Vibrational spectroscopy

Gian-Marco Rignanese

ETSF

UCLouvain

European Theoretical Spectroscopy Facility
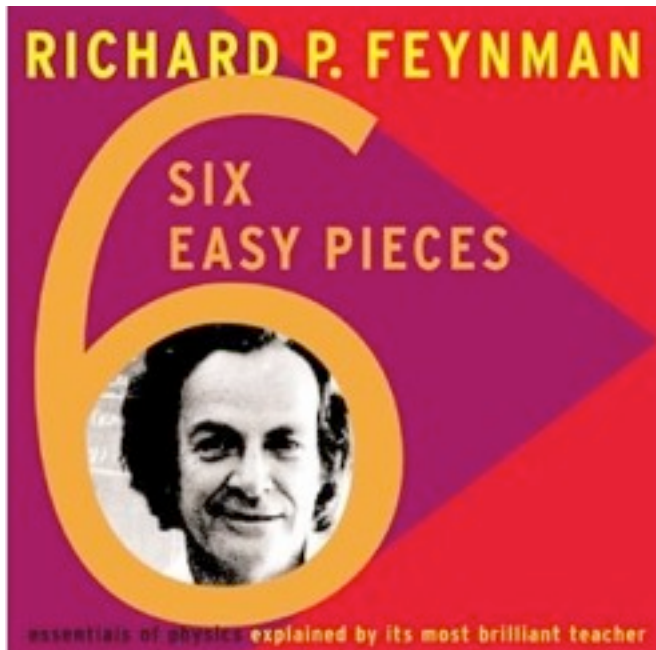
Unité de Physico-Chimie et de Physique des Matériaux, B-1348 Louvain-la-Neuve, Belgique
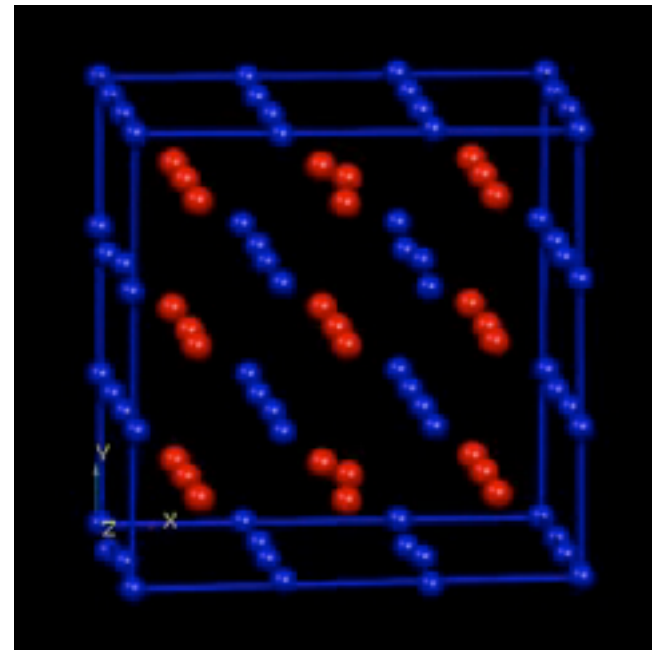
KITP programme on Excitations in Condensed Matter

Santa Barbara (CA), 20 november 2009

- "..everything that living things do can be understood in terms of the jigglings and wigglings of atoms.."

(Addison-Wesley, Reading MA)
p. 59. (1991)

atomic motion at 300K
(http://wolf.ifj.edu.pl/phonon)

Infrared spectroscopy

- IR light over a broad frequencies is passed through a sample.
- The matter absorbs the light only for some specific frequencies corresponding to the vibrational modes of the system and which fulfill some selection rules (the IR-active modes).
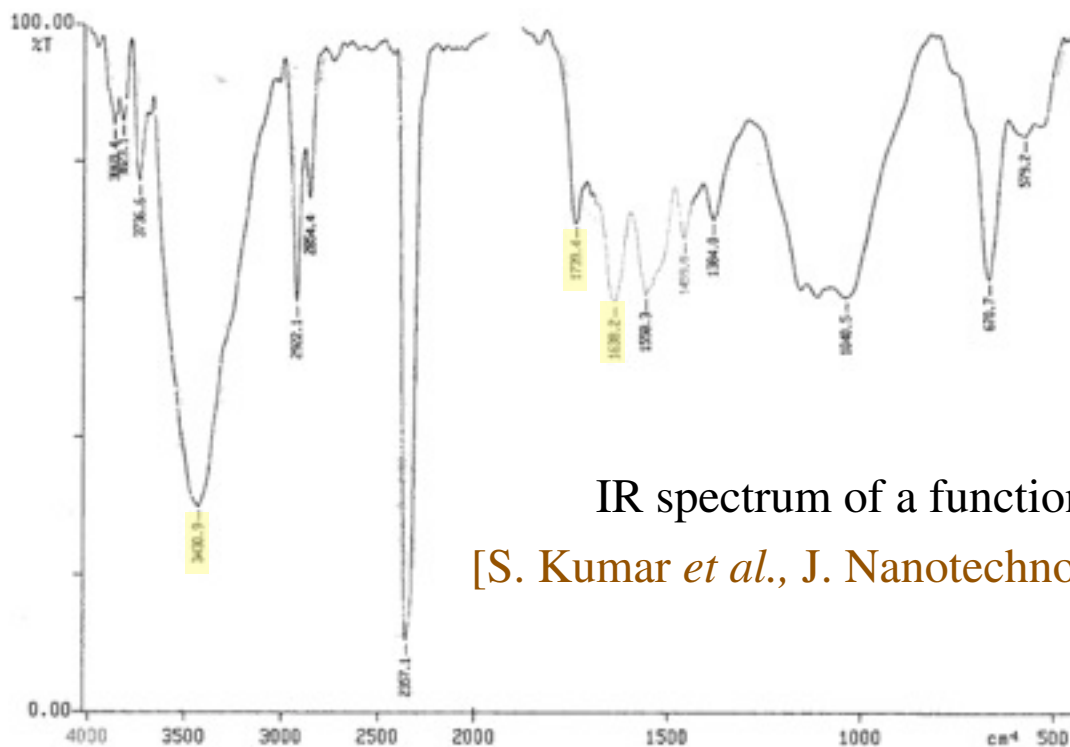
IR spectrum of a functionalized CNT

[S. Kumar *et al.*, J. Nanotechno. Onl., **112** (2006)]

Raman spectroscopy

- A sample is illuminated with a monochromatic light.
- The light interacts with some specific vibrational modes of the system, which fulfill selection rules (Raman-active modes).
- The energy of the laser photons (and hence, the frequency of the light) may be shifted up or down.
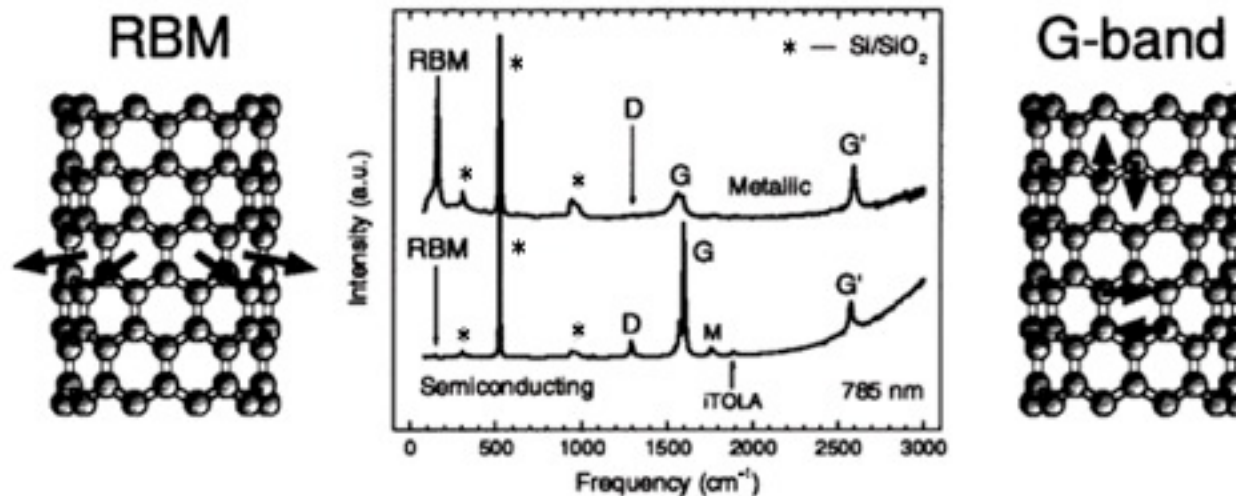
Raman spectrum of CNTs

[M. Dresselhaus *et al.,* An. Acad. Bras. Ciênc. **78**, 423 (2006)]

Born-Oppenheimer approximation

- Quantum treatment for electrons → **Kohn-Sham equation**

$$E_{el}[n] = \sum_v \langle \psi_v | T + V_{ext} | \psi_v \rangle + E_{Hxc}[n]$$
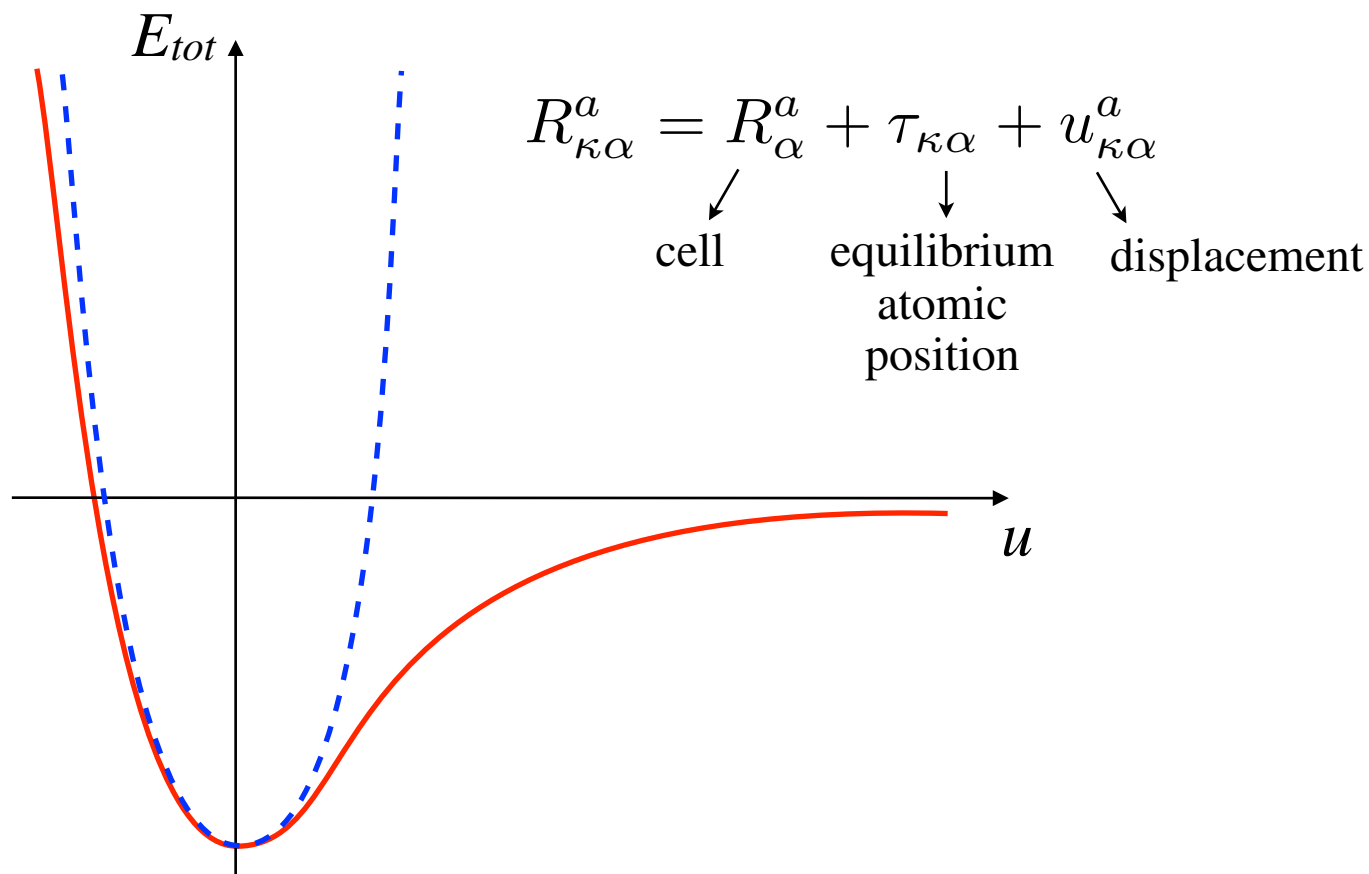
$$n(\mathbf{r}) = \sum_v \psi_v^*(\mathbf{r})\psi_v(\mathbf{r})$$

