{R} \cdot \vec{\mu}^S}{R^5} + \dots$$

- $\vec{\mu} = \alpha \vec{E}$, con α 's empíricas.
- Los dipolos modifican $\vec{E}$. Problema autoconsistente : $\vec{E}_i = \vec{E}_i^{\text{ind}} + \sum_j \mathbf{B}_{ij} \vec{\mu}_j$
- Y $\vec{\mu}_i = \alpha_i \vec{E}_i = \alpha_i \vec{E}_i^{\text{ind}} + \alpha_i \sum_j \mathbf{B}_{ij} \vec{\mu}_j$.
- Que puede transformarse en un problema lineal: $\mathbf{C} \vec{\mu} = \vec{E}^{\text{ind}}$
- $\text{CuNaF}_{18}\text{F}_{14}^{5+}:\text{NaF}$



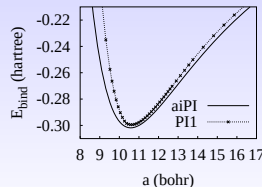
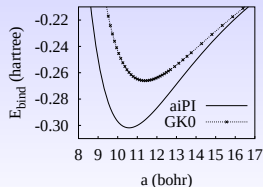
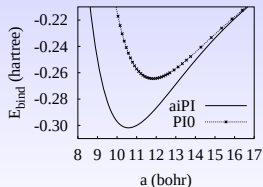
El método gPI

- Liberar la ligadura de simetría esférica: $\varphi_{plm}(\vec{r}) = \chi_{pl}(r)S_{lm}(\hat{r})$
- Así: $\lambda_{pl}^{\Gamma\mu,k}(\vec{r}) = \sum_m u_{lm}^{\Gamma\mu,k} \varphi_{plm}(\vec{r})$
- Gran cantidad de trabajo para:
 - Obtener funciones de simetría.
 - Las integrales monocéntricas entre ellas: monoelectrónicas $(\mathbf{O}^R)_{\Gamma pq} = \frac{1}{n_\Gamma} \sum_{\mu=1}^{n_\Gamma} \langle \lambda_p^{\Gamma\mu} | \hat{O}(r) | \lambda_q^{\Gamma\mu} \rangle$ y bielectrónicas de Coulomb y Cambio.
 - las integrales bicéntricas de red.
 - Las interacciones multipolares de largo rango: Potencial de Madelung multipolar: $V_{\text{mad}}^{lm}(\vec{x}) = \sum_{\vec{R}}^{\text{red}} \frac{S_{lm}(\vec{R}+\vec{x})}{|\vec{R}+\vec{x}|^{l+1}}$
 - Para este último generalizó el método de Ewald habitual.

$$V_{\text{mad}}^{lm}(\vec{x}) = \frac{4\pi^{l!}}{\Delta(2l-1)!!} \sum_{\vec{R}} K^l S_{lm}(\hat{K}) \frac{e^{-K^2/4p}}{K^2} e^{-i\vec{K}\cdot\vec{x}} + \frac{2^l}{\sqrt{\pi}(2l-1)!!} \sum_{\vec{R}} \Gamma(l+1/2, p|\vec{R}+\vec{x}|^2) \frac{S_{lm}(\vec{R}+\vec{x})}{|\vec{R}+\vec{x}|^{l+1}} - 2\sqrt{\frac{p}{\pi}} \delta_{\vec{x}0} \delta_{l0} \delta_{m0}$$
- Codificado por Carlos Fernández Solano.

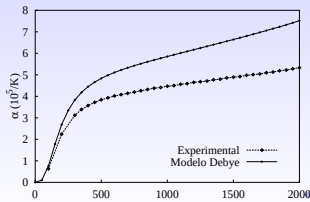
Métodos Semiclásicos

- En TSE: $E_{\text{bind}} = \sum_R E_{\text{def}}^R + \sum_{R>S} E_{\text{int}}^{RS}$
- Potenciales *ab initio* basados en la TSE
 - Modelo de Gordon y Kim (DFT no-SCF): $\rho = \rho^R + \rho^S$
Usando las ρ cristalinas *aiPI*:
 $E_{\text{pair}}^{RS}(r_{RS}; \rho) = E_C^{RS}(r_{RS}; \rho) + \int_V (\rho F[\rho] - \rho^R F[\rho^R] - \rho^S F[\rho^S]) dv$
 - Potenciales interiónicos *aiPI*
 $E_{\text{int}}^{RS} = \langle \Phi_r^R | \hat{V}_{\text{int}}^S | \Phi_r^R \rangle - Z^R \hat{V}_{\text{int}}^S(\vec{r}^R)$
 - Rígidos y Relajados $E_{\text{bind}}(\vec{a}) = \sum_R E_{\text{def}}^R(\vec{a}_0) + \frac{1}{2} \sum'_{R,S} E_{\text{int}}^{RS}(\vec{a}_0; R_{RS}(\vec{a}))$.
 - PIIP: E_{def} se incorpora al potencial $E_{\text{def}}^R = \sum_{S \neq R} E_{\text{def}}^{RS} + \sum_{S,T \neq R} E_{\text{def}}^{RST} + \dots$



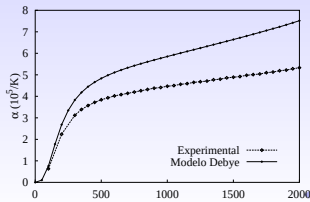
Termodinámica de cristales

- Aproximación armónica: $A(N, V, T) = -k_B T \ln Q(N, V, T) = E_0(N, V) + A_{\text{vib}}$
 $A_{\text{vib}} = \int_0^\infty \left\{ \frac{1}{2} h\nu + k_B T \ln (1 - e^{-h\nu/k_B T}) \right\} g(\nu) d\nu,$
- Modelo de Debye: $g(\nu) = \frac{12\pi V}{c^3} \nu^2$ (corte ν_D) $\Rightarrow \alpha = 0$
- Anarmonicidad: Modelo cuasiarmónico de Debye ($\nu_D \equiv \Theta_D = f(V)$)
 $\Theta_D = \frac{h}{k_B} f(\nu) \left(6\pi^2 n_r V_r^{\frac{1}{3}} \right)^{\frac{1}{3}} \left(\frac{B_{\text{static}}}{M_r} \right)^{\frac{1}{2}}, B_{\text{static}} = V \left(\partial^2 E_0 / \partial V^2 \right)$
- Termodinámica: $G^*(T, p, \vec{a}) = E_0(\vec{a}) + pV(\vec{a}) + A_{\text{vib}}(T, \Theta_D(V(\vec{a})))$
 - Implementación del modelo: Gibbs.
 - Ajuste numérico a funciones $E(V)$ y a ecuaciones de estado universales: Vinet, Birch-Murnaghan, BCNT



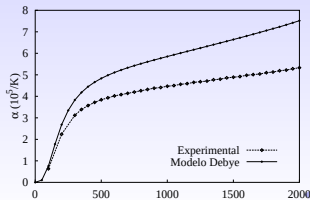
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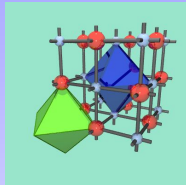
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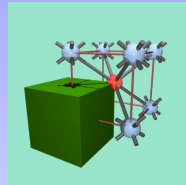


Transiciones de fase inducidas por presión

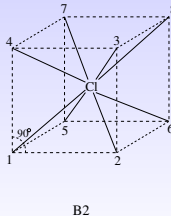
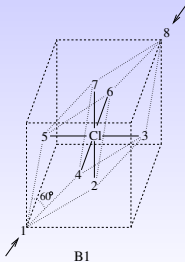
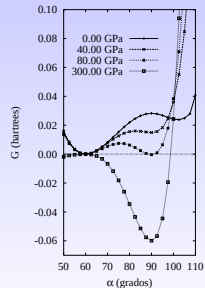
Mecanismo de transición B1-B2 en haluros alcalinos



NaCl

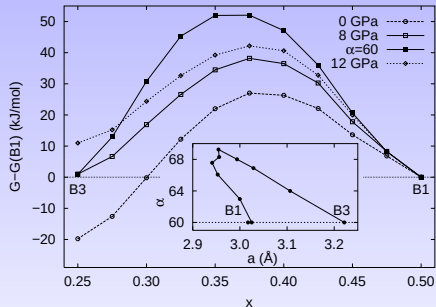
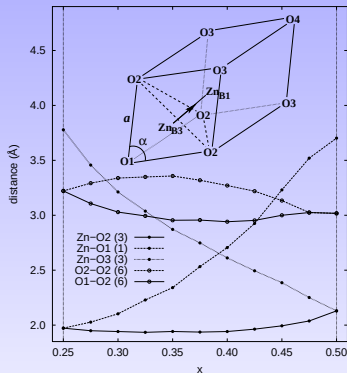


CsCl


 (a, α)


Transiciones de fase inducidas por presión

Mecanismo de transición B3-B1 en ZnO (semiconductores)



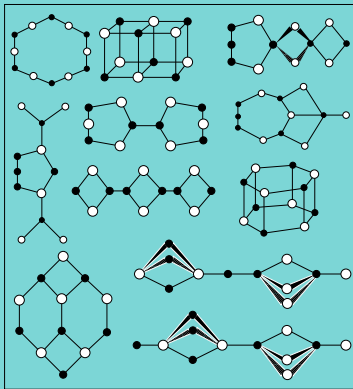
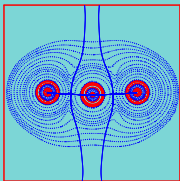
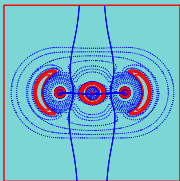
- Ga_2O_3 , PbF_2 y otros.

Nanoagregados III-V

Estructura, estabilidad, enlace

 $M_n N_n$

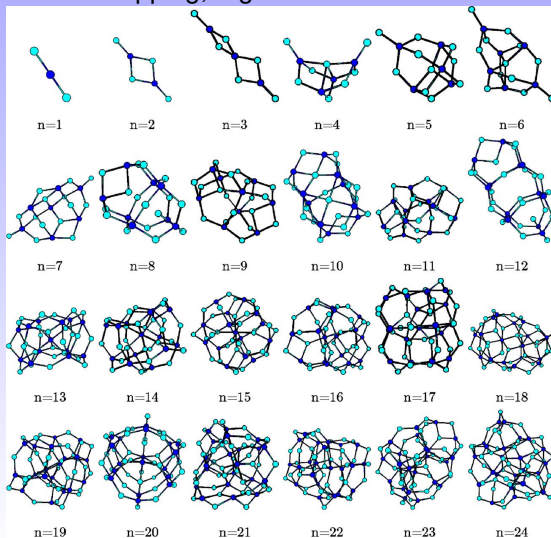
- Evolución y segregación de unidades nitrogenadas.
- Evolución del enlace al pasar de Al a In



Nanoagregados

Optimización Global, MgF_2

Potenciales a/PI . Basin Hopping, Algoritmos Genéticos.

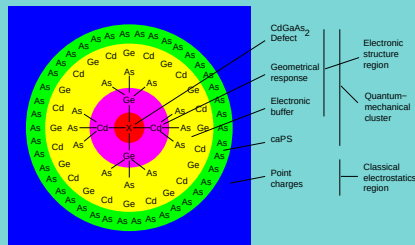
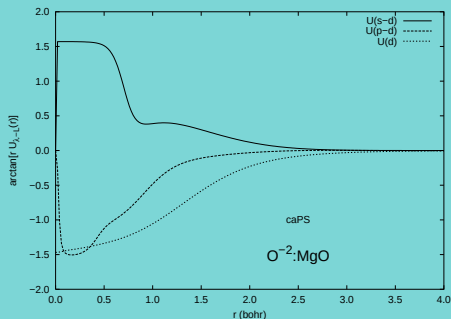


Pseudopotenciales adaptados al cristal (caPS)

- Adaptación del potencial de red aiPI o gPI a la estructura estándar ECP:

$$\hat{U} = -\frac{q}{r} + \mathcal{U}_L(r) + \sum_{\lambda=0}^{L-1} \sum_{\mu=-\lambda}^{\lambda} |Y_{\lambda\mu}\rangle \mathcal{U}_{\lambda-L}(r) \langle Y_{\lambda\mu}|$$

- Ajuste radial: $\mathcal{U}_{\ell}(r) = \sum_{i=1}^N B_i^{\ell} r^{n_i^{\ell}} \exp(-\alpha_i^{\ell} r^2)$.



Enlace Químico en el Espacio Real

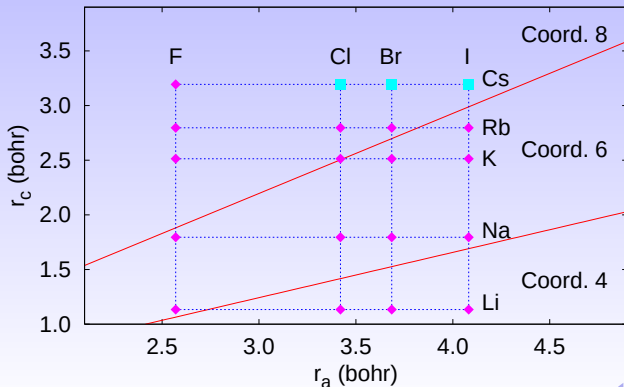
Geometrización del espacio cristalino

- Desde Pauling, relación **imperfecta** estabilidad $\Leftrightarrow$ radios iónicos
- QTIC proporciona el marco adecuado
- Relaciones de Pauling B1-B2 correctas entre radios topológicos

Enlace Químico en el Espacio Real

Geometrización del espacio cristalino

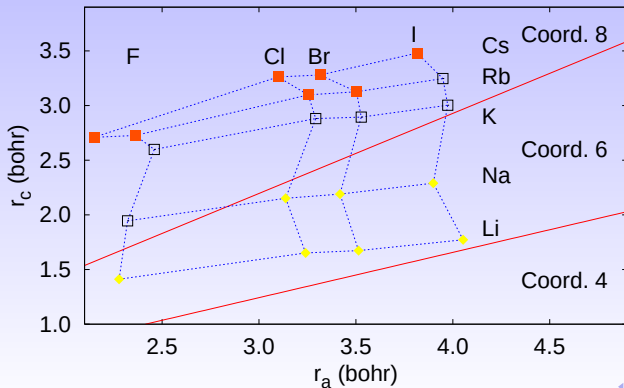
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Enlace Químico en el Espacio Real

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Enlace Químico en el Espacio Real

- En QTAIM, $R^3 = \bigcup_i \Omega_i \Rightarrow \langle \hat{O} \rangle = \sum_i \Rightarrow \langle o \rangle_i$
 - QTIC: Partición de propiedades macroscópicas (Termodinámicas)

Partición Prop. Intensivas

- $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right) = \sum_{\Omega} f_{\Omega} \kappa_{\Omega},$
 $f_{\Omega} = \frac{V_{\Omega}}{V}, \kappa_{\Omega} = -\frac{1}{V_{\Omega}} \left(\frac{\partial V_{\Omega}}{\partial p} \right)$
- Cambios topológicos en transiciones de fase inducidas por presión.

Enlace Químico en el Espacio Real

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$$f_{\Omega} = \frac{V_{\Omega}}{V}, \quad \kappa_{\Omega} = -\frac{1}{V_{\Omega}} \left(\frac{\partial V_{\Omega}}{\partial p} \right)$$

B en $A_2MO_4 \simeq 200$ GPa

	$f(A)$	$f(M)$	$f(O)$
MgAl ₂ O ₄	0.09	0.10	0.81
MgGa ₂ O ₄	0.09	0.16	0.75
ZnAl ₂ O ₄	0.14	0.10	0.77
ZnGa ₂ O ₄	0.14	0.16	0.71

- Cambios topológicos en transiciones de fase inducidas por presión.

Enlace Químico en el Espacio Real

Mejoras algorítmicas en IQA

- $$E = \sum_A \overbrace{\{T_A + V_{ee}^{AA} + V_{en}^{AA}\}}^{E_{\text{self}}^A} + \sum_{A>B} \overbrace{\{V_{en}^{AB} + V_{ne}^{AB} + V_{nn}^{AB} + V_{ee}^{AB}\}}^{E_{\text{int}}^{AB}}$$
- $\rho_2 = \rho_2^C + \rho_2^{xc}, V_{ee}^{AB} = V_C^{AB} + V_{xc}^{AB}, \text{ luego } E_{\text{int}}^{AB} = V_{\text{clas}}^{AB} + V_{xc}^{AB}$
- $E_{\text{bind}} = \sum_A (E_{\text{self}}^A - E^{A,0}) + \sum_{A>B} E_{\text{int}}^{AB} = \sum_A E_{\text{def}}^A + \sum_{A>B} \{V_{\text{clas}}^{AB} + V_{xc}^{AB}\}$
- V_{clas} mide la ionicidad. V_{xc} la covalencia
- Mensaje: **Deformarse para interaccionar**
- Formalización y extensión a otras particiones
- Nueva visión del enlace de hidrógeno
- Bidimensionalidad del eje covalente-iónico
- Enlace metal-carbonilo
- Nueva interpretación de los BCPs

Enlace Químico en el Espacio Real

Generalización de QTAIM

Generalización de IQA

- No solo ρ_2 , cualquier nRDM se pueden condensar: CGDM

$$\rho_i(\mathbf{r}_1, \dots, \mathbf{r}_i)[C] = \frac{N!}{i!c_1! \dots c_m!} \int_{D_C} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N \rho_N$$
- Partición de electrones en cuencas: Estructuras resonantes

$$S = (s_1, \dots, s_m), s_j = s^{\Omega_j}$$
- $p(S) = \rho_0()[S] = p(n_1, \dots, n_m)$: Función de distribución (EDF)
- IQA generalizable a estructuras
 - $E = \sum_S \tilde{E}(S)p(S)$
 - $\tilde{E}(S) = \sum_i^m \tilde{E}_{\text{self}}^i(S) + \sum_{i>j}^m \tilde{E}_{\text{int}}^{ij}(S)$

Enlace Químico en el Espacio Real

Generalización de QTAIM y de IQA

EDFs y DAFHs

- Interpretación Estadística del enlace químico: $\delta^{AB} = -2\text{cov}(n_A, n_B)$

- EDFs prácticamente binomiales:

$$p_N = \bigotimes_i p_1^i$$

- e localizados (Pauli en ER)
- e deslocalizados (enlace)

- DAFH

$$G^\Omega(\mathbf{r}_2) = - \int_\Omega d\mathbf{r}_1 \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \sum_i n_i \phi_i(\mathbf{r})^2$$

- $\delta^{AB} = 2 \sum_i n_i (1 - n_i)$
- $V_{xc}^{AB} \approx \sum_i V_i$

- Recuperación de imágenes orbitales

Bond bundle

- Existen regiones de flujo nulo asociadas a pares libres, y enlaces
- Trabajo inconcluso
- Definición, algoritmos...

