Elastic and piezoelectric tensorial properties

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Tensorial physical properties of crystals

Tensor of rank n:

set of 3^n coefficients with n subscripts, associated with a given Cartesian basis, which transform according to the formula:

$$y'_{ihkl..} = \sum_{1}^{3}{}_{p,q,r,s}.. \, T_{ip}T_{hq}T_{kr}T_{ls}....y_{pqrs..} \, ,$$

when the basis is transformed into a new one by action of the

T matrix

Tensor of first order:
vectorial quantity (3 vector components)
electric polarization intensity: P_i (i=1,2,3)
magnetic polarization intensity

Tensor of second order:
linerar relationship between two vectorial quantities

strain s_{ij} (i,j=1,2,3): $u_i = x_i' - x_i = \sum_{j=1}^{3} s_{ij} x_j$

symmetrical strain: $\varepsilon_{ij} = \frac{1}{2}(s_{ij} + s_{ji}) = \varepsilon_{ji}$

Voigt notation: $\varepsilon_{ij} \rightarrow \varepsilon_h \rightarrow \varepsilon = [\varepsilon_1\ \varepsilon_2\ \varepsilon_3\ \varepsilon_4\ \varepsilon_5\ \varepsilon_6]$
(11→1, 22→2, 33→3, 23→4, 13→5, 12→6)

stress τ_{ij} (i,j=1,2,3): $p_i = \sum_{j=1}^{3} \tau_{ij} n_j$

symmetrical stress: $\tau_{ij} = \tau_{ji}$

Voigt notation: $\tau_{ij} \rightarrow \tau_h \rightarrow \tau = [\tau_1 \ \tau_2 \ \tau_3 \ \tau_4 \ \tau_5 \ \tau_6]$
(11$\rightarrow$1, 22$\rightarrow$2, 33$\rightarrow$3, 23$\rightarrow$4, 13$\rightarrow$5, 12$\rightarrow$6)

Tensor of fourth order:
linerar relationship between two second-order tensorial
 quantities

elasticity tensor c_{ijpq} (i,j,p,q=1,2,3): $\tau_{ij} = \sum_{1}^{3} pq \ c_{ijpq} \varepsilon_{pq}$

Voigt notation:
$c_{ijpq} \rightarrow c_{hk}$ (h,k=1,2,3,4,5,6) $\tau_h = \sum_{k=1}^{6} c_{hk} \varepsilon_k$

<u>Tensor of third order</u>:

linerar relationship between a first- and a second-order
tensorial quantity

piezoelectricity tensor e_{ijp} (i,j,p=1,2,3): $\quad P_i = \displaystyle\sum_{1}^{3} {}_{jp}\ e_{ijp}\varepsilon_{jp}$

Voigt notation:

$e_{ijp} \to e_{ih}$ (i=1,2,3; h=1,2,3,4,5,6) $\quad P_i = \displaystyle\sum_{h=1}^{6} e_{ih}\varepsilon_h$

Elastic constants $c_{hk} = c_{kh}$:

linear coefficients relating stress components to the ensuing strain components

Mechanical work (linear régime): $W = V\sum\limits_{h=1}^{6} \tau_h \varepsilon_h$

Elastic energy: $W = \frac{1}{2}(V\sum\limits_{1}^{6}{}_{hk}c_{hk}\varepsilon_h\varepsilon_k)$

Suitable strains $\varepsilon = [\varepsilon_1\ \varepsilon_2\ \varepsilon_3\ \varepsilon_4\ \varepsilon_5\ \varepsilon_6]$ have to be selected, so as to obtain a quadratic dependence of the elastic energy on the 'amplitude' of the deformation

Example: CaF_2 (cubic Fm-3m)
three independent elastic constants (c_{11}, c_{12}, c_{44})

$$
\begin{bmatrix}
c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\
c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\
c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & c_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & c_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & c_{44}
\end{bmatrix}
$$

$c_{12}=c_{13}=c_{23}$
$c_{44}=c_{55}=c_{66}$

1) $\varepsilon = [\varepsilon \; \varepsilon \; 0 \; 0 \; 0 \; 0] \; \rightarrow \; \Delta a/a = \Delta b/b = \varepsilon$ strain amplitude
   (the symmetry is lowered to tetragonal I4/mmm)

   $W = V(c_{11}+c_{12})\varepsilon^2 \; \rightarrow$
   $c_{11}+c_{12}$ coefficient of the parabolic $W(\varepsilon)$ numerical fit

2) $\varepsilon = [\varepsilon \; \varepsilon \; -2\varepsilon \; 0 \; 0 \; 0] \; \rightarrow \; \Delta a/a = \Delta b/b = -2\Delta c/c = \varepsilon$
   tetragonal strain amplitude

   $W = 3V(c_{11}-c_{12})\varepsilon^2 \; \rightarrow$
   $c_{11}-c_{12}$ coefficient of the parabolic $W(\varepsilon)$ numerical fit

3) $\varepsilon = [0\ 0\ 0\ \varepsilon\ \varepsilon\ \varepsilon] \rightarrow \varepsilon \propto \cos\alpha = \cos\beta = \cos\gamma$ strain amplitude
    (the symmetry is lowered to rombohedral R-3m)