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_{Hxc}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- Classical treatment for nuclei → **Newton equation**

unit cell

$$F_{\kappa\alpha}^a = -\left.\frac{\partial E_{tot}}{\partial R_{\kappa\alpha}^a}\right|_{\{\mathbf{R}\}} = M_\kappa \frac{d^2 R_{\kappa\alpha}^a}{dt^2}$$

atom   direction
(α=1,2,3)

$$E_{tot} = E_{ion} + E_{el}$$

Harmonic approximation

$$R^a_{\kappa\alpha} = R^a_\alpha + \tau_{\kappa\alpha} + u^a_{\kappa\alpha}$$

cell   equilibrium atomic position   displacement

$$E_{tot}\left(\{\mathbf{u}\}\right) = E^{(0)}_{tot} + \sum_{a\kappa\alpha}\sum_{a'\kappa'\alpha'} \frac{1}{2}\left(\frac{\partial^2 E_{tot}}{\partial u^a_{\kappa\alpha}\partial u^{a'}_{\kappa'\alpha'}}\right) u^a_{\kappa\alpha} u^{a'}_{\kappa'\alpha'}$$

Phonons

- The matrix of **interatomic force constants** (IFCs) is defined as

$$C_{\kappa\alpha,\kappa'\alpha'}(a, a') = \left(\frac{\partial^2 E_{tot}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\alpha'}^{a'}} \right)$$

- Its Fourier transform (using translational invariance)

$$\tilde{C}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) = \sum_{a'} C_{\kappa\alpha,\kappa'\alpha'}(0, a') e^{i\mathbf{q}\cdot\mathbf{R}_{\mathbf{a'}}}$$

allows one to compute phonon frequencies and eigenvectors as solutions of the following **generalized eigenvalue problem**:

$$\sum_{\kappa'\alpha'} \tilde{C}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) U_{m\mathbf{q}}(\kappa'\alpha') = M_\kappa \omega_{m\mathbf{q}}^2 U_{m\mathbf{q}}(\kappa\alpha)$$
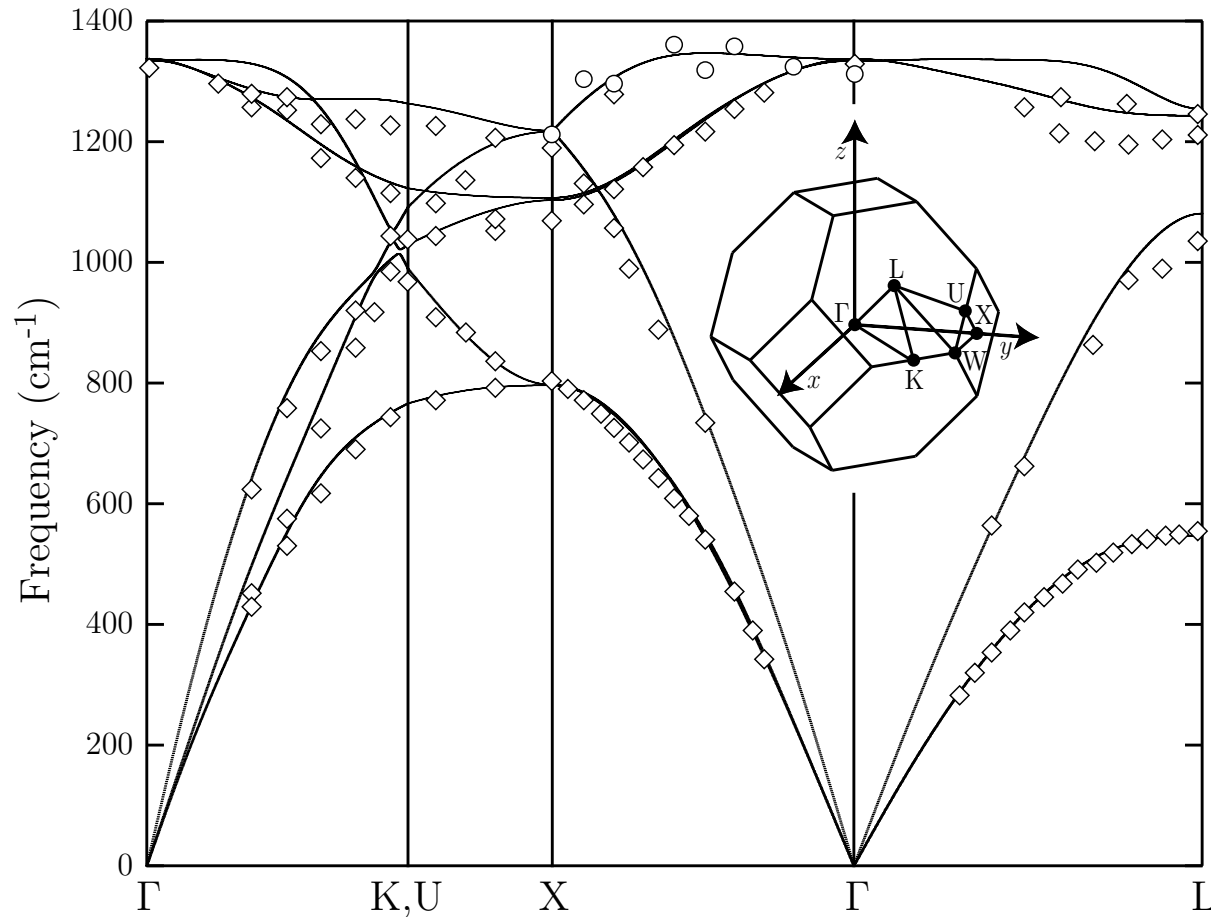
phonon displacement pattern   masses   square of phonon frequencies

Example: Diamond

Theory vs. Experiment

[X. Gonze, GMR, and R. Caracas, Z. Kristallogr. **220**, 458 (2000)]

Density-functional perturbation theory

- For a perturbation characterized by a small parameter λ, all the quantities ($X=H$, E_{tot}, ε_i, ψ_i) are written as a perturbation series:

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \lambda^3 X^{(3)} + \cdots$$

$$\text{with } X^{(n)} = \frac{1}{n!} \left. \frac{d^n X}{d\lambda^n} \right|_{\lambda=0}$$

- <u>Hypothesis:</u> $V_{ext}(\lambda) = V_{ext}^{(0)} + \lambda V_{ext}^{(1)} + \lambda^2 V_{ext}^{(2)} + \cdots$

  known at all orders, as well as $E_{tot}^{(0)}, \varepsilon_i^{(0)}, \psi_i^{(0)}, n^{(0)}$

First order derivatives

- **Hellman-Feynman theorem** → energy:

$$\varepsilon_i^{(1)} = \left\langle \psi_i^{(0)} \left| H^{(1)} \right| \psi_i^{(0)} \right\rangle$$

$$E_{el}^{(1)} = E_{el}^{(1)} \left\{ \psi_i^{(0)} \right\} \quad \text{(non-variational)}$$

- **Sternheimer equation** → wavefunctions:

$$\left(H^{(0)} - \varepsilon_i^{(0)} \right) \left| \psi_i^{(1)} \right\rangle = - \left(H^{(1)} - \varepsilon_i^{(1)} \right) \left| \psi_i^{(0)} \right\rangle$$

$$\left| \psi_i^{(1)} \right\rangle = \sum_{j \neq i} \left| \psi_j^{(0)} \right\rangle \frac{1}{\varepsilon_i - \varepsilon_j} \left\langle \psi_j^{(0)} \left| H^{(1)} \right| \psi_i^{(0)} \right\rangle$$

$$P_c \left(H^{(0)} - \varepsilon_i^{(0)} \right) P_c \left| \psi_i^{(1)} \right\rangle = - P_c H^{(1)} \left| \psi_i^{(0)} \right\rangle$$

where P_c is the projector upon the conductions bands

Second and third order derivatives

- Only 1st order wavefunctions are needed to get 2nd order in energy

$$\varepsilon_i^{(2)} = \left\langle \psi_i^{(0)} \left| H^{(2)} \right| \psi_i^{(0)} \right\rangle$$

$$+ \frac{1}{2} \left(\left\langle \psi_i^{(1)} \left| H^{(1)} \right| \psi_i^{(0)} \right\rangle + \left\langle \psi_i^{(0)} \left| H^{(1)} \right| \psi_i^{(1)} \right\rangle \right)$$

$$E_{el}^{(2)} = E_{el}^{(2)} \left\{ \psi_i^{(0)}; \psi_i^{(1)} \right\} \quad \text{(variational with respect to } \psi_i^{(1)})$$

- Actually, 1st order wavefunctions suffice to get 3rd order energy

$$\varepsilon_i^{(3)} = \left\langle \psi_i^{(0)} \left| H^{(3)} \right| \psi_i^{(0)} \right\rangle + \left\langle \psi_i^{(1)} \left| H^{(2)} \right| \psi_i^{(0)} \right\rangle$$

$$+ \left\langle \psi_i^{(0)} \left| H^{(2)} \right| \psi_i^{(1)} \right\rangle + \left\langle \psi_i^{(0)} \left| H^{(1)} - \varepsilon_i^{(1)} \right| \psi_i^{(1)} \right\rangle$$

$$E_{el}^{(3)} = E_{el}^{(3)} \left\{ \psi_i^{(0)}; \psi_i^{(1)} \right\} \quad \text{(non-variational)}$$

Higher order and mixed derivatives

- More generally, the nth order wavefunctions give access to the $(2n)^{\text{th}}$ and $(2n+1)^{\text{th}}$ order energy [**"2n+1" theorem**]

$$E_{el}\left\{\psi_{trial} + O(\eta)\right\} = E_{el}\left\{\psi_{trial}\right\} + O(\eta^2)$$

- Similar expressions for mixed derivatives (related to two different perturbations j1 and j2):

$$E_{el}^{j_1 j_2} = E_{el}^{j_1 j_2}\left\{\psi_i^{(0)}; \psi_i^{j_1}; \psi_i^{j_2}\right\}$$

- The extremal principle is lost but the expression is stationary:
  - ★ the error is proportional to the product of errors made in the 1st order quantities for the first and second perturbations;
  - ★ if these errors are small, their product will be much smaller;
  - ★ however, the sign of the error is undetermined, unlike for the variational expressions.

Types of perturbation

- Possible perturbations include: atomic displacements, expansion or contraction of the primitive cell, homogeneous external field (electric or magnetic), alchemical change, ...

- Related derivatives of the total energy ($E_{el} + E_{ion}$)
  - ★ 1st order: forces, stress, dipole moment, ...
  - ★ 2nd order: dynamical matrix, elastic constants, dielectric susceptibility, Born effective charge tensors, piezoelectricity, internal strains
  - ★ 3rd order: non-linear dielectric susceptibility, phonon-phonon interaction, Grüneisen parameters, ...

- Further properties can be obtained by integration over phononic degrees of freedom (e.g., entropy, thermal expansion, ...)

Electronic dielectric permittivity tensor

- The **dielectric permittivity tensor** is the coefficient of proportionality between the macroscopic displacement field and the macroscopic electric field, in the linear regime:

$$\mathcal{D}_{\text{mac},\alpha} = \sum_{\alpha'} \epsilon_{\alpha\alpha'} \mathcal{E}_{\text{mac},\alpha'}$$

$$\epsilon_{\alpha\alpha'} = \frac{\partial \mathcal{D}_{\text{mac},\alpha}}{\partial \mathcal{E}_{\text{mac},\alpha'}} = \delta_{\alpha\alpha'} + 4\pi \frac{\partial \mathcal{P}_{\text{mac},\alpha}}{\partial \mathcal{E}_{\text{mac},\alpha'}}$$

- At high frequencies of the applied field, the dielectric permittivity tensor only includes a contribution from the electronic polarization:

$$\epsilon_{\alpha\alpha'}^{\infty} = \delta_{\alpha\alpha'} - \frac{4\pi}{\Omega_0} 2 E_{el}^{\mathcal{E}_\alpha^* \mathcal{E}_{\alpha'}}$$

$$\sum_{\alpha\alpha'} \hat{q}_\alpha \epsilon_{\alpha\alpha'}^{\infty} \hat{q}'_\alpha = \frac{1}{\epsilon_{\mathbf{G}=0,\mathbf{G}'=0}^{-1}(\mathbf{q} \to 0)}$$

$\downarrow$
unit vector

Born effective charge tensor

- It is defined as the proportionality coefficient relating at linear order, the polarization per unit cell, created along the direction α, and the displacement along the direction α' of the atoms belonging to the sublattice κ:

$$Z^*_{\kappa\alpha\alpha'} = \Omega_0 \left. \frac{\partial \mathcal{P}_{\mathrm{mac},\alpha}}{\partial u_{\kappa\alpha'}(\mathbf{q}=0)} \right|_{\mathcal{E}_\alpha=0} = \left. \frac{\partial F_{\kappa\alpha'}}{\partial \mathcal{E}_\alpha} \right|_{u_{\kappa\alpha'}=0}$$

- It also describes the linear relation between the force in the direction α' on an atom κ and the macroscopic electric field
- Both can be connected to the mixed 2nd order derivative of the energy with respect to $u_{\kappa\alpha'}$ and $\mathcal{E}_\alpha$
- <u>Sum rule:</u> $\sum_\kappa Z^*_{\kappa\alpha\alpha'} = 0$

Static dielectric permittivity tensor

- The **mode oscillator strength tensor** is defined as

$$S_{m,\alpha\alpha'} = \left(\sum_{\kappa\beta} Z^*_{\kappa\alpha\beta} U^*_{m\mathbf{q}=0}(\kappa\beta) \right) \left(\sum_{\kappa\beta'} Z^*_{\kappa\alpha'\beta'} U_{m\mathbf{q}=0}(\kappa\beta') \right)$$