Modelización de transiciones de fase inducidas por presión en compuestos ABO_4 y A_2BO_4

Lourdes Gracia, Armando Beltrán y Juan Andrés

Efecto de la Presión

CÁLCULOS MECANOCUÁNTICOS

Programas
- CRYSTAL
- VASP

Metodología
DFT (B3LYP)

Optimización de la geometría



Curva E_T -V



código GIBBS:
Ecuación de Estado



V_0, B_0, B_0'

$$B = \frac{1}{\kappa} = -V \left[\frac{\partial P}{\partial V} \right]_T$$

SISTEMAS

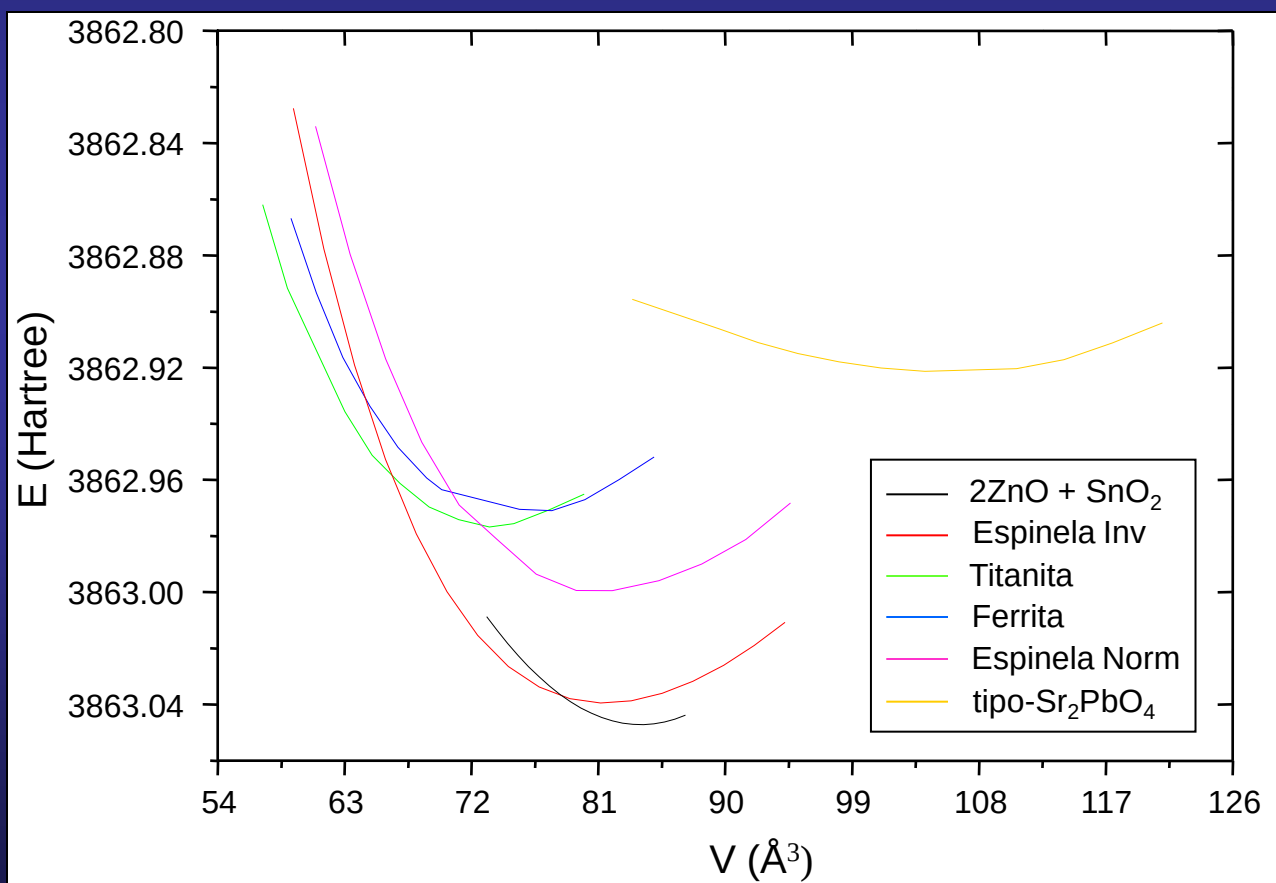
- Zn_2SnO_4
- AgClO_4
- CaSO_4
- SrMoO_4
- BaSO_4

Zn_2SnO_4

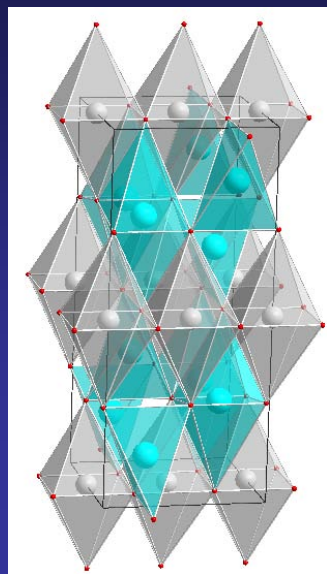
	<u>bases</u>
Sn	[DB]-21G*
Zn	8-411G*
O	6-31G*

Óxido ternario modelo
Propiedades ópticas y electrónicas

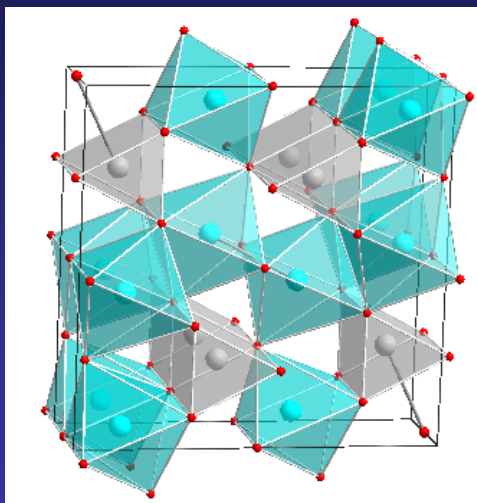
↓
composición y estructura



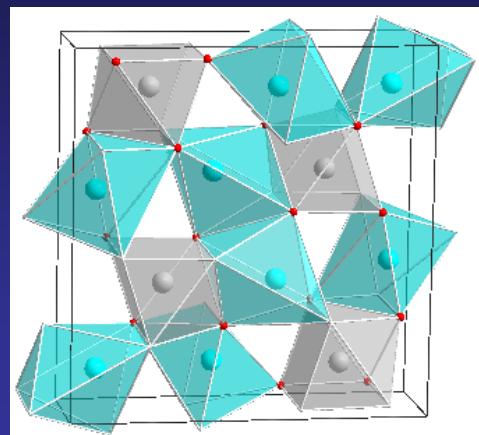
Espinela Inversa (*Imma*)



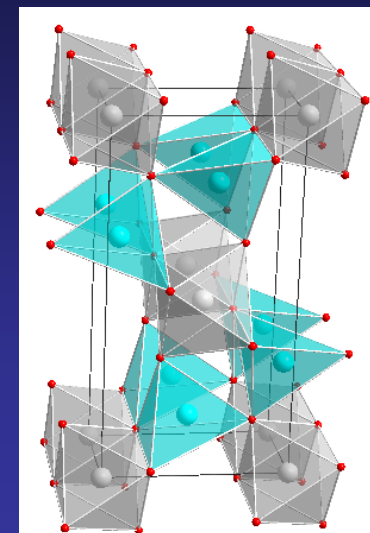
tipo-Titanita (*Cmcm*)



tipo-Ferrita (*Pnam*)



tipo-Sr₂PbO₄ (*Pbam*)



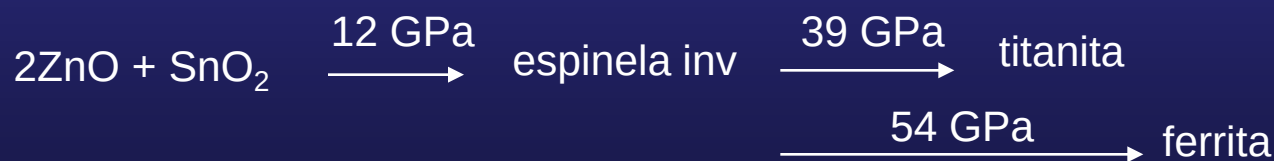
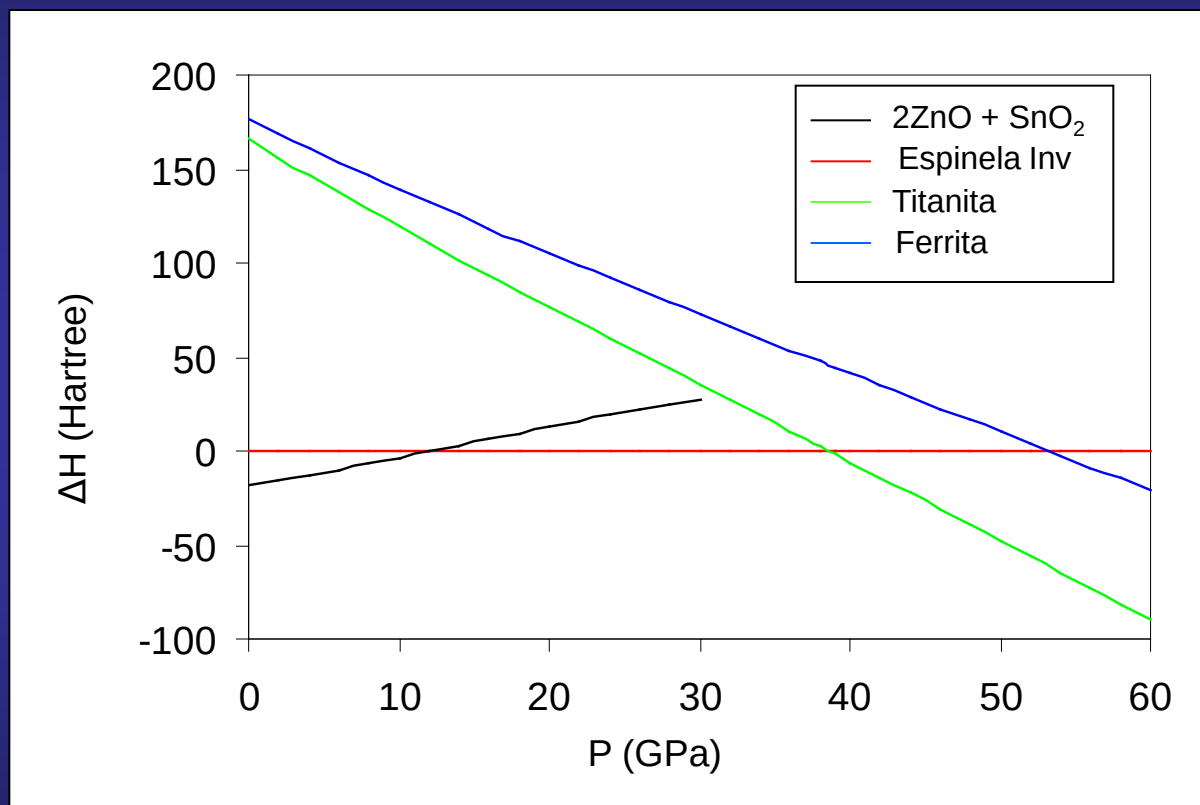
Parámetros estructurales a P=0 GPa de las fases estudiadas

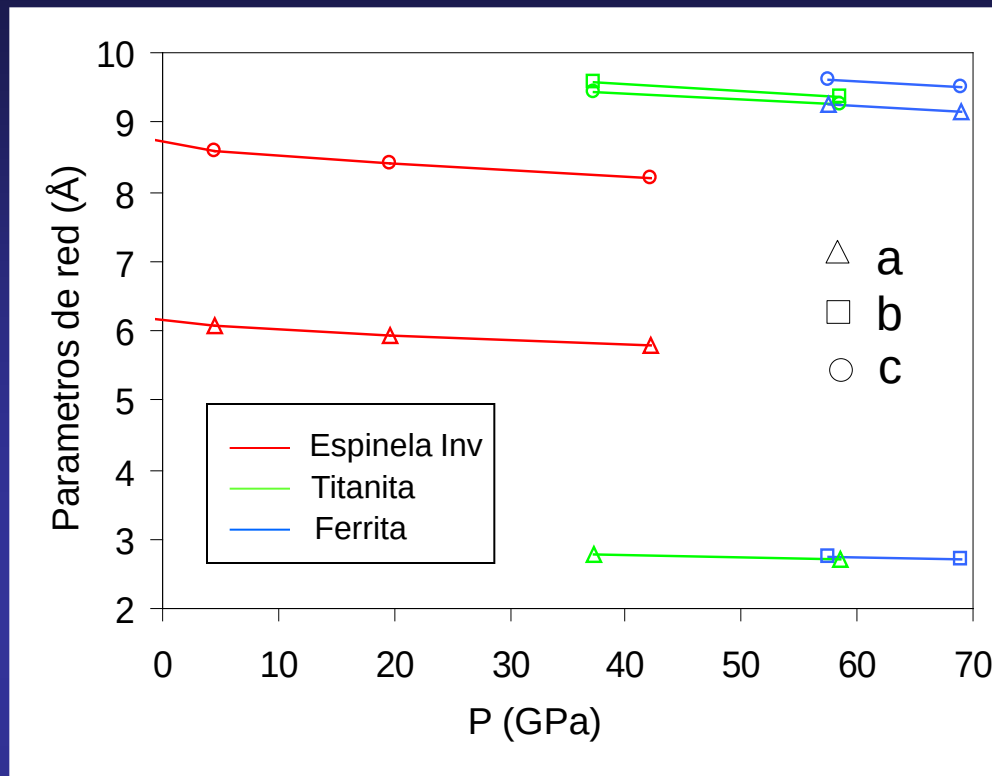
		a	b	c	β	B (GPa)	B'
ZnO	<i>P6₃mc</i>	3.277		5.244	120°	114.0	4
SnO ₂	<i>P4₂/mnm</i>	4.715		3.194		256.6	4
Espinela Inv		6.187		8.750		185.6	4
Espinela Norm		8.688				193.4	4
Titanita		2.922	10.084	9.948		178.5	4
Ferrita		9.949	2.936	10.325		161.4	4
tipo-Sr ₂ PbO ₄		6.752	10.862	3.018		23.8	4

X. Shen *et al* *J. Appl. Phys.* **106**, 113523 **2009**

$P = 21.1 \text{ GPa} \rightarrow$ fase intermedia ortorrómbica $a=4.92 \text{ \AA}$, $b=4.36 \text{ \AA}$, $c=4.19 \text{ \AA}$

$P = 32.7 \text{ GPa} \rightarrow$ posible fase ferrita $a=5.68 \text{ \AA}$, $b=5.26 \text{ \AA}$, $c=?$





distancia Sn-O (Å)

espinela inv

octahedros SnO_6 , 2.076 (4) y 2.025 (2)

titanita

prisma trigonal SnO_6 , 2.136 (4) y 2.052 (2)

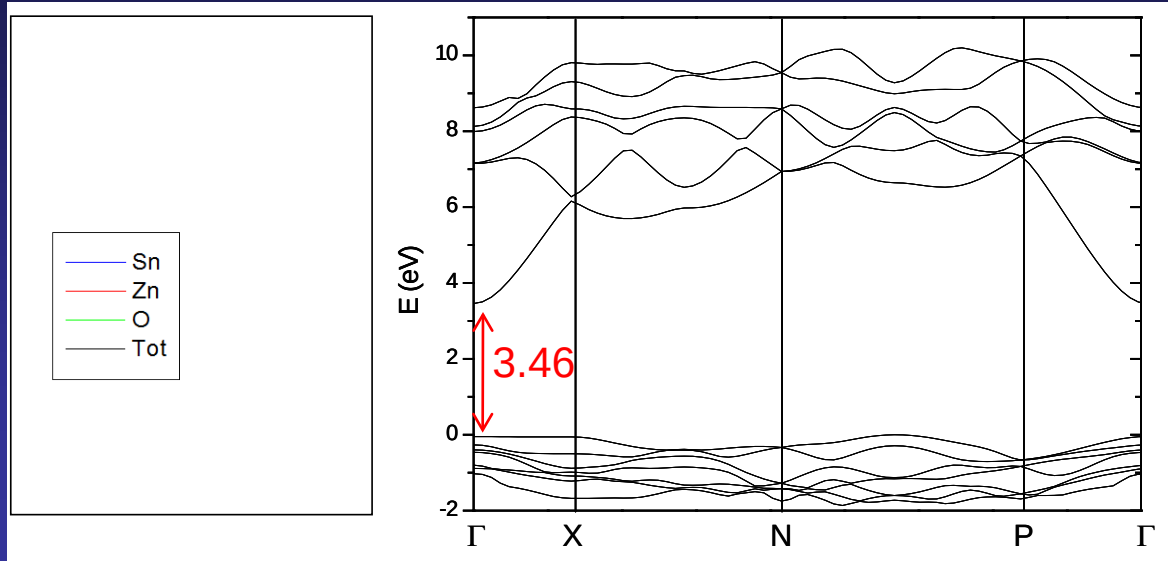
ferrita

pseudoprisma trigonal SnO_7 , 2.083-2.223

Espinela Inversa

BV $\rightarrow$ O p (p_x)

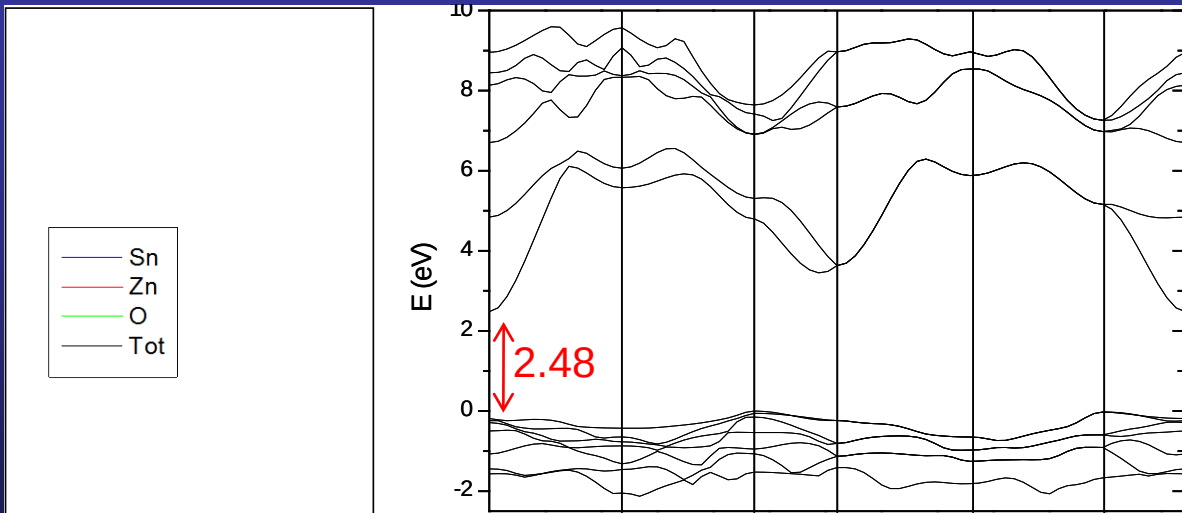
BC $\rightarrow$ Sn 5s (octahedros)
dominan sobre O 2s
y Zn 4s (tetrahedros)



