



UNIVERSIDAD
DE LA REPÚBLICA
URUGUAY



Facultad
de Química
UDELAR - Uruguay

Introducción a los métodos de modelado
computacional en ciencias de los materiales

Propiedades Vibracionales desde Métodos *ab initio*

Dr. Ricardo Faccio
Facultad de Química
Universidad de la República
rfaccio@fq.edu.uy

Noviembre de 2025

http://cryssmat.fq.edu.uy/ricardo/cursos/prop-vibracionales_RFaccio.pdf

1

1

1. Punteo

1. Introducción
 - Oscilaciones
 - Frecuencias y Autovectores
 - Diagramas de Dispersión y Densidad de Estados Fonónica
2. Fonones en 3D
 - Tensor de constantes de fuerza
 - Matriz dinámica
3. Propiedades Vibracionales y Térmicas
 - Ejemplo: Rutilo
4. Phonopy
5. Ejemplos
6. Nuevas herramientas
7. Sistemas discretos

Noviembre de 2025

http://cryssmat.fq.edu.uy/ricardo/cursos/prop-vibracionales_RFaccio.pdf

2

2

1. Punteo

- Introducción:
 - Oscilaciones de 1 y N grados de libertad
- Frecuencias y Autovectores
- Diagramas de Dispersión y Densidad de Estados Fonónica
- Propiedades Eléctricas
 - Matriz dieléctrica
 - Cargas de Born
- Propiedades Térmicas
 - Entropía Configuracional
 - Energía Libre de Helmholtz
 - Capacidad Calorífica
 - Transporte térmico

Noviembre de 2025

3

3

1. Introducción: Espectro Fonónico

- Estudiar estabilidad de fases:
 - Presencia de modos de frecuencia imaginaria
- Determinar propiedades térmicas:
 - Entropía, Energía Libre de Helmholtz y Gibbs, Entropía y Capacidad calorífica (C_v y C_p)
- Determinar propiedades vibracionales:
 - espectros IR y Raman
 - Dispersión de Neutrones
- Propiedades estructurales dinámicas:
 - Tensor de agitación térmica (XRD y ND)
 - Coeficiente de dilatación térmica
 - Propiedades estructurales dependientes de Temperatura
- Determinar propiedades de Transporte:
 - Conductividad térmica
 - Aplicaciones en materiales termoelectrónicos

Noviembre de 2025

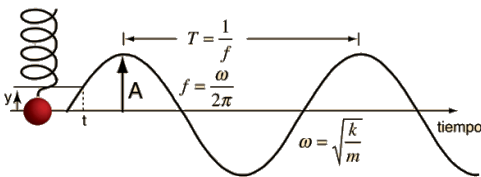
4

4

1. Oscilaciones

▣ Sistema masa resorte Simple

$$-kx = m\ddot{x}$$

$$\omega = \sqrt{\frac{k}{m}}$$


Noviembre de 2025

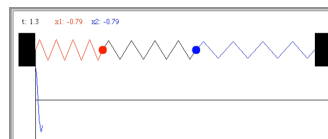
5

1. Osciladores con dos grados

▣ Dos grados de libertad

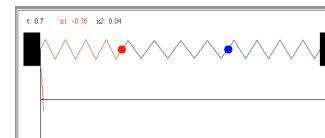
$$-kx_1 - k(x_1 - x_2) = m\ddot{x}_1$$

$$-kx_2 - k(x_2 - x_1) = m\ddot{x}_2$$



$$x_1 = x_2$$

$$\omega_a = \sqrt{\frac{k}{m}}$$



$$x_1 = -x_2$$

$$\omega_b = \sqrt{\frac{3k}{m}}$$

6

6

1. Osciladores con dos grados

□ Dos grados de libertad

$$\begin{aligned} -kx_1 - k(x_1 - x_2) &= m\ddot{x}_1 & \frac{-2k}{m}x_1 + \frac{k}{m}x_2 &= -\omega^2 mx_1 \\ -kx_2 - k(x_2 - x_1) &= m\ddot{x}_2 & \frac{k}{m}x_1 - \frac{2k}{m}x_2 &= -\omega^2 mx_2 \end{aligned}$$

$$\begin{aligned} \left(\omega^2 - \frac{2k}{m}\right)x_1 + \left(\frac{k}{m}\right)x_2 &= 0 \\ \left(\frac{k}{m}\right)x_1 + \left(\omega^2 - \frac{2k}{m}\right)x_2 &= 0 \end{aligned} \quad \begin{bmatrix} \left(\omega^2 - \frac{2k}{m}\right) & \left(\frac{k}{m}\right) \\ \left(\frac{k}{m}\right) & \left(\omega^2 - \frac{2k}{m}\right) \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

Noviembre de 2025

7

7

1. Oscilaciones con dos Grados

□ Determinamos frecuencias

$$\det \begin{bmatrix} \left(\omega^2 - \frac{2k}{m}\right) & \left(\frac{k}{m}\right) \\ \left(\frac{k}{m}\right) & \left(\omega^2 - \frac{2k}{m}\right) \end{bmatrix} = 0$$

$$\omega_A = \sqrt{\frac{k}{m}}$$

$$\omega_B = \sqrt{\frac{3k}{m}}$$

□ Determinamos Configuraciones

$$\begin{bmatrix} \left(\omega^2 - \frac{2k}{m}\right) & \left(\frac{k}{m}\right) \\ \left(\frac{k}{m}\right) & \left(\omega^2 - \frac{2k}{m}\right) \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = 0$$

$$\left(\frac{x_2}{x_1}\right)_A = +1$$

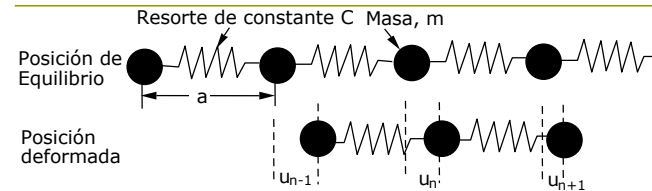
$$\left(\frac{x_2}{x_1}\right)_B = -1$$

Noviembre de 2025

8

8

1. Osciladores acoplados



u_n : Es el desplazamiento del átomo n respecto de su posición de equilibrio

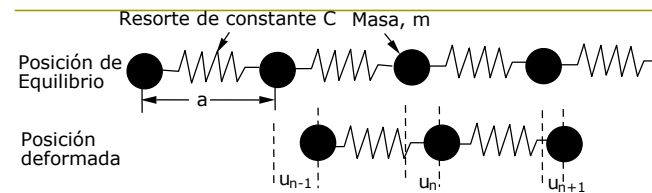
□ 2ª Ley de Newton:
$$M \frac{d^2 u_n}{dt^2} = F_n = c [u_{n+1} + u_{n-1} - 2u_n]$$

□ u_n : tiene que tener forma de onda:

$$u_n = u \exp \left(-i \vec{k} \cdot \vec{r}_{na} - \omega t \right) = u \exp \left(-ik(na) - \omega t \right)$$

9

1. Cadena lineal de osciladores



□ Dependencia temporal:
$$u_n(t) = u_n \exp(-i\omega t)$$

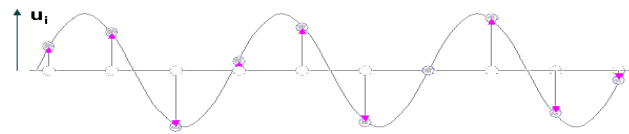
□ Luego aparece una ecuación de diferencias en los desplazamientos:

$$M \omega^2 u_n = c [u_{n+1} + u_{n-1} - 2u_n] \quad \Rightarrow \quad -M \omega^2 u_n = c [u_{n+1} + u_{n-1} - 2u_n]$$

$$\Rightarrow M \omega^2 = c [\exp(ika) + \exp(-ika) - 2] \quad \Rightarrow \quad \omega^2 = \frac{2c}{M} [1 - \cos(ka)]$$

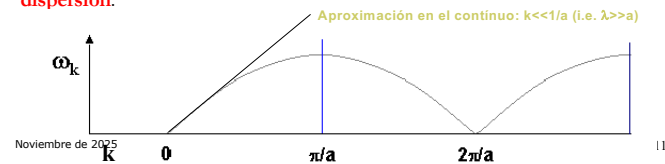
10

1. Relación de dispersión



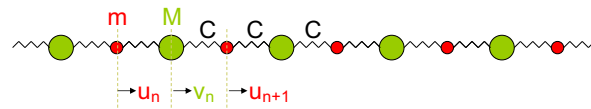
- La solución para cada oscilador con vector de onda $\mathbf{k}$ y frecuencia
- Relación de ω_k en función de k se llama **relación de dispersión**.

$$\omega_k = 2\sqrt{\frac{c}{M}} \left| \sin\left(\frac{1}{2}ka\right) \right|$$



11

1. Red diatómica



$$m\ddot{u}_n = C(v_n - u_n) - C(u_n - v_{n-1})$$

$$M\ddot{v}_n = C(u_{n+1} - v_n) - C(v_n - u_n)$$

$$\text{Modo normal: } u_n(t) = u_n e^{-i\omega t}; v_n(t) = v_n e^{-i\omega t}$$

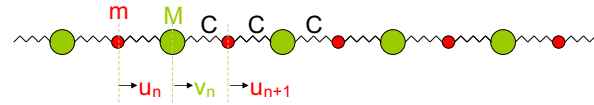
$$\Rightarrow \begin{cases} (m\omega^2 - 2C)u_n + C(v_n + v_{n-1}) = 0 \\ (M\omega^2 - 2C)v_n + C(u_n + u_{n+1}) = 0 \end{cases} \Rightarrow \det \begin{bmatrix} \end{bmatrix} = 0$$

Noviembre de 2025

12

12

1. Red diatómica



- Resultado:
$$\omega^4 - 2C \left(\frac{m+M}{mM} \right) \omega^2 + 2 \frac{C^2}{mM} (1 - \cos ka) = 0$$
- Ecuación se puede resolver para ω^2 , pero es más simple examinar casos límite:
 - $ka \ll 1$: $\cos(ka) = 1 - \frac{1}{2}(ka)^2 + \dots$
 - $ka = \pi$ (borde 1ZB)
- Para $ka \ll 1$:
$$\omega^2 \cong 2C \left(\frac{1}{m} + \frac{1}{M} \right) \quad (\text{rama óptica})$$

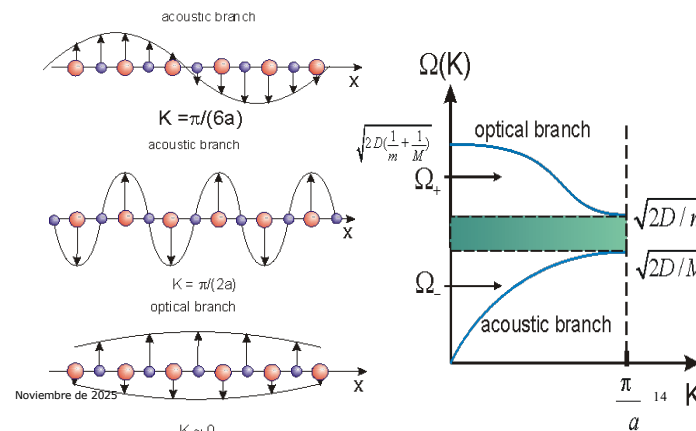
$$\omega^2 \cong \frac{C}{m+M} \frac{k^2 a^2}{2} \quad (\text{rama acústica})$$

Noviembre de 2025

13

13

1. Relación de Dispersión

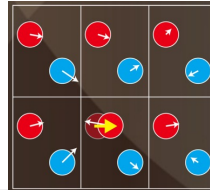


Noviembre de 2025

14

2. Fonones a partir de Constantes de Fuerza:

- El desplazamiento de átomos respecto de su posición de equilibrio aumenta las fuerzas.
- Los métodos de ab-initio nos permiten calcular las fuerzas con buena precisión.
- El análisis sistemático del conjunto de fuerzas asociado a desplazamientos simétricos nos provee las frecuencias de los fonones.
- Es posible trabajar con Density Functional Perturbation Theory (DFPT)