- The macroscopic **static** (low-frequency) **dielectric permittivity tensor** is calculated by adding the ionic contribution to the electronic dielectric permittivity tensor:

$$\epsilon_{\alpha\alpha'}(\omega) = \epsilon^\infty_{\alpha\alpha'} + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\alpha'}}{\omega_m^2 - \omega^2}$$

$$\epsilon^0_{\alpha\alpha'} = \epsilon^\infty_{\alpha\alpha'} + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\alpha'}}{\omega_m^2}$$

LO-TO splitting

- The macroscopic electric field that accompanies the collective atomic displacements at $\mathbf{q} \to 0$ can be treated separately:

$$\tilde{C}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q} \to 0) = \tilde{C}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q} = 0) + \tilde{C}^{\mathrm{NA}}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q} \to 0)$$

where the nonanalytical, direction-dependent term is:

$$\tilde{C}^{\mathrm{NA}}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q} \to 0) = \frac{4\pi}{\Omega_0} \frac{\left(\sum_\beta q_\gamma Z^*_{\kappa\beta\alpha}\right)\left(\sum'_\beta q'_\beta Z^*_{\kappa'\beta'\alpha'}\right)}{\sum_{\beta\beta'} q_\beta \epsilon^\infty_{\beta\beta'} q'_\beta}$$

- The transverse modes are common to both $\tilde{C}$ matrices but the longitudinal ones may be different, the frequencies are related by

$$\omega^2_m(\mathbf{q} \to 0) = \omega^2_m(\mathbf{q} = 0) + \frac{4\pi}{\Omega_0} \frac{\sum_{\alpha\alpha'} q_\alpha S_{m,\alpha\alpha'} q'_\alpha}{\sum_{\alpha\alpha'} q_\alpha \epsilon^\infty_{\alpha\alpha'} q'_\alpha}$$

- S. Baroni, P. Giannozzi & A. Testa, Phys. Rev. Lett. **58**, 1861 (1987)

- X. Gonze & J.-P. Vigneron, Phys. Rev. B **39**, 13120 (1989)

- X. Gonze, Phys. Rev. A **52** , 1096 (1995)

- S. de Gironcoli, Phys. Rev. B **51**, 6773 (1995)

- X. Gonze, Phys. Rev. B. **55**, 10337 (1997)

- X. Gonze & C. Lee, Phys. Rev. B. **55**, 10355 (1997)

- S. Baroni, S. de Gironcoli, A. Dal Corso, P. Giannozzi, Rev. Mod. Phys. 73, 515 (2001)
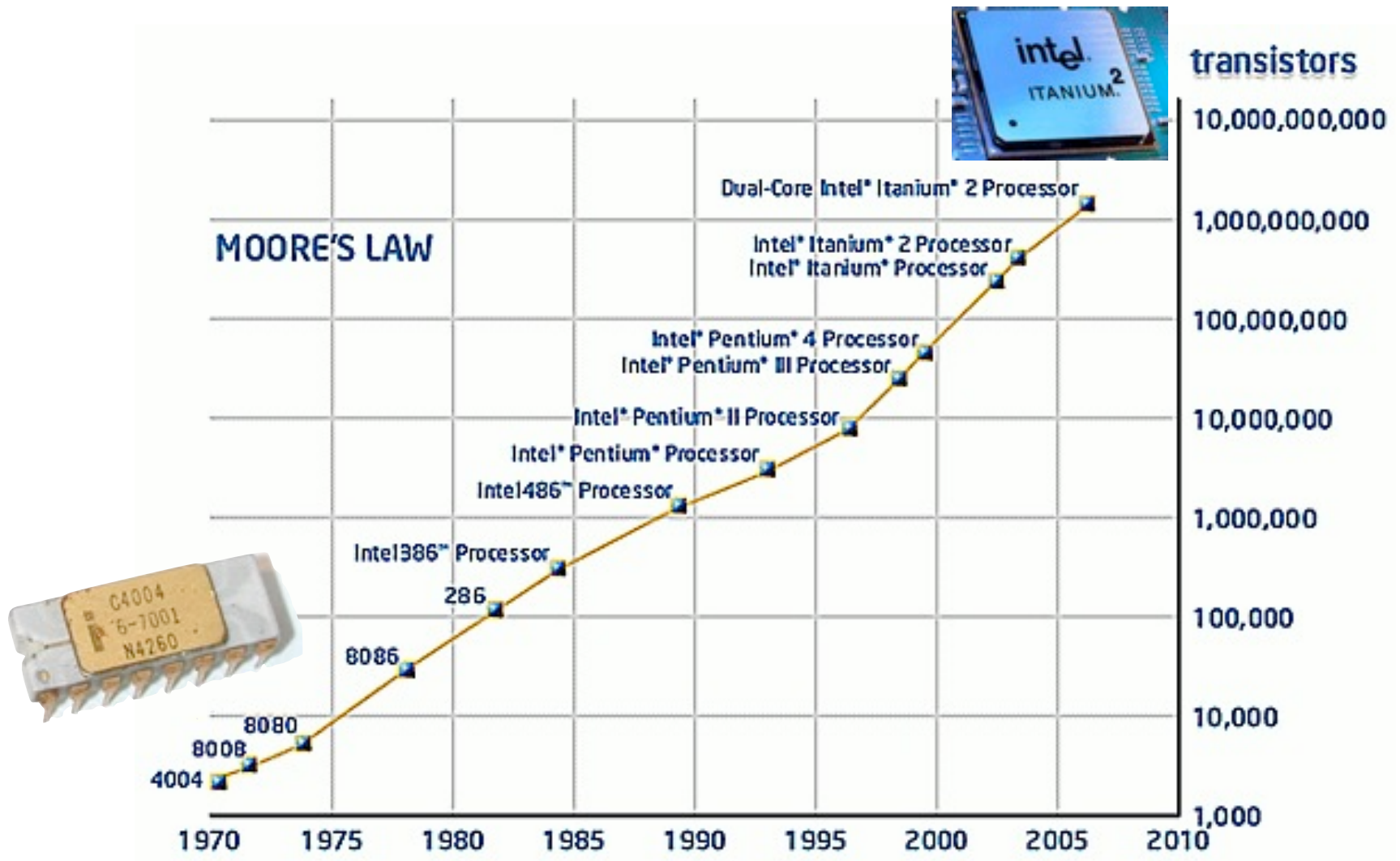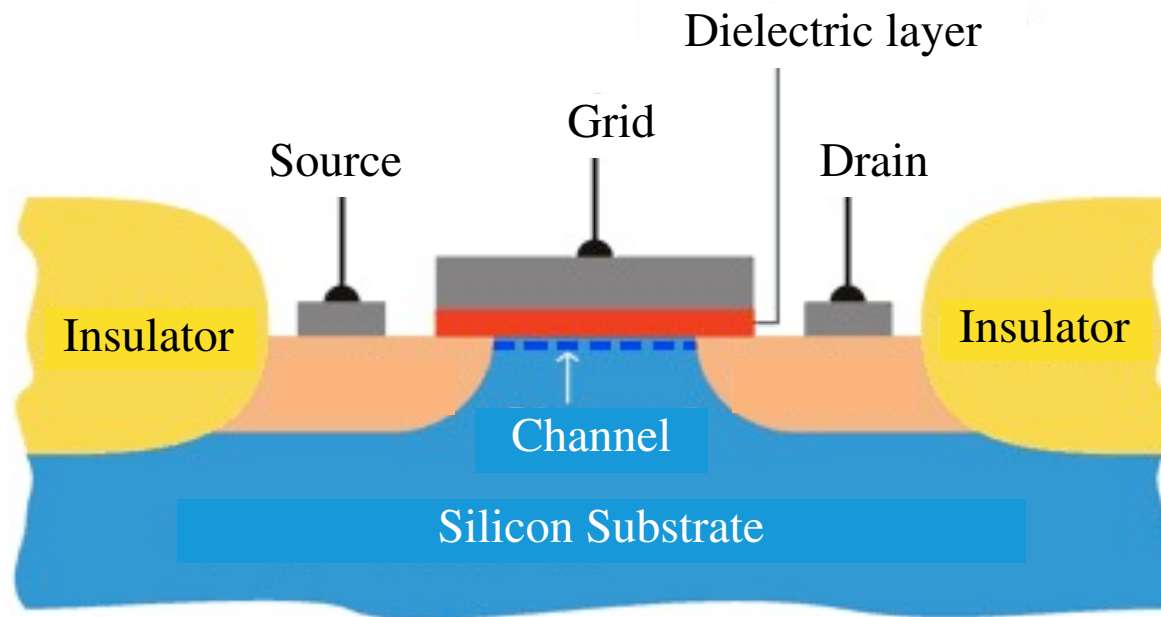
ETSF vibrational spectroscopy beamline
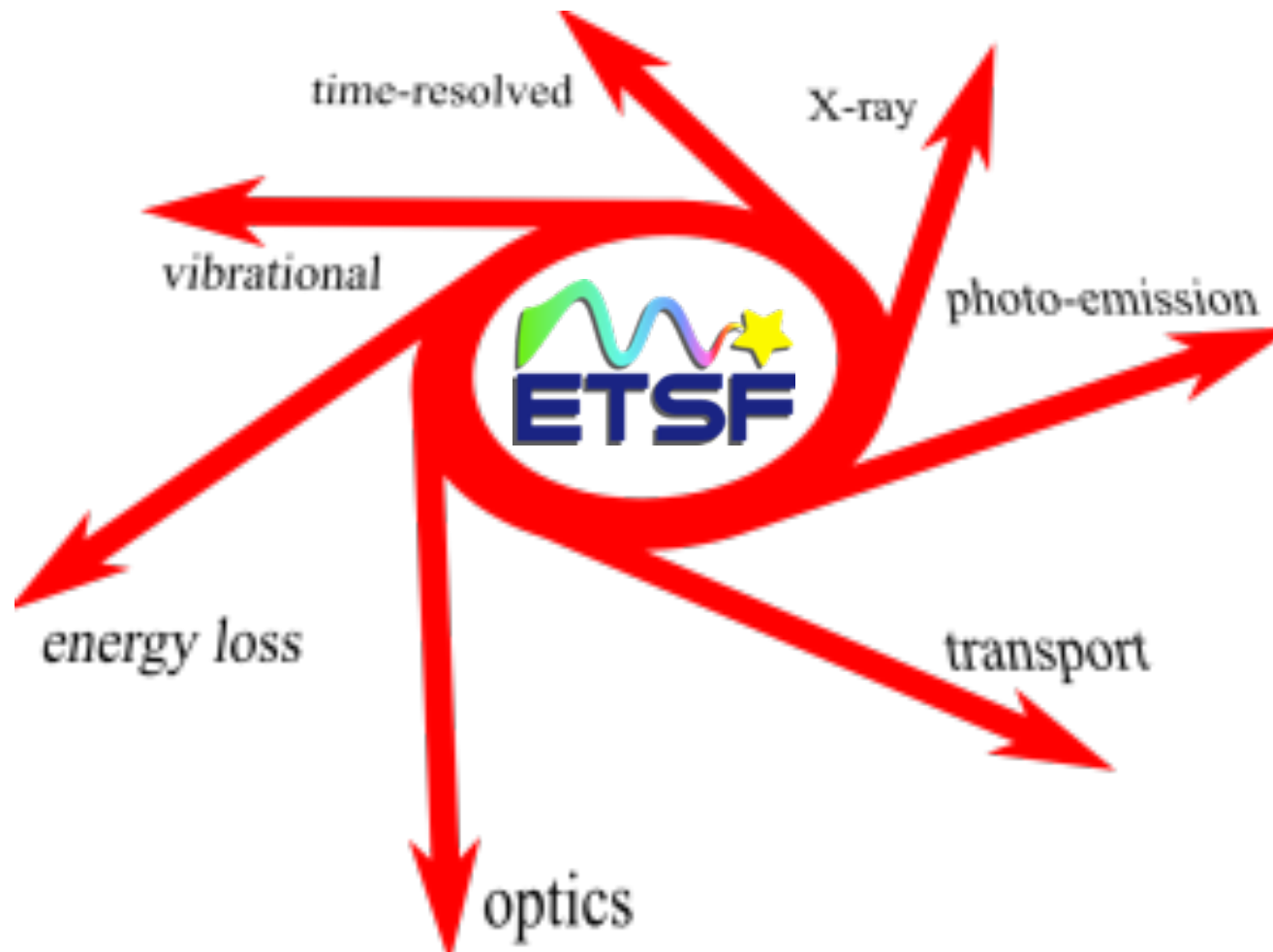
Quest for high-k materials

Moore's law

KITP programme on Excitations in Condensed Matter, Santa Barbara (CA), 20 November 2009

MOS transistor

Dielectric layer

Grid

Source

Drain

Insulator

Insulator

Channel

Silicon Substrate

	L (nm)	t (nm)
2000	100-150	1.5-2.0
2008	45	1.0
2015	25	0.5

$L \approx 40\text{-}50\ t$

The problem...