Titanita

BV $\rightarrow$ O p ($p_x p_y p_z$)

BC $\rightarrow$ Sn 5s y Zn 4s
dominan sobre O 2s



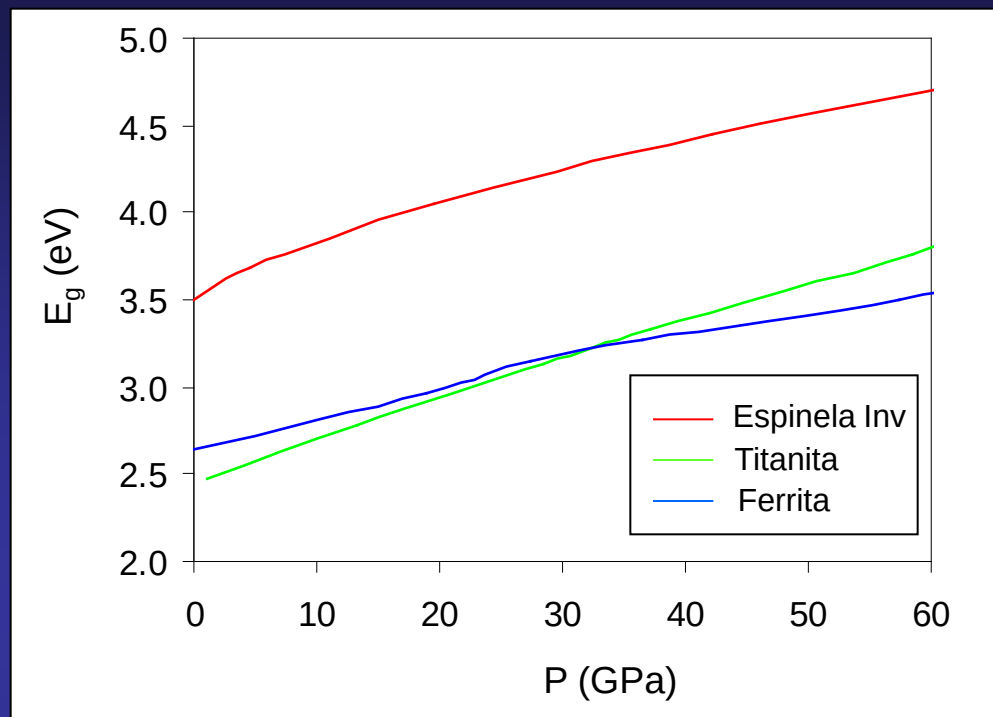
Ferrita

$E_g = 2.64\text{ eV}$

BC $\rightarrow$ participación Zn 3p_y

Variación del band gap
con la presión

Análisis vibracional
(modos Raman)

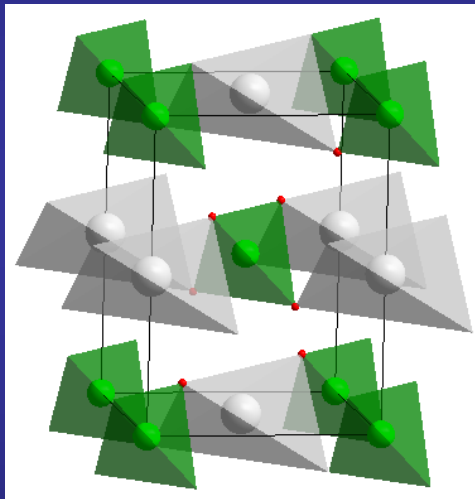


	dw/dP (cm ⁻¹ /GPa)
Espinela Inv	0.7 a 5.4
Titanita	0.3 a 4.2
Ferrita	→

Dos modos A_g blandos (a 95 y 920 cm⁻¹)
contracción-expansión de octaedros ZnO_6 en la
región diagonal del plano ac .

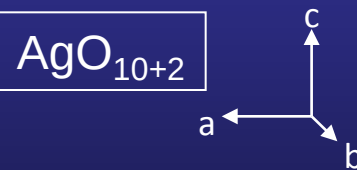
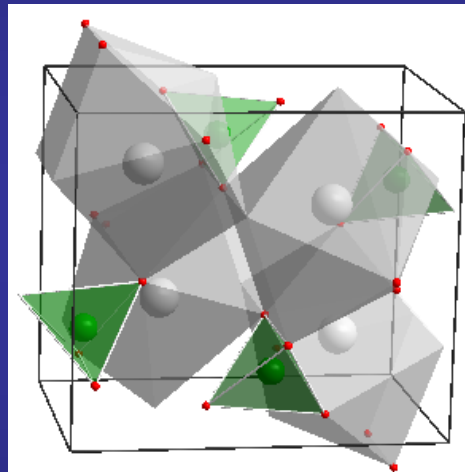
AgClO₄

Tetragonal
(*I*-42m)

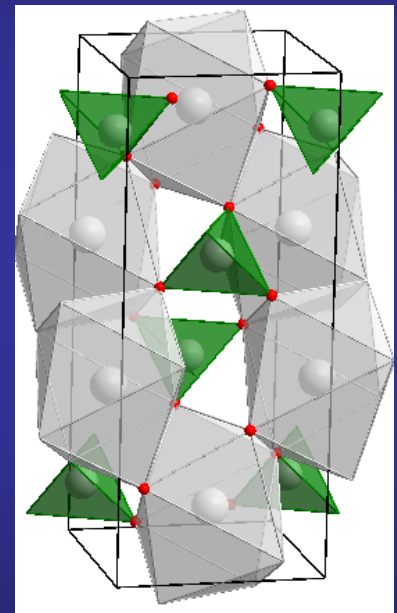


tetrahedros ClO₄
bisdisfenoides AgO₈

Barita
(*Pnma*)

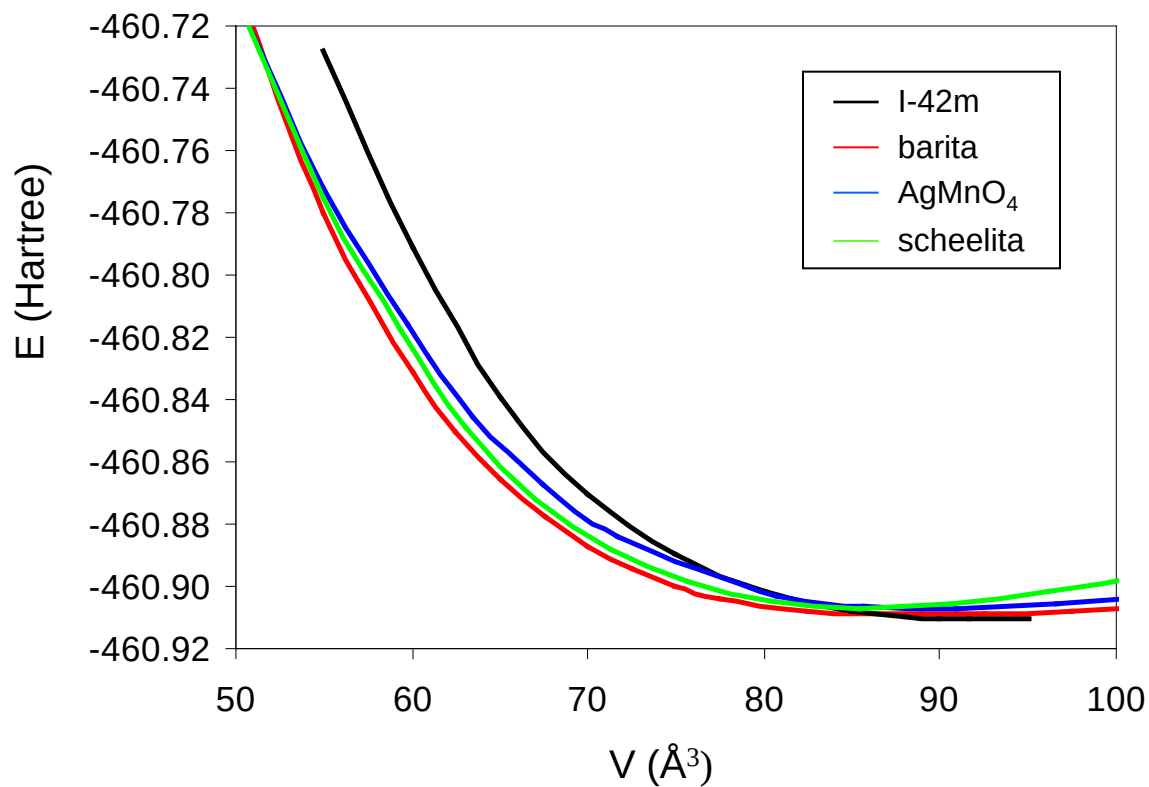


Scheelita
(*I*41/a)



AgMnO₄
(*P*21/*n*)

	<u>bases</u>
Ag	HAYWSC-311d31G
Cl	HAYWLC-31G
O	6-31G*



Datos teóricos

	I -4 2m tetragonal		
	a	c	V/2
	5.0912	6.9443	90.0000
Ag (2b)	0.0	0.0	0.5
Cl (2a)	0.0	0.0	0.0
O1 (8i)	0.1829	0.1829	0.1416
B0 = 34.0 GPa B0' = 9.1			

	Pnma barita			
	a	b	c	V/4
	8.2169	5.5509	7.8059	88.9988
Ag (4c)	0.1864	0.25	0.2579	
Cl (4c)	0.0615	0.25	0.8110	
O1 (4c)	0.2301	0.25	0.9212	
O3 (8d)	0.4401	0.5073	0.1872	
O2 (4c)	0.4032	0.25	0.5654	
B0 = 37.0 GPa B0' = 5.0				

	I41/a scheelite		
	a	c	V/4
	5.0761	13.2630	85.4363
Ag (4b)	0.0	0.25	0.625
Cl (4a)	0.0	0.25	0.125
O (16f)	0.2372	0.1221	0.0554
B0 = 49.97 B0' = 6.0875			

P21/n AgMnO4				
a	b	c	beta	V/4
5.7513	8.5776	7.3769	90.97	90.968
B0 = 49.97 B0' = 6.0875				

Datos experimentales (difracción en polvo a RT, APS)

Daniel Errandonea (Universidad de Valencia)

Tetragonal

$a = 4.976(3) \text{ \AA}$ y $c = 6.746(4) \text{ \AA}$; $V = 167.0(3) \text{ \AA}^3$; $Z = 2$				
Atomo		x	y	z
Ag	2b	0	0	0.5
Cl	2a	0	0	0
O	8i	0.1645(9)	0.1645(9)	0.1341(9)

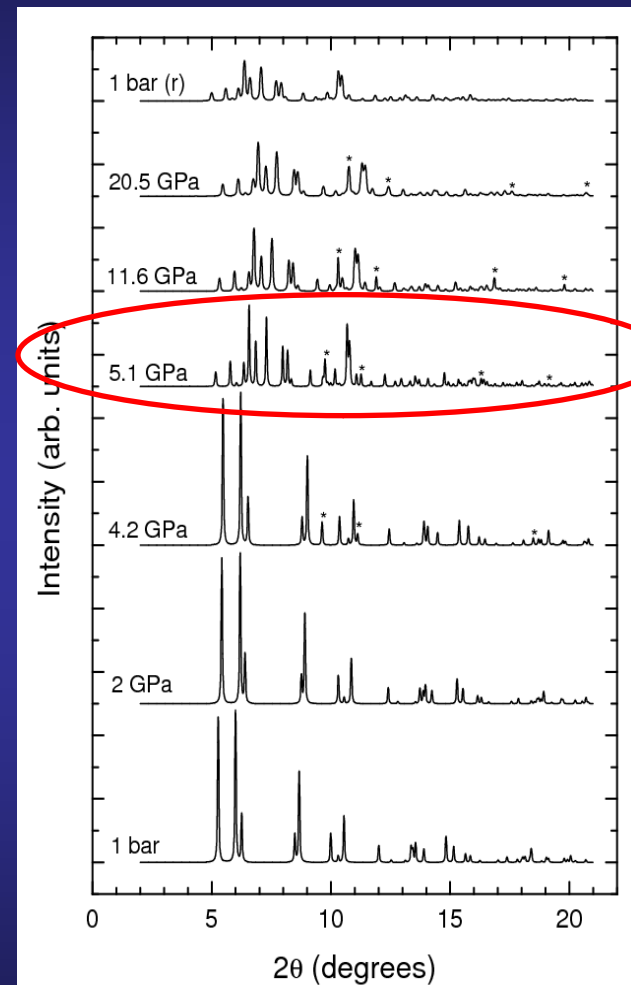
$B_0 = 29.0$ $B_0' = 4.1$

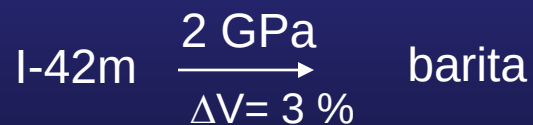
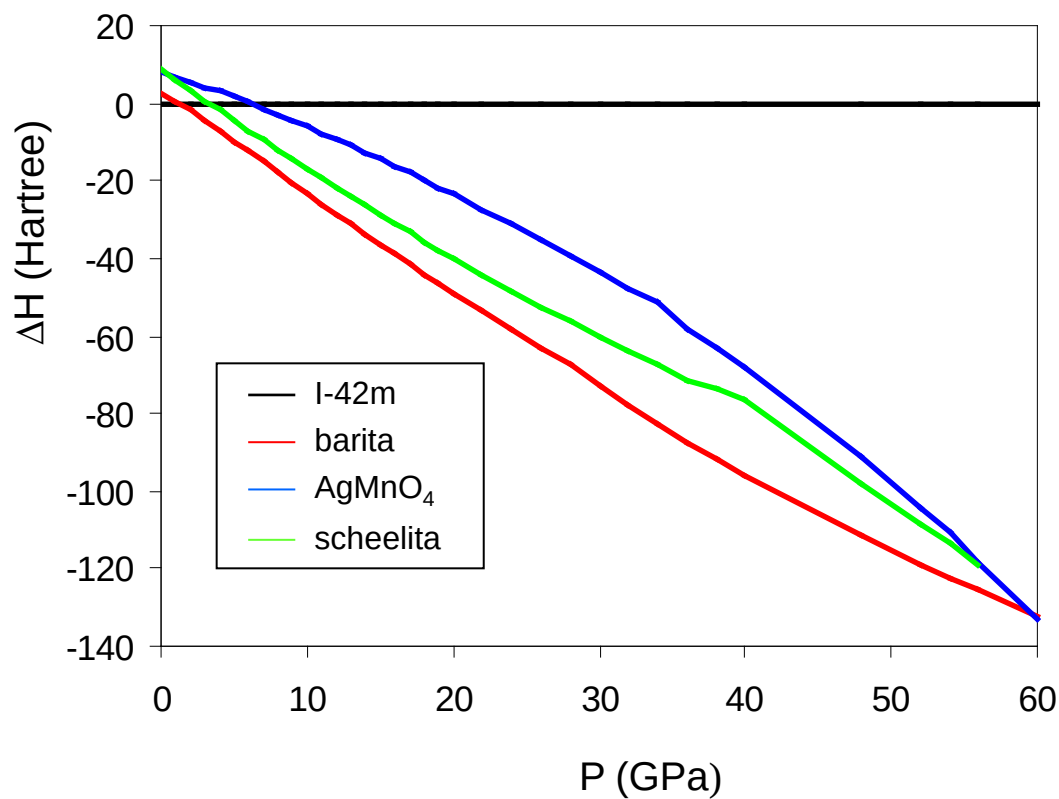
5.1 GPa ↓ Colapso de volumen del 7 %

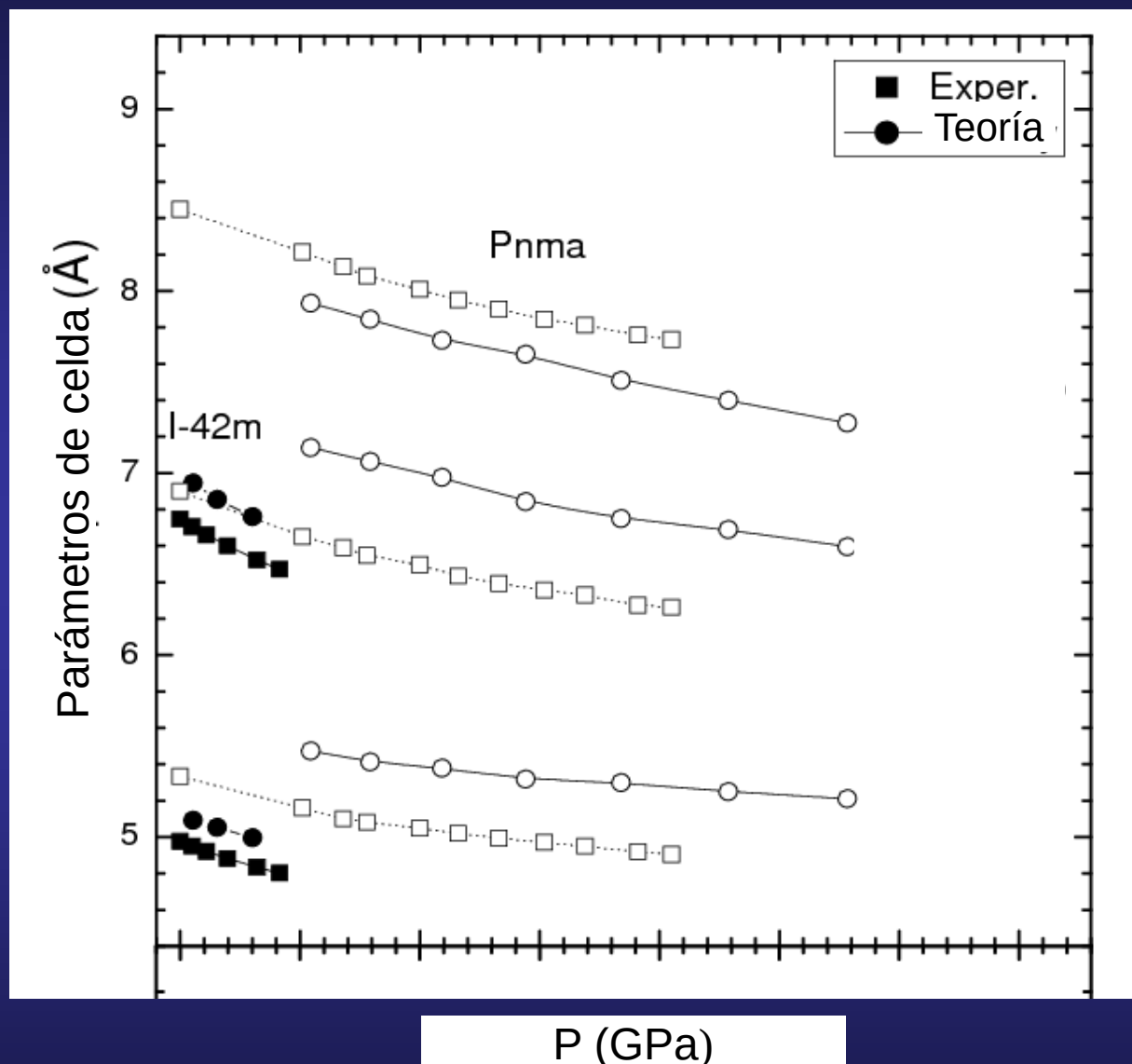
Barita

$a = 8.214(8) \text{ \AA}$, $b = 5.160(5) \text{ \AA}$, y $c = 6.651(6) \text{ \AA}$; $V = 281.9(8) \text{ \AA}^3$; $Z = 4$				
Atomo		x	y	Z
Ag	4c	0.1822(2)	0.25	0.3345(3)
Cl	4c	0.0697(1)	0.25	0.8122(9)
O	4c	0.1902(2)	0.25	0.9503(9)
O	8d	0.4033(4)	0.5433(4)	0.1961(2)
O	4c	0.4253(4)	0.25	0.5901(5)