Noviembre de 2025

15

15

2. Fonones

- Energía Potencial: Expansión

$$H = T + V$$

$$V = \Phi_0 + \sum_M \sum_i \Phi_i(M) \Phi_i(M) + \frac{1}{2} \sum_{MN} \sum_{ij} \Phi_{ij}(M, N) U_i(M) U_j(N) + \dots$$

Φ = constantes de Fuerza (FCs)

i, j, k = componentes cartesianas

M, N, P = puntos de red

$$\Phi_{ij}(M, N) \approx - \frac{F_i(M; \Delta r_j(N))}{\Delta r_j(N)}$$

Noviembre de 2025

16

16

2. Fonones

- Aproximación armónica: $H = T + V$

$$H = T + \frac{1}{2} \sum_{MN} \sum_{ij} \Phi_{ij}(M_\mu, N_\nu) U_i(M_\mu) U_j(N_\nu)$$

$\mu, \nu = \text{coordenadas internas}$

- Ecuación de valores propios y matriz dinámica:

$$D_{ij}(\mu\nu, \vec{q}) = \frac{N_0^{-1}}{\sqrt{M_\mu M_\nu}} \sum_{MN} \sum_{ij} \Phi_{ij}(M_\mu, N_\nu) e^{i\vec{q}(\vec{R}(M_\mu) - \vec{R}(N_\nu))}$$

Noviembre de 2025 $M = \text{masa}, N_0 = \text{número de átomos}, R = \text{posición}$

17

17

2. Fonones

- Problemas de autovalores, diagonalización:

$$D(\vec{q}) w(\vec{q}s) = [\omega(\vec{q}s)]^2 w(\vec{q}s)$$

$D_{ij}(\mu\nu, \vec{q})$ para dos átomos por red

- D: matriz dinámica, w: autovector, s: índice de banda

$$D(\vec{q}) = \begin{pmatrix} D_{xx}(11) & D_{xy}(11) & D_{xz}(11) & D_{xx}(12) & D_{xy}(12) & D_{xz}(12) \\ D_{yx}(11) & D_{yy}(11) & D_{yz}(11) & D_{yx}(12) & D_{yy}(12) & D_{yz}(12) \\ D_{zx}(11) & D_{zy}(11) & D_{zz}(11) & D_{zx}(12) & D_{zy}(12) & D_{zz}(12) \\ D_{xx}(21) & D_{xy}(21) & D_{xz}(21) & D_{xx}(22) & D_{xy}(22) & D_{xz}(22) \\ D_{yx}(21) & D_{yy}(21) & D_{yz}(21) & D_{yx}(22) & D_{yy}(22) & D_{yz}(22) \\ D_{zx}(21) & D_{zy}(21) & D_{zz}(21) & D_{zx}(22) & D_{zy}(22) & D_{zz}(22) \end{pmatrix} w(\vec{q}, s) = \begin{pmatrix} \sqrt{M_1} U_x(1, \vec{q}, s) \\ \sqrt{M_1} U_y(1, \vec{q}, s) \\ \sqrt{M_1} U_z(1, \vec{q}, s) \\ \sqrt{M_2} U_x(2, \vec{q}, s) \\ \sqrt{M_2} U_y(2, \vec{q}, s) \\ \sqrt{M_2} U_z(2, \vec{q}, s) \end{pmatrix}$$

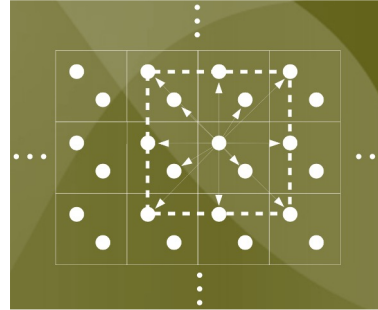
Noviembre de 2025

18

2. Fonones:

□ Método en práctica

- Uso de Superceldas para determinar los Potenciales:



Noviembre de 2025

19

19

2. Fonones: Constantes de Fuerza

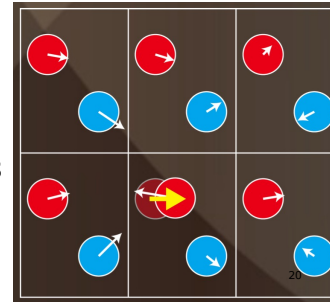
□ Método de diferencias finitas

- Movemos un átomo
- Medimos la fuerza en los otros átomos

$$\Phi_{ij}(M\mu, N\nu) \approx -\frac{F_i(M\mu; \Delta r_j(N\nu))}{\Delta r_j(N\nu)}$$

□ Métodos perturbativos

- DFPT
- QE, VASP, etc.



Noviembre de 2025

20

20

2. Fonones: DFPT

- Permite cálculos precisos y eficientes de las energías totales y sus subsecuentes derivadas utilizando diferentes perturbaciones.
- Las constantes de fuerza se obtienen como derivadas segundas.
- En el caso de polarizabilidades (Raman) y propiedades de transporte, es necesario derivadas terceras.

Noviembre de 2025

21

21

2. Fonones: Matriz Dinámica

- Problemas de autovalores, diagonalización:

$$D(\vec{q})w(\vec{q}s) = [\omega(\vec{q}s)]^2 w(\vec{q}s)$$

$D_{ij}(\mu\nu, \vec{q})$ para dos átomos por red

- D: matriz dinámica, w: autovector, s: índice de banda

$$D(\vec{q}) = \begin{pmatrix} D_{xx}(11) & D_{xy}(11) & D_{xz}(11) & D_{xx}(12) & D_{xy}(12) & D_{xz}(12) \\ D_{yx}(11) & D_{yy}(11) & D_{yz}(11) & D_{yx}(12) & D_{yy}(12) & D_{yz}(12) \\ D_{zx}(11) & D_{zy}(11) & D_{zz}(11) & D_{zx}(12) & D_{zy}(12) & D_{zz}(12) \\ D_{xx}(21) & D_{xy}(21) & D_{xz}(21) & D_{xx}(22) & D_{xy}(22) & D_{xz}(22) \\ D_{yx}(21) & D_{yy}(21) & D_{yz}(21) & D_{yx}(22) & D_{yy}(22) & D_{yz}(22) \\ D_{zx}(21) & D_{zy}(21) & D_{zz}(21) & D_{zx}(22) & D_{zy}(22) & D_{zz}(22) \end{pmatrix} w(\vec{q}, s) = \begin{pmatrix} \sqrt{M_1} U_x(1, \vec{q}, s) \\ \sqrt{M_1} U_y(1, \vec{q}, s) \\ \sqrt{M_1} U_z(1, \vec{q}, s) \\ \sqrt{M_2} U_x(2, \vec{q}, s) \\ \sqrt{M_2} U_y(2, \vec{q}, s) \\ \sqrt{M_2} U_z(2, \vec{q}, s) \end{pmatrix}$$

Noviembre de 2025

22

3. Ejemplo:

□ Rutilo:

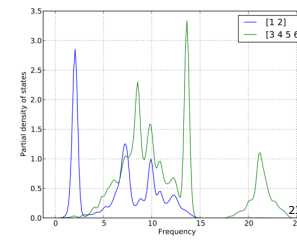
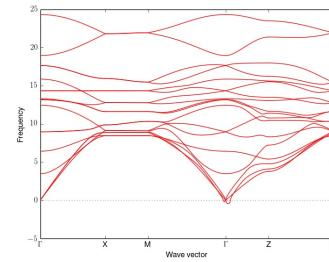
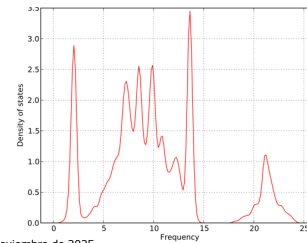
Grupo Espacial $P 4_2/m n m$

$a=b= 4.5977(4) \text{ \AA}$ y $c=2.9564(2) \text{ \AA}$

Átomo Wyckoff $x \ y \ z$

$Ti^{4+} \ 2a \ 0.0 \ 0.0 \ 0.0$

$O^{2-} \ 4f \ 0.3023(3) \ 0.3023(3)$



23

3. Fonones: LO-TO splitting

□ Los cálculos estáticos no dan cuenta de interacciones dipolo-dipolo a longitud de onda larga ($q \rightarrow 0$).

□ Necesario incluir aspectos dinámicos:

■ Desplazamiento atómico induce cargas atómicas

■ Estas cargas interaccionan entre si

■ Deben ser incorporadas:

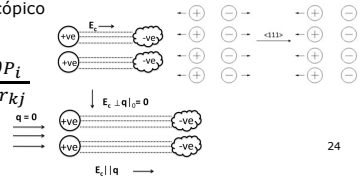
□ Cargas de Born

□ Tensor Dieléctrico Macroscópico

→ Incorporación de Términos No-Analíticos (NAC)

□ Cargas de Born: $Z_{k,ij}^* = \frac{\Omega}{|e|} \frac{\partial P_i}{\partial r_{kj}}$

□ Tensor dieléctrico: ϵ_{ij}



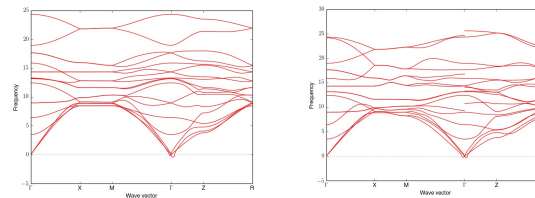
24

24

3. Fonones: NAC

- Los cálculos estáticos no dan cuenta de interacciones dipolo-dipolo a longitud de onda larga ($q \rightarrow 0$).

$$D_{\alpha\beta}(jj', \vec{q} \rightarrow 0) = D_{\alpha\beta}(jj', \vec{q} = 0) + \frac{1}{\sqrt{m_j m_{j'}}} \frac{4\pi (\sum_{\gamma} q_{\gamma} Z_{j,\gamma\alpha}^*) (\sum_{\gamma'} q_{\gamma'} Z_{j',\gamma'\beta})}{\sum_{\alpha\beta} q_{\alpha} \epsilon_{\alpha\beta}^{\infty} q_{\beta}}$$



Noviembre de 2025

25

25

3. Cargas de Born: Rutilo

- Cargas de Born

$$Z_{k,ij}^* = \frac{\Omega}{|e|} \frac{\partial P_{k,i}}{\partial r_{k,j}}$$

MACROSCOPIC STATIC DIELECTRIC TENSOR
(including local field effects in DFT)

7.423904	0.000000	0.000000
0.000000	7.423904	0.000000
0.000000	0.000000	8.849335

BORN EFFECTIVE CHARGES (e)

ion 1 (Ti)			
1	6.35763	1.04091	0.00000
2	1.04090	6.35765	0.00000
3	0.00000	0.00000	7.68997
ion 2 (Ti)			
1	6.35763	-1.04091	0.00000
2	-1.04090	6.35765	0.00000
3	0.00000	0.00000	7.68997
ion 3 (O)			
1	-3.16931	-1.82350	0.00000
2	-1.82348	-3.16930	0.00000
3	-0.00077	-0.00077	-3.84183
ion 4 (O)			
1	-3.16968	-1.82377	0.00000
2	-1.82381	-3.16974	0.00000
3	0.00077	0.00077	-3.84183
ion 5 (O)			
1	-3.16968	1.82377	0.00000
2	1.82348	-3.16930	0.00000
3	0.00077	-0.00077	-3.84183
ion 6 (O)			
1	-3.16931	1.82350	0.00000
2	1.82381	-3.16974	0.00000
3	-0.00077	0.00077	-3.84183