- SiO$_2$ is now reaching its limits:
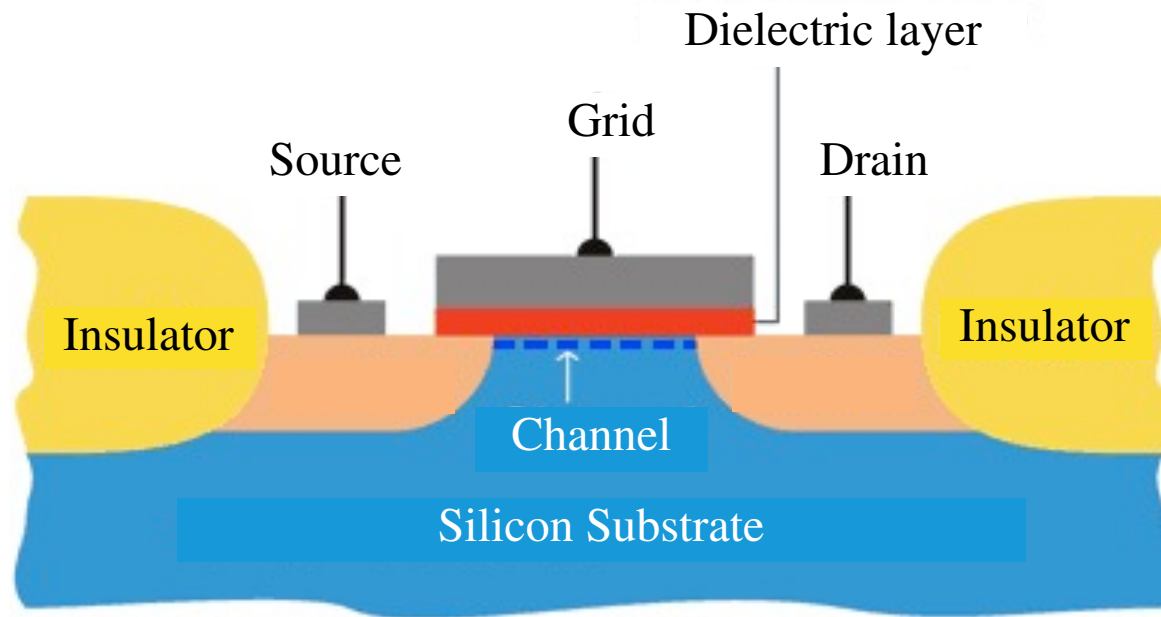
- ★ tunnel current through the grid oxide
- ★ degradation and rupture
- ★ penetration of dopants through the grid oxide
- ★ increased presence of defects

... and the solution

- Use dielectrics with high-permittivity (**high-κ**):

  for the same **equivalent thickness** (t_{eq}),

  the **physical thickness** (t) can be increased

  when the permittivity (κ) is higher

  ⇒ tunnel current decreases

$$C \propto \frac{\kappa}{t} \qquad t_{eq} = t\frac{\kappa_{ox}}{\kappa}$$

$\kappa \approx 4$

$t=20\text{Å}$

$\kappa \approx 8$

$t=40\text{Å}$

$\kappa \approx 20$

$t=100\text{Å}$

SiO$_2$ (3.9)　　　Si$_3$N$_4$ (7), Al$_2$O$_3$ (9)　　　Y$_2$O$_3$ (15), Hf/ZrO$_2$ (25)
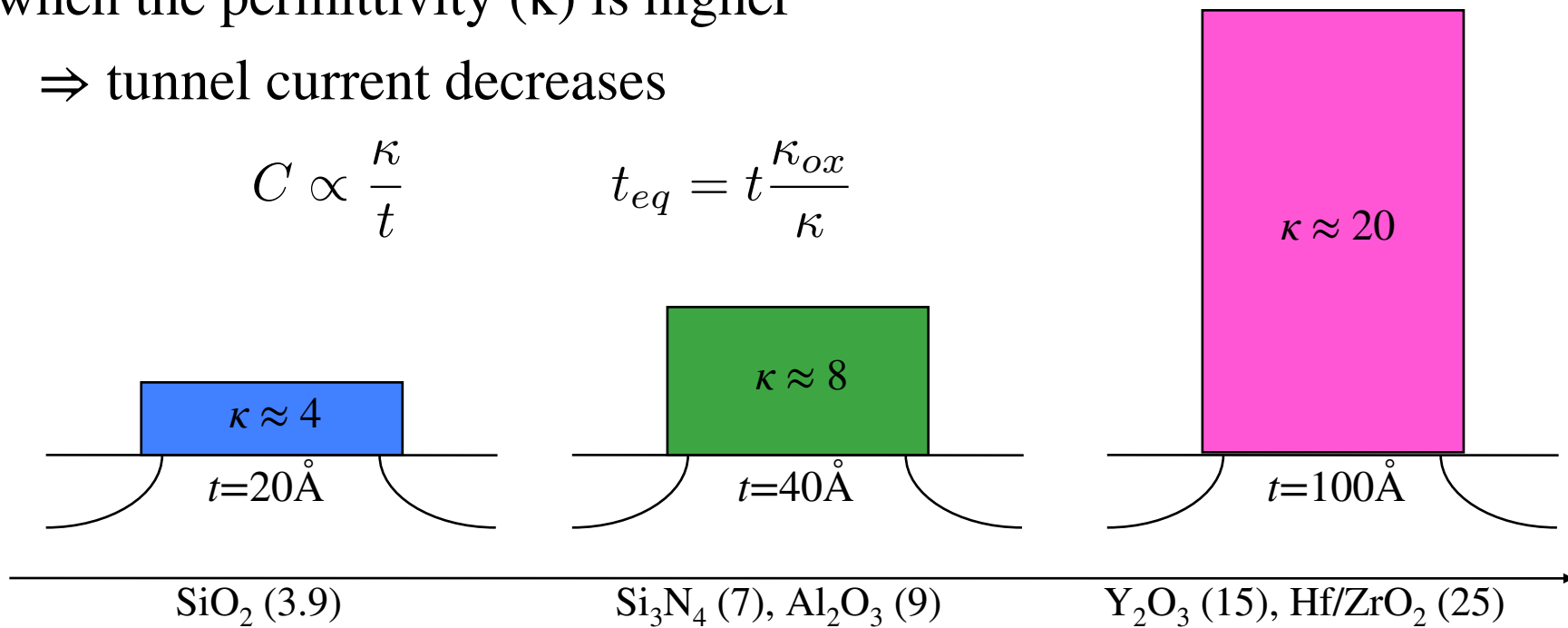
Not such a simple change...
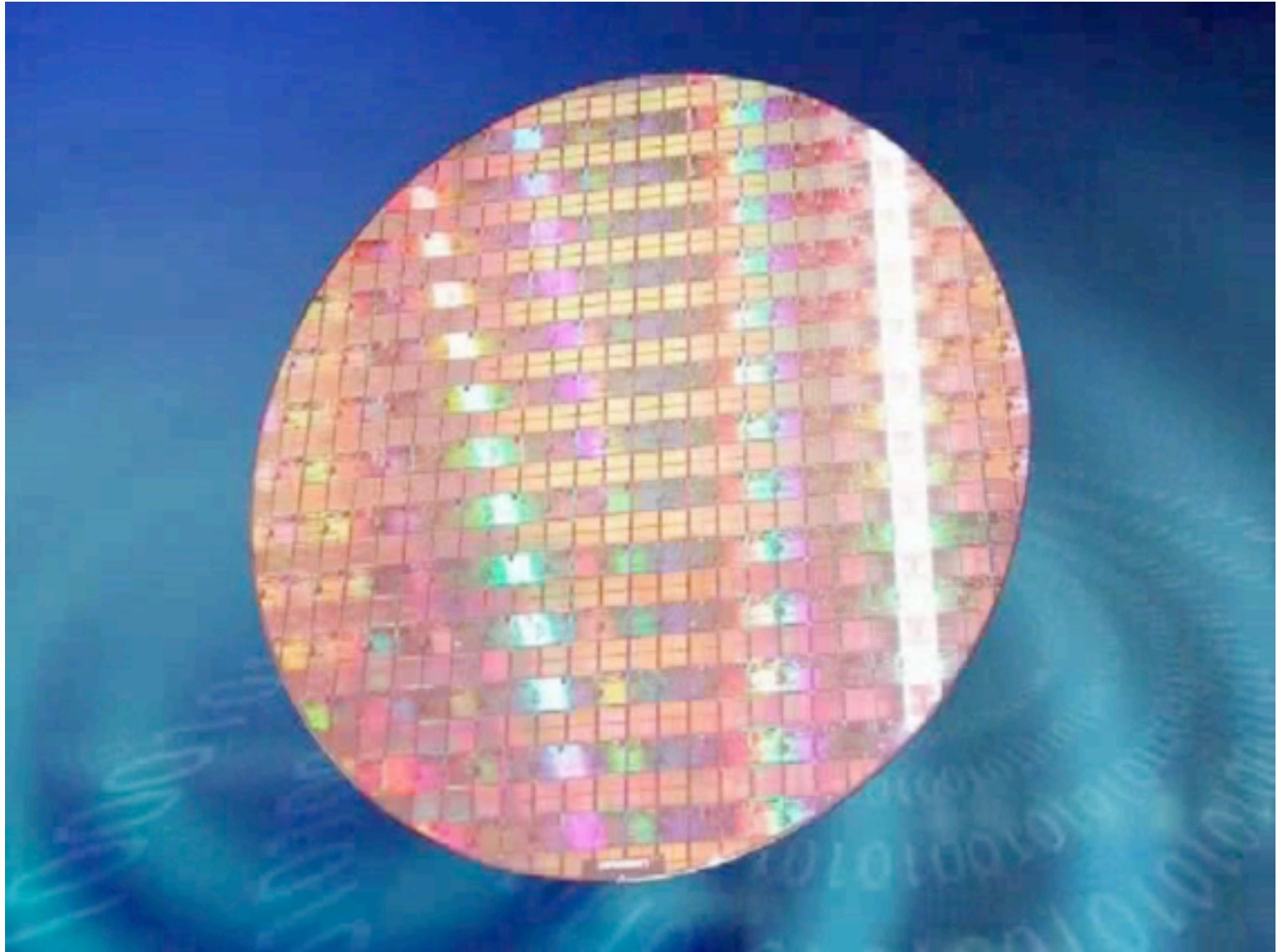
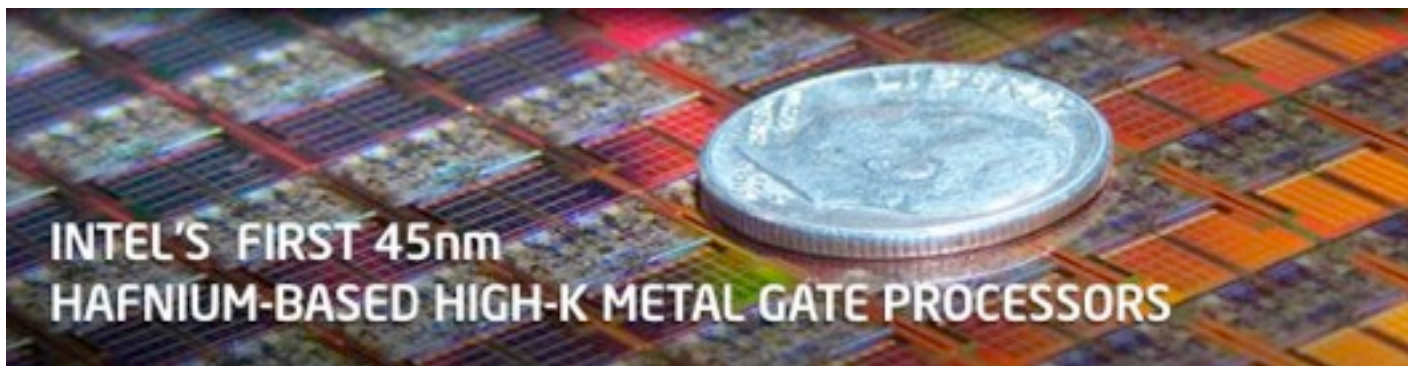# The most promising candidates

- Group IVb oxides and silicates:

  $(MO_2)_x(SiO_2)_{1-x}$ with M=(Hf, Zr, Ti)

  ★ amorphous compounds **stable** in contact with the Si substrate
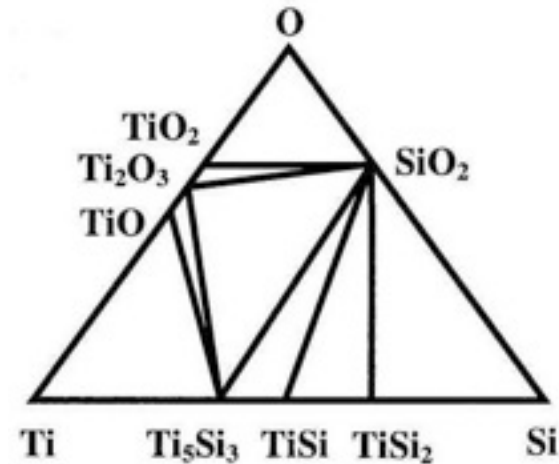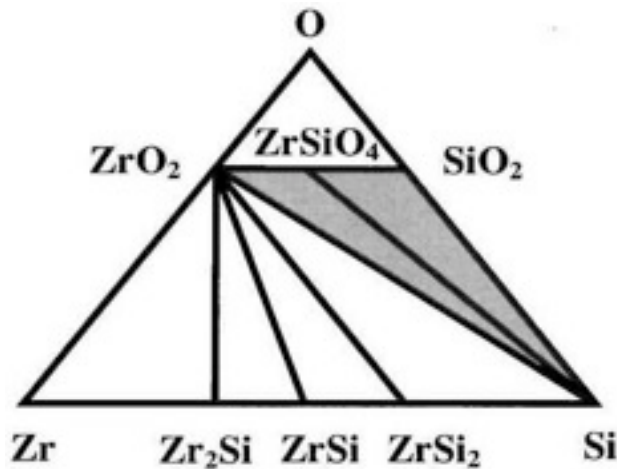
 ★ ϵ_0 can be **modulated** with the quantity of M=(Hf, Zr, Ti) incorporated