   The F atom acquires a degree of freedom along the
   trigonal axis, which has to be relaxed

 $W = 3/2(Vc_{44})\varepsilon^2 \rightarrow$

   c_{44} coefficient of the parabolic $W(\varepsilon)$ numerical fit

Symmetry and physical properties of crystals

- <u>Neumann's principle</u>:

  The symmetry of a matter ('intrinsic') tensorial

  physical property can not be lower than the point
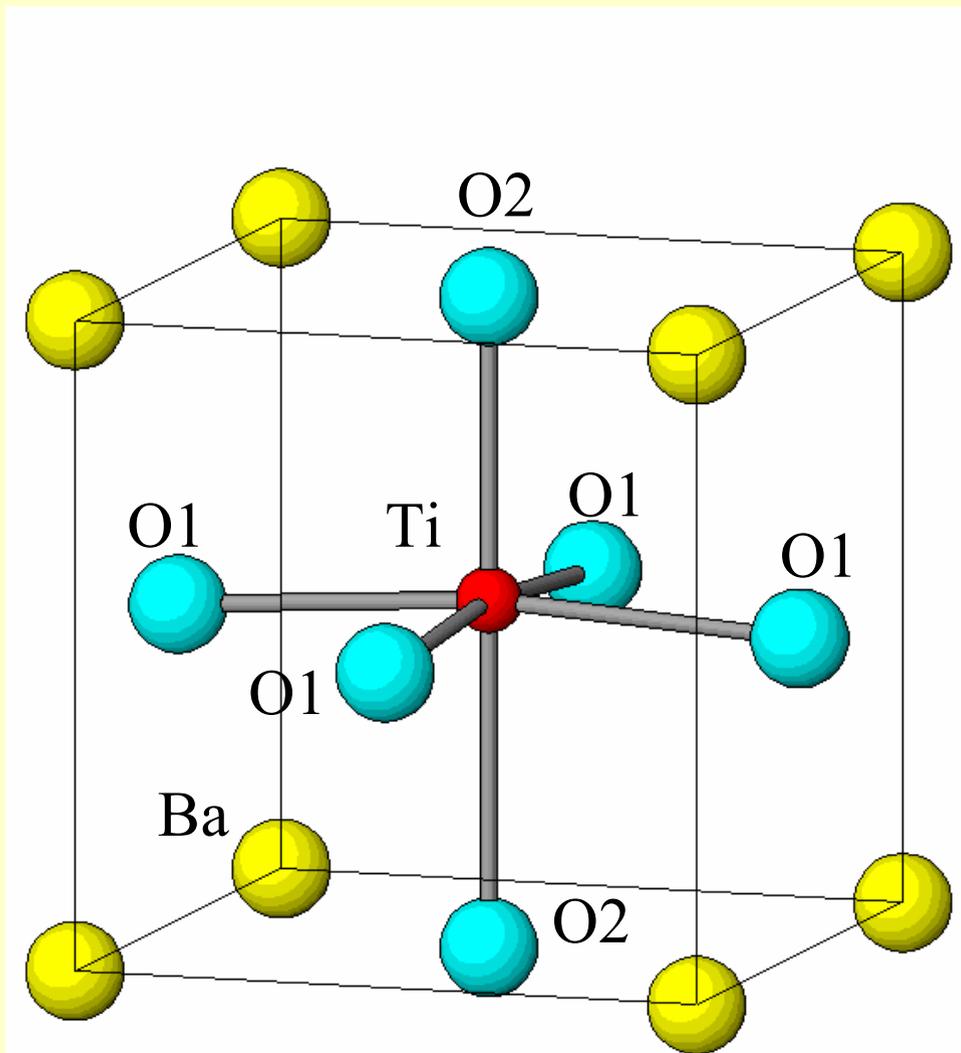
  group symmetry of the crystal

- <u>Ferroelectricity</u>, <u>pyroelectricity</u>:
  "spontaneous" electric dipole moment per unit volume P_0

- Polar vector with symmetry ∞m

$$\Downarrow$$
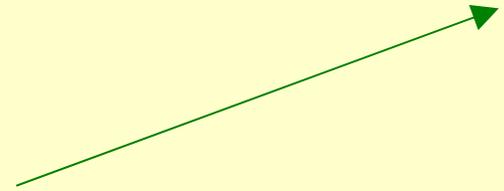
only subgroups of ∞m are allowed as point groups of ferroelectric crystals (non-centrosymmetrical polar groups):

1, 2, 3, 4, 6, m, mm2, 3m, 4mm, 6mm

BaTiO$_3$ - P4mm – ferroelectric phase at RT

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- **Piezoelectricity**

  - in ferroelectric crystals: the spontaneous polarization **P** changes under strain

$$\Downarrow$$

  all ferroelectric crystals are also piezoelectric

  - in non-ferroelectric crystals: a non-spontaneous polarization **P** arises under strain, which lowers the point symmetry from non-polar to polar

$$\Downarrow$$

  only non-centrosymmetrical non-polar point groups are allowed for piezoelectric non-ferroelectric crystals:

$$-4, -6, 222, \ 32, \ 422, \ 622, \ 23, -42m, -6m2, -43m$$

- $P_i = P_{0i} + \sum_k e_{ik}\varepsilon_k$ electric dipole moment per unit volume