Noviembre de 2025

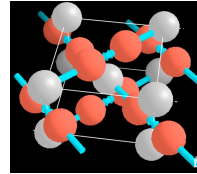
26

26

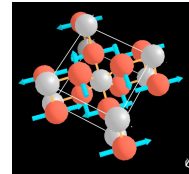
3. Representación Irreducible

Character table:

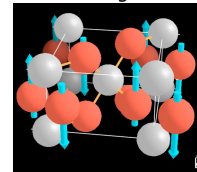
- 1 (0.000): A2u
- 2 (0.000): Eu
- 4 (0.847): A2u
- 5 (2.264): B1u
- 6 (3.181): Eu
- 8 (4.161): B1g
- 9 (11.160): Eu
- 11 (11.205): B1u
- 12 (12.674): A2g
- 13 (13.163): Eg
- 15 (14.261): Eu
- 17 (17.497): A1g
- 18 (23.857): B2g



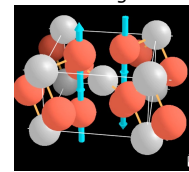
A1g



B1g



Eg



Eg

Noviembre de 2025

27

27

Propiedades Térmicas

Helmholtz free energy: $F_{vib} = E_{vib} - TS_{vib}$

Vibrational internal energy: $E_{vib} = \sum_{qv} \hbar \omega(qv) \left[\frac{1}{2} + \frac{1}{e^{\frac{\hbar \omega(qv)}{k_B T}} - 1} \right]$

Vibrational Entropy:

$$S_{vib} = -\frac{\partial F_{vib}}{\partial T} = \frac{1}{2T} \sum_{qv} \hbar \omega(qv) \coth \left(\frac{\hbar \omega(qv)}{2k_B T} \right) - k_B \sum_{qv} \ln \left[2 \sinh \left(\frac{\hbar \omega(qv)}{2k_B T} \right) \right]$$

Heat capacity:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \sum_{qv} k_B \left(\frac{\hbar \omega(qv)}{k_B T} \right)^2 \left\{ \frac{e^{\frac{\hbar \omega(qv)}{k_B T}}}{\left(e^{\frac{\hbar \omega(qv)}{k_B T}} - 1 \right)^2} \right\}$$

Noviembre de 2025

28

28

Phonopy

Introducción

Noviembre de 2025

29

29

4. Phonopy

- ❑ Es un paquete de cálculo de fonones
- ❑ Escrito en Python
- ❑ Utiliza resultados de cálculos de primero principios: VASP, WIEN2k, QE, SIESTA, DFTB+ etc.
- ❑ Requiere como input cálculos de fuerzas.
- ❑ Permite realizar un postprocesamiento completo: fonones y propiedades térmicas

Noviembre de 2025

30

30

4. Phonopy: Esquema

- Estructura de equilibrio.
- Se generan superceldas con desplazamientos
- Se realiza el cálculo de Fuerzas y se colectan:
 - Set of Forces
 - Force Constants
- Análisis de fonones:
 - DOS, bandas, propiedades térmicas, etc.
- Más allá de la aproximación armónica:
 - Dilatación térmica y propiedades en función de T.

Noviembre de 2025

31

31

4. Phonopy: Estructura de Equilibrio

- | | |
|--|--|
| <ul style="list-style-type: none"> □ VASP: <ul style="list-style-type: none"> ■ POSCAR □ QE <ul style="list-style-type: none"> ■ Archivo.in □ WIEN2k <ul style="list-style-type: none"> ■ Archivo.struct □ SIESTA <ul style="list-style-type: none"> ■ Archivo.fdf | <ul style="list-style-type: none"> □ En todos los casos se debe partir de una estructura adecuadamente convergida en Energía y Fuerzas. |
|--|--|

Noviembre de 2025

32

32

4. Phonopy: Creación de Desplazamientos

- ❑ Se deben crear los desplazamientos para la celda pristina o para la supercelda:
 - Phonopy -d -dim="X Y Z"
 - X,Y y Z corresponden a las dimensiones de la supercelda seleccionada
- ❑ Si se utiliza otro código que no se VASP se debe indicar el código e input:
 - Phonopy --qe -c archivo.in -d -dim="X Y Z"

Noviembre de 2025

33

33

4. Phonopy: Cálculo de Fuerzas

- ❑ Una vez generados los inputs se deben calcular las fuerzas
- ❑ Esto implica la utilización del código ab-initio:

QE:

```
&control
  calculation = 'scf'
  pseudo_dir = './'
  tstress = .true.
  tprnfor = .true.
  verbosity = 'high',
```

VASP:

```
PREC = Accurate
ENCUT = 500
IBRION = -1
NELMIN = 5
EDIFF = 1.0e-08
IALGO = 38
ISMear = 0;
SIGMA = 0.1
LREAL = .FALSE.
ADDGRID = .TRUE.
LWAVE = .FALSE.
LCHARG = .FALSE.
```

Noviembre de 2025

34

34

4. Phonopy: Colección de Fuerzas

- Colectar las Fuerzas de los cálculos realizados:

- VASP

- % phonopy --dim="X Y Z" -f 001/vapsrun.xml 002/vapsrun.xml 003/vapsrun.xml

- QE

- % phonopy --qe -c tio2.in --dim="X Y Z" -f 001/tio2-001.out 002/tio2-002.out 003/tio2-003.out

Noviembre de 2025

35

35

4. Phonopy: DFPT (VASP)

- Por el momento sólo con VASP es posible procesar los datos de fonones con phonopy:

- INCAR:

```
SYSTEM = TiO2
ISTART = 1
ICHARG = 1
NWRITE = 3
PREC = Medium
ISMear = -5
LREAL=.FALSE.
IBRION= 8
#ISIF= 3
NSW= 1
EDIFF= 1.0e-08
EDIFFG = -1.0e-08
IALGO = 38
LREAL = .FALSE.
ADDGRID = .TRUE.
LWAVE = .FALSE.
LCHARG = .FALSE.
```

→ DFPT

Con esto se obtiene directamente las constantes de Fuerza

Noviembre de 2025

36

36

4. Phonopy: Archivos de Fuerzas y Constantes de Fuerza

Sample FORCE_SETS file:

```
128
2

1
d1x d1y d1z
F1x F1y F1z
F2x F2y F2z
...
2
d2x d2y d2z
F1x F1y F1z
F2x F2y F2z
...
```

Sample FORCE_CONSTANTS file:

```
128
1 1
Φxx Φxy Φxz
Φyx Φyy Φyz
Φzx Φzy Φzz
1 2
Φxx Φxy Φxz
Φyx Φyy Φyz
Φzx Φzy Φzz
...
```

$$\Phi_{ij}(M\mu, N\nu) \approx -\frac{F_i(M\mu; \Delta r_j(N\nu))}{\Delta r_j(N\nu)}$$

Noviembre de 2025

37

37

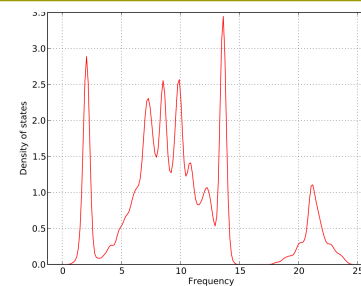
4. Phonopy: DOS

■ Mesh.conf

```
ATOM_NAME = Ti O
DIM = 1 1 1
MP = 20 20 20
```

```
% phonopy -p mesh.conf
% phonopy -p -s mesh.conf
```

- -p: plot
- -s: save



Noviembre de 2025

38

38

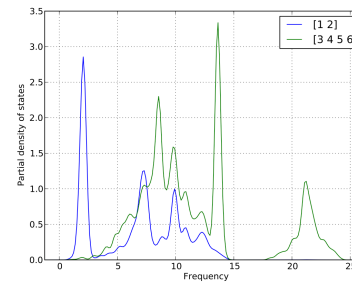
4. Phonopy: PDOS

□ Mesh.conf

```
ATOM_NAME = Ti O
DIM = 1 1 1
MP = 20 20 20
PDOS= 1 2, 3 4 5 6
```

```
% phonopy -p mesh.conf
% phonopy -p -s mesh.conf
```

- -p: plot
- -s: save



Noviembre de 2025

39

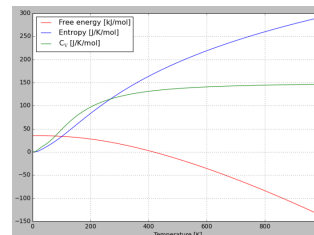
39

4. Phonopy: Prop. Térmicas

□ Mesh.conf

```
ATOM_NAME = Ti O
DIM = 1 1 1
MP = 20 20 20
```

```
% phonopy -p -t mesh.conf
% phonopy -p -s -t mesh.conf
```



Calculating thermal properties...#

T [K]	F [kJ/mol]	S [J/K/mol]	C _v [J/K/mol]	E [kJ/mol]
0.000	35.1058142	0.0000000	0.0000000	35.1058142
10.000	35.1056943	0.0866117	0.4911589	35.1065604
20.000	35.0986108	1.6954350	5.1965987	35.1325195
30.000	35.0669392	4.7579191	10.0095416	35.2096768
40.000	35.0023507	8.1834766	13.9485985	35.3296898
50.000	34.9028845	11.7323259	18.1171969	35.4895007
60.000	34.7671120	15.4585352	23.0451455	35.6946241
70.000	34.5928920	19.4295747	28.7336199	35.9529623

40

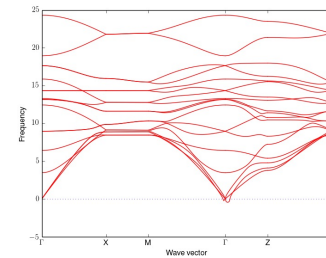
40

4. Phonopy: Bandas (D. Dispersión)

□ band.conf

```
DIM = 1 1 1
BAND = 0 0 0 1/2 0 1/2 1/2 1/2 1/2 1/2 1/4 3/4 0 0 0
BAND_LABELS = /Gamma X L W /Gamma
BAND_POINTS = 201
```

```
% phonopy -p band.conf
% phonopy -p -s band.conf
```



41

4. Phonopy: Bandas (NAC)

□ band.conf

```
DIM = 1 1 1
BAND = 0 0 0 1/2 0 1/2 1/2 1/2 1/2 1/2 1/4 3/4 0 0 0
BAND_LABELS = /Gamma X L W /Gamma
BAND_POINTS = 201
NAC = .TRUE.
```

```
% phonopy -p --nac band.conf
% phonopy -p -s --nac band.conf
```

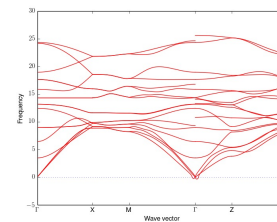
□ Archivo BORN

Sample BORN file:

```
<Conversion Factor>
  εxx εxy εxz εyx εyy εyz εzx εzy εzz
  Zxx Zxy Zxz Zyx Zyy Zyz Zzx Zzy Zzz
  εxx εxy εxz εyx εyy εyz εzx εzy εzz
  Zxx Zxy Zxz Zyx Zyy Zyz Zzx Zzy Zzz
```

Dielectric tensor

Born charge tensors
for unique atoms

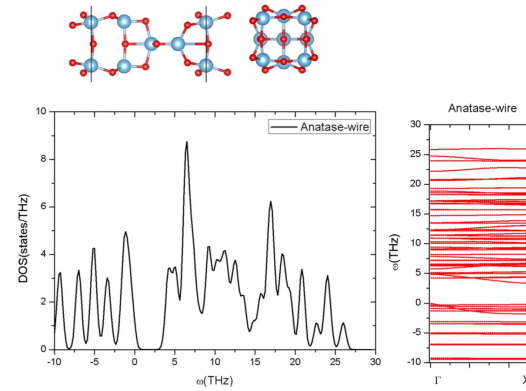


```
# epsilon and Z* of atoms 1 3
7.6697240 -0.0000000 0.0000000 0.0000000 7.6697240 0.0000000 0.0000000 0.0000000 9.4960260
6.4698600 1.0376900 0.0000000 1.0377200 6.4698400 0.0000000 0.0000000 0.0000000 7.9652900
-3.2332500 -1.8710000 0.0000000 -1.8710100 -3.2331800 0.0000000 -0.0007800 -0.0007800 -4.0431800
```

42

42

2. Ejemplo: Nanohilos de Anatasa



Noviembre de 2025

43

43

3 Ejemplo 2: Nanohilos de Anatasa

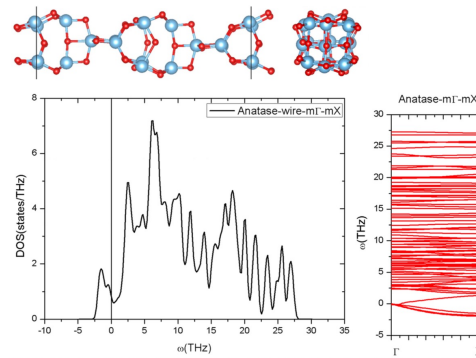


Figura 9.5.2-3. Esquema de nanohilos de Anatasa (001) modulada- Γ / modulada-X y su correspondiente diagrama de dispersión con densidad de estados fonónica.