The most promising candidates

INTEL'S FIRST 45nm
HAFNIUM-BASED HIGH-K METAL GATE PROCESSORS

Metal

High-k

SiGe   SiGe

Silicon

intel
Core™2 Extreme
quad-core
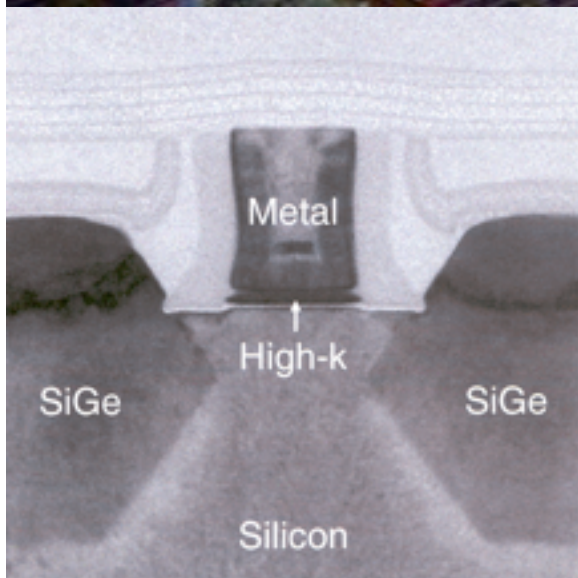
30 Million transistors fit on the head of a pin. Using an entirely new transistor formula, the processor incorporate 410 million transistors for each dual core chip, and 820 million for each quad core chip.
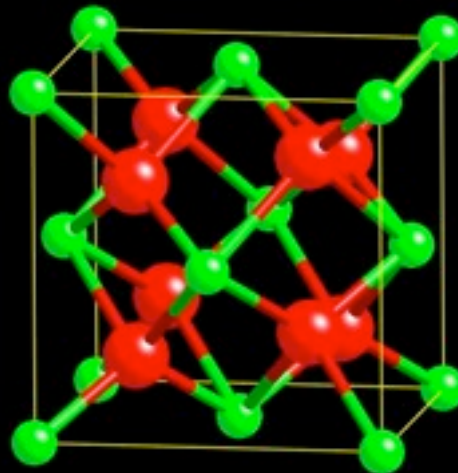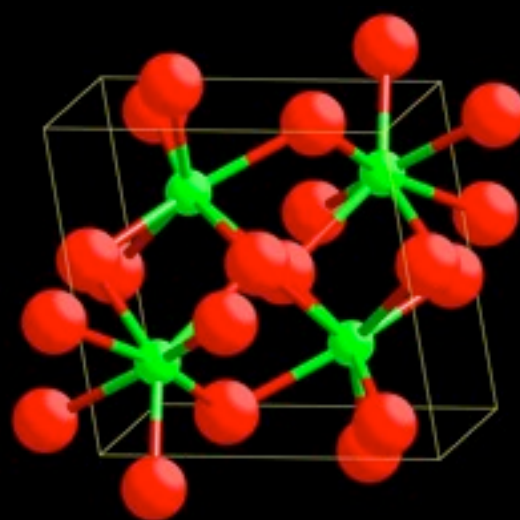
Crystalline oxides and silicates

c-MO$_2$ (cubic)   **t-MO$_2$ (tetragonal)**   **m-MO$_2$ (monoclinic)**
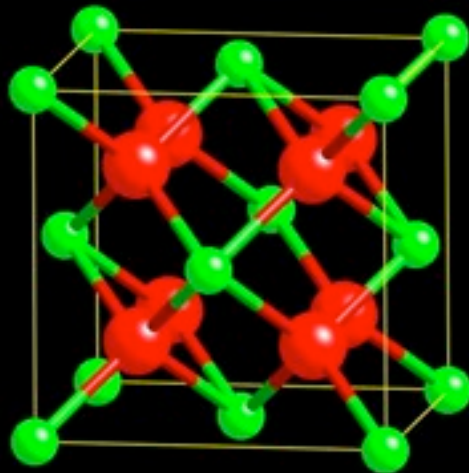
c-MO$_2$ (cubic)	t-MO$_2$ (tetragonal)	m-MO$_2$ (monoclinic)
• Space group Fm$\bar{3}$m (fluorite)	• Space group P4$_2$/nmc	• Space group I4$_1$/amd (baddeleyite)
• 1 formula unit of MO$_2$	• 2 formula unit of MO$_2$	• 4 formula unit of MO$_2$
• M 8-fold coordinated	• M 8-fold coordinated	• M 7-fold coordinated
• O 4-fold coordinated	• O 4-fold coordinated	• O 4-fold coordinated
		• O 3-fold coordinated

Crystalline oxides and silicates

o1-MO$_2$ **o2-MO$_2$**   **MSiO$_4$**

(orthorhombic)
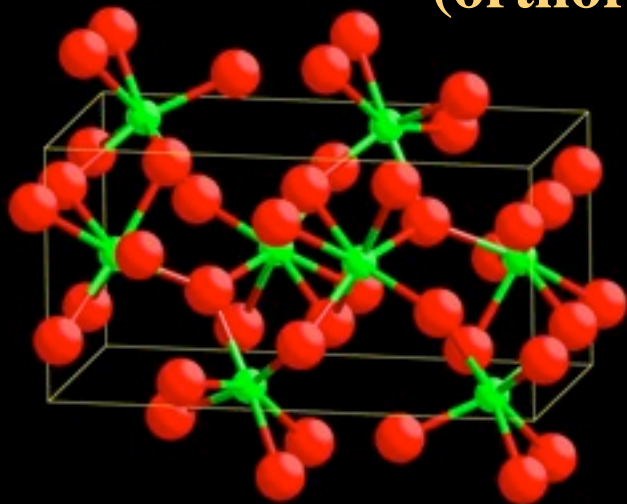
- Space group Pbca
- 8 formula unit of MO$_2$
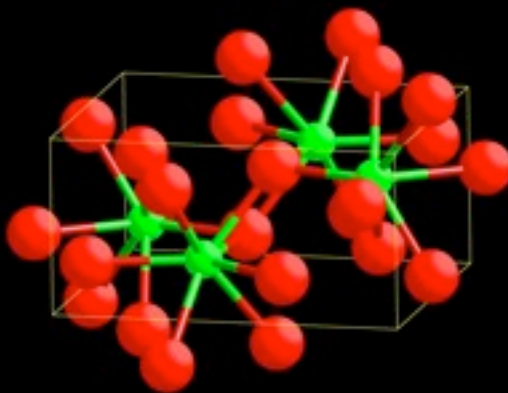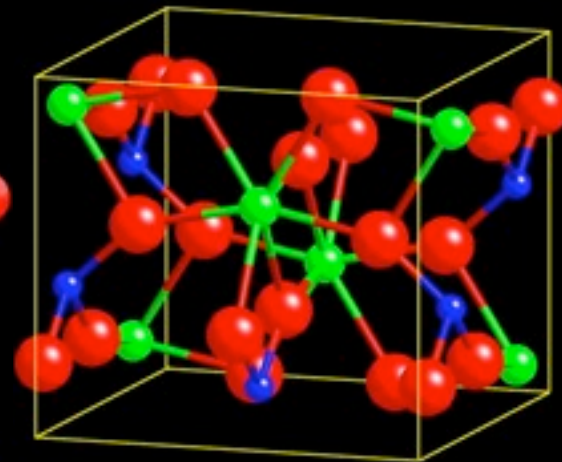- M 7-fold coordinated
- O 4-fold coordinated
- O 3-fold coordinated

- Space group Pnma (cotunnite)
- 4 formula unit of MO$_2$
- M 9-fold coordinated
- O 4-fold coordinated
- O 5-fold coordinated

- Space group I4$_1$/amd (zircon)
- 4 formula unit of MSiO$_4$
- M 8-fold coordinated
- Si 4-fold coordinated
- O 3-fold coordinated

Comparison with experiments

		$\parallel$		$\perp$	
		ϵ^∞	ϵ^0	ϵ^∞	ϵ^0
t-MO$_2$	Hf	5.1	20.0 (16-20)	5.4	32.8 (16-20)
	Zr	5.3 (5)	20.3 (35-40)	5.7 (5)	48.1 (35-40)
MSiO$_4$	Hf	4.1	10.7 (11-25)	3.9	10.6 (11-25)
	Zr	4.3 (4)	11.5 (11)	4.1 (4)	12.0 (11)

- ϵ^∞ is overestimated by 10-15% due to the well-known band-gap problem of DFT-LDA
- ϵ^0 is overestimated because the Born effective charges are overemphasized by DFT-LDA

[A. Filipetti & N.A. Spaldin, PRB **68**, 045111 (2003)]

... and with other theoretical works

		c-MO$_2$	t-MO$_2$			m-MO$_2$				
			$\parallel$	$\perp$	avg.	xx	yy	zz	xz	avg.
ϵ^∞	Hf	5.37	5.13	5.39	5.30	5.10	5.12	4.80	0.18	5.30
	Zr	5.74	5.28	5.74	5.59	5.41	5.49	5.05	0.20	5.59
ϵ^0	Hf	26.2	20.0	32.8	28.5	18.9	17.1	14.0	0.88	16.7
	Zr	33.6	20.3	48.1	38.9	21.6	19.8	15.5	1.11	19.0
$\Delta\epsilon$	Hf	20.8	14.9	27.4	23.2	13.8	12.0	9.15	0.70	11.4
	Ref. [1]	23.9	10.7	92.3	65.1	13.1	10.8	7.53	1.82	10.5
	Zr	27.9	15.0	42.4	33.3	16.2	14.3	10.5	0.91	13.4
	Ref. [2]	31.8	14.9	41.6	32.7	16.7	15.6	11.7	0.98	14.7

[1. X. Zhao & D. Vanderbilt, PRB **65**, 233106 (2002)]

[2. X. Zhao & D. Vanderbilt, PRB **65**, 075105 (2002)]

tend to be larger than the LDA results by $\sim 18\%$.) When compared with ZrO$_2$, the off-diagonal elements of $\epsilon^{\text{latt}}_{\text{mono}}$ are roughly doubled, while the diagonal elements become smaller. Most surprisingly, the x-y components of $\epsilon^{\text{latt}}_{\text{tetra}}$ become more than twice as large as for ZrO$_2$, while the z component decreases by $\sim 28\%$. We find the isotropic $\epsilon^{\text{latt}}_{\text{cubic}}$ to be 23.9, somewhat smaller than the value of 31.8 for ZrO$_2$.[4]

Crystalline alloys Hf$_x$ Zr$_{1-x}$ O$_2$

- Experimental results:

## Hafnium zirconate gate dielectric for advanced gate stack applications

R. I. Hegde,[a)] D. H. Triyoso, S. B. Samavedam, and B. E. White, Jr.
Austin Silicon Technology Solutions (ASTS), Freescale Semiconductor Inc.,
3501 Ed Bluestein Boulevard, Austin, Texas 78721