- $\mathbf{P_0}$:   spontaneous polarization vector
  - present in ferroelectric and pyroelectric crystals, with polar symmetry
  - absent in other (non-centrosymmetrical but non-polar) piezoelectric crystals

- <u>Warning</u>:

  The absolute macroscopic polarization $\mathbf{P}$ of a crystal cannot be measured as a bulk property, independent of sample termination

- finite polarization changes $\Delta \mathbf{P}$ between two different crystal states (ferroelectricity), or polarization derivatives $\partial \mathbf{P}/\partial f$ with respect to a physical effect f (piezoelectricity, pyroelectricity) are the measurable observables

- $$\text{div}(\mathbf{J} + \partial \mathbf{P}/\partial t) = 0 \quad \rightarrow \quad \Delta \mathbf{P} = -\!\int \mathbf{J}\,dt$$

$$\Downarrow$$

  the polarization change is equal to the integrated macroscopic current density $\mathbf{J}$ passing through the crystal while the perturbation is switched on

Quantum-mechanical calculations of spontaneous polarization and/or piezoelectric properties

$$\Delta \mathbf{P} = \mathbf{P}^{(2)} - \mathbf{P}^{(1)} = -\int \mathbf{J} dt$$

- the current density depends on the phase of the wave function in addition to its modulus
- the charge density $\rho(\mathbf{x}) = |\Psi(\mathbf{x})|^2$ does not determine $\Delta \mathbf{P}$ uniquely

R.D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993)

R. Resta, Rev. Mod. Phys. 66, 899 (1994)

R. Resta, in "Quantum-mechanical ab initio calculation of the properties of crystalline materials" (Ed. by C. Pisani), pp. 273-288, Springer (1996)

D. Vanderbilt, J. Phys. Chem. Solids 61, 147 (2000)

$$\mathbf{P}_{nucl}^{(\alpha)} = (e/V) \sum_s Z_s \mathbf{x}_s$$

$$\mathbf{P}_{el}^{(\alpha)} = (e/8\pi^3) \sum_n \int < f_{n\mathbf{K}}^{(\alpha)} | -i\nabla_{\mathbf{K}} | f_{n\mathbf{K}}^{(\alpha)} > d\mathbf{K}$$

α denotes the crystal structure configuration (positions of nuclei)

$$\mathbf{P}^{(\alpha)} = \mathbf{P}_{nucl}^{(\alpha)} + \mathbf{P}_{el}^{(\alpha)}; \qquad \Delta\mathbf{P} = \mathbf{P}^{(2)} - \mathbf{P}^{(1)}$$

$$< f_{n\mathbf{K}} | -i\nabla_{\mathbf{K}} | f_{n\mathbf{K}} > = -i \int f_{n\mathbf{K}}(\mathbf{x})^* \nabla_{\mathbf{K}} f_{n\mathbf{K}}(\mathbf{x}) d\mathbf{x};$$

$$f_{n\mathbf{K}}(\mathbf{x}) = \psi_{n\mathbf{K}}(\mathbf{x}) \, e^{-i\mathbf{K} \cdot \mathbf{x}}$$

$\psi_{n\mathbf{K}}(\mathbf{x})$:   eigenfunctions of the one-electron Hamiltonian H

$f_{n\mathbf{K}}(\mathbf{x})$:   cell-periodic Bloch functions; $f_{n\mathbf{K}}(\mathbf{x} + \mathbf{l}) = f_{n\mathbf{K}}(\mathbf{x})$

Berry phases

Berry phases are related to the crystallographic components of the **P** vector, and can be computed quantum-mechanically:

$$\varphi_i = 2\pi(V/e)\mathbf{P} \cdot \mathbf{a}_i^* = (V/4\pi^2) \sum_n \int < f_{n\mathbf{K}}^{(\alpha)} \big| -i\mathbf{a}_i^* \cdot \nabla_{\mathbf{K}} \big| f_{n\mathbf{K}}^{(\alpha)} > d\mathbf{K}$$

Derivatives $(\partial\varphi_i/\partial\varepsilon_k)$ are invariant with respect to $(e/V)\mathbf{l}$ vectors added to **P**:

$$\partial\varphi_i(\mathbf{P})/\partial\varepsilon_k = \partial\varphi_i[\mathbf{P} + (e/V)\mathbf{l}]/\partial\varepsilon_k$$

Berry phases and piezoelectric constants

- The derivatives $\partial\varphi_i/\partial\varepsilon_k$ are computed numerically for a given strain $[\varepsilon_1 \ \varepsilon_2 \ \varepsilon_3 \ \varepsilon_4 \ \varepsilon_5 \ \varepsilon_6]$

- Then phase derivatives are transformed into polarization derivatives (piezoelectric constants):

$$e_{ik} = (\partial P_i/\partial\varepsilon_k)_E = (e/2\pi V)\sum_h a_{ih}(\partial\varphi_h/\partial\varepsilon_k)_{\varepsilon=0} = \underline{e}_{ik},$$

where the a_{ih} quantities are Cartesian components of the direct unit-cell vectors