Noviembre de 2025

44

44

3 Ejemplo 2: Nanohilos

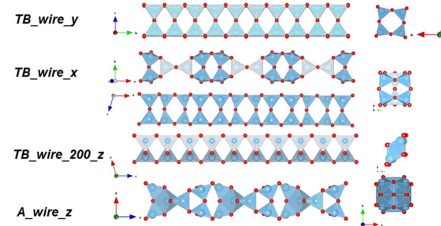


Figura 9.5.3-3 – Reconstrucción estructural de los hilos estudiados.

Tabla 9.5.3-2- Energías de formación y de gap para hilos de $\text{TiO}_2(\text{B})$ y Anatasa.

Sistema	$E_{\text{form}}(\text{eV})$	$E_{\text{gap}}(\text{eV})$	$E_{\text{gap,bun}}(\text{eV})$
TBx	1.16	3.19	2.73
TBy	0.41	3.62	2.73
Az	0.95	2.71	2.23

Noviembre de 2025

45

45

3 Ejemplo 2: Nanohilos

$$F = E - TS$$

$$E = \sum_{q\nu} \hbar \omega(q\nu) \left[\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar \omega(q\nu)}{k_B T}\right) - 1} \right]$$

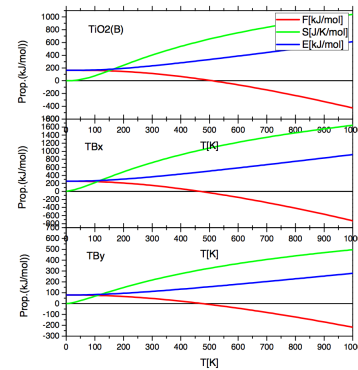
$$S = -\frac{\partial F}{\partial T} = \frac{1}{2T} \sum_{q\nu} \hbar \omega(q\nu) \coth\left(\frac{\hbar \omega(q\nu)}{2k_B T}\right) - k_B \sum_{q\nu} \ln \left[2 \sinh\left(\frac{\hbar \omega(q\nu)}{2k_B T}\right) \right]$$

Noviembre de 2025

46

46

3 Ejemplo 2: Nanohilos



Noviembre de 2025
Figura 9.5.3-4. Energía vibracional E , entropía vibracional S y energía libre de Helmholtz F para los sistemas $TiO_2(B)$, TBx y TBy .

47

3 Ejemplo 2: Nanohilos

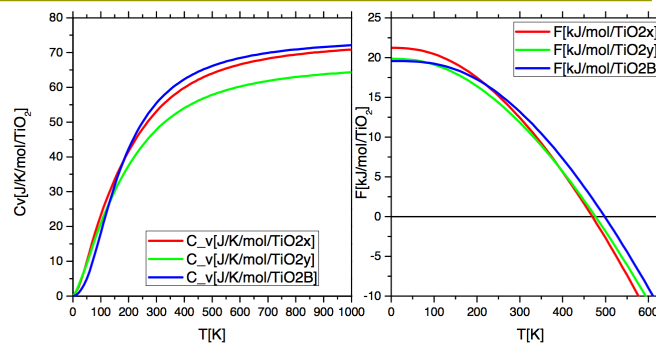
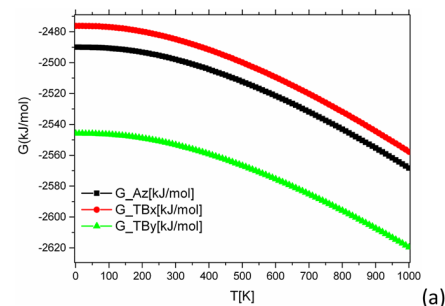


Figura 9.5.3-5. Energía Libre de Helmholtz normalizada $F [kJ/mol/TiO_2]$ y la respectiva capacidad calorífica.
 Noviembre de 2025

48

3 Ejemplo 2: Nanohilos

$$\square G(V, T) \cong E_{\text{wire}}(V) - F_{\text{vib}}(V, T)$$



Noviembre de 2025

49

49

3 Ejemplo 2: Detalles

THE JOURNAL OF
PHYSICAL CHEMISTRY C

Cite This: *J. Phys. Chem. C* 2018, 122, 3363–3370

Article
pubs.acs.org/JPCA

TiO₂(B) and Anatase Angstrom-Scale Wires: A Theoretical Study

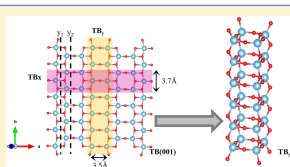
Luciana Fernández-Werner,^{*,†} Estela A. González,[‡] Ricardo Faccio,^{*,†} and Álvaro W. Mombro[†]

[†]Centro NanoMat/CrystMat-Lab, DETEMA, Facultad de Química, Universidad de la República, Montevideo, Uruguay

[‡]Instituto de Física del Sur (IFISUR), Departamento de Física, Universidad Nacional del Sur (UNS), CONICET, Av. L. N. Alem 1253, B8000CPB - Bahía Blanca, Argentina

Supporting Information

ABSTRACT: In this work, we model TiO₂(B) angstrom-scale wires derived from TiO₂(B) (001) ultrathin sheets. By means of density functional theory (DFT) calculations, we study their structural, electronic and thermodynamic properties, comparing with anatase angstrom scale wire with z as growing direction, of which there is experimental evidence. We found locally stable structures. TiO₂(B) atomic wire oriented along y direction exhibits significantly lower formation energy (0.33 eV) than the other studied systems (1.05 eV for TiO₂(B) wire oriented along x and 0.88 eV for anatase wire oriented along z -direction). Additionally, we present the simulated X-ray powder diffraction diagrams in order to help the experimental identification of this potential titanium dioxide polymorph's nanostructures. These results could be interesting for their potential applications, such as energy storage and photovoltaic applications, and for fundamental studies as well.



Noviembre

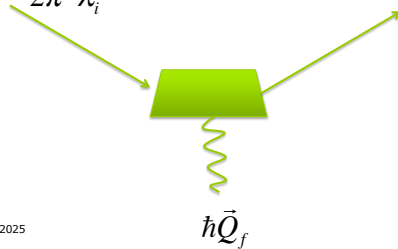
50

50

4. Interacción Radiación materia

■ Fotones y Fonones

$$\vec{p}_i = \hbar \vec{k}_i = \frac{h}{2\pi} \frac{2\pi}{\lambda_i}$$

$$\vec{p}_f = \hbar \vec{k}_f = \frac{h}{2\pi} \frac{2\pi}{\lambda_f}$$


Noviembre de 2025

51

4. Interacción Radiación materia

■ Principios de conservación y simetría

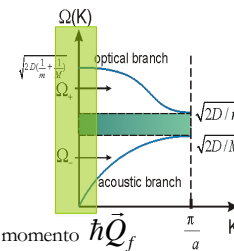
- Todo principio de conservación surge de una relación de simetría

- Tiempo $\rightarrow$ Energía
- Posición $\rightarrow$ Momento Lineal
- Rotación $\rightarrow$ Momento Angular

■ Sólido Cristalino

- Conservación del momento cristal

- El fonón interactúa como si tuviera un momento $\hbar \vec{Q}_f$
- Conservación de energía
- El fotón tiene un momento muy bajo, $Q \approx 0$



Noviembre de 2025

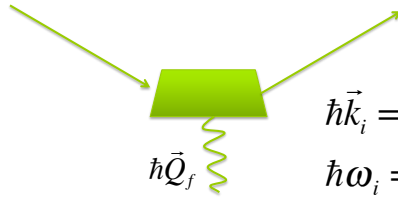
52

52

4. Interacción Radiación materia

■ Fotones y Fonones

$$\vec{p}_i = \hbar \vec{k}_i = \frac{h}{2\pi} \frac{2\pi}{\lambda_i}$$

$$\vec{p}_f = \hbar \vec{k}_f = \frac{h}{2\pi} \frac{2\pi}{\lambda_f}$$


$$\hbar \vec{k}_i = \pm \hbar \vec{Q} + \hbar \vec{k}_f$$

$$\hbar \omega_i = \hbar \omega_{\vec{Q}} + \hbar \omega_f$$

Noviembre de 2025

53

53

4. Propiedades eléctricas

■ Permitividad dieléctrica:

$$\vec{D} = \epsilon \vec{E}$$

$$D_i = \epsilon_{ij} E_j$$

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}$$

$$D_i = \epsilon_0 E_i + P_i$$

■ Relación entre polarizabilidad y constante dieléctrica macroscópica:

$$\alpha_{ij} = \left(\frac{V}{4\pi} \right) \frac{\partial \epsilon_{ij}}{\partial u_{ij}} = \left(\frac{V}{4\pi} \right) \frac{\partial \epsilon_{ij}}{\partial q_{ij}}$$

Noviembre de 2025

54

54

4. Secciones eficaces

▣ IR:

$$I^{IR} = \left(\frac{N\pi}{3c} \right) \left| \frac{d\vec{\mu}}{dQ_i} \right|^2$$

$$I^{IR} \propto \sum_{\alpha} \left| \frac{d\mu_{\alpha}}{dQ_m} \right|^2 = \sum_{\alpha} \left| \sum_{k\beta} \frac{d\mu_{\alpha}}{d\tau_{k\beta}} U_m(k\beta) \right|^2$$

$$I^{IR} \propto \sum_{\alpha} \left| \sum_{k\beta} Z_{k,\alpha\beta}^* e_m(k\beta) \right|^2$$

▣ Cargas de Born

$$Z_{k,\alpha\beta}^* = \frac{\Omega}{|e|} \frac{\partial P_{\alpha}}{\partial \varepsilon_{k\beta}}$$

Noviembre de 2025

55

55

4. Secciones eficaces

▣ Raman

$$\frac{d\sigma_i}{d\Omega} = \left(\frac{2\pi v_s}{c} \right)^4 \left| \hat{e}_s \frac{\partial \tilde{\alpha}}{\partial Q_i} \hat{e}_L \right|^2 \frac{h(n_i^b + 1)}{8\pi^2 v_i}$$

$$n_i^b = \left(\exp \left(\frac{h\nu_i}{k_B T} \right) - 1 \right)^{-1}$$

$$\frac{d\sigma_i}{d\Omega} = \left(\frac{2\pi v_s}{c} \right)^4 \frac{I^{Ram}}{45} \frac{h(n_i^b + 1)}{8\pi^2 v_i}$$

$$\frac{I^{Ram}}{45} = 45 \left(\frac{d\alpha}{dQ} \right)^2 + 7 \left(\frac{d\beta}{dQ} \right)^2 = 45\alpha'^2 + 7\beta'^2$$