HfO$_2$ and ZrO$_2$ have very similar physical and chemical properties.[28] They are completely miscible in the solid solution as shown in Fig. 1. Separating the two from each other can be difficult. The correlation between dielectric properties and lattice structures of HfO$_2$ and ZrO$_2$ has been studied through simulation.[29–31] Authors performed first-principles density functional theory calculations on all crystal phases of HfO$_2$ and ZrO$_2$, where it was reported that the dielectric response and band gap of the material are strongly phase dependent. The tetragonal phase for both HfO$_2$ and ZrO$_2$ has the highest dielectric constant ($k \sim 30-40$), while the monoclinic phase has the lowest dielectric constant ($k \sim 20$).
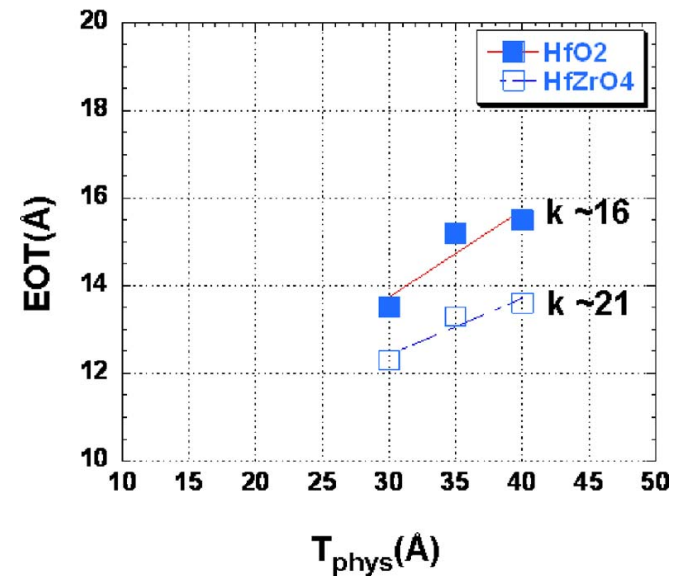
XRD for HfO$_2$
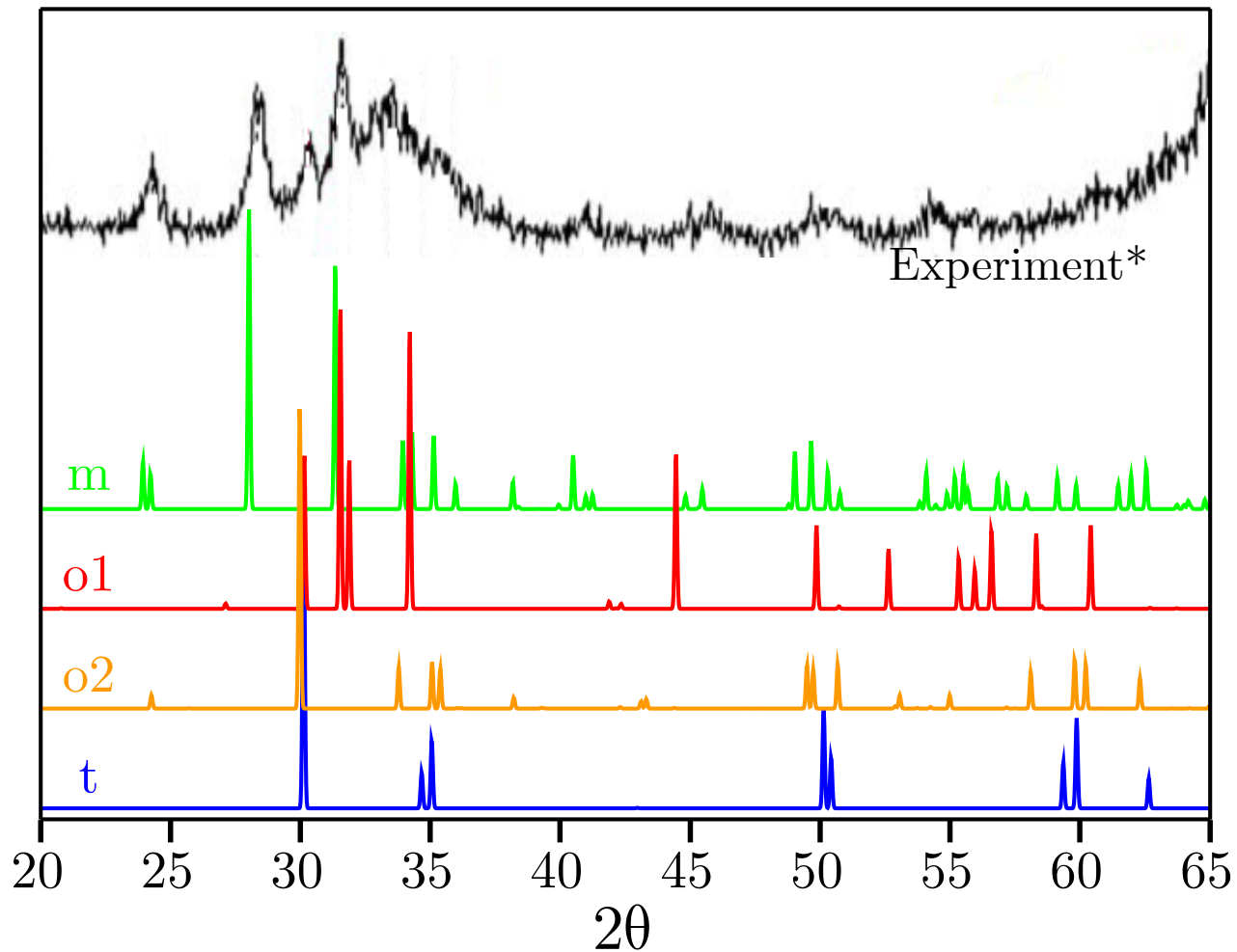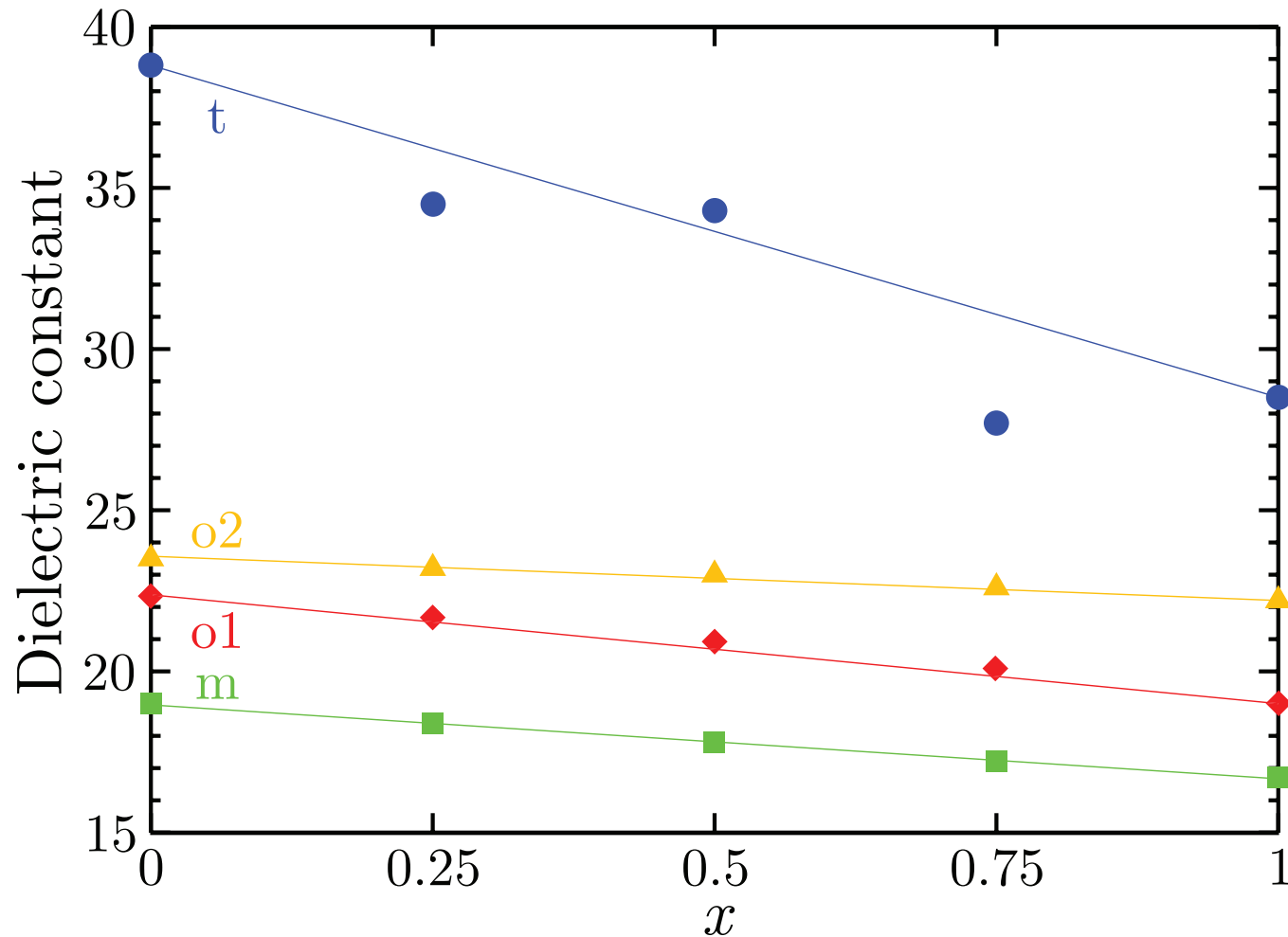

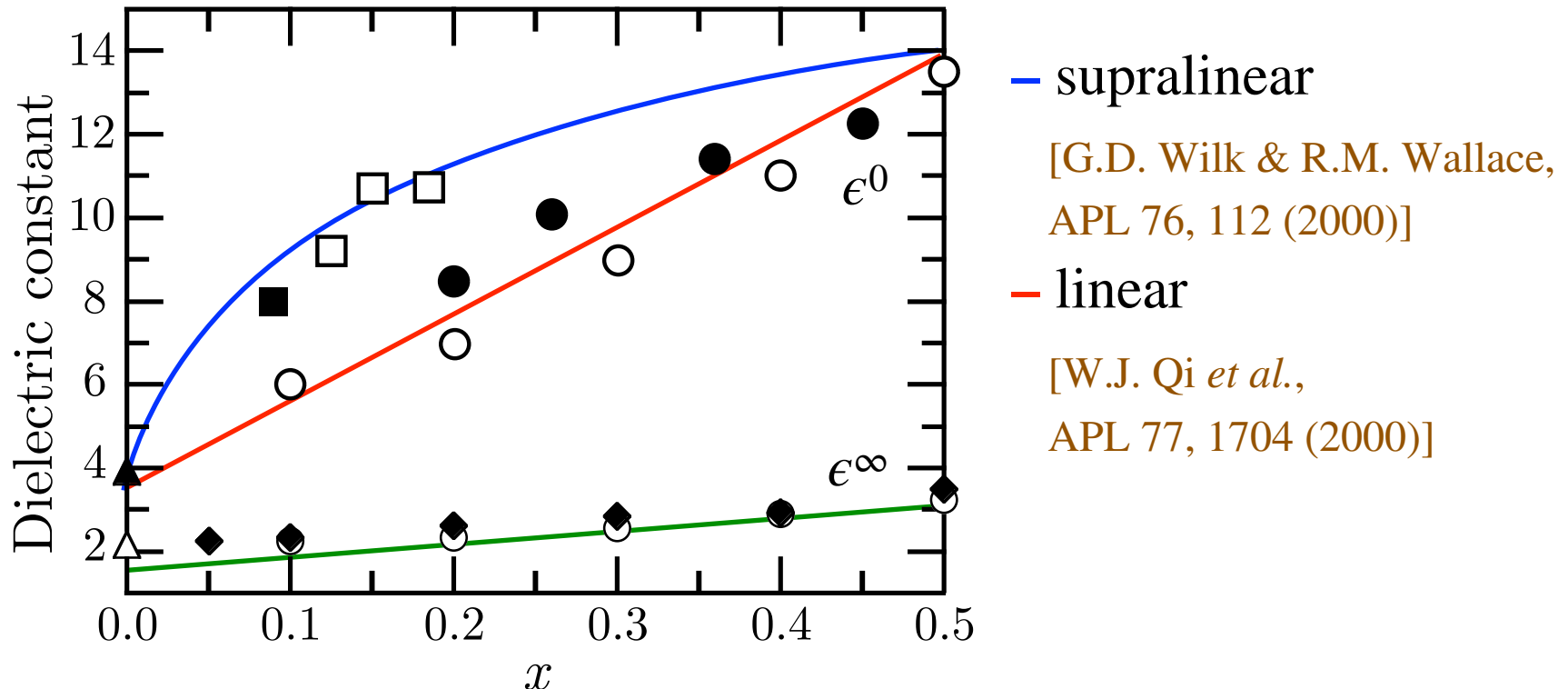[(*) from Triyoso *et al.*, J. Vac. Sci. Technol B **25**, 845 (2007)]

Crystalline alloys $Hf_x Zr_{1-x} O_2$

- Theoretical results

Amorphous silicates

- How does the dielectric constant ϵ^0 vary with the M=(Hf, Zr, Ti) concentration x in $M_x Si_{1-x} O_2$ amorphous silicates?

supralinear

[G.D. Wilk & R.M. Wallace, APL 76, 112 (2000)]

linear

[W.J. Qi *et al.*, APL 77, 1704 (2000)]

- How does the dielectric constant ϵ^0 depend on the underlying atomic structure?
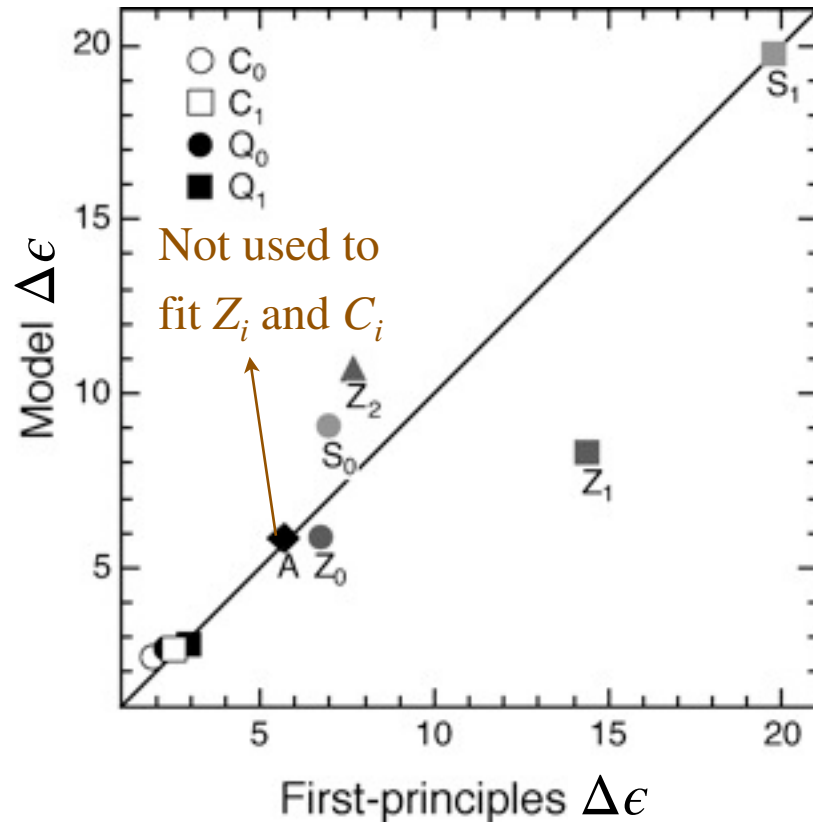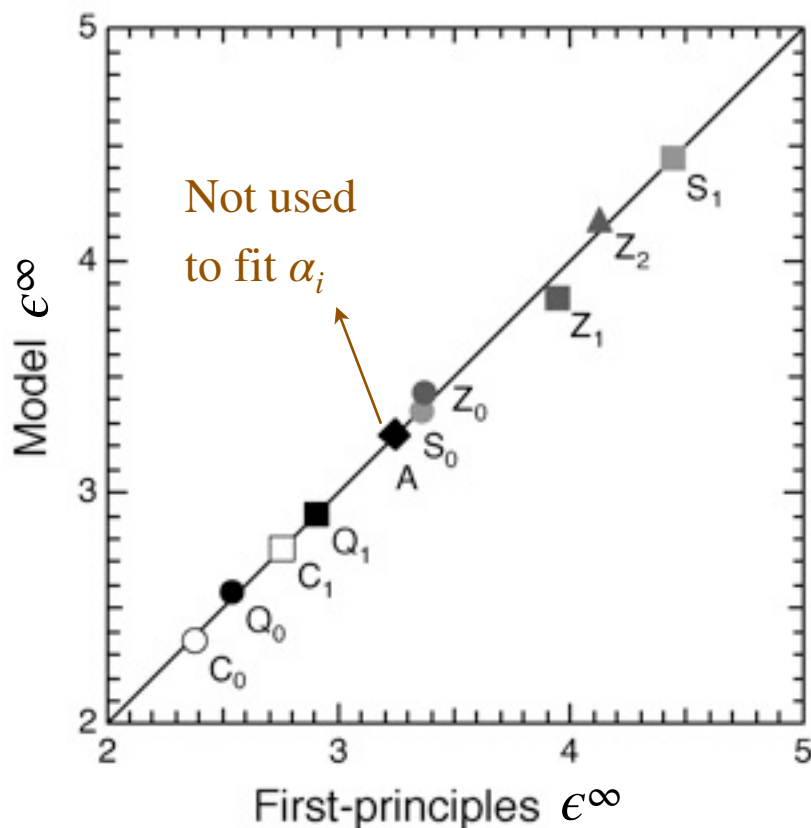
Coordination model (I)