$B_0 = 38.0$ $B_0' = 5.1$

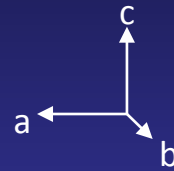
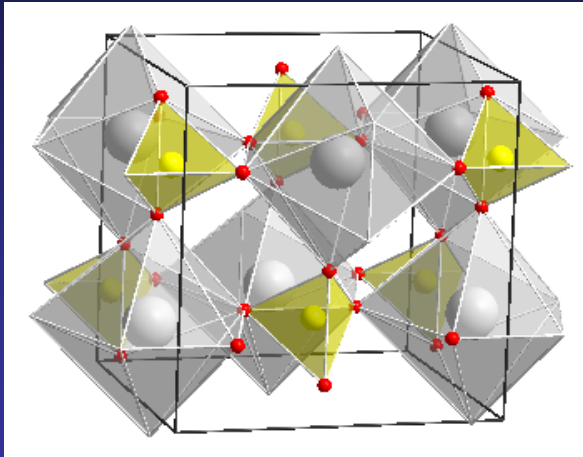




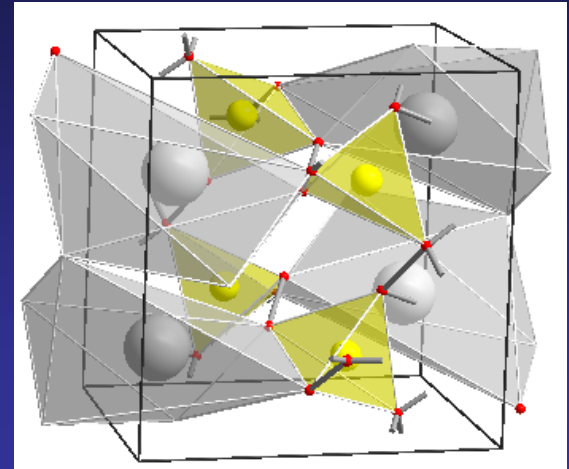


CaSO_4

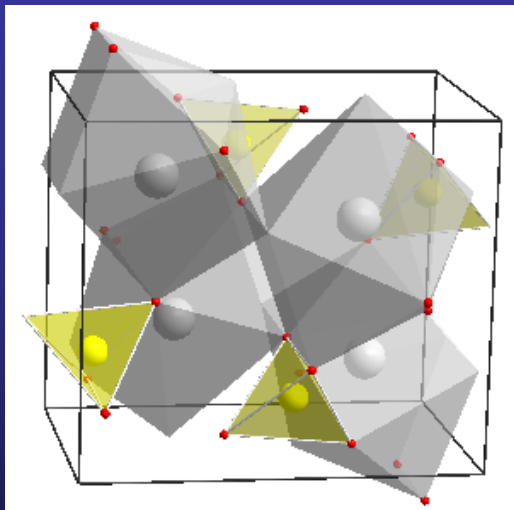
Anhidrita



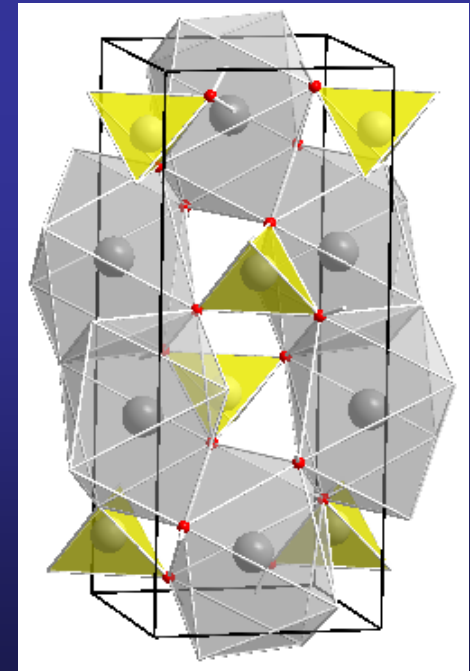
Monacita



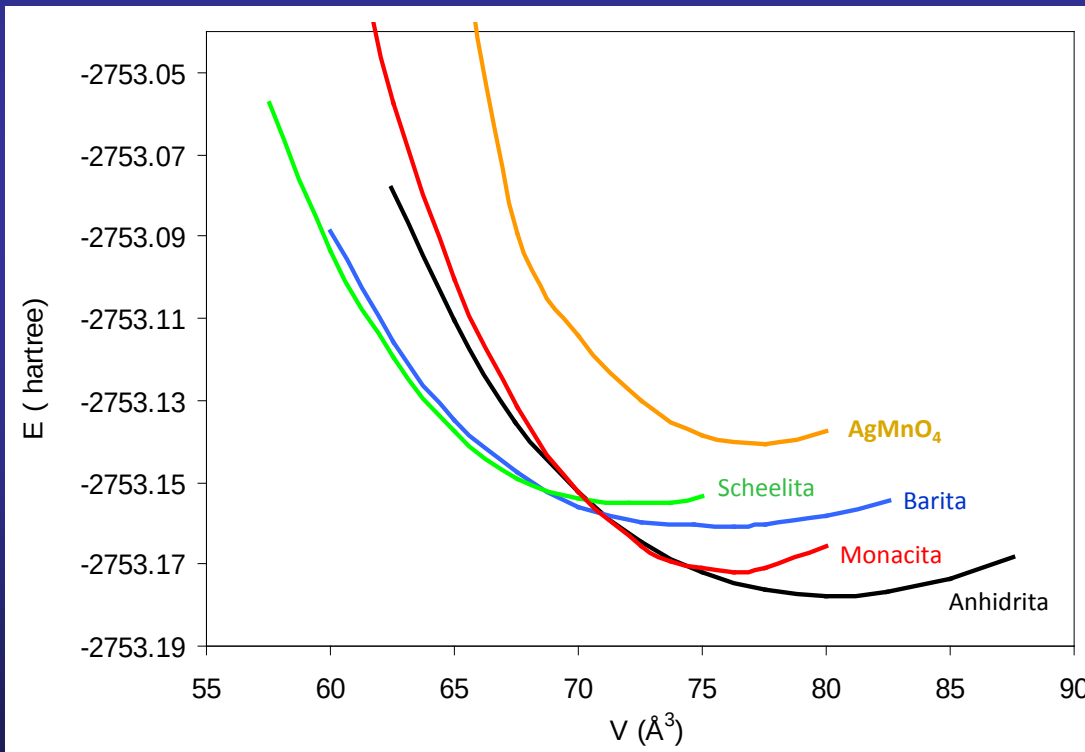
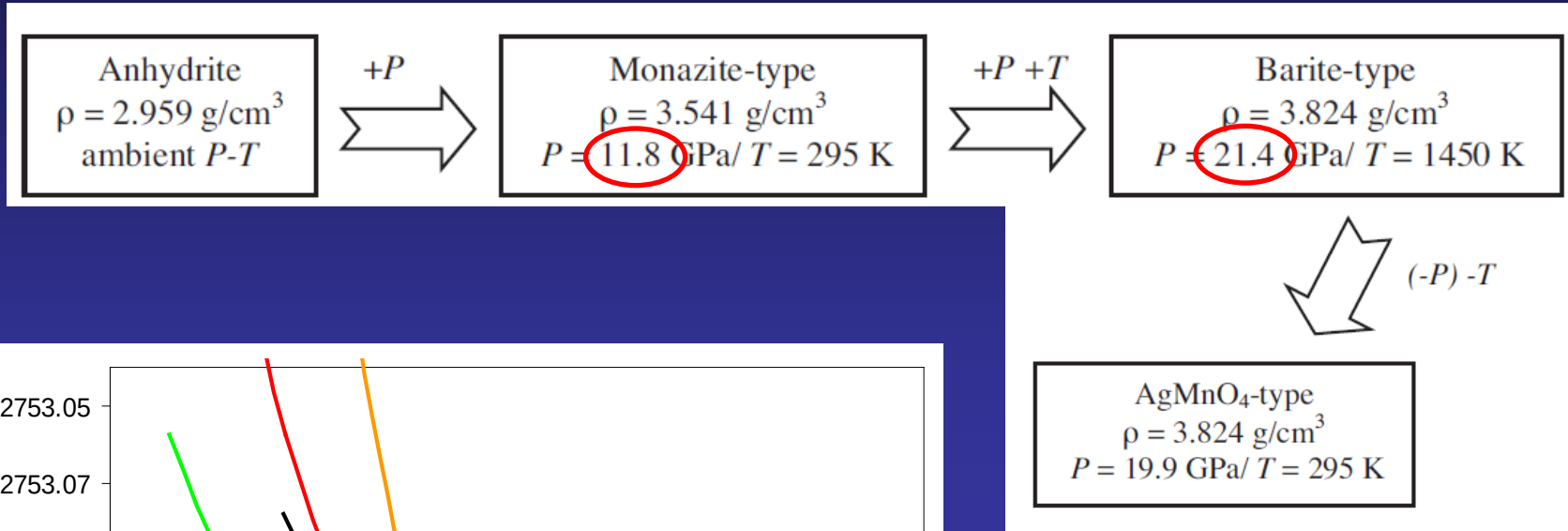
Barita



Scheelita



W. A. Crichton et al. *American Mineralogist*, 90, 22–27, 2005



<u>bases</u>	
Ca	86-511d21G
S	86-311G*
O	6-31G*86

Datos teóricos

Estructura	anhidrita	monacita	barita	scheelita	AgMnO ₄
a (Å)	7.1051	6.8283	7.9635	4.9251	5.4260
b (Å)	6.3048	7.0597	5.3395	11.8752	8.2350
c (Å)	7.1434	6.5037	7.0241	2.4112	6.9385
β		103.38			90.83

Datos experimentales

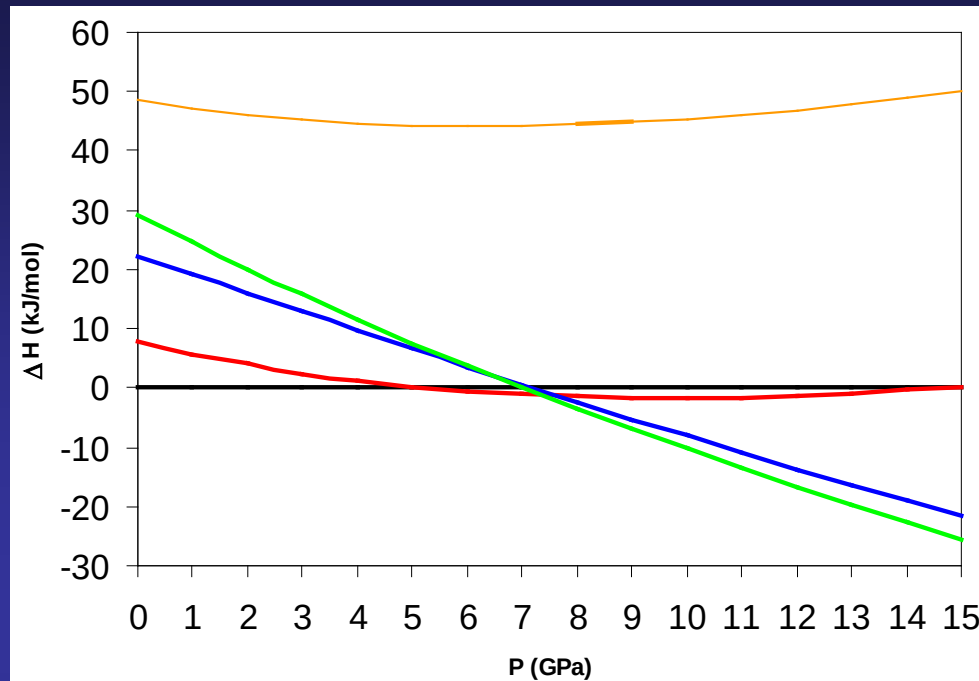
YM Ma et al. *J. Phys.: Condens. Matter* 19 (2007) 425221

W. A. Crichton et al.

Estructura	anhidrita	monacita
a (Å)	6.992	6.829
b (Å)	6.999	7.134
c (Å)	6.240	6.228
β		104.39

monacita	barita	AgMnO ₄
6.3769	6.3365	4.9577
6.6439	7.5347	7.5243
6.1667	4.9532	6.3397
102.22		90.829

2 GPa 



Structura	anhidrita	monacita	barita	scheelita	AgMnO ₄
B ₀ (B ₀ ')	67.7 (5.61)	146.2 (4.28)	64.8 (6.94)	84.1 (5.86)	144.9 (4.19)
Exp B ₀ (B ₀ ')	≈45 (-)	149.4 (4.25)			

S.E. Bradbury *et al* J Phys Chem Solids 70 (2009) 134–141

anhidrita → monacita a $P_{\dagger} \geq 5$ GPa , reducción de volumen -2% a 5GPa

monacita → barita (y/o scheelita) a 8 GPa

Análisis vibracional

Anhidrita

18 modos Raman

$$\Gamma = 6 A_g + 5 B_{1g} + 5 B_{2g} + 2 B_{3g}$$

Modo blando A_g
Indicativo de transición

Monacita

36 modos Raman

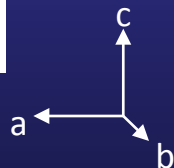
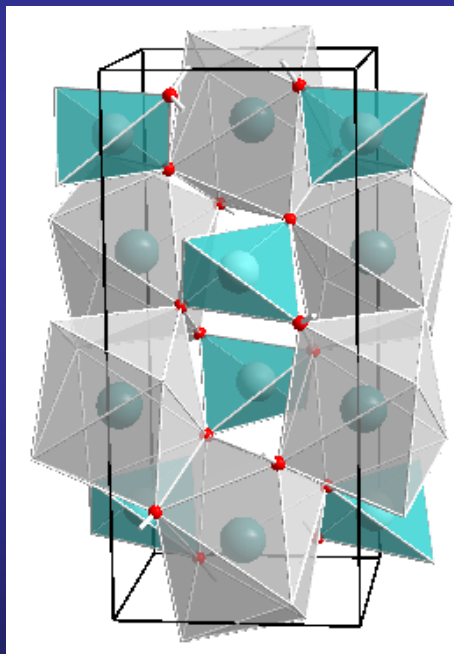
$$\Gamma = 18 A_g + 18 B_{1g}$$

Modo	$\omega(0)$ (cm ⁻¹)	Ma et al ^a	d ω /dP	d ω /dP ^a	γ
T (B _{1g})	51.75		6.275		8.671
T(A_g)	139.96	123	-4.068		-2.078
T (B _{1g})	156.19	131	0.924		0.423
R (B _{2g})	164.25		3.787		1.649
R (B _{3g})	174.61	168	4.076		1.669
R+T (B _{2g})	198.17		2.011		0.725
R+T (B _{1g})	212.49		11.866		3.993
T (A _g)	228.34	235	7.898		2.473
T (B _{2g})	300.50		4.569		1.087
ν_2 (B _{3g})	349.15	416	0.300	0.038	0.061
ν_2 (A _g)	451.53	498	3.198	2.171	0.506
ν_4 (B _{1g})	535.79	608	1.835	0.950	0.245
ν_4 (B _{2g})	558.13	626	2.496	1.365	0.320
ν_4 (A _g)	622.23	674	4.147	1.635	0.477
ν_1 (A _g)	948.17	1016	4.814	2.722	0.363
ν_3 (B _{1g})	1058.84	1128	3.863	3.226	0.261
ν_3 (A _g)	1086.82	1159	3.420	3.780	0.225
ν_3 (B _{2g})	1123.91	1111	4.312	3.888	0.275

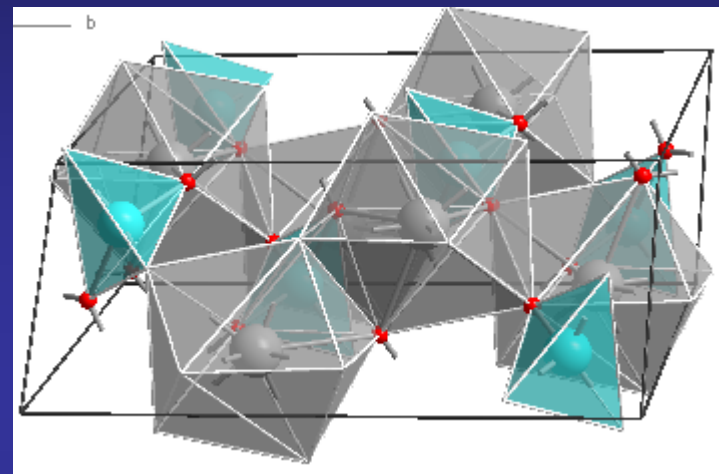
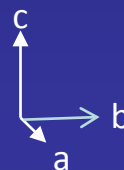
SrMoO_4

Programa VASP
bases: PAW-PBE

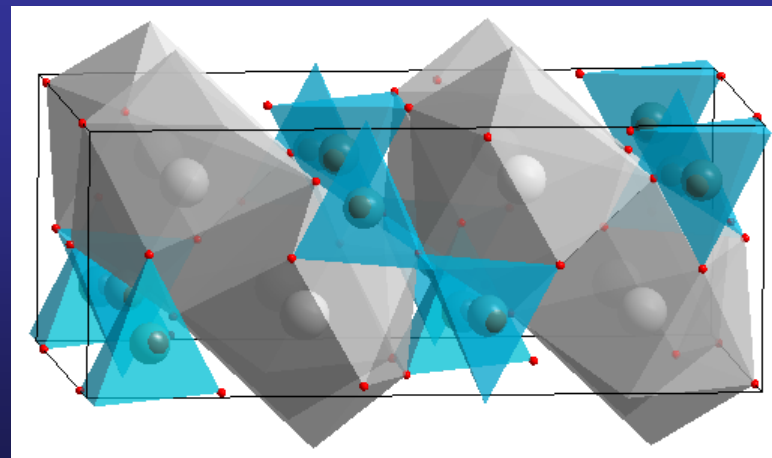
Scheelita
($I41/a$)



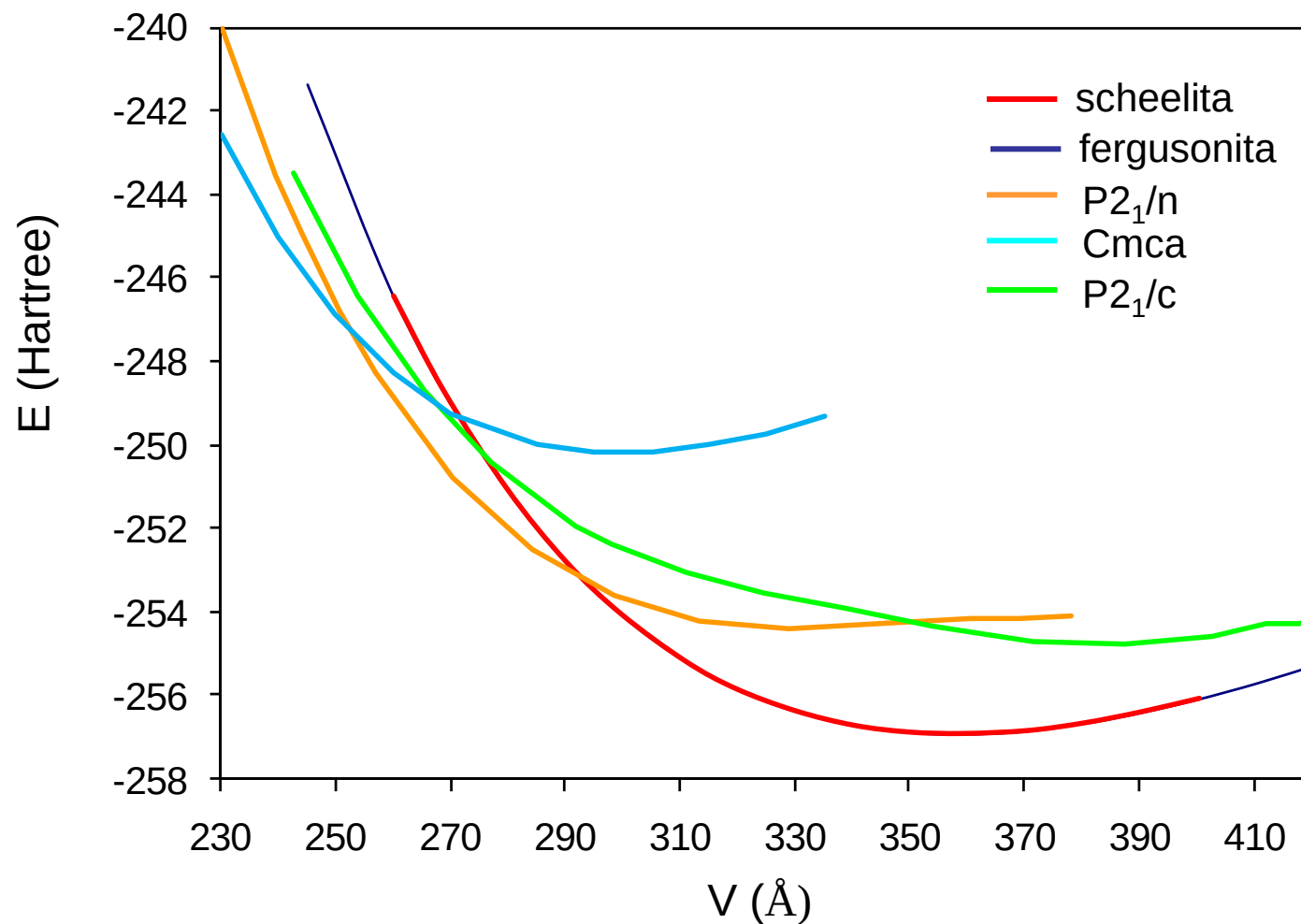
Fergusonita
($I2/a$)



($Cmca$)



Curva E-V



Parámetros estructurales a P=0 GPa de las fases de SrMoO₄

scheelite I4 ₁ /a: a = 5.448 c = 12.112 B = 74.7 GPa B' = 4				
Sr	4b	0	0.25	0.625
Mo	4a	0	0.25	0.125
O	16f	0.2371	0.1113	0.0433
fergusonite I2/a: a = 5.431 b = 12.072 c = 5.402 β = 89.38 B = 84.2 GPa B' = 4				
Sr	4e	0.25	0.6252	0
Mo	4e	0.25	0.1246	0
O	8f	0.8902	0.9571	0.2374
O	8f	0.4885	0.2067	0.8602
P2 ₁ /n: a = 12.734 b = 7.091 c = 7.286 β = 91.67 B = 87.8 GPa B' = 4				
Cmca: a = 7.983 b = 13.664 c = 5.406 B = 104.5 GPa B' = 4				
P2 ₁ /c: a = 8.141 b = 5.965 c = 8.587 β = 111.68 B = 18.3 GPa B' = 4				

D. Errandonea et al J Solid State Chem 181 (2008) 355–364

(a) Structural parameters of scheelite SrMoO₄ at 0.5 GPa: I4₁/a, Z = 4, a = 5.380(5) Å, c = 12.019(9) Å

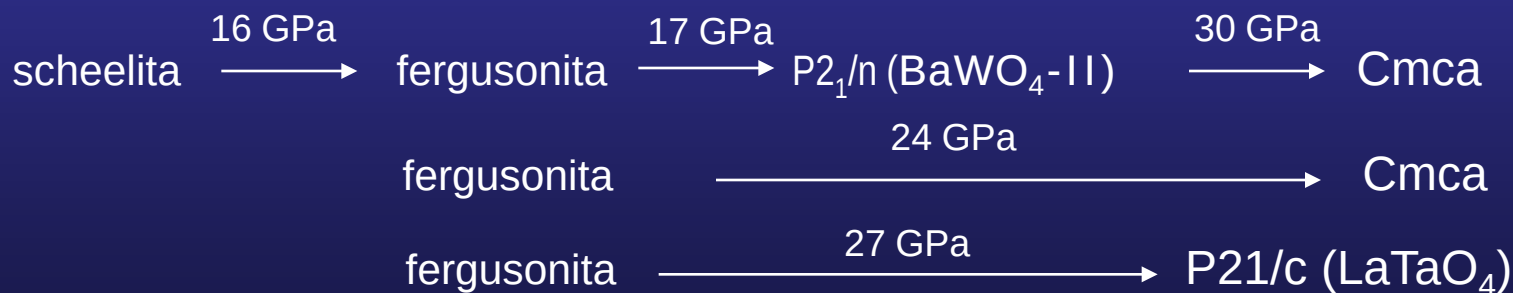
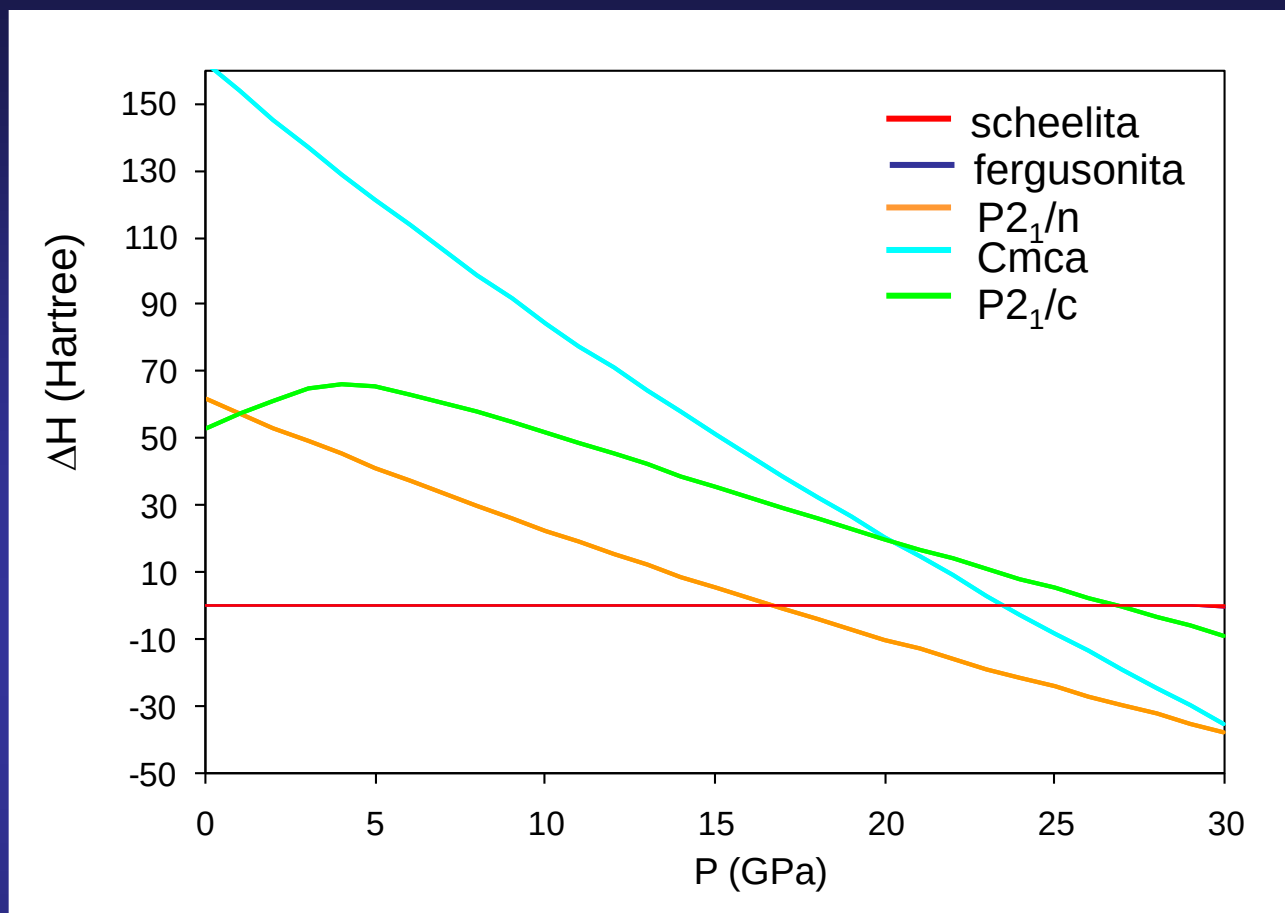
Sr	4b	0	0.25	0.625
Mo	4a	0	0.25	0.125
O	16f	0.248(9)	0.110(6)	0.051(6)

(c) Structural parameters of fergusonite SrMoO₄ at 13.1 GPa: I2/a, Z = 4, a = 5.256(5) Å, b = 11.191(9) Å, c = 5.195(5) Å, β = 90.9(1)°

Sr	4e	0.25	0.615(2)	0
Mo	4e	0.25	0.123(1)	0
O	8f	0.910(6)	0.951(6)	0.248(5)
O	8f	0.492(6)	0.239(5)	0.797(6)

$$B_0 = 71.0 \text{ B}'_0 = 4.2$$

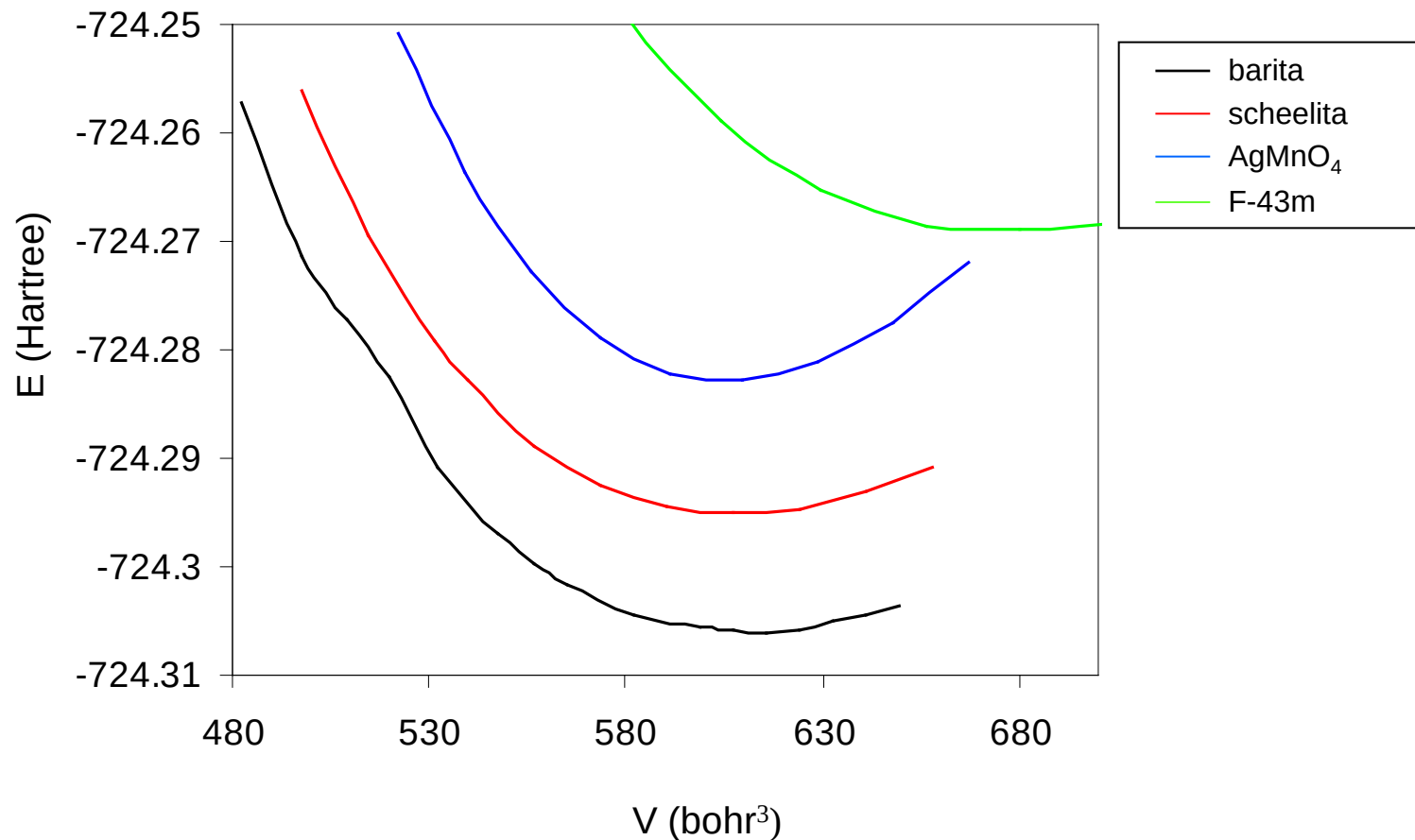
$$P_T = 12.2 \text{ GPa}$$



BaSO₄

Parámetros estructurales a P=0 GPa de las fases de BaSO₄

		a	b	c	β	B (GPa)	B'
Barita	<i>Pnma</i>	9.148	5.454	7.316		64.0	7.2
Scheelita	<i>I41/a</i>	5.174		13.448		71.8	6.7
AgMnO ₄	<i>P21/n</i>	5.910	8.436	7.252	90.97	125.6	4.4
	<i>F-43m</i>	7.386				53.9	7.4





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Departament de Química Física i Analítica



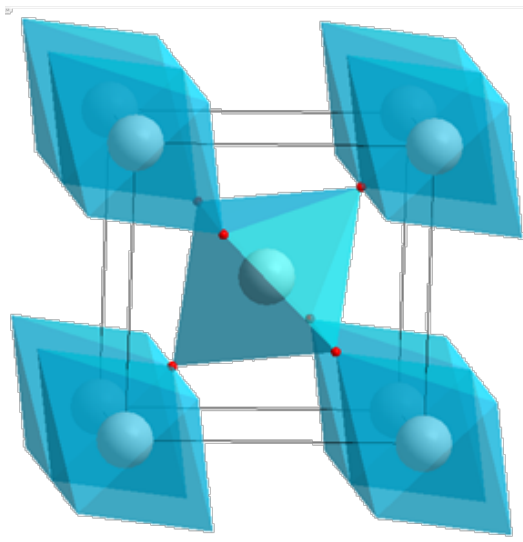
Estudio teórico (y experimental) del efecto de la presión sobre el TiO_2 y el SbPO_4

Marcilene Cristina Gomes*

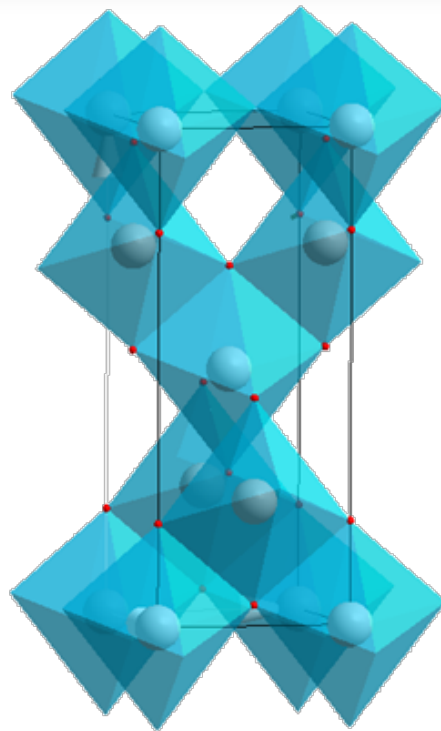
I Symposium MALTA-Consolider 23-27 Enero 2011

*Instituto Federal de Mato Grosso/Campus Cáceres - Brasil

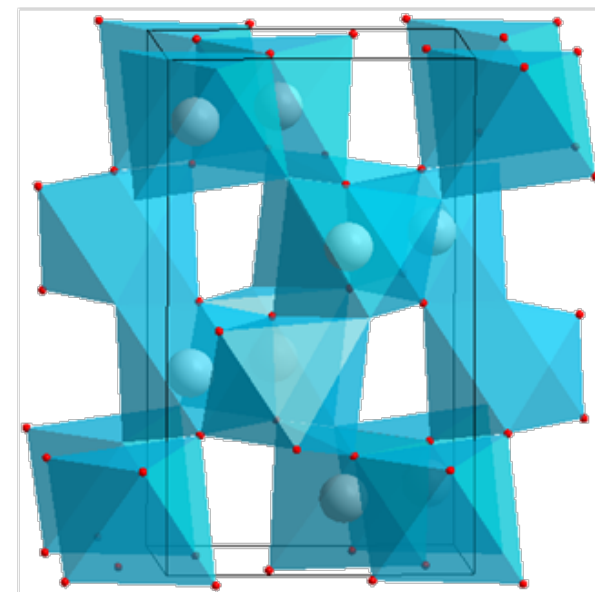
TiO₂ polimorfos



Rutilo



Anatasa



Brookita

TiO₂ síntesis

Método → Sol-Gel

Fuente Ti → Isopropóxido de Titanio (Ti[OCH(CH₃)₂]₄) (99% Aldrich)