Noviembre de 2025

56

56

4. Secciones eficaces

$$\alpha'_{ij} = \tilde{\alpha}' = \begin{bmatrix} \tilde{\alpha}'_{xx} & \tilde{\alpha}'_{xy} & \tilde{\alpha}'_{xz} \\ \tilde{\alpha}'_{yz} & \tilde{\alpha}'_{yy} & \tilde{\alpha}'_{yz} \\ \tilde{\alpha}'_{zx} & \tilde{\alpha}'_{zy} & \tilde{\alpha}'_{zz} \end{bmatrix} \quad \tilde{\alpha}' = \frac{1}{3}(\tilde{\alpha}'_{xx} + \tilde{\alpha}'_{yy} + \tilde{\alpha}'_{zz})$$

$$\beta'^2 = \frac{1}{2} \left((\tilde{\alpha}'_{xx} - \tilde{\alpha}'_{yy})^2 + (\tilde{\alpha}'_{xx} - \tilde{\alpha}'_{zz})^2 + (\tilde{\alpha}'_{yy} - \tilde{\alpha}'_{zz})^2 + 6(\tilde{\alpha}'_{xy}{}^2 + \tilde{\alpha}'_{xz}{}^2 + \tilde{\alpha}'_{yz}{}^2) \right)$$

$$\frac{d\sigma_i}{d\Omega} = \left(\frac{2\pi v_s}{c} \right)^4 \frac{I^{Ram}}{45} \frac{h(n_i^b + 1)}{8\pi^2 v_i}$$

$$\frac{I^{Ram}}{45} = 45 \left(\frac{d\alpha}{dQ} \right)^2 + 7 \left(\frac{d\beta}{dQ} \right)^2 = 45\alpha'^2 + 7\beta'^2$$

Noviembre de 2025

57

57

4. Ejemplo

▣ Rutilo:

▣ Grupo Espacial P 4₂/m n m

▣ a=b= 4.5977(4) Å y c=2.9564(2) Å

Átomo Wyckoff	x	y	z
Ti ⁴⁺ 2a	0.0	0.0	0.0
O ²⁻ 4f	0.3023(3)	0.3023(3)	0.0

▣ <http://www.cryst.ehu.es>

Noviembre de 2025

58

58

60

60

4 Ejemplo:

Bilbao Crystallographic Server → IR Raman Hyper-Raman Modes

IR Raman and Hyper-Raman Activity for the Space Group $P4_2/mnm$ (No. 136)

Input Structure:

```

136
4.5977 4.5977 4.5977 90 90 90
2
Ti 1 2a 0.000000 0.000000 0.000000
O 1 4f 0.302300 0.302300 0.000000
    
```

The space group it has been introduced is $P4_2/mnm$ (No. 136), its point group is D_{4h} ($4/mmm$)

Mechanical representation

$$M = A_{1g} + A_{2g} + 2A_{2u} + B_{1g} + 2B_{1u} + B_{2g} + 4E_u + E_g$$

More information about the mechanical representation: [show](#) [hide](#)

Acoustic and Optic modes:

$$\Gamma_{\text{acoustic}} = A_{2u} + E_u$$

$$\Gamma_{\text{optic}} = A_{1g} + A_{2g} + A_{2u} + B_{1g} + 2B_{1u} + B_{2g} + 3E_u + E_g$$

Noviembre de 2025

61

61

4 Ejemplo

IR, Raman and Hyper-Raman Active Modes

IR Active Modes

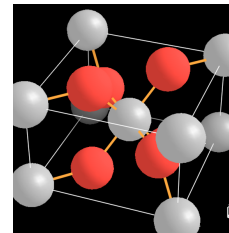
WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	E_u	E_g
4f	·	·	·	1	·	·	·	·	2	·
2a	·	·	·	1	·	·	·	·	2	·

Infrared active modes: $A_{2u} + 3E_u$ (Acoustic modes not included)

Raman Active Modes

WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	E_u	E_g
4f	1	·	·	·	1	·	1	·	·	1
2a	·	·	·	·	·	·	·	·	·	·

Raman active modes: $A_{1g} + B_{1g} + B_{2g} + E_g$

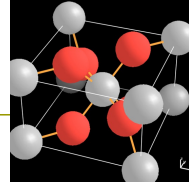


62

62

4. Ejemplo:

▣ Frecuencias



1 f =	24.163760 THz	151.825382 2PiTHz	806.016250 cm-1	99.933315 meV
2 f =	17.858403 THz	112.207657 2PiTHz	595.692194 cm-1	73.856446 meV
3 f =	14.425855 THz	90.640323 2PiTHz	481.194726 cm-1	59.660564 meV
4 f =	14.425855 THz	90.640323 2PiTHz	481.194726 cm-1	59.660564 meV
5 f =	13.549475 THz	85.133864 2PiTHz	451.961834 cm-1	56.036146 meV
6 f =	13.549475 THz	85.133864 2PiTHz	451.961834 cm-1	56.036146 meV
7 f =	12.767136 THz	80.218282 2PiTHz	425.865805 cm-1	52.800649 meV
8 f =	11.630951 THz	73.079419 2PiTHz	387.966746 cm-1	48.101763 meV
9 f =	11.320651 THz	71.129750 2PiTHz	377.616271 cm-1	46.818467 meV
10 f =	11.320651 THz	71.129750 2PiTHz	377.616271 cm-1	46.818467 meV
11 f =	3.017258 THz	24.612861 2PiTHz	130.665672 cm-1	16.200484 meV
12 f =	3.075099 THz	19.321416 2PiTHz	102.574256 cm-1	12.717591 meV
13 f =	3.075099 THz	19.321416 2PiTHz	102.574256 cm-1	12.717591 meV
14 f =	2.461587 THz	15.460605 2PiTHz	82.109687 cm-1	10.180307 meV
15 f =	2.416689 THz	15.184503 2PiTHz	80.612056 cm-1	9.994625 meV
16 f/i =	0.021903 THz	0.137620 2PiTHz	0.730600 cm-1	0.090583 meV
17 f/i =	0.021903 THz	0.137620 2PiTHz	0.730600 cm-1	0.090583 meV
18 f/i =	0.021903 THz	0.137620 2PiTHz	0.730600 cm-1	0.090583 meV

Noviembre de 2025

63

63

4 Ejemplo:

▣ Autovectores

▣ Ejemplo: Modo N° 2

2 f = 17.858403 THz 112.207657 2PiTHz 595.692194 cm-1 73.856446 meV

X	Y	Z	dx	dy	dz
0.000000	0.000000	0.000000	-0.000000	0.000000	0.000000
2.294651	2.294651	1.476306	0.000000	-0.000000	-0.000000
1.394810	1.394810	0.000000	-0.353553	-0.353553	-0.000000
3.194493	3.194493	0.000000	0.353553	0.353553	0.000000
0.899841	3.689461	1.476306	0.353553	-0.353553	-0.000000
3.689461	0.899841	1.476306	-0.353553	0.353553	-0.000000

Noviembre de 2025

64

64

4. Ejemplo: Rutilo

□ Clasificación de los modos

freq (cm ⁻¹)	Irrep
1 (0.000):	A _{2u}
2 (0.000):	E _u
4 (2.428):	B _{1u}
5 (2.464):	A _{2u}
6 (3.075):	E _u
8 (3.918):	B _{1g}
9 (11.322):	E _u
11 (11.631):	B _{1u}
12 (12.767):	A _{2g}
13 (13.550):	E _g
15 (14.427):	E _u
17 (17.859):	A _{1g}
18 (24.164):	B _{2g}

IR, Raman and Hyper-Raman Active Modes

IR Active Modes

WP	A _{1g}	A _{1u}	A _{2g}	A _{2u}	B _{1g}	B _{1u}	B _{2g}	B _{2u}	E _u	E _g
4f	.	.	.	1	.	.	.	.	2	.
2a	.	.	.	1	.	.	.	.	2	.

Infrared active modes: A_{2u} + 3E_u (Acoustic modes not included)

Raman Active Modes

WP	A _{1g}	A _{1u}	A _{2g}	A _{2u}	B _{1g}	B _{1u}	B _{2g}	B _{2u}	E _u	E _g
4f	1	.	.	.	1	.	1	.	.	1
2a	.	.	.	.	.	.	.	.	.	.

Raman active modes: A_{1g} + B_{1g} + B_{2g} + E_g

Noviembre de 2025

65

65

4. Ejemplo: Rutilo

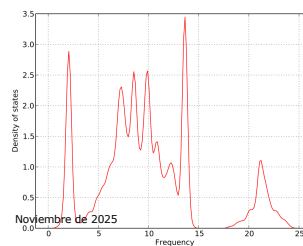
□ Rutilo:

□ Grupo Espacial P 4₂/m n m

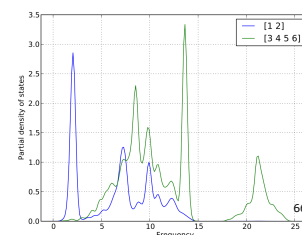
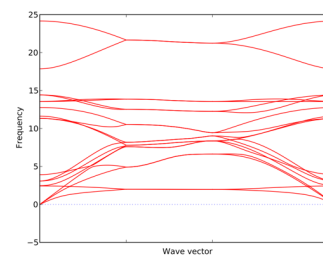
□ a=b= 4.5977(4)Å y c=2.9564(2) Å

Ti⁴⁺ 2a 0.0 0.0 0.0

O²⁻ 4f 0.3023(3) 0.3023(3)



Noviembre de 2025



66

4. Ejemplo: Rutilo

Tensor Dieléctrico: ϵ_{ij}

MACROSCOPIC STATIC DIELECTRIC TENSOR
(including local field effects in DFT)

7.423904	0.000000	0.000000
0.000000	7.423904	0.000000
0.000000	0.000000	8.849335

Noviembre de 2025

67

67

4. Ejemplo: Rutilo

Cargas de Born

$$Z_{k,\alpha\beta}^* = \frac{\Omega}{|e|} \frac{\partial P_\alpha}{\partial \epsilon_{k\beta}}$$

MACROSCOPIC STATIC DIELECTRIC TENSOR
(including local field effects in DFT)

7.423904	0.000000	0.000000
0.000000	7.423904	0.000000
0.000000	0.000000	8.849335

BORN EFFECTIVE CHARGES (e)

ion 1 (Ti)			
1	6.35763	1.04091	0.00000
2	1.04090	6.35765	0.00000
3	0.00000	0.00000	7.68997
ion 2 (Ti)			
1	6.35763	-1.04091	0.00000
2	-1.04090	6.35765	0.00000
3	0.00000	0.00000	7.68997
ion 3 (O)			
1	-3.16931	-1.82350	0.00000
2	-1.82348	-3.16930	0.00000
3	-0.00077	-0.00077	-3.84183
ion 4 (O)			
1	-3.16968	-1.82377	0.00000
2	-1.82381	-3.16974	0.00000
3	0.00077	0.00077	-3.84183
ion 5 (O)			
1	-3.16968	1.82377	0.00000
2	1.82348	-3.16930	0.00000
3	0.00077	-0.00077	-3.84183
ion 6 (O)			
1	-3.16931	1.82350	0.00000
2	1.82381	-3.16974	0.00000
3	-0.00077	0.00077	-3.84183