- Calculations of optical (ϵ^∞) and static (ϵ^0) dielectric constants for a series of Zr silicates crystalline models

- **Microscopic scheme** relating ϵ to structural units (SUs) centered on Si and Zr atoms through characteristic parameters: a **polarizability** α, a **dynamical charge** Z, and a **force constant** C which depend on the **coordination** of the central atom (Si or Zr):

	SiO_4	SiO_6	ZrO_4	ZrO_6	ZrO_8
α	19.68	16.14	37.37	35.35	32.69
Z	4.29	4.92	5.66	7.16	6.73
C	0.360	0.218	0.420	0.082	0.115

★ α decreases with coordination (for Si and Zr)

★ no such regular trend for Z and C : ZrO_6 SUs max.

Coordination model (II)

- The model was validated by comparing the results of the model with those of first-principles calculations for the set of crystalline systems as well as for an amorphous model: ($\Delta\epsilon = \epsilon^0 - \epsilon^\infty$)

Comparison with experiments

- The dielectric constants ϵ^∞ and ϵ^0 can be estimated for Zr_xSi_{1-x} O_2 amorphous silicates (with x known) with some additional information about the cationic coordination:
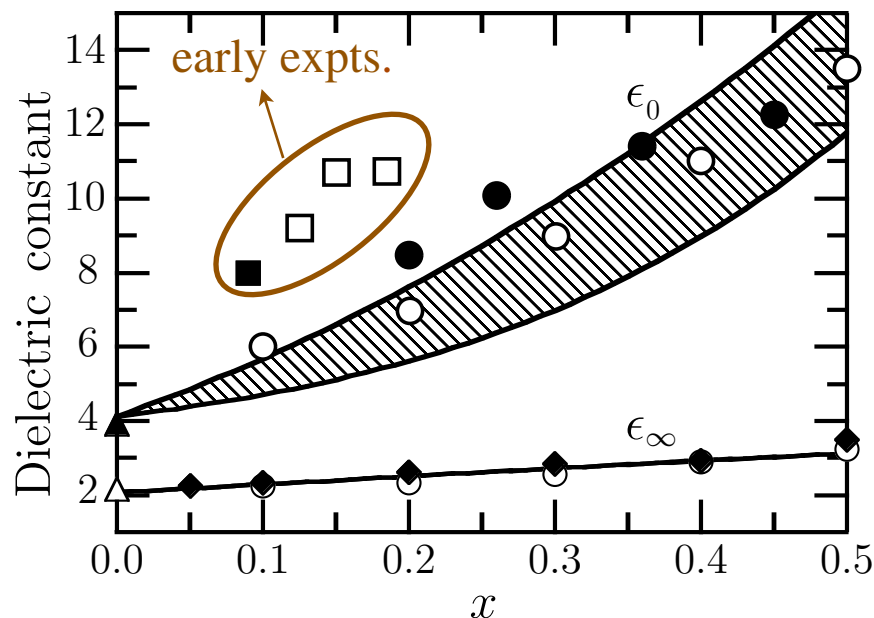
- Si atoms 4-fold like in SiO_2
- Zr atoms: quadratic distribution between ZrO_4, ZrO_6, ZrO_8

↪upper curve: only ZrO_6

↪lower curve: without ZrO_6

- For ϵ^∞ → excellent agreement with available experimental data
- For ϵ^0 → supra-linear behavior with a sufficient amount of ZrO_6 but limited effect compared to early experiments

...with other theoretical works

Anomalous Behavior of the Dielectric Constant of Hafnium Silicates: A First Principles Study

Carlo A. Pignedoli, Alessandro Curioni, and Wanda Andreoni[*]

IBM Research, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland
(Received 23 June 2006; published 18 January 2007)

We present an extensive *ab initio* study of the structural and dielectric properties of hafnium silicates $Hf_xSi_{1-x}O_2$ that accounts for the observed anomalous dependence on composition of the static dielectric constant in the entire x range. The results reveal that this complex behavior reflects that of the structural development with x, from silica to hafnia, and clarify how different growth processes can also lead to scattered sets of data. Several simple models proposed thus far to explain part of the experimental data are shown to be inadequate. It is argued that silicate layers with low hafnium content form at the HfO_2/Si interface and play a crucial role in preserving high electron mobility in the channel.

50 amorphous structures with 192-324 atoms

Our *ab initio* results allow us to evaluate the models proposed so far to account for the variation of the dielectric constant of ternary high-k dielectrics: (i) We have applied the CN-dependent model of Ref. [25], in which, in analogy with the electronic polarizability, also the lattice term was decomposed into local and additive contributions associated with the different CN units present in the alloy [33]. The effective charges Z^2 and the "inverse force constant" C^{-1} are written as sums over these units with weights given by their relative concentrations. Our calculations reveal that although the former approximation is a good one, the latter is not appropriate and leads to a significant overestimate of the dielectric constant [Fig. 3(a)] in the Hf-rich region. (ii) The important role of atomic CN discounts the
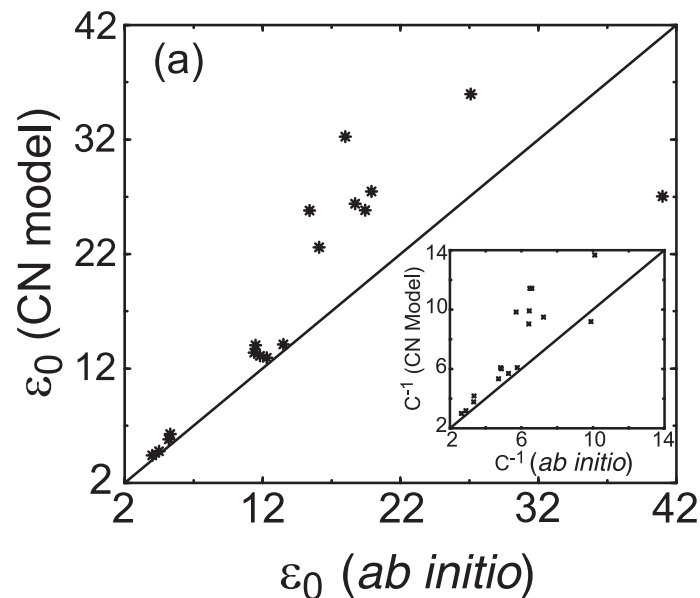
... and within group IVb

	HfO_6	ZrO_6	TiO_6	HfO_8	ZrO_8	TiO_8
α	35.28	34.54	33.49	32.21	31.66	32.87
Z	7.19	7.45	8.59	6.77	6.95	7.70
C	0.128	0.105	0.044	0.163	0.142	0.078

● The **enhancement** of the dielectric permittivities are:
  ★ larger for Ti-centered SUs than for Hf- and Zr-centered ones
  ★ larger for MO_6 SUs than MO_8 ones

● For **Ti amorphous silicates**, the dielectric permittivities should be considerably larger than for **Hf and Zr amorphous silicates**
  ★ for Ti, the MO_6 SUs tend to be more stable (as in rutile) than the MO_8 ones whereas, for Hf and Zr, the MO_8 SUs prevail
  ★ all the characteristic parameters of Ti-centered SUs produce a larger enhancement than Hf and Zr ones.
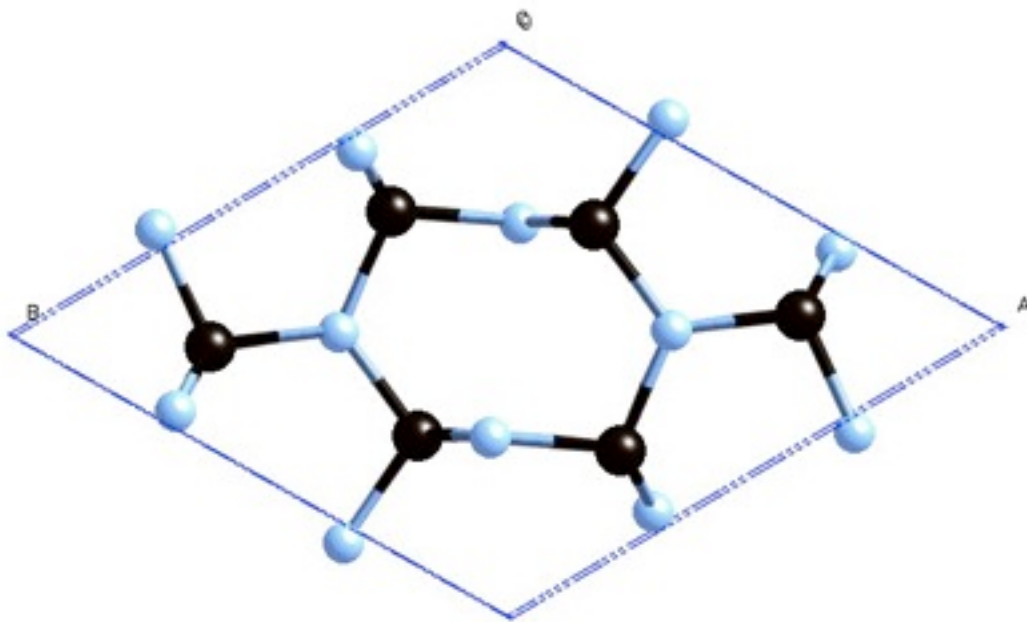
Quest for superhard materials
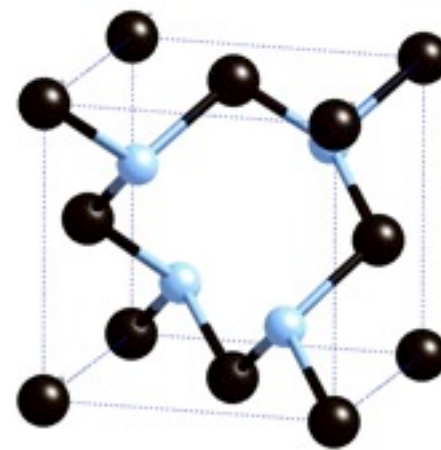
Possible crystalline phases of C$_3$N$_4$

β-C$_3$N$_4$

Defect Zinc Blende-C$_3$N$_4$

(B=427 GPa)

[A.Y. Liu & M.L. Cohen,
Science **245**, 841 (1989)]
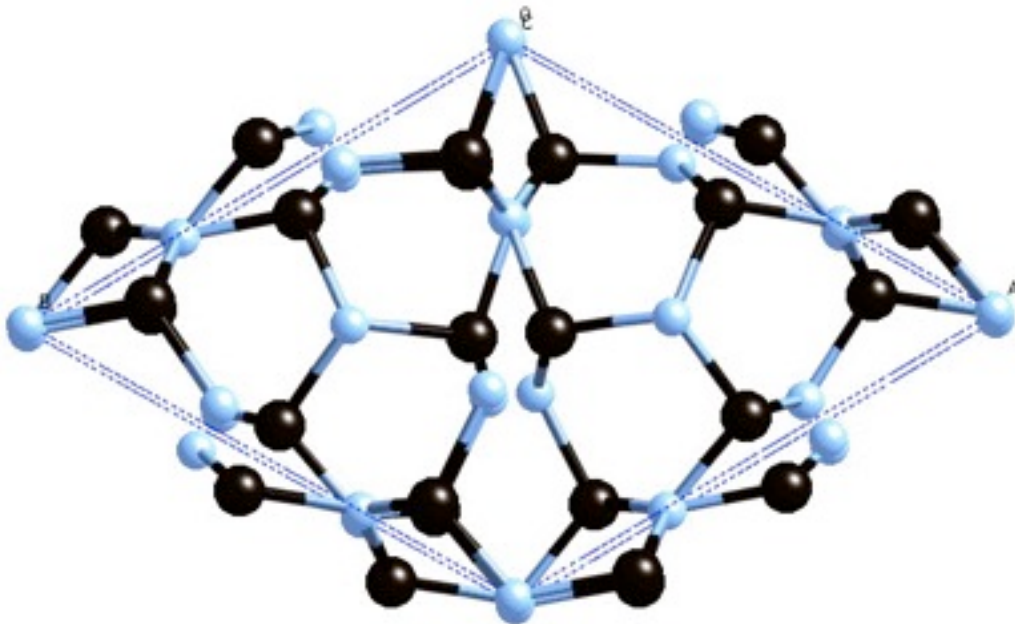