Wurtzite and zinc blende phases of ZnO and ZnS

M. Catti, Y. Noel, R. Dovesi, J. Phys. Chem. Solids 11, 2183 (2003)

wurtzite: 6mm   zinc blende: -43m

$$\begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \qquad \begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{bmatrix}$$

$$\begin{bmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{bmatrix} \qquad \begin{bmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{14} \end{bmatrix}$$

Ab initio (Hartree-Fock and DFT-GGA) and experimental structural data for wurtzite and zinc blende ZnO and ZnS

	ZnO			ZnS		
	HF	GGA	exp.	HF	GGA	exp.
Wurtzite						
a (Å)	3.286	3.275	3.25	3.982	3.875	3.82
c (Å)	5.241	5.251	5.20	6.500	6.307	6.25
u	0.383	0.382	0.380	0.377	0.377	0.378
Zinc blende						
a (Å)	4.619	4.610	---	5.627	5.511	5.413

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Wurtzite and zinc blende phases of ZnO and ZnS

- <u>Strains chosen appropriately for each piezoelectric constant</u>

     wurtzite: 6mm   zinc blende: -43m

e_{33}:   [0 0 ε 0 0 0] e_{14}:   [0 0 0 ε ε ε]

e_{31}:   [ε ε 0 0 0 0]

e_{15}:   [0 0 0 ε $\sqrt{3}\varepsilon$ 0]

- <u>Structural optimization at each value of ε for every strain</u>

Wurtzite

$$\mathbf{a}_1 = (\sqrt{3}/2)a\,\mathbf{i}_1 - (1/2)\mathbf{i}_2; \qquad \mathbf{a}_2 = a\,\mathbf{i}_2; \qquad \mathbf{a}_3 = c\,\mathbf{i}_3$$

$$\varepsilon = [0\ 0\ \varepsilon\ 0\ 0\ 0] \qquad\qquad e_{33} = (e/2\pi V)c(\partial\varphi_3/\partial\varepsilon)$$

$$\varepsilon = [\varepsilon\ \varepsilon\ 0\ 0\ 0\ 0] \qquad\qquad e_{31} = (e/2\pi V)c/2(\partial\varphi_3/\partial\varepsilon)$$

$$\varepsilon = [0\ 0\ 0\ \varepsilon\ \sqrt{3}\varepsilon\ 0] \qquad\qquad e_{15} = (e/2\pi V)a/2(\partial\varphi_1/\partial\varepsilon)$$

Zinc blende

$$\mathbf{a}_1 = (a/2)\mathbf{i}_2 + (a/2)\mathbf{i}_3; \qquad \mathbf{a}_2 = (a/2)\mathbf{i}_1 + (a/2)\mathbf{i}_3; \qquad \mathbf{a}_3 = (a/2)\mathbf{i}_1 + (a/2)\mathbf{i}_2$$

$$\varepsilon = [0\ 0\ 0\ 2\varepsilon\ 2\varepsilon\ 2\varepsilon] \qquad\qquad e_{14} = (e/2\pi V)a/2(\partial\varphi_1/\partial\varepsilon)$$