Noviembre de 2025

68

68

4. Ejemplo: Rutilo

▣ Actividad Raman

mode	freq(cm-1)	alpha	beta2	activity	Irrep.
001	806.01625	0.0111139	0.119	0.842	B2g
002	595.69219	3.6897265	126.828	1500	A1g
003	481.19473	0.0093502	0.000	0.005	Eu
004	481.19473	0.0017736	0.000	0.001	Eu
005	451.96183	-0.0246816	43.201	302	Eg
006	451.96183	0.0092582	43.239	302	Eg
007	425.86581	0.0028455	0.000	0.001	A2g
008	387.96675	0.0016885	0.000	0.000	B1u
009	377.61627	0.0072289	0.000	0.002	Eu
010	377.61627	0.0039901	0.000	0.001	Eu
011	130.66567	0.0017733	0.042	0.3	B1g
012	102.57426	0.0134835	0.000	0.008	Eu
013	102.57426	0.0080623	0.000	0.004	Eu
014	82.10969	0.0392713	0.000	0.071	A2u
015	80.61206	-0.0024535	0.000	0.000	B1u

Noviembre de 2025

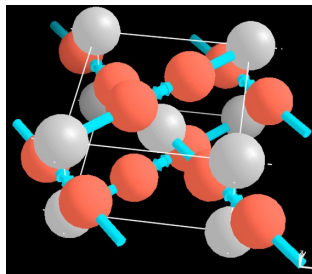
69

$$\frac{d\sigma_i}{d\Omega} = \left(\frac{2\pi\nu_i}{c} \right)^4 \frac{I^{Ram}}{45} \frac{h(n_i^2 + 1)}{8\pi^2\nu_i}$$

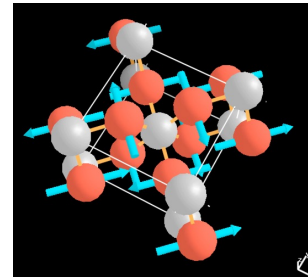
$$\frac{I^{Ram}}{45} = 45 \left(\frac{d\alpha}{dQ} \right)^2 + 7 \left(\frac{d\beta}{dQ} \right)^2 = 45\alpha'^2 + 7\beta'^2$$

4. Ejemplo: Rutilo

▣ Modos Raman Activos



A1g



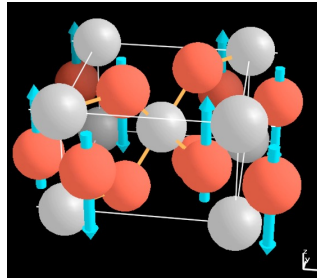
B1g

Noviembre de 2025

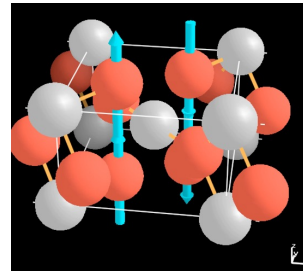
70

4. Ejemplo: Rutilo

▣ Modos Raman Activos



E_g



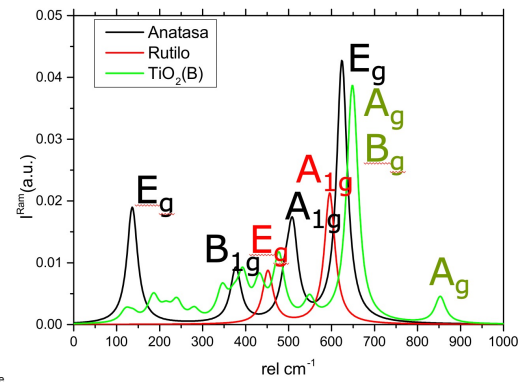
E_g

Noviembre de 2025

71

71

Raman:



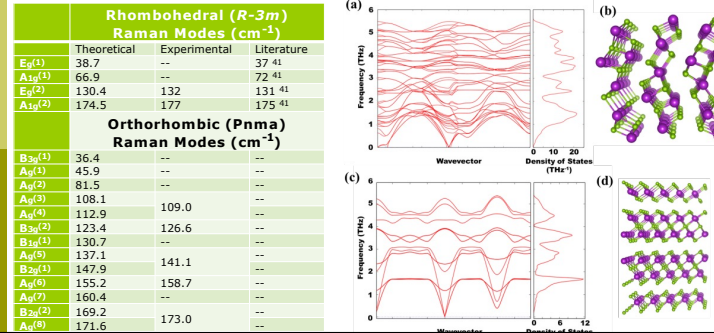
Noviembre

72

72

5. Ejemplo: Fases del Bi_2Se_3

Síntesis electroquímica de fase metaestable del Bi_2Se_3 (ortorrómbica, Pnma) y su transformación hacia la fase estable (Rombohédrica, R-3m)



73

5. Ejemplo Bi_2Se_3

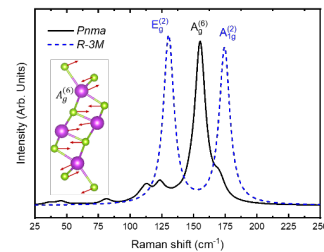


Figure 2: Simulated Raman spectra for both Pnma and R-3m crystallographic structure of Bi_2Se_3 . The inset with the atomic scheme shows the displacement vectors for the $A_g^{(6)}$ mode of Pnma phase.

P. B. Souza¹, M. A. Tumelero², R. Faccio³, R. Ahmed⁴, C. C. Plá Cid¹, G. Zangari⁵, & A. A. Pasa, Submitted 2021

74

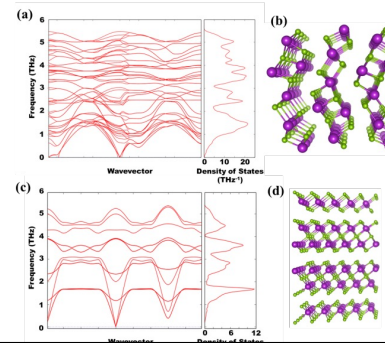
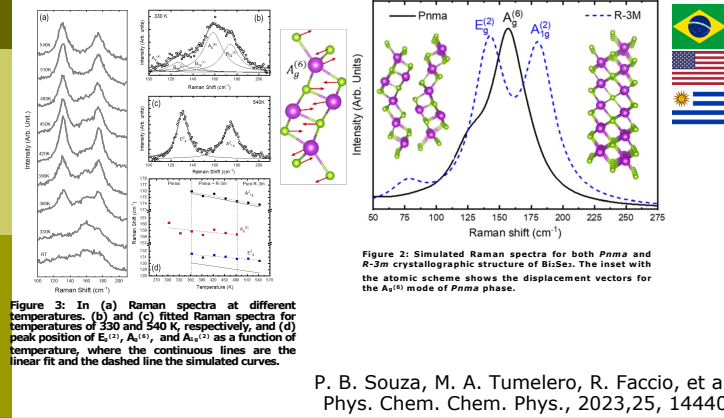


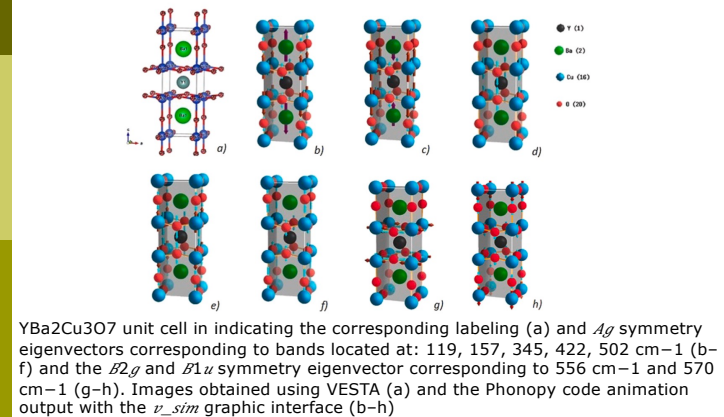
Figure 3: In (a) Raman spectra at different temperatures. (b) and (c) fitted Raman spectra for temperatures of 330 and 540 K, respectively, and (d) peak position of $E_g^{(2)}$, $A_g^{(6)}$, and $A_{1g}^{(2)}$ as a function of temperature, where the continuous lines are the linear fit and the dashed line the simulated curves.

5. Ejemplo Bi_2Se_3



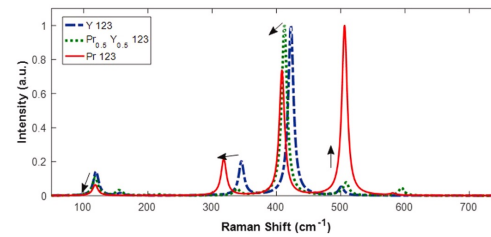
75

6. $\text{REBa}_2\text{Cu}_3\text{O}_{7-d}$



76

6. REBa₂Cu₃O_{7-d}



Calculated Raman spectra for Y_{1-x}Pr_xBa₂Cu₃O₇ with $x = 0, 0.5$ and 1 . The arrows indicate the modification of the peaks as Pr content increases

77

6. REBa₂Cu₃O_{7-d}

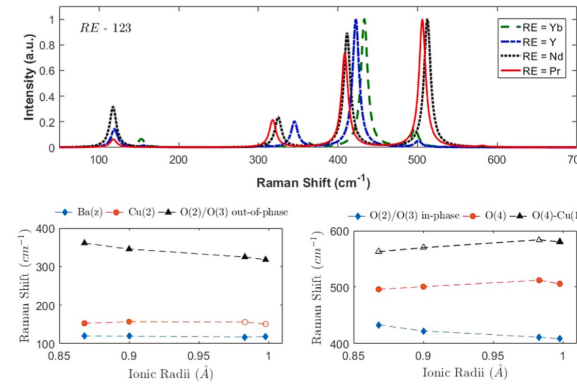
Table 3

Cell parameters (top) and frequency modes by DFT calculation (bottom), for different Rare Earth substitution in RE-123.

Cell parameters								
RE	<i>a</i> (Å)	<i>α</i> (°)	<i>b</i> (Å)	<i>β</i> (°)	<i>c</i> (Å)	<i>γ</i> (°)	<i>ΔV</i> ₀ (%)	
Yb	3.7546	90.0	3.8764	90.0	11.6022	90.0	-2.0%	
Y	3.8051	90.0	3.8928	90.0	11.6330	90.0	0.0%	
Nd	3.8496	90.0	3.9267	90.0	11.7264	90.0	2.9%	
Pr	3.8590	90.0	3.9334	90.0	11.7547	90.0	3.8%	
Mode assignment								
RE	Ion radius (Å)	Ba ₂	Cu(2) ₂	O(2)/O(3) ₂ out-of-phase <i>A_g</i>	O(2)/O(3) ₂ in-phase <i>A_g</i>	O(4) ₂	O(2)/O(3) ₂	O(4)-Cu(1) ₂
		<i>B_{2g}</i>			<i>A_g</i>	<i>A_g</i>	<i>B_{2g}</i>	<i>B_{1u}</i>
Yb	0.868	120 cm ⁻¹	153 cm ⁻¹	363 cm ⁻¹	433 cm ⁻¹	497 cm ⁻¹	580 cm ⁻¹	563 cm ⁻¹
Y	0.900	119 cm ⁻¹	157 cm ⁻¹	345 cm ⁻¹	422 cm ⁻¹	501 cm ⁻¹	556 cm ⁻¹	570 cm ⁻¹
Nd	0.983	117 cm ⁻¹	156 cm ⁻¹	325 cm ⁻¹	411 cm ⁻¹	512 cm ⁻¹	520 cm ⁻¹	584 cm ⁻¹
Pr	0.998	118 cm ⁻¹	151 cm ⁻¹	318 cm ⁻¹	409 cm ⁻¹	506 cm ⁻¹	513 cm ⁻¹	581 cm ⁻¹

78

6. $\text{REBa}_2\text{Cu}_3\text{O}_{7-d}$



79

6. $\text{REBa}_2\text{Cu}_3\text{O}_{7-d}$

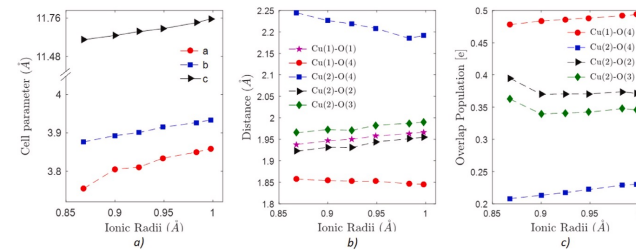


Fig. 12. (a) Cell parameters, (b) most relevant Cu-O distances and (c) Overlap Populations for different Pr content, RE atoms and Yttrium.