(B=425 GPa)

[A.Y. Liu & R.M. Wentzcovitch,
Phys. Rev. B **50**, 10362 (1994)]
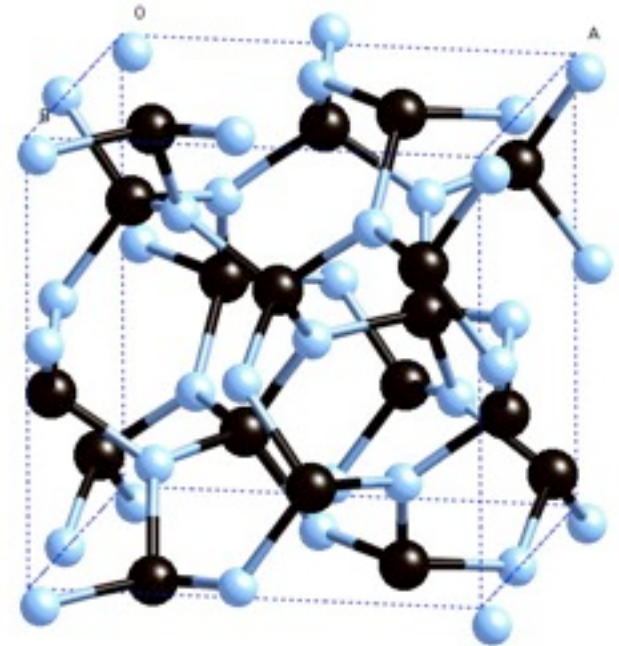
Possible crystalline phases of C_3N_4

α-C_3N_4

Cubic-C_3N_4

(B=425 GPa)

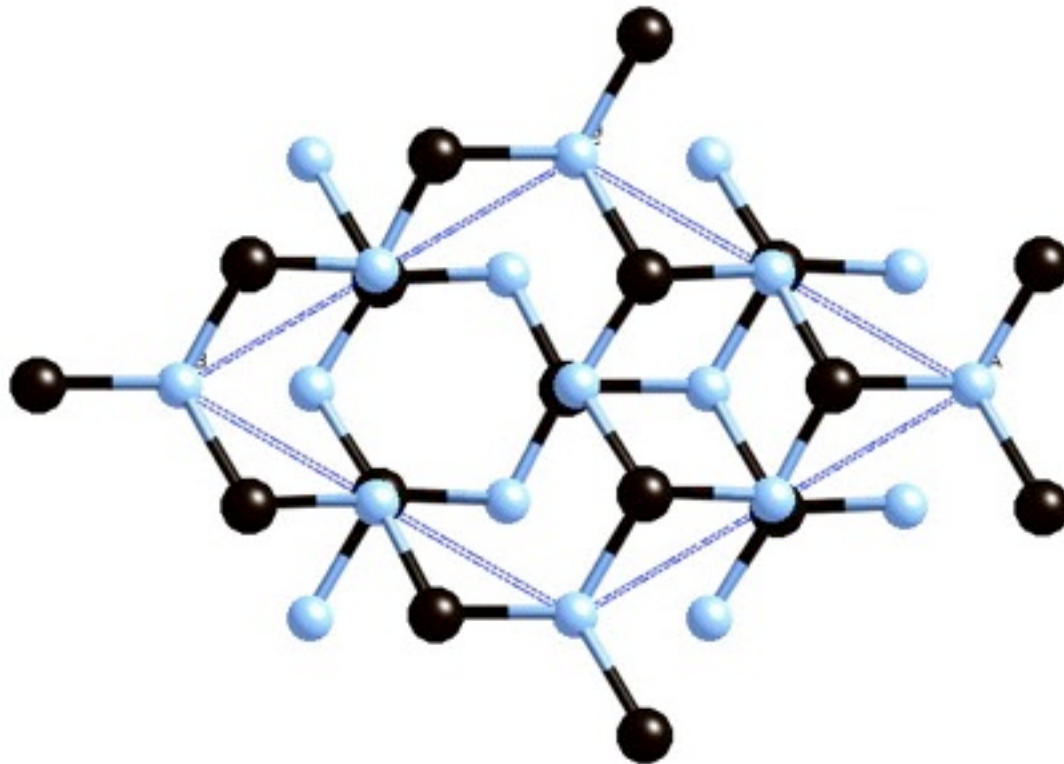[Y.J. Guo & W.A. Goddard,
Chem. Phys. Lett. **237**, 72 (1995)]

(B=496 GPa)

[D.M. Teter & R.J. Hemley,
Science **271**, 53 (1996)]
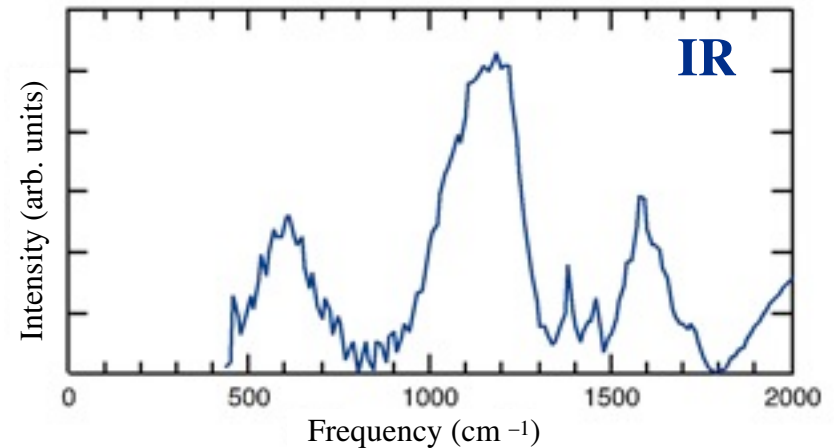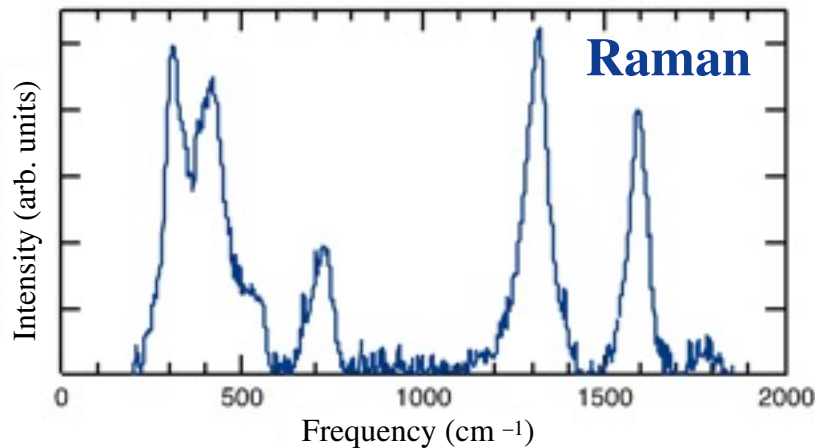
Possible crystalline phases of C₃N₄

Graphitic-C_3N_4

(B=51 GPa)

[A.Y. Liu & R.M. Wentzcovitch,

Phys. Rev. B **50**, 10362 (1994)]

Experimental synthesis?

- <u>Problem:</u> spectrum unknown a priori

  ★ work by analogy with Si_3N_4

  ★ definition of a scaling factor (**Hooke's law**):

$$\rho = \frac{\nu_{Si_3N_4}}{\nu_{C_3N_4}} = \sqrt{\frac{B_{Si_3N_4} d_{SiN} u_{Si_3N_4}}{B_{C_3N_4} d_{CN} u_{C_3N_4}}} = 1.43 - 1.47$$

bulk modulus   interatomic distance   reduced mass

[M. Wixom, J. Am. Ceram. Soc. **73**, 1973 (1990)]

Vibrational properties

	β−Si_3N_4		β−C_3N_4	ρ
	Expt.	*Th.*		
$E_{2g}(1)$	185	180	305	1.69
$A_g(1)$	208	201	442	2.20
$E_{1g}(1)$	230	223	412	1.85
$E_{2g}(2)$	452	447	717	1.60
$A_g(2)$	—	460	637	1.39
$E_{2g}(3)$	620	614	890	1.45
$A_g(3)$	733	729	1078	1.48
$E_{1g}(2)$	866	863	1197	1.39
$E_{2g}(4)$	930	927	1148	1.24
$A_g(4)$	940	936	1290	1.38
$E_{2g}(5)$	1048	1042	1377	1.32

the model works **fine for stretching modes** but

very poorly for bending modes (low frequency)

Vibrational properties

- the three lowest frequency modes are

  very pronounced → **spectral signature** :

  ★ Si_3N_4 :

      185   208   230 (cm–1)

  ★ C_3N_4 :
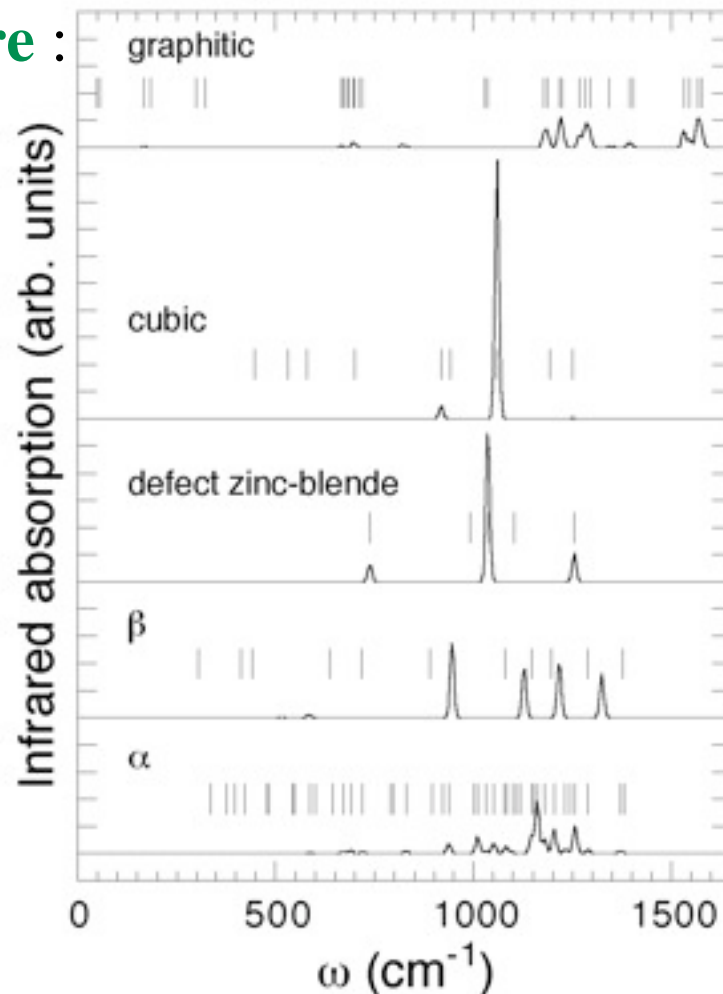
     →   using scaling factor

      266   300   327 (cm–1)

     →   from first-principles

      305   442   412 (cm–1)

- this raises serious doubts about the

  possible identification of β-C_3N_4

  phase in several experiments

Dielectric properties

	ε_∞	ε_0
$\alpha-C_3N_4$	(5.03 5.03 4.91)	(7.01 7.01 6.90)
$\beta-C_3N_4$	(5.15 5.15 4.73)	(7.81 7.81 6.13)
Defect Zinc Blende	5.21	7.37
Cubic	5.59	8.37
Graphitic	(6.15 6.15 2.84)	(8.82 10.34 2.92)

- Experimentally, $\varepsilon_\infty \approx 5.5$ for a-CN$_x$ ($x=25\%$)

- Highest values $\rightarrow$ for the in-plane components of
  the systems with sp^2-bonded C atoms

- For the systems with sp^3-bonded C atoms:
  highest value $\rightarrow$ for the cubic phase
  (*i.e.* the one with the highest bulk modulus)

Born effective charge tensors

- For the systems with sp^3-bonded C atoms:

  the tensors are quite isotropic: $Z^*(\text{C}) \approx +2.3$ and $Z^*(\text{N}) \approx -1.7$

- For the systems with sp^2-bonded C atoms:

  the tensors are very anisotropic

  - ★ in-plane components are bigger (up to +4 for C and −3 for N)
  - ★ very small values perpendicularly to the plane
  - ★ the N atoms that are threefold coordinated present an homogeneous in-plane value; while those that are twofold coordinated present two well separated values

- The **signs** of the Born effective charges reflect the difference in **electronegativity** between C and N atoms