Dopaje → Mn

Co

Fe

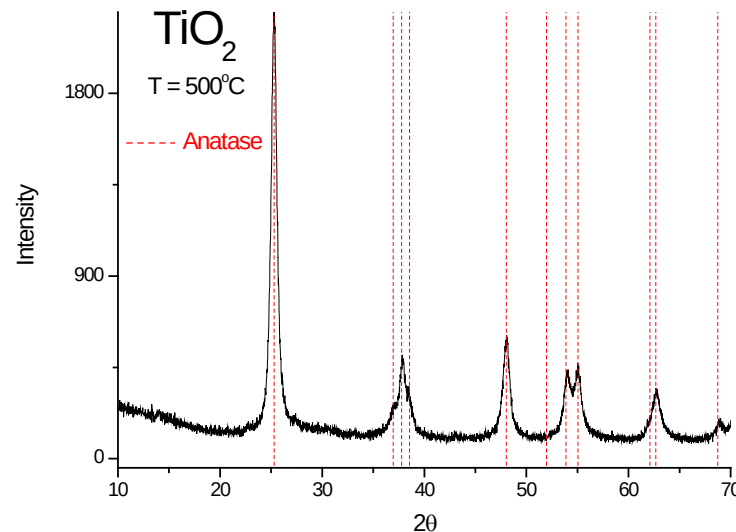
MnO (99% Aldrich)

CoO (99% Aldrich)

FeO (99,9% Aldrich)

Concentración → 0,2%, 2%, 5%, 10%, 20%

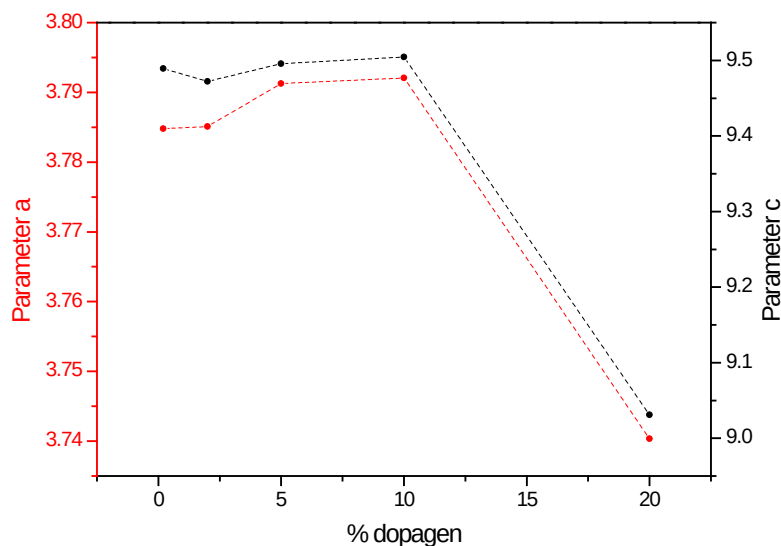
Temperatura → 500°C (6h) ~ TiO₂ Anatasa



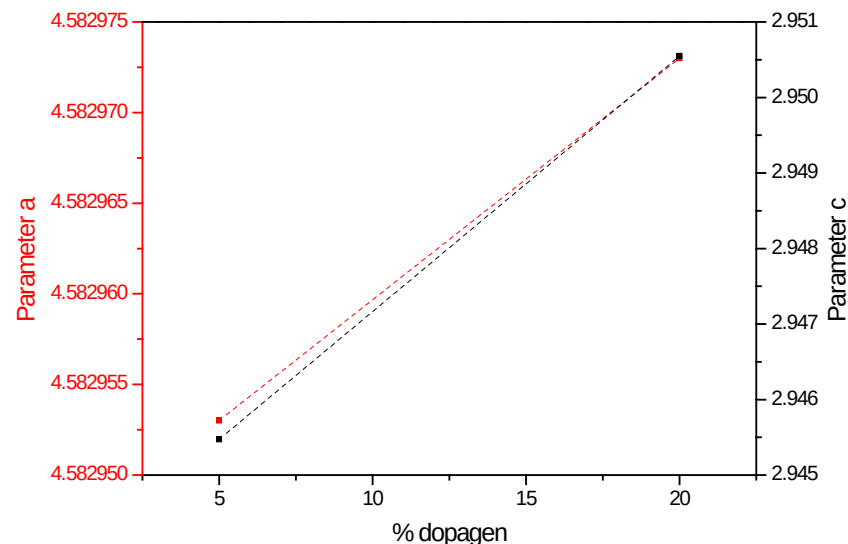
TiO₂ síntesis

El TiO₂ rutilo cristaliza en el grupo espacial tetragonal P4₂/mmm (spg nº136). Cristales prismáticos con terminaciones bipiramidales y su polimorfo anatasa en el grupo tetragonal I4₁/amd (spg nº141).

Anatasa



Rutilo

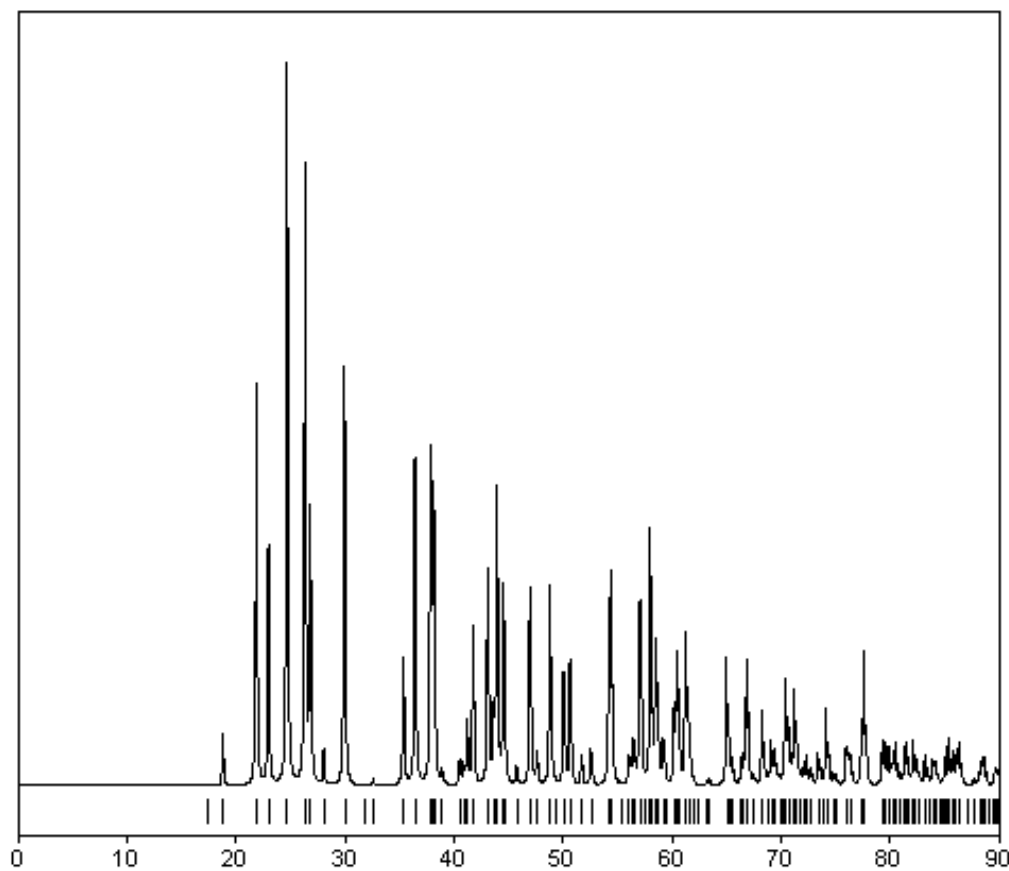


TiO₂ Comparación entre el efecto de la presión «física» y la concentración de dopante (Mn, Co, Fe) (presión «química»)

- Programa CRYSTAL, DFT (Funcionales B3LYP y B3PW)
- Estudios de difracción de rayos X y Raman con celdas MALTA

SbPO₄ síntesis

El ortofosfato de antimonio fue preparado a partir de SbCl₃, (Alfa 99+%) y H₃PO₄ (concentrato, Prolabo). El precipitado se secó y calentó durante 2 y 4 h a 200°C y 400°C, respectivamente, al aire, en un recipiente de platino.



B. Kinberger, *Acta Chem. Scand.* 24 (1970) 320.

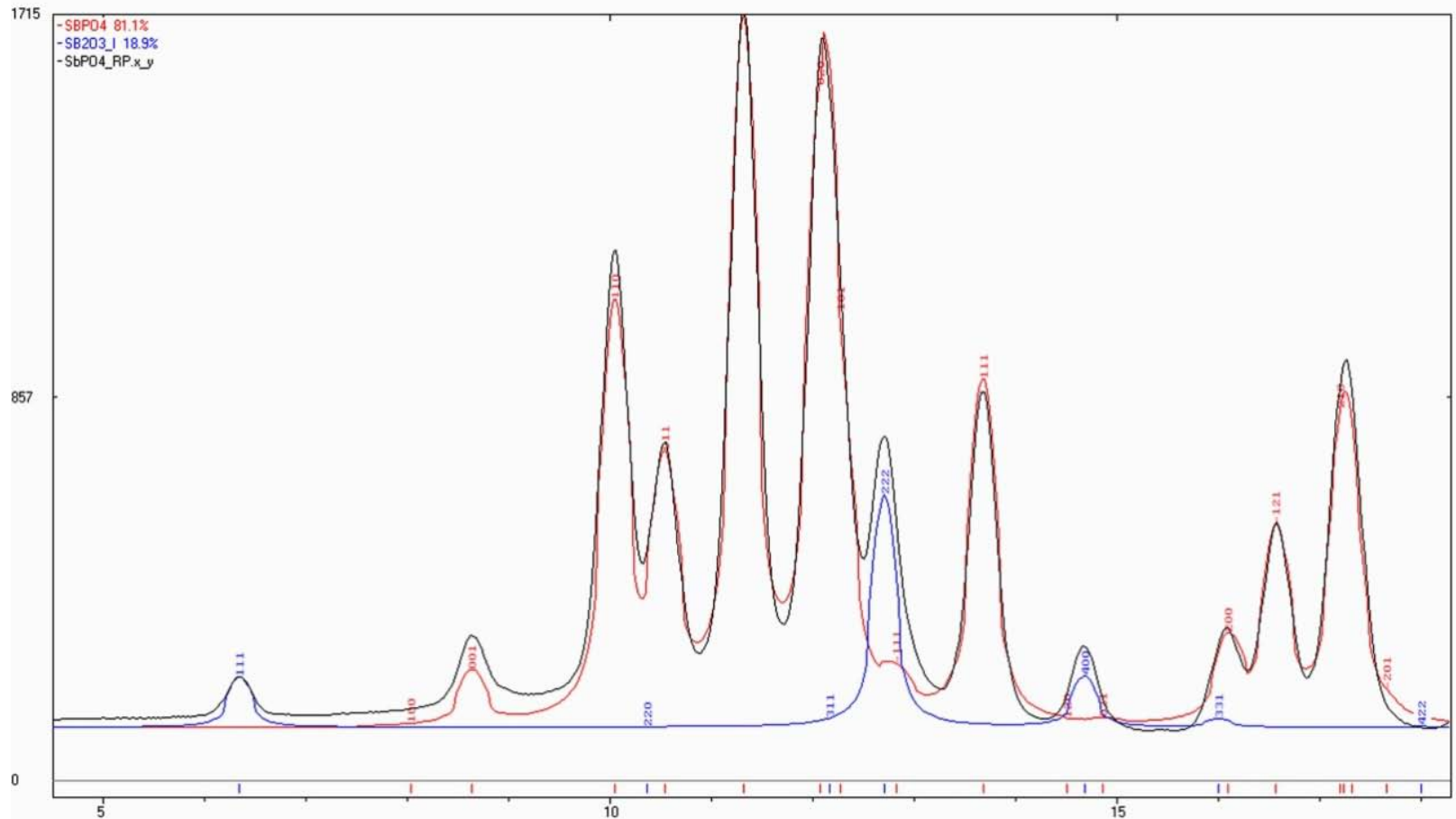
M. Nalin, S.J.L. Ribeiro, M. Poulain, M. Poulain, Y. Messaddeq, *J. Non-Cryst. Sol.* 284 (2001) 110.

W. Brockner, L.P. Hoyer / *Spectrochimica Acta Part A* 58 (2002) 1911–1914

Estudio a alta presión del SbPO_4

Difracción de rayos-X

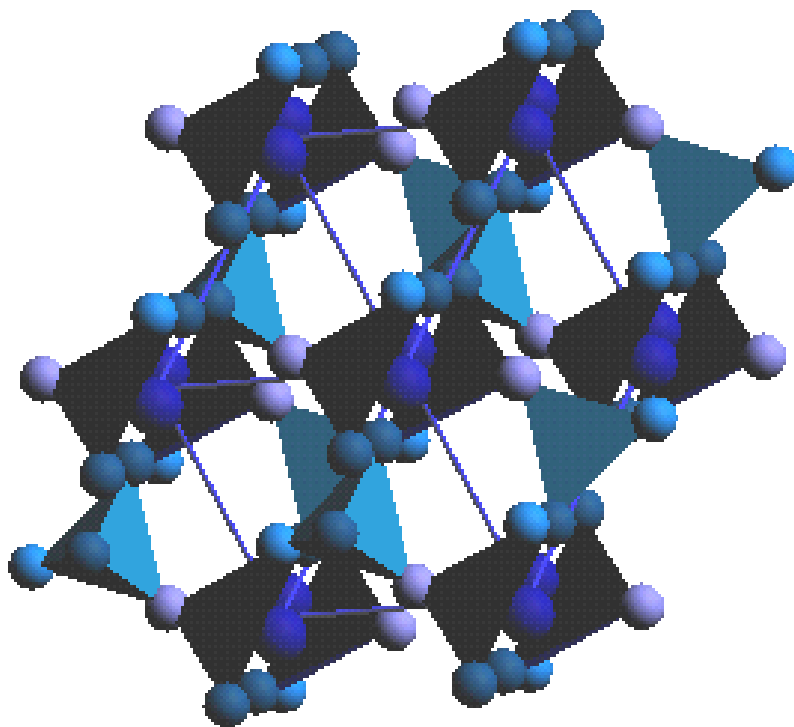
El difractograma a temperatura ambiente ha sido indexado como una mezcla fases: $\text{SbPO}_4 + \text{Sb}_2\text{O}_3$ (~5% en volumen) con parámetros de red ligeramente mayores de los ICSD correspondientes (figura: contribuciones de SbPO_4 y Sb_2O_3 en rojo y azul, respectivamente)



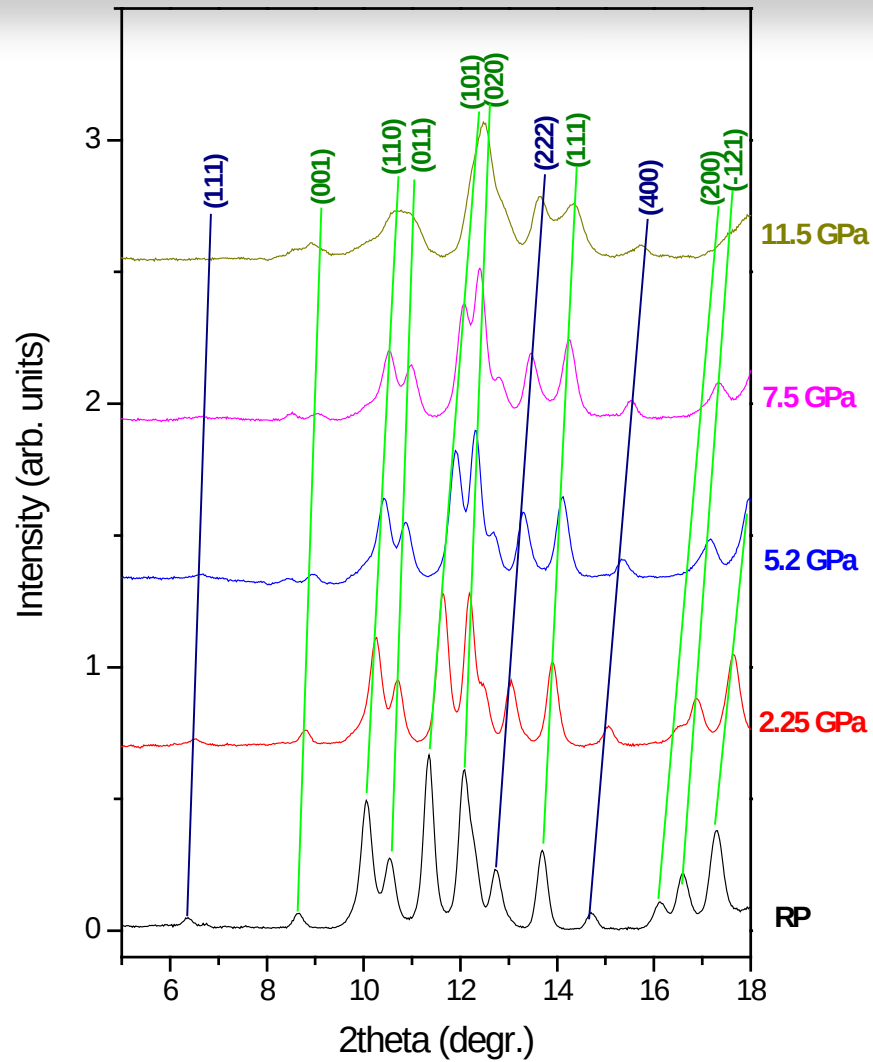
SbPO₄

SbPO₄

- $P2_1/m$ (n° 11), $a = 5.0984 \text{ \AA}$; $b = 6.7598 \text{ \AA}$; $c = 4.7308 \text{ \AA}$; $\beta = 94.6144$; $V = 162.515 \text{ \AA}^3$
- ICSD: $a = 5.0868 \text{ \AA}$; $b = 6.7547 \text{ \AA}$; $c = 4.7247 \text{ \AA}$; $\beta = 94.66$; $V = 161.8 \text{ \AA}^3$ (Kinberger, 1970)



SbPO_4

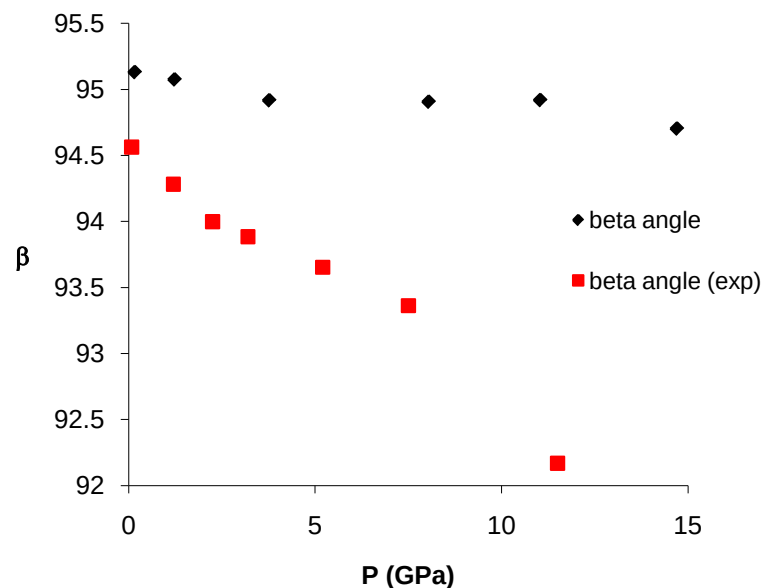
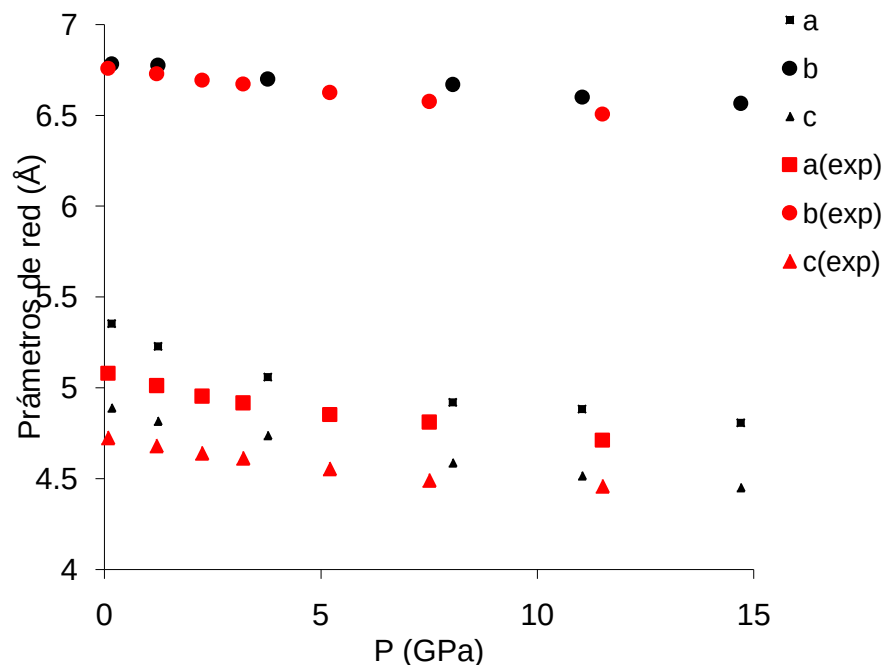


¡No se observan transiciones de fase hasta la presión máxima (12 GPa) alcanzada en estas medidas!

SbPO₄

Evolución de los parámetros de red

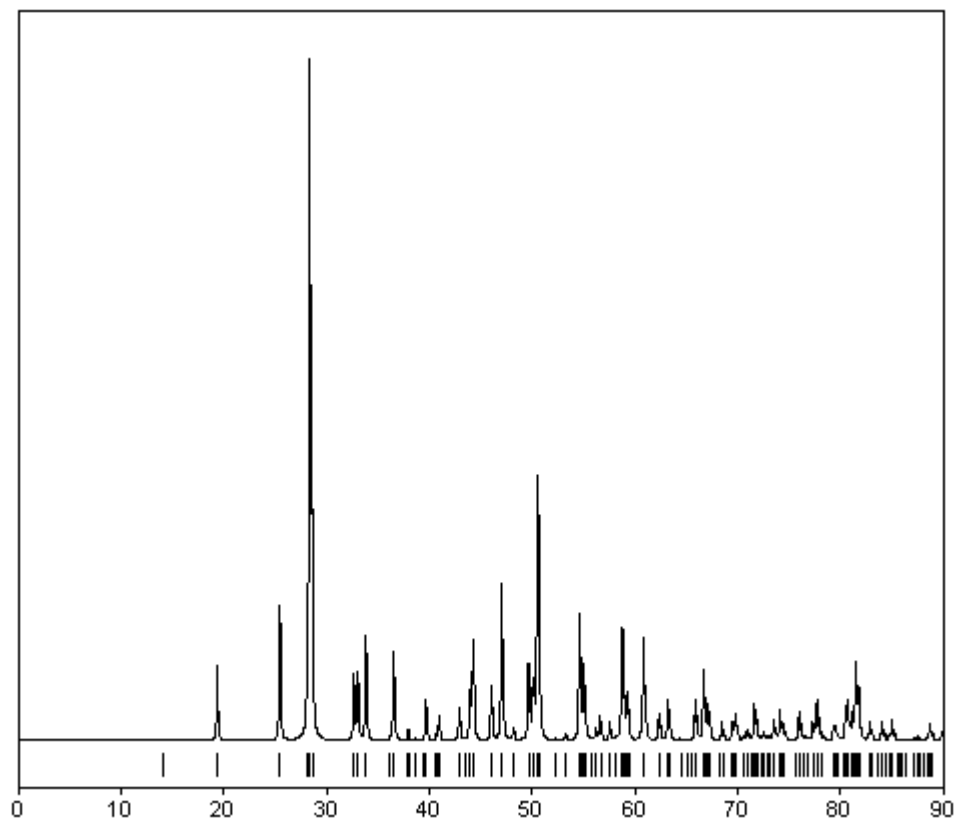
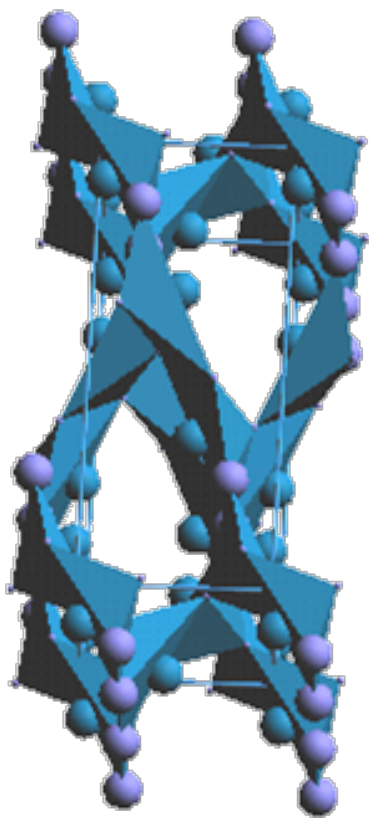
La variación de las constantes de red de la fase inicial con la presión es continua y bastante isotrópica. Los ejes a, b y c decrecen con la presión (véase la figura de la derecha). El ángulo beta de esta estructura monoclinica decrece considerablemente con la presión acercándose gradualmente a 90° aunque mucho menos en los cálculos teóricos que en los datos experimentales (véase figura de la derecha).



Sb_2O_3

Sb_2O_3

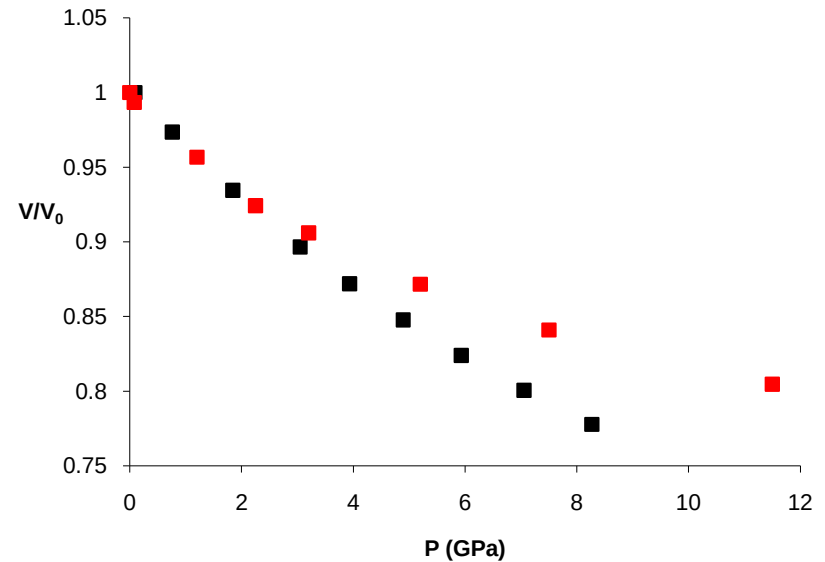
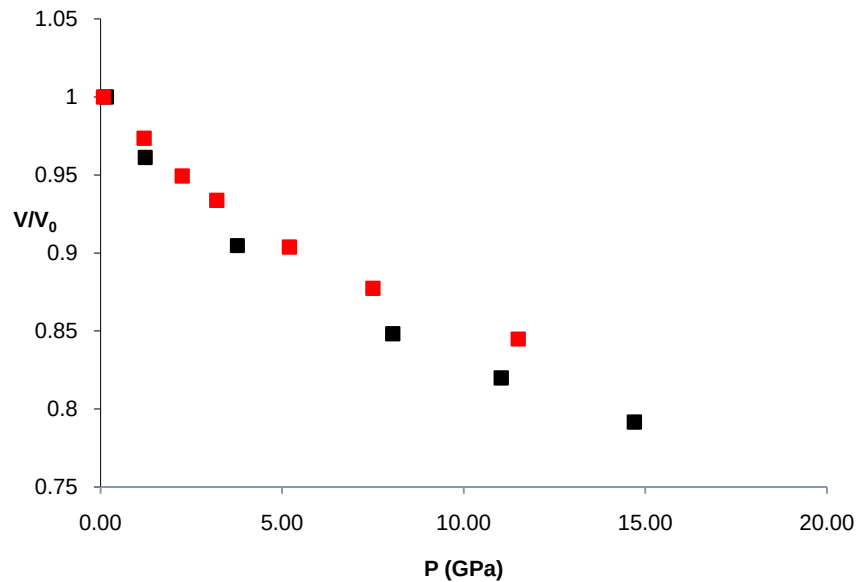
- S.G. $Fd\bar{3}m$ (n° 227) $a = 11.1294 \text{ \AA}$; $V = 1378.527 \text{ \AA}^3$
- ICSD: $a = 11.1519 \text{ \AA}$; $V = 1386.9 \text{ \AA}^3$ (Svensson, 1974)



SbPO₄ – Sb₂O₃

Ecuaciones de estado

Los volúmenes de las celdas unidad de SbPO₄ y Sb₂O₃ decrecen de forma continua con la presión dando los valores de B_0 (GPa) y B'_0 de la tabla (véanse las dos figuras) a partir de un ajuste a la ecuación de Birch-Murnaghan de tercer orden (en rojo valores experimentales y en negro los teóricos).



Estructure	SbPO4	Sb2O3
B_0 (B'_0)	32.41 (6) 41.37 (4)	17.81 (5.9) 20.81 (4.0)
Exp B_0 (B'_0)	34.24 (6.4)	22.35 (7.0)

Perspectivas

Estudio de otras fases y de las posibles transiciones de fase a $P > 12$ GPa

SbPO₄

Ortorrómbicas: *Pnma* (spg nº62) ; *Cmcm* (spg nº 63)

Tetragonal: zircón (*I41/amd*)

Monoclínica: fergusonita (*C2/c*)

A P ambiente el orden de estabilidad encontrado es:

Monoclínica *P21/m* > *Pnma* > *Cmcm* > zircón > fergusonita

Estamos calculando las EOS , los B_0 , P_{trans} (¿?)

Estudio de Propiedades Ópticas No Lineales (NLO) (en unidades atómicas)

$$P = \epsilon_0 E (\chi^{(1)} + \chi^{(2)}E + \chi^{(3)}E^2 + \dots) = \epsilon_0 (E_0 - E)$$

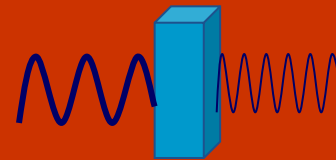
$$E_0 = E (1 + \chi^{(1)} + \chi^{(2)}E + \chi^{(3)}E^2)$$

P_0 : polarización permanente
 $\chi^{(n)}$: susceptibilidad no lineal de orden n
 E : campo eléctrico



Fibra óptica

- generación del segundo armónico



Duplicación de frecuencia

- Efecto Pockels

- Generación del tercer armónico

- Efecto Kerr (índice no lineal de segundo orden n_2)

NLO (a.u.)

$$\varepsilon = E_0/E = (\varepsilon^{(0)} + \varepsilon^{(1)} E + \varepsilon^{(2)} E^2) = n^2$$

$$\varepsilon^{(0)} = 1 + \chi^{(1)} ; \quad \varepsilon^{(1)} = \chi^{(2)} ; \quad \varepsilon^{(2)} = \chi^{(3)}$$

$$n_0 = \sqrt{\varepsilon^{(0)}} ; \quad n_1 = \varepsilon^{(1)} / 2\sqrt{\varepsilon^{(0)}} = \varepsilon^{(1)} / 2n_0 ; \quad n_2 = \varepsilon^{(2)} / 2n_0$$

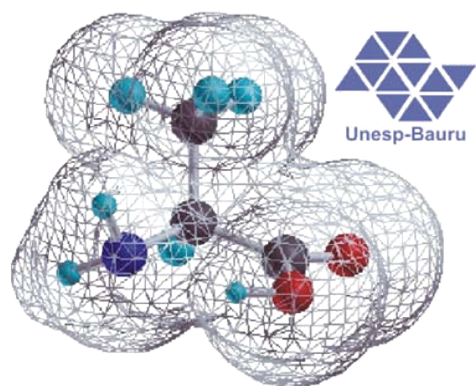
- Estudio teórico con el programa de cálculo CRYSTAL, UJI
- Estudio experimental en colaboración con Philippe Thomas del SPCTS, Université de Limoges (Francia)

$\chi^{(n)}$: susceptibilidad

$\varepsilon^{(n-1)}$: constante dieléctrica

$n^{(n-1)}$: índice de refracción

Agradecimentos



Grupo de Modelagem e
Simulação Molecular





Aguinaldo Robinson de Souza
José Humberto Dias da Silva
Marcelo Nalin
André Luis de Jesus Pereira
Marcilene Cristina Gomes

**Gracias por
su atención**

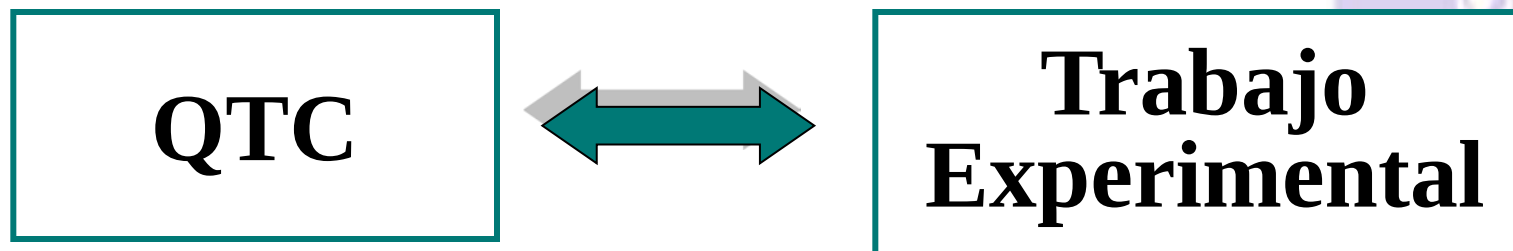
Química Teórica y Computacional (QTC)



Química del Estado Sólido

- *Propiedades estructurales de materiales cerámicos.
Procesos de sustitución y dopaje.
Efecto de la presión, transiciones de fase*
- *Propiedades electrónicas y ópticas de materiales piezoeléctricos y catalíticos.*
- *Procesos de adsorción en superficies de óxidos metálicos.*

Cooperación



- *Predicción*
- *Interpretación*
- *Caracterización de especies químicas de detección experimental difícil*

QTC Aplicada a Medios Condensados

Efecto de la presión

Propiedades ópticas

Superficies y crecimiento

Experimento y Teoría en Armonía

Las dos caras de la química física se han desarrollado juntas, y su sinergia dicta la dirección de la investigación contemporánea.



$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$$

$$\psi \approx e^{i(\vec{k}\vec{x} - \omega t)}$$

$$i\hbar \frac{\partial}{\partial t} \psi = -\frac{\hbar^2}{2m} \nabla^2 \psi$$

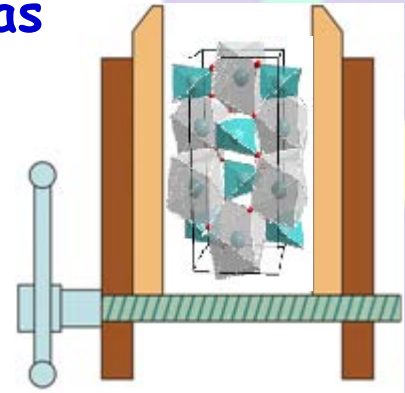
$$\hat{H} \psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t)$$

Mark A. Johnson , *Nature Chemistry*, **1**, 8 (2009)

QTC Aplicada a Medios Condensados

Efecto de la presión

- Propiedades estructurales y electrónicas
(Transformaciones de fase)
- Modelización de mecanismos
de reacción incluyendo la presión



CÁLCULOS MECANOCUÁNTICOS

- Metodología:
 - Teoría del funcional de la densidad (DFT)
 - Modelos periódicos
 - Programas: CRYSTAL, VASP
- Propiedades obtenidas:
 - Geometrías optimizadas, parámetros macroscópicos: EOS, B_0 , ε , n y propiedades ópticas no lineales
 - Propiedades electrónicas: ρ , DOS, estructura de bandas, dE_g/dP
 - Espectros vibracionales teóricos (Raman, IR), asignación de modos de vibración, ω , $d\omega/dP$.
- Caracterización del mecanismo de transiciones de fase