It is found that the Raman band associated with oxygen vibrations in the CuO_2 planes is shifted to lower frequencies when Pr content is increased in both, measured and calculated spectra, explained in the simulations by the reduction of the overlap population of $\text{Cu}(1)-\text{O}(2/3)$ bonds.

80

6. REBa₂Cu₃O_{7-d}

Materials Chemistry and Physics 256 (2020) 123737

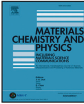


ELSEVIER

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys



Experimental and theoretical Raman study on the HTSC Pr_xY_{1-x}Ba₂Cu₃O₇ family for different Pr concentrations and synthesis methods[☆]

Sofia Favre ^{a,*}, Marcos Mazini ^a, Carla Yelpe ^a, Daniel Ariosa ^a, Ricardo Faccio ^b

^a Instituto de Física, Facultad de Ingeniería, Universidad de la República, Herrera y Reaistg 565, CC 30, CP 11300 Montevideo, Uruguay

^b Área Física & Centro NanoMat, DEHEMA, Facultad de Química, Universidad de la República, Av. Gral. Flores 2124, CC 1157, CP 11800 Montevideo, Uruguay

Noviembre de 2025

81

7. Bi₂Sr₂CaCu₂O₈

Superconductor con poca bibliografía en referencia a asignación de modos.

Fonones y Propiedades Electrónicas

Table 1. Lattice parameters, unit cell volume and total energy of Bi2212 before and after performing the modulation correction.

Before (tetragonal)		After (distorted)	
$a = 3.72135 \text{ \AA}$	$\alpha = 90.0000^\circ$	$a = 3.77550 \text{ \AA}$	$\alpha = 90.5047^\circ$
$b = 3.72135 \text{ \AA}$	$\beta = 90.0000^\circ$	$b = 3.75719 \text{ \AA}$	$\beta = 87.6678^\circ$
$c = 30.6050 \text{ \AA}$	$\gamma = 90.0000^\circ$	$c = 30.30016 \text{ \AA}$	$\gamma = 90.0722^\circ$
$V = 424.462641 \text{ \AA}^3$		$V = 429.443151 \text{ \AA}^3$	
$E_{\text{tot}} = -162.61456 \text{ eV}$		$E_{\text{tot}} = -163.65998 \text{ eV}$	

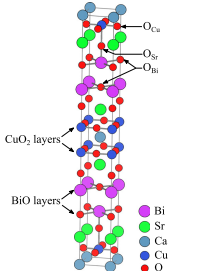
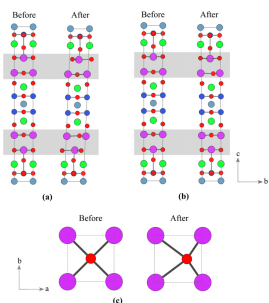


Figure 1. Idealized tetragonal crystal structure of Bi₂Sr₂CaCu₂O₈. O_{Cu}: apical oxygens, O_{Sr}: oxygens in the BiO layers, O_{Bi}: oxygens in the CuO₂ layers.



7. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

J. Phys.: Condens. Matter **33** (2021) 185705

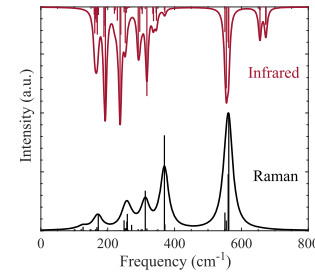


Figure 3. Calculated IR (top) and Raman (bottom) spectrum of Bi2212. The vertical lines show the individual cross sections for each vibrational mode. A complete table with all the phonon frequencies and cross sections is included in the supplementary material (<https://stacks.iop.org/JPCM/33/185705/mmedia>).

Novembre de 2025

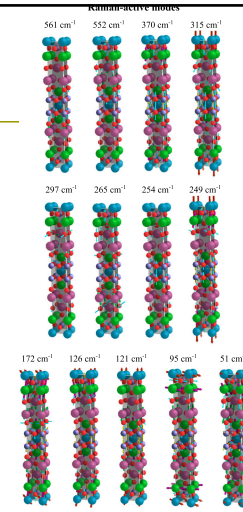


Figure 5. Schematic representation of the most relevant Raman-active vibrational modes and their corresponding frequencies for Bi2212. The atomic displacements, associated to each eigenvector, are represented with arrows.

83

7. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

Table 2. Phonon frequencies (ω in cm^{-1}) and assignments of the Raman-active modes in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$, compared with previous experimental reports.

Present work	Cardona <i>et al</i> 1988 [4]	Denisov <i>et al</i> 1989 [5]	Sugai and Sato 1989 [6]	Boekholt <i>et al</i> 1990 [7]	Liu <i>et al</i> 1992 [8]	Martin and Lee 1995 [9]	Kakihana <i>et al</i> 1996 [10]
ω	Assignments ^a	ω	Assignments ^b	ω	Assignments ^c	ω	Assignments ^d
51	Bi(z)	65	Bi(z) Ag	63	Bi(z) Ag	62	Bi(z) Ag
95	Cu(y-Sr(y))	122	Bi(z) Ag	121	Sr Ag	110	Cu(x) Ag
121	Cu(z)	133	Bi(z) Ag	132	Sr Ag	129	Cu(z) Ag
126	Cu(z)	156	(Sr/Cu) Ag	141	Cu(z) Ag	129	Cu(z) Ag
172	Sr(z)	184	(Sr/Cu) Ag	141	Cu(z) Ag	182	Sr(z) Ag
249	Cu(z)	219	(Sr/Cu) Ag	187	Cu(x) Ag	180	Sr(z) Ag
254	$\text{O}_{\text{Cu}}(z)$ B1g	282	$\text{O}_{\text{Cu}}(z)$ B1g	289	$\text{O}_{\text{Cu}}(z)$ B1g	285	$\text{O}_{\text{Cu}}(z)$ B1g
265	$\text{O}_{\text{Bi}}(z)$	296	$\text{O}_{\text{Bi}}(z)$ Ag	295	$\text{O}_{\text{Bi}}(z)$ Ag	287	$\text{O}_{\text{Bi}}(z)$ Ag
297	$\text{O}_{\text{Bi}}(z)$	313	$\text{O}_{\text{Bi}}(z)$ Ag	327	$\text{O}_{\text{Bi}}(z)$ Ag	310	$\text{O}_{\text{Bi}}(z)$ Ag
315	$\text{O}_{\text{Cu}}(z)$	391	$\text{O}_{\text{Cu}}(z)$ Ag	394	$\text{O}_{\text{Cu}}(z)$ Ag	355	$\text{O}_{\text{Cu}}(z)$ Ag
370	$\text{O}_{\text{Cu}}(z)$	469	$\text{O}_{\text{Bi}}(z)$ Ag	469	$\text{O}_{\text{Bi}}(z)$ Ag	386	$\text{O}_{\text{Bi}}(z)$ Ag
552	$\text{O}_{\text{Bi}}(z)$	631	$\text{O}_{\text{Bi}}(z)$ Ag	632	$\text{O}_{\text{Bi}}(z)$ Ag	627	$\text{O}_{\text{Bi}}(z)$ Ag
561	$\text{O}_{\text{Bi}}(z)$	659	$\text{O}_{\text{Bi}}(z)$ Ag	663	$\text{O}_{\text{Bi}}(z)$ Ag	660	$\text{O}_{\text{Bi}}(z)$ Ag

Novembre de 2025

84

84

7. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

Table 3. Phonon frequencies (ω in cm^{-1}) and assignments of the IR active modes in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x}$, compared with previous experimental reports.

Present work	Piro <i>et al</i> 1989 [15]	Zheng <i>et al</i> 1991 [16]	Pal <i>et al</i> 1991 [17]	Hudkovič <i>et al</i> 1996 and 2004 [18, 19]	Tsvetkov <i>et al</i> 1999 [20]	Kovaleva <i>et al</i> 2004 [21]
ω Assign	ω Assign	ω Assign	ω Assign	ω Assign	ω Assign	ω Assign
		129 Cu axial stretching		95 Originated in Bi-O layers	98 Involves Cu atoms	97 Bi against Cu,Ca and Sr (A _{2u})
161 Sr-Cu-O ₆ (z) stretching involving Cu		169 Symmetric stretching of Sr planes		157 Sr-CuO ₆	174 Cu-O ₆ bending + Bi and Sr	168 Sr-Cu stretching (A _{2u})
193 Bi-Sr(y)				200 Sr-O ₆	220 In-plane optical phonon	210 Sr-Cu stretching (A _{2u})
237 Sr-O ₆ O ₆ (z) stretching involving Cu		331 Sr-O vibrations		252 Sr-O ₆ stretching involving Cu		282 —
252 Bi-O ₆ O ₆ (y)	275 Cu-O ₆ in-plane Bending (B _u)			298 Cu-O ₆ in-plane Bending		
294 Bi-O ₆ O ₆ (x)		406 Cu-O-Cu out-of-plane bending (A _{2u})				304 O ₆ -O ₆ vibrations (A _{2u})
317 O ₆ -O ₆ (xz) + Cu-O ₆ (z) stretching involving Cu				345 Bi-O ₆ O ₆ Stretching	328 O ₆ -O ₆	
336 Cu(x)-O ₆ in-plane bending	360 Bi-O ₆ -Cu Bending (B _u)	418 Bi-O ₆ -Cu Bending (B _u)		383 O ₆ -O ₆ against Cu	358 O ₆ against Cu and O ₆ (A _{2u})	
345 Cu(y)-O ₆ in-plane bending	300-450 Cu-O-Cu out-of-plane bending (A _{2u})	488 Bi-O ₆ -Cu stretching (A _{2u})		460 O ₆ -O ₆	469 Zone boundary mode ^a	462 —
370 O ₆ (z)					472 Zone boundary mode ^a	521 —
557 O ₆ (z)	500-570 Bi-O ₆ -Cu stretching (A _{2u})		609 O ₆ -O ₆ stretching	566 O ₆ -O ₆ stretching	628 O ₆ -O ₆ out of plane vibration ^b	583 O ₆ -O ₆ stretching (A _{2u})
655 Cu-O ₆ (x) stretching					655 O ₆ -O ₆ out of plane vibration ^b	
673 Cu-O ₆ (y) stretching	600 Cu-O ₆ in-plane stretching (B _u)	612 Cu-O ₆ stretching (B _u)	637 Cu-O ₆ in-plane stretching	632 Cu-O ₆ stretching		640 —

Novembre de 2025

85

7. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

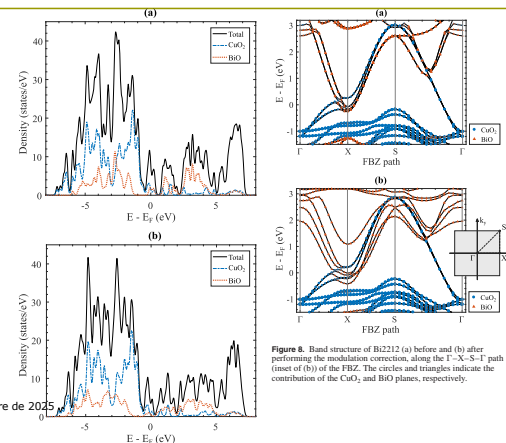


Figure 8. Band structure of Bi2212 (a) before and (b) after performing the modulation correction, along the Γ -X-S- Γ path (inset of (b)) of the FBZ. The circles and triangles indicate the contribution of the CuO₂ and BiO planes, respectively.