ZnO wurtzite: Berry phases along **a** and **c** vs. the ε_4 strain $\Rightarrow$ e_{15} piezoelectric constant
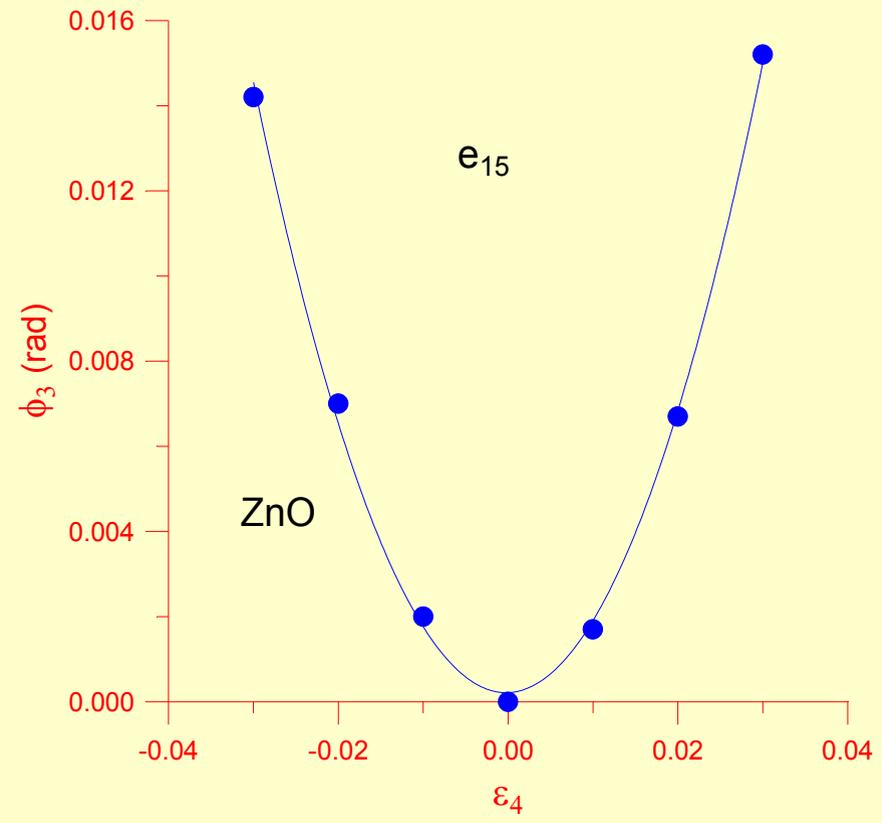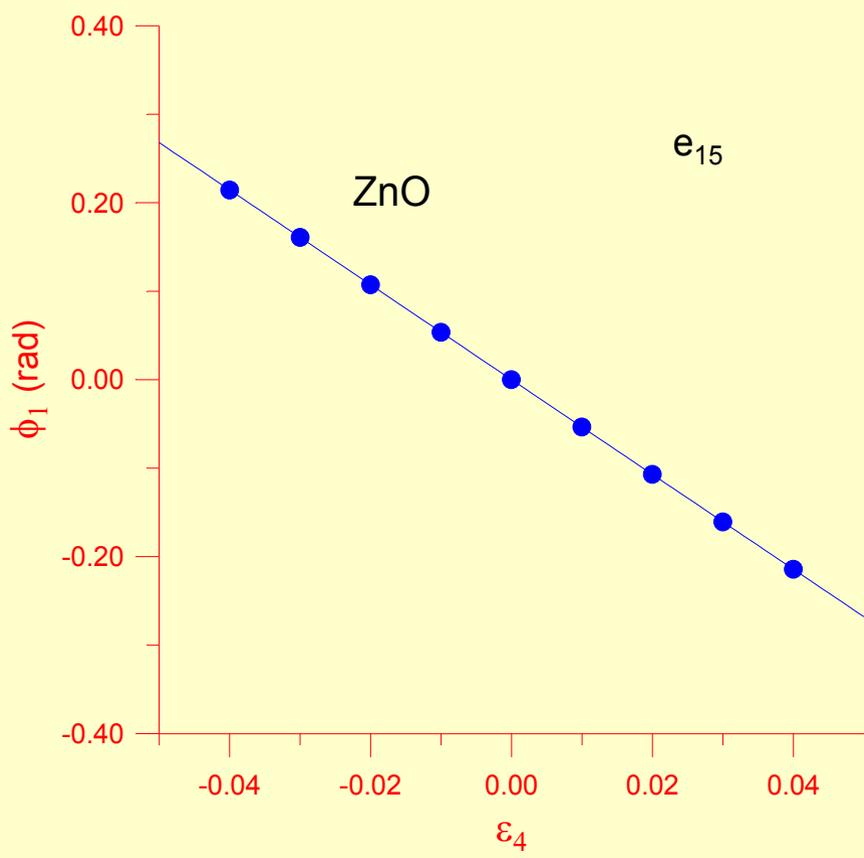
Ab initio and experimental proper piezoelectric constants $\underline{e}_{ik}$ (Cm^{-2}) for wurtzite and zinc blende ZnO and ZnS

	Wurtzite			Zinc blende
	$\underline{e}_{33}$	$\underline{e}_{31}$	$\underline{e}_{15}$	$\underline{e}_{14}$
ZnO				
HF	1.19	-0.55	-0.46	0.69
GGA	1.20	-0.59		
exp.[a]	0.96	-0.62	-0.37	---
ZnS				
HF	0.18	-0.13	-0.13	0.11
GGA	0.21	-0.16		
exp.[b]	0.34	-0.10	-0.08	0.14

External- (clamped-ion) and internal-strain components of piezoelectric constants

$$e_{ik} = \partial P_i/\partial \varepsilon_{jk} = (\partial P_i/\partial \varepsilon_{jk})_u + (\partial P_i/\partial u)_{\varepsilon=0}(\partial u/\partial \varepsilon_{jk})_{\varepsilon=0} = e_{ik}^{(0)} + e_{ik}^{int}$$

- <u>Clamped-ion component</u> $e_{ik}^{(0)} = (\partial P_i/\partial \varepsilon_{jk})_u$:

  atomic fractional coordinates are kept fixed along the strain (homogeneous deformation)

- <u>Internal-strain component</u> $e_{ik}^{int} = (\partial P_i/\partial u)_{\varepsilon=0}(\partial u/\partial \varepsilon_{jk})_{\varepsilon=0}$:

  atomic fractional coordinates are relaxed at fixed strain

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<u>Rigid-ion point-charge model</u>,
<u>and pure ionic (nuclear) contribution to piezoelectricity</u>:

vanishing clamped-ion component of the proper piezoelectric constan
$$\Downarrow$$

<u>Clamped-ion component from ab initio calculations</u>:

a measure of the deviation of the electronic behaviour from the
simple point-charge RI model (pure electronic contribution to
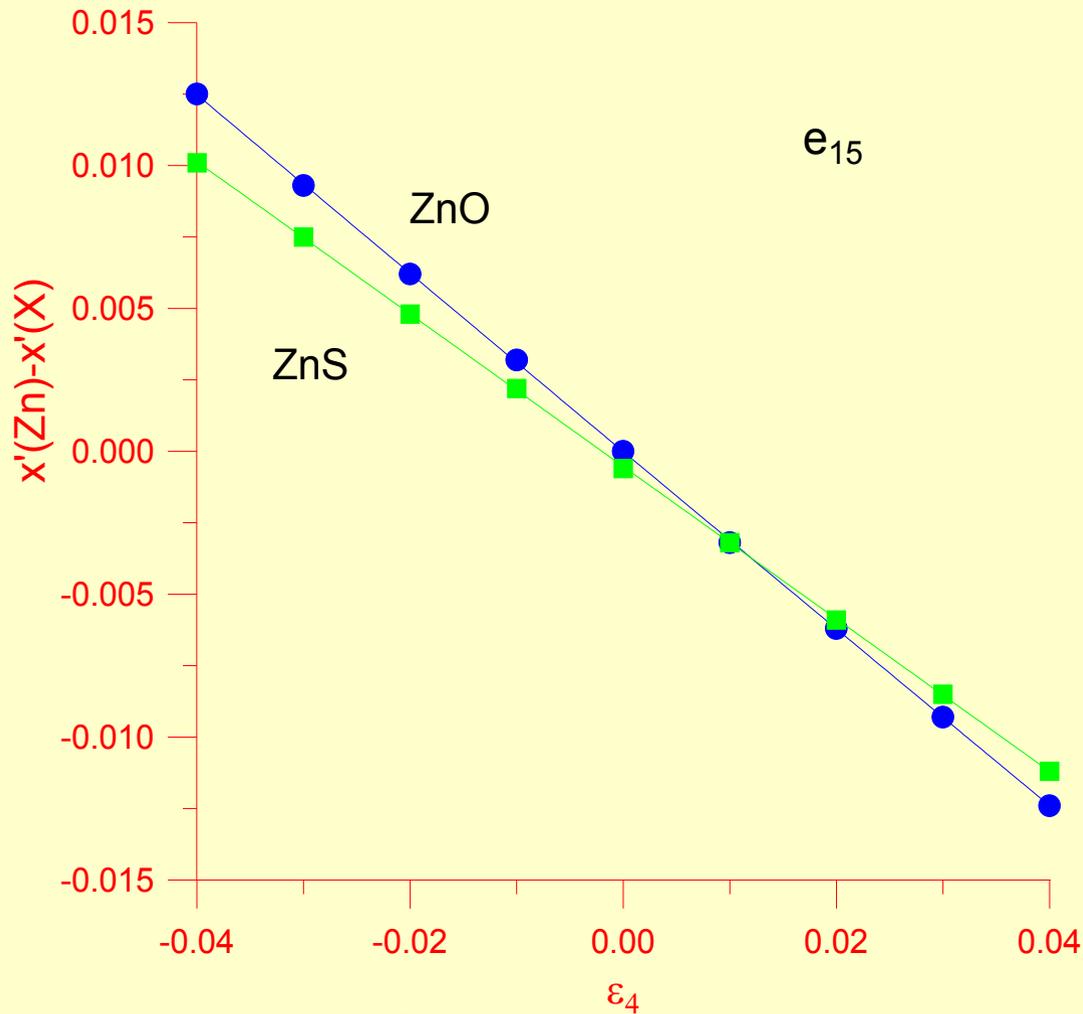piezoelectricity)
$$\Downarrow$$

a pure homogeneous strain yet induces polarization effects on the
atomic electron distributions, which give rise to non-vanishing
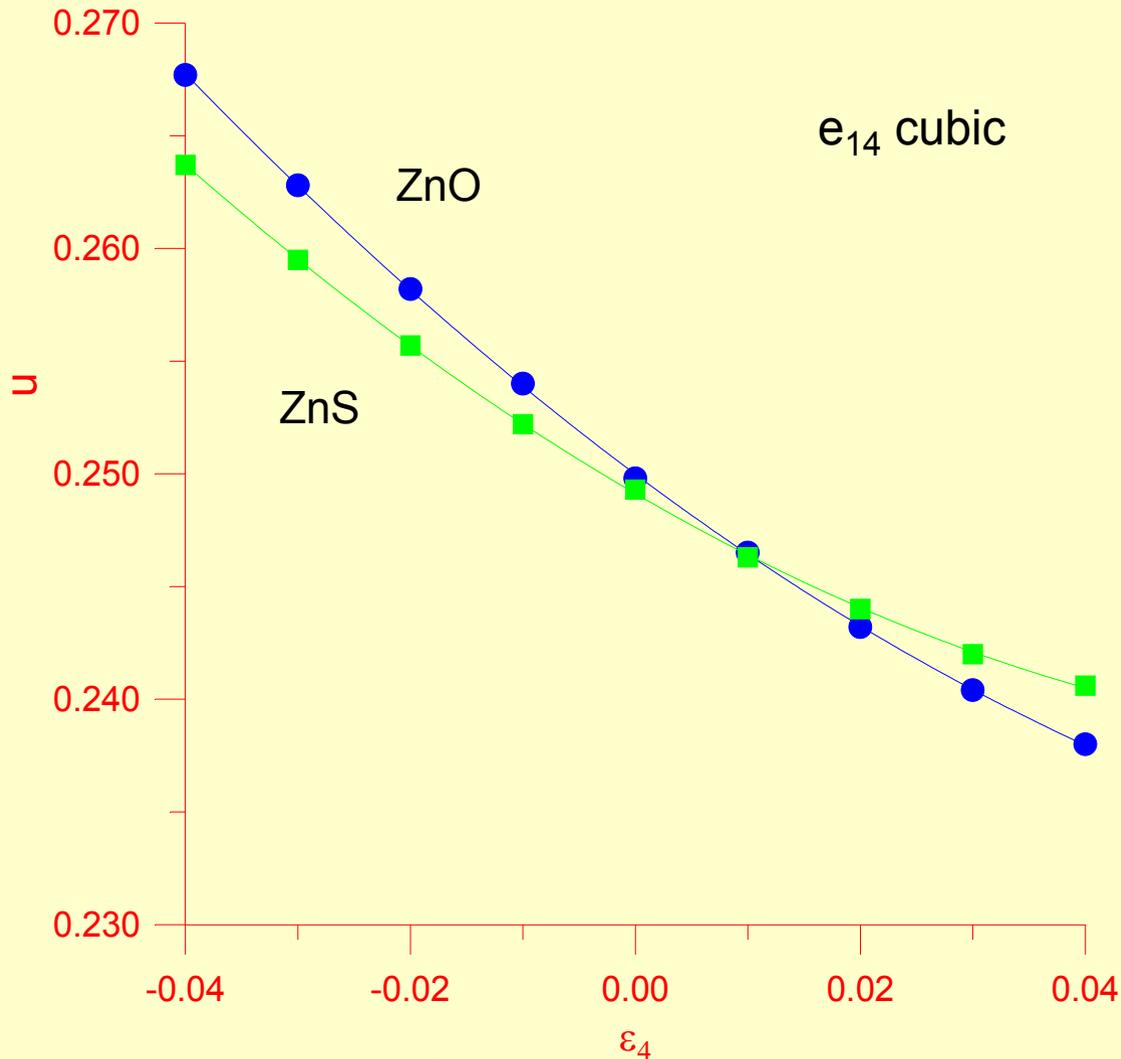clamped-ion terms of the piezoelectric constants

[001] fractional component of Zn-X spacing vs. ε_3 strain in wurtzite

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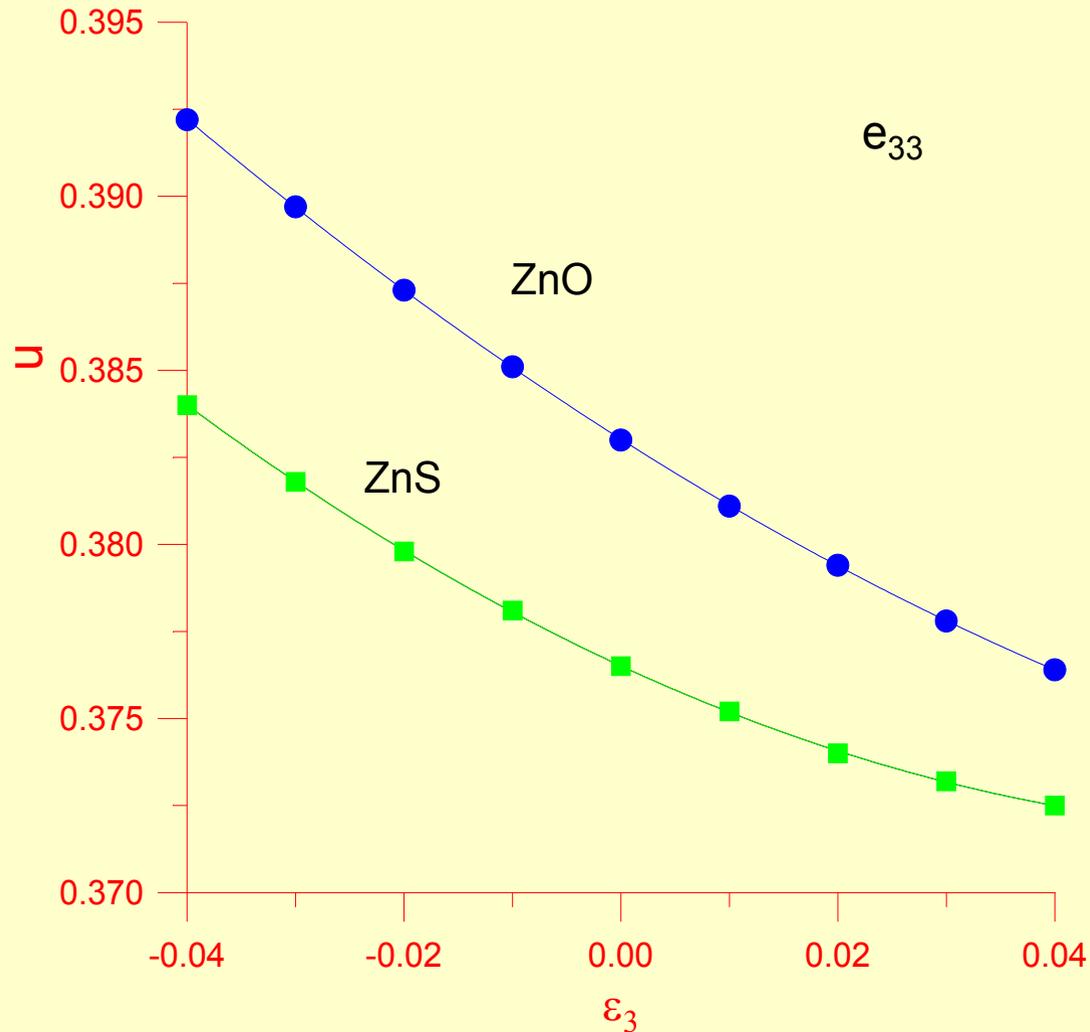
[110] fractional component of Zn-X spacing vs. ε_4 strain in wurtzite

# [111] fractional component of Zn-X spacing vs. ε_4 strain in zinc blende

Ab initio, classical (rigid ion model) and experimental proper piezoelectric constants $\underline{e}_{ik}$ (Cm^{-2}) for ZnO and ZnS

|	$\underline{e}_{33}$ (H)		$\underline{e}_{31}$ (H)		$\underline{e}_{15}$ (H)		$\underline{e}_{14}$ (C)	
	ZnO	ZnS	ZnO	ZnS	ZnO (H)	ZnS	ZnO	ZnS
HF	1.19	0.18	-0.54	-0.13	-0.46	-0.13	0.69	0.11
HF(ext.)	-0.45	-0.59	0.22	0.29	0.22	0.28	-0.45	-0.53
HF(int.)	1.63	0.74	-0.76	-0.42	-0.68	-0.41	1.14	0.64
HF(ext.)/HF(int.)	28%	80%	29%	69%	33%	69%	40%	83%
du/dε (HF)	-0.228	-0.147	0.215	0.160	0.320	0.270	-0.372	-0.290
exp.[a]	0.96	0.34	-0.62	-0.10	-0.37	-0.08	---	0.14

Analysis of *ab initio* results on piezoelectric constants of ZnO and ZnS

- Signs and values of the e_{ik} constants and of their $e_{ik}^{(0)}$ and e_{ik}^{int} components

$$\Downarrow$$

- the internal-strain term e_{ik}^{int} is always dominant, and has thus the same sign as the total value e_{ik}

- the sign is opposite to that of $du/d\varepsilon$, because the Zn to X inter-layer distance is $(1/2-u)c$ (W) or $(1/3-u)c$ (ZB)

- the clamped-ion term $e_{ik}^{(0)}$ has opposite sign to that of e_{ik}^{int} and e_{ik}

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ZnO/ZnS hexagonal • ε_3 strain • $e_{33} > 0$
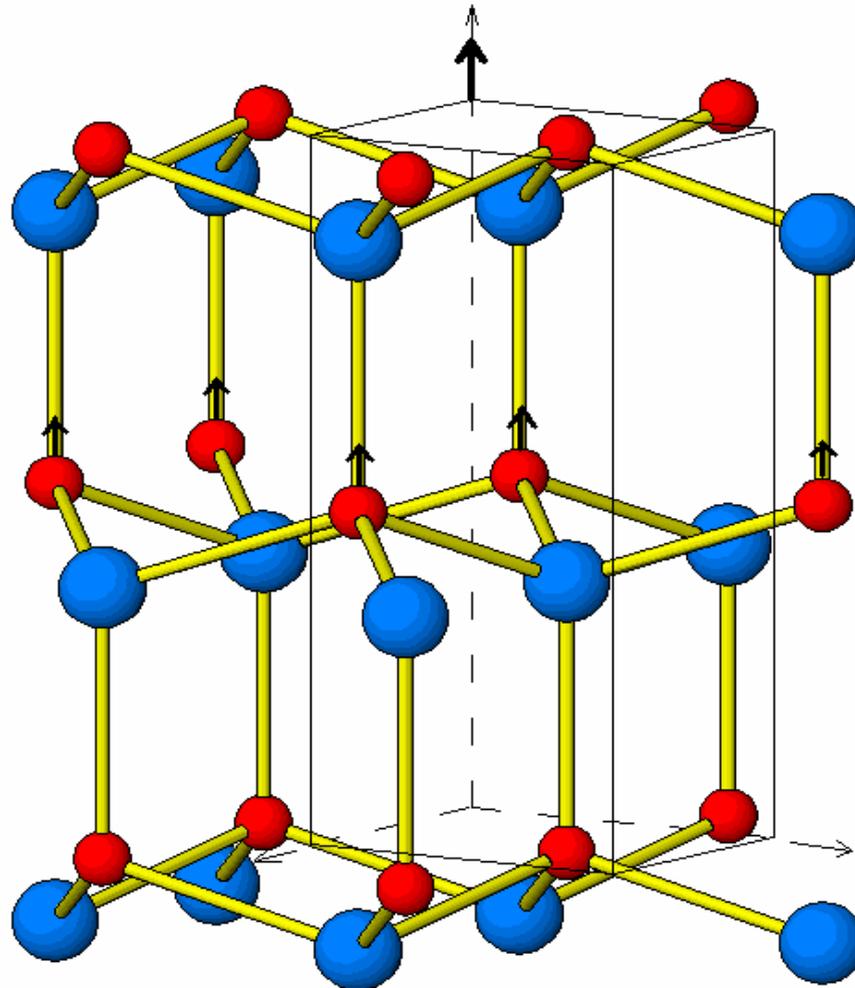