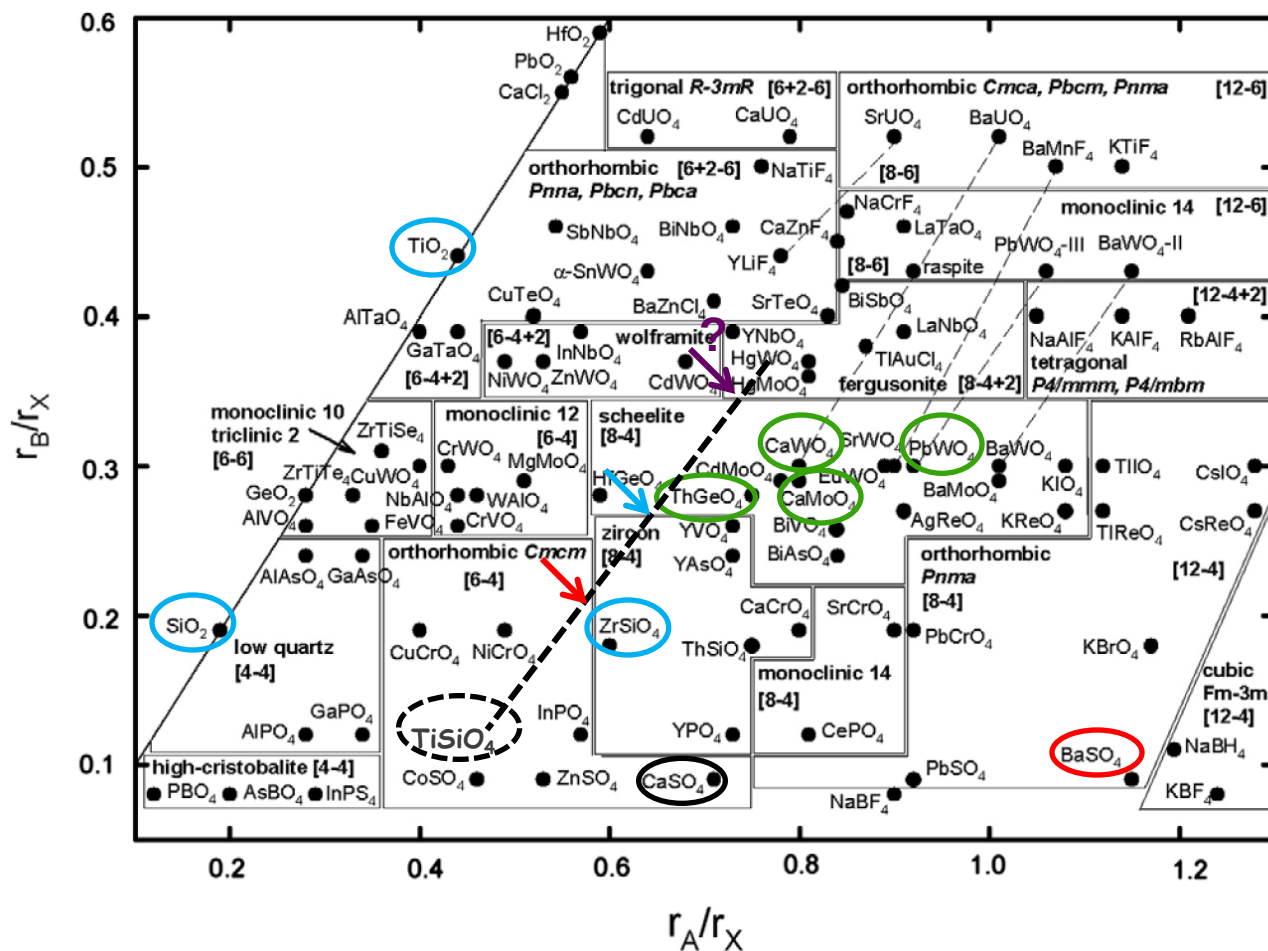


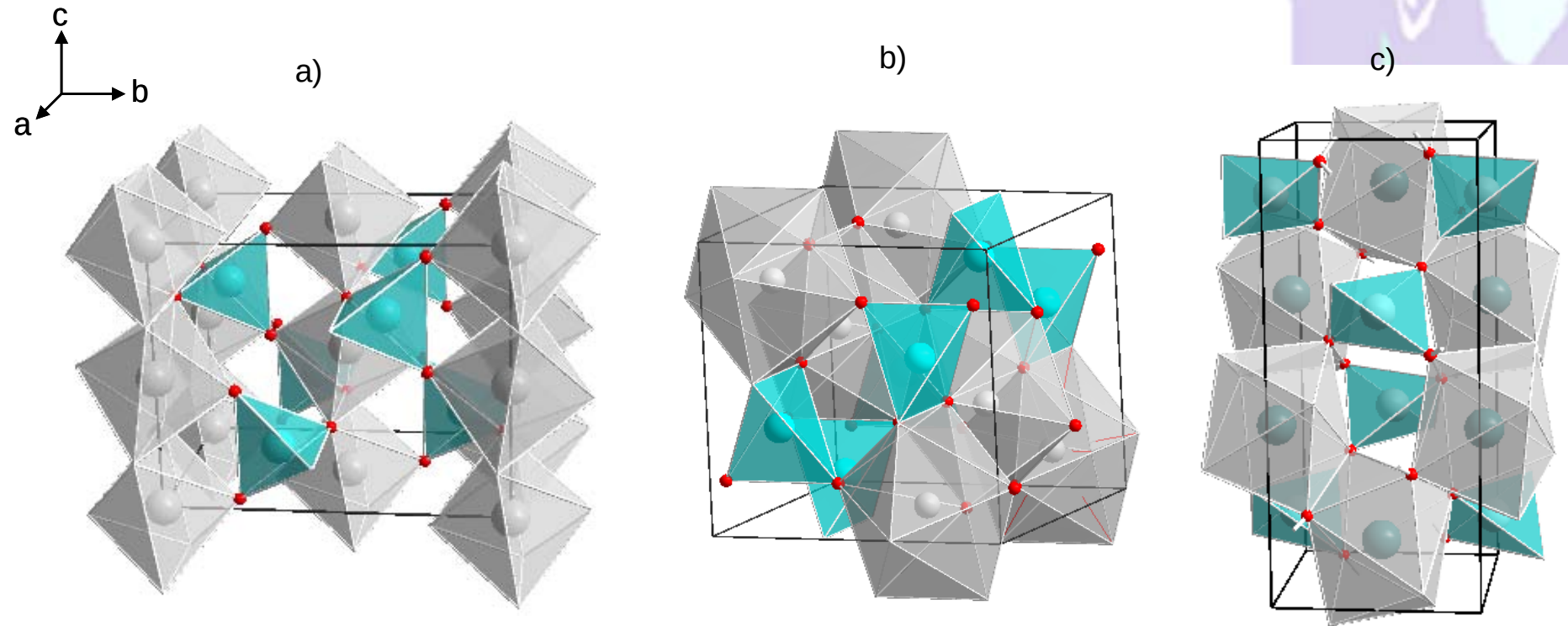
Diagrama de Bastide para compuestos ABX_4

Las líneas a trazos representan la evolución del cociente de radios iónicos con la presión

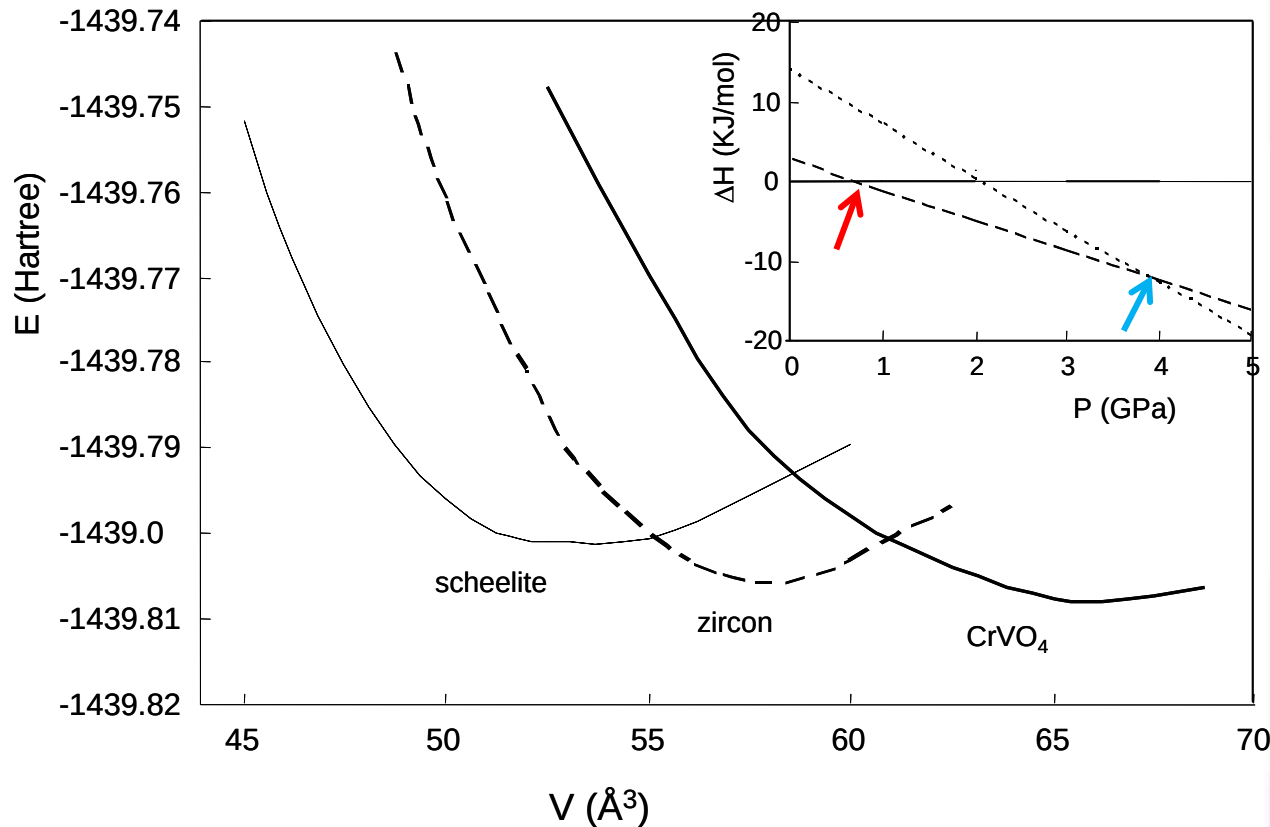
D. Errandonea, F.J. Manjón, *Progress in Materials Science*, **53**, 711 (2008)

Estructuras de TiSiO_4

a) tipo CrVO_4 , (b) zircón y (c) scheelita



Curva E-V



A **0.8 GPa** la transición desde la fase tipo CrVO_4 a la fase zircón muestra un gran cambio de volumen de 11.8%, y a **3.8 GPa** se obtiene la transición zircón-scheelita con una reducción de volumen significativa del 8.5%.

TABLE II. Phonon frequencies and Grüneisen parameters for CrVO_4 -type, zircon and scheelite phases (Raman modes).

CrVO_4			Zircon				Scheelite		
Mode	$\omega(0) \text{ cm}^{-1}$	γ	Mode	$\omega(0) \text{ cm}^{-1}$	$\omega^a \text{ cm}^{-1}$	γ	Mode	$\omega(0) \text{ cm}^{-1}$	γ
$T(A_g)$	215.17	1.45	$T(E_g)$	211.61	194.3	-1.77	$T(B_g)$	235.95	-0.11
$T(B_{1g})$	270.51	0.46	$T(B_{1g})$	248.69	258.9	3.55	$T(E_g)$	256.60	1.36
$R(B_{1g})$	328.34	2.27	$T(E_g)$	254.34	242.4	1.12	$T(B_g)$	292.66	0.35
$R(B_{2g})$	337.99	0.02	$T(B_{1g})$	300.16	262.9	-1.96	$T(E_g)$	375.11	0.59
$T(B_{3g})$	379.86	1.93	$\nu_2(A_{1g})$	416.45	383.2	1.88	$R(A_g)$	400.42	1.68
$R(B_{3g})$	466.62	1.24	$R(E_g)$	428.61	430.1	2.71	$\nu_2(A_g)$	412.71	0.84
$\nu_2(A_g)$	474.80	0.98	$\nu_2(B_{2g})$	433.89	417.6	1.69	$\nu_2(B_g)$	511.83	0.51
$\nu_4(B_{1g})$	538.18	0.50	$\nu_4(E_g)$	592.72	544.3	0.92	$R(E_g)$	531.92	0.70
$\nu_2(B_{2g})$	538.60	1.18	$\nu_4(B_{1g})$	674.85	627.2	1.26	$\nu_4(E_g)$	594.63	0.80
$\nu_4(A_g)$	583.54	0.59	$\nu_1(A_{1g})$	966.07	1011.4	2.01	$\nu_4(B_g)$	698.67	0.58
$\nu_4(B_{3g})$	692.00	0.64	$\nu_3(E_g)$	976.56	945.4	2.01	$\nu_3(B_g)$	889.55	0.81
$\nu_3(B_{1g})$	837.95	0.76	$\nu_3(B_{1g})$	1077.50	1047.2	2.10	$\nu_1(A_g)$	930.96	0.66
$\nu_3(A_g)$	962.28	0.45					$\nu_3(E_g)$	974.19	0.79
$\nu_1(A_g)$	1014.14	0.57							
$\nu_3(B_{3g})$	1070.41	0.51							

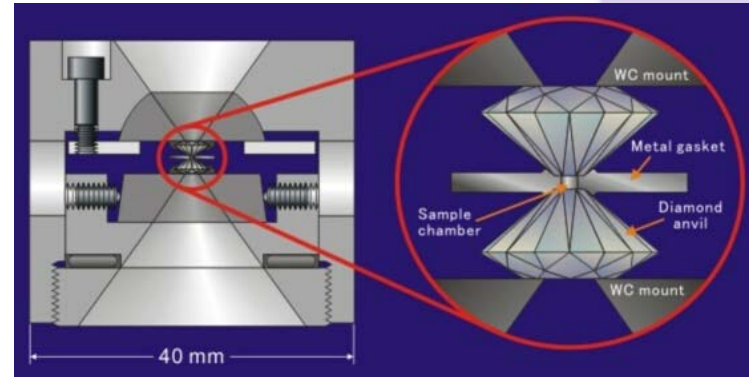
^aRaman modes data from Reference 19.

En la scheelita el modo de baja frecuencia con $\gamma < -0.11 (B_g)$, sugiere la posibilidad de una transición a una estructura post-scheelita: fergusonita o wolframita

Estudio Experimental

DAC →

Múltiples técnicas de caracterización



Necesitamos "super microscopios" (**Sincrotrón**)

Experimentos en colaboración con Daniel Errandonea y David Santamaría

Sincrotrones



Nuevos Beamlines dedicados a altas presiones
(APS/ESRF/SPring8/Diamond/Soleil/ALBA)

Actividades Científicas Concluidas

ABO₄

SiTiO₄: Estudio teórico, cálculos periódicos a nivel B3LYP con el programa CRYSTAL
 EOS, B_0, P_t, ω (Raman, IR), $\gamma, dE_g/dP, \varepsilon, n$

**Characterization of the TiSiO₄ Structure and its Pressure-Induced Phase Transformations:
A Density Functional Theory Study**

L. Gracia, A. Beltrán, and D. Errandonea

Physical Review B **2009**, 80, 094105

ThGeO₄: estudio teórico-experimental (zircón → scheelita → fergusonita)

Experimental and theoretical investigation of ThGeO₄ at high pressure

D. Errandonea, R. S. Kumar, L. Gracia, A. Beltrán, S.N. Achary, A.K. Tyagi,

Physical Review B **2009**, 80, 094101

Actividades Científicas Concluidas

ABO₃

SrTiO₃ estudio teórico-experimental (fotoluminiscencia, estudio de estados excitados)

A Theoretical Study on the Photoluminescence of SrTiO₃

L. Gracia, J. Andrés, V.M. Longo, J. A. Varela and E. Longo

Chem. Phys. Lett. **2010**, 493, 141-146

AO₂

SiO₂ estudio teórico del mecanismo de transición de fase

Bonding changes across the α -cristobalite $\rightarrow$ stishovite transition path in silica

L. Gracia, J. Contreras-García, A. Beltrán and J.M. Recio

High Pressure Research **2009**, 29, 93–96

SnO₂ estudio teórico-experimental del crecimiento de nanoestructuras

Anomalous Oriented Attachment Growth Behavior on SnO₂ Nanocrystals

D. G. Stroppa, L. A. Montoro, A. Beltrán, T. G. Conti, R. O. da Silva, J. Andrés, E. R. Leite, A. J. Ramirez, *Chem Comm* **2011**, accepted

Actividades Científicas Concluidas

Reactividad

Unraveling the mechanisms of the Selective Oxidation of Methanol to Formaldehyde in Vanadia Supported on Titania Catalyst

P. González-Navarrete, L. Gracia, M. Calatayud and J. Andrés
J. Phys. Chem. C **2010**, *114*, 6039-6046

DFT Study of the Oxidation of Methanol to Formaldehyde on a Hydrated Vanadia Cluster

P. González-Navarrete, L. Gracia, M. Calatayud and J. Andrés
J. Comput. Chem. C **2010**, *114*, 2493-2501

Actividades Científicas Iniciadas

ABO₄

estudios teórico-experimentales

En colaboración con UV /UCM

- CaSO_4 anhidrita $\rightarrow$ monacita $\rightarrow$ (scheelita, barita) $\rightarrow$ tipo- AgMnO_4 $\rightarrow$ tipo- RbAlO_4
- BaSO_4 Barita ;(?) Scheelita, AgMnO_4 , $\overline{\text{F}}43\text{m}$
- AgClO_4 $\overline{\text{I}}42\text{m} \rightarrow$ barita $\rightarrow \text{AgMnO}_4$ / scheelita; monacita, anhidrita, cúbica HT
(?) zircón, NaClO_4 (Cmcm)
- SrMoO_4 scheelita $\rightarrow$ fergusonita $\rightarrow \text{P}21/\text{n} \rightarrow \text{Cmca}$; $\text{P}21/\text{c}$

En colaboración con UCM - UFSCar /UNESP (Brasil)

- SbPO_4 $\text{P}21/\text{m} > \text{Pnma} > \text{Cmcm} > \text{zircón} > \text{fergusonita}$
estudio de propiedades ópticas no lineales de la fase $\text{P}21/\text{m}$

En colaboración con UFSCar /UNESP (Brasil)

- CaWO_4 / CaMoO_4 scheelita (fotoluminiscencia, estudio de estados excitados)

Actividades Científicas Iniciadas

 A_2BO_4

estudio teórico

- Zn_2SnO_4 $ZnO + SnO_2 \rightarrow$ espinela inversa $\rightarrow$ (titanita, ferrita)
A Theoretical Study on the Pressure-induced Phase Transitions in Inverse Spinel Structure $Zn_{1-x}Sn_xO_4$
L. Gracia, A. Beltrán and J. Andrés, *J. Phys. Chem. C*, **2011**, enviado

estudio teórico - experimental

En colaboración con UCM - UNESP (Brasil)

 ABO_3

- $Pb(Zr_{0.5}Ti_{0.5})O_3$ monoclinica $\rightarrow$ tetragonal $\rightarrow$ cúbica

AB

- $Ga_{1-x}Mn_xN$ estudio de las superficies $(10\bar{1}0)$ and $(11\bar{2}0)$

CHITEL 2010 (19-24 Septiembre, Anglet, Francia)

Actividades Científicas Iniciadas

ABF₃

estudio teórico-experimental

Estabilidad de las estructuras cúbica ($P\bar{m}3m$), tetragonal ($I4/mcm$ y $P4/mbm$) y ortorrómbica ($Pbcn$) en función de P :

- NaMgF_3 , KMgF_3 , KMnF_3 , KCoF_3 , KNiF_3 , KZnF_3 , KCaF_3 , RbCaF_3

Programa VASP y CRYSTAL, metodología DFT (Funcionales GGA y B3LYP).

L. Gracia, F. Aguado

AO₂

Estudio teórico – experimental de la transición de fase anatasa – rutilo

En colaboración con UNESP (Brasil) - UPV

TiO_2 Comparación entre el efecto de la presión «física» y la concentración de dopante (Mn, Co, Fe) (presión «química»)

- Programa CRYSTAL, DFT (Funcionales B3LYP y B3PW)
- Estudios de difracción de rayos X y Raman con celdas MALTA