Novembre de 2025

86

7. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

IOP Publishing

Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **33** (2021) 185705 (11pp)

<https://doi.org/10.1088/1361-648X/abed17>

Electronic and vibrational properties of the high T_c superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$: an *ab initio* study

Carla Yelpe¹, Ricardo Faccio^{2,*}, Daniel Ariosa¹ and Sofía Favre¹

¹ Instituto de Física, Facultad de Ingeniería, Universidad de la República, Herrera y Reissig 565, CC 30, CP 11300 Montevideo, Uruguay

² Área Física and Centro NanoMat, DETEMA, Facultad de Química, Universidad de la República, Av. Gral. Flores 2124, CC 1157, CP 11800 Montevideo, Uruguay

E-mail: rfaccio@fq.edu.uy

Received 21 December 2020, revised 22 February 2021

Accepted for publication 9 March 2021

Published 23 April 2021



Noviembre de 2025

87

87

Machine Learning Force Field (MLFF)

New Implementation in
VASP 6.3

Noviembre de 2025

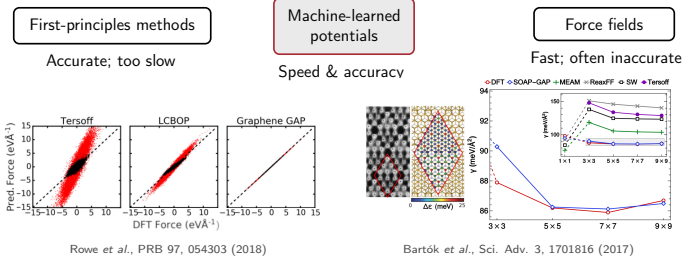
88

88

Force Field Machine Learning

✓ Molecular dynamics (MD) simulations allow to calculate many finite-temperature properties of materials and molecules (free energies and phase transitions, thermal expansion, diffusivity, heat transport...).

! How energies and forces are computed determines the accessible time and size scales.

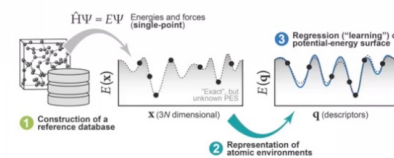


Novembre de 2025

89

Force Field Machine Learning

- Basic principle for solids is very simple
 - 1) Database: Ab initio calculations for some 1000 structures
 - 2) Chose a representation for the local environment (descriptor)
 - 3) Fit the data using a neural network or a regression method



V.L. Deringer, M.A. Caro, and G. Csányi, Adv. Mater. 31, 1902765 (2019)

Database → Features/Descriptors/Representation → Regression

- 1) Database: Select the structures on the fly from MD

90

Force Field Machine Learning

Database → Descriptors → Regression

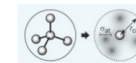
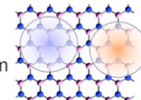
Local environment mapped onto set of descriptors

Behler & Parrinello, Phys. Rev. Lett. 98, 146401 (2007): symmetry functions

Bartók, Kondor, Csányi, PRB 87, 184115 (2013): power spectrum

some other ideas: bag of bonds, Coulomb matrix, long range descriptors, ...

Descriptors calculated from classical density distribution of the atoms around central atom (translationally invariant)

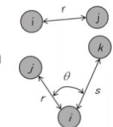


$$\rho(\mathbf{r}) = c^{lmn} Y_{lm}(\Omega_r) j_l(q_n r) \quad \text{not rotationally invariant}$$

$$\rho^1(r) = g(r) = c^{00n} j_0(q_n r) \quad \text{pair correlation function}$$

$$\rho^2(r, s, \theta) \quad \text{angular correlation function}$$

likelihood to find one particle at distance r
another one at s at angle θ



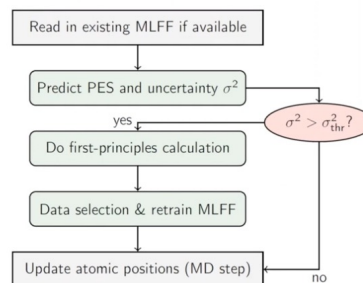
Jinnouchi et al., J. Chem. Phys. 152, 234102 (2020)

91

91

Force Field Machine Learning

Database → Descriptors → Regression



The error in the force is calculated for each atom in the to be considered structure

- If the error exceeds the threshold for any atom, a DFT calculation is performed
- All atoms, for which the error is exceeding the threshold, are added to the set of "reference atoms" i_B
- We need only few first principles calculations
- With this trick, the number of "reference atomic environments" grows also slowly

Jinnouchi, Karsai, and Kresse, PRB 100, 014105 (2019)

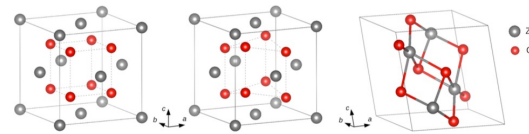
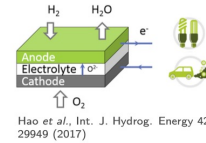
92

92

MLFF: VASP

Applications: zirconia (ZrO_2)

- Many technological applications.
- Strongly anharmonic solid.
- Complex phase diagram: monoclinic $\rightarrow$ tetragonal $\rightarrow$ cubic.

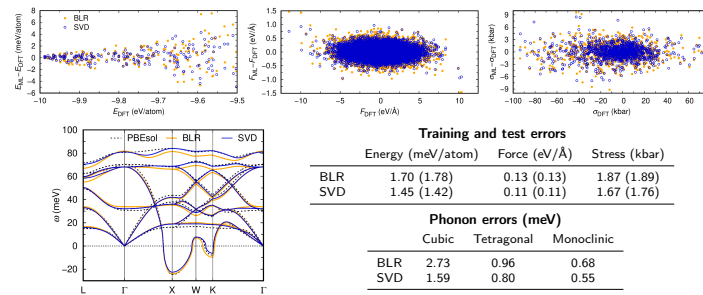


Novembre de 2025

93

MLFF: VASP

Training on the fly: 592 DFT calculations (PBEsol) vs. 1.5×10^5 total MD steps (T up to 2800 K).



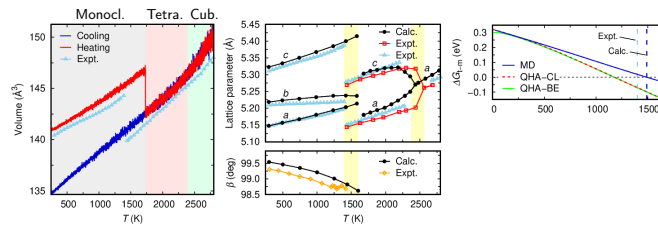
Novembre de 2025

94

MLFF: VASP

Temperature-induced structural phase transitions

Monoclinic to tetragonal to cubic phase:



$$\text{Fully anharmonic Gibbs free energy: } G(T) = -T \int_{T_0}^T \frac{H(T')}{T'^2} dT' + \frac{G_0}{T_0} T$$

Verdi, Karsai, Liu, Jinnouchi & Kresse, npj Comput. Mater. 7, 156 (2021)

Noviembre de 2025

95

95

7. Sistemas Discretos

▣ Cálculos *ab initio* o *Primeros Principios*

▣ DFT

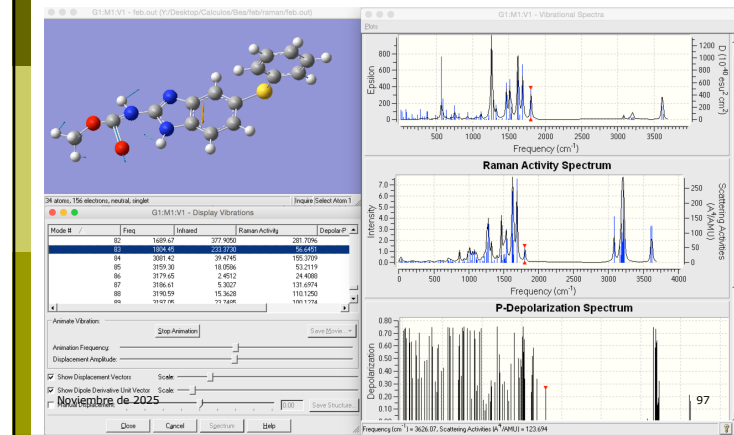
- Gaussian 09
- Gaussian 16
- VASP
- Quantum-Espresso

Noviembre de 2025

96

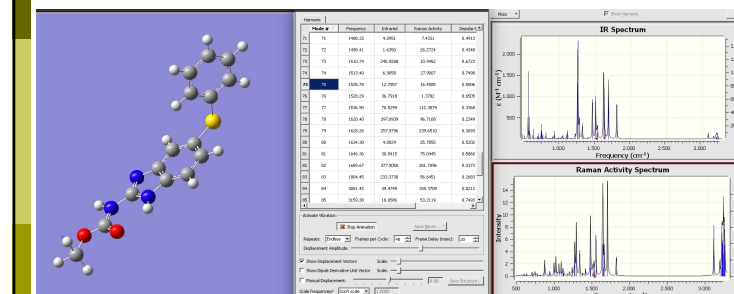
96

7. Simulación de IR y Raman



97

FBZ Simulation

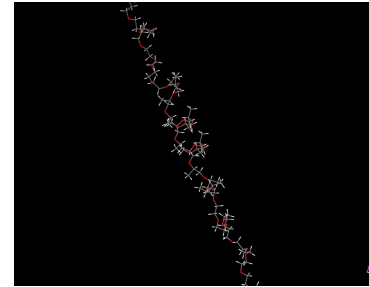
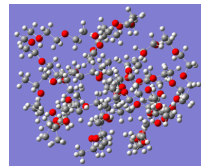
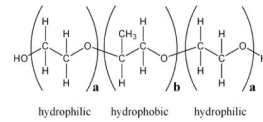


17/11/25

98

98

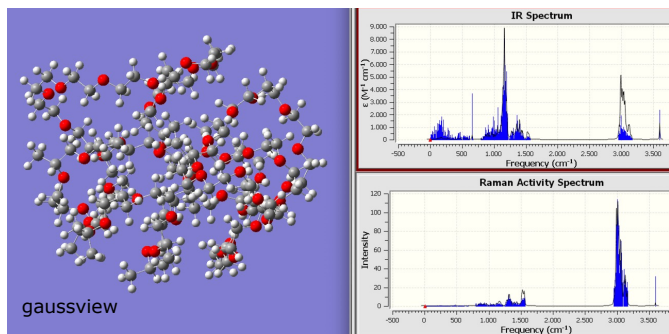
Poloxamer P184



poly(ethyleneoxide)/poly(propyleneoxide)/poly(ethylene oxide)
Molecular Dynamics Simulation

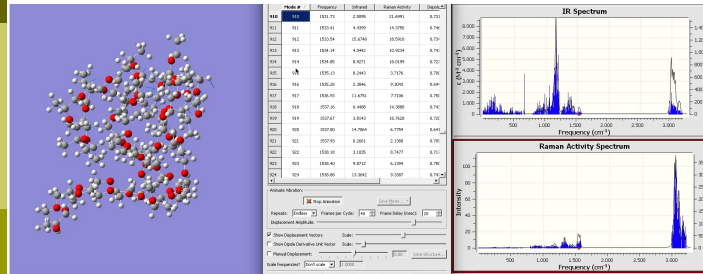
99

Poloxamer P184 Simulation



100

Poloxamer P184 Simulation



17/11/25

101

101

Gracias!



Noviembre de 2025



UNIVERSIDAD
DE LA REPÚBLICA
URUGUAY

102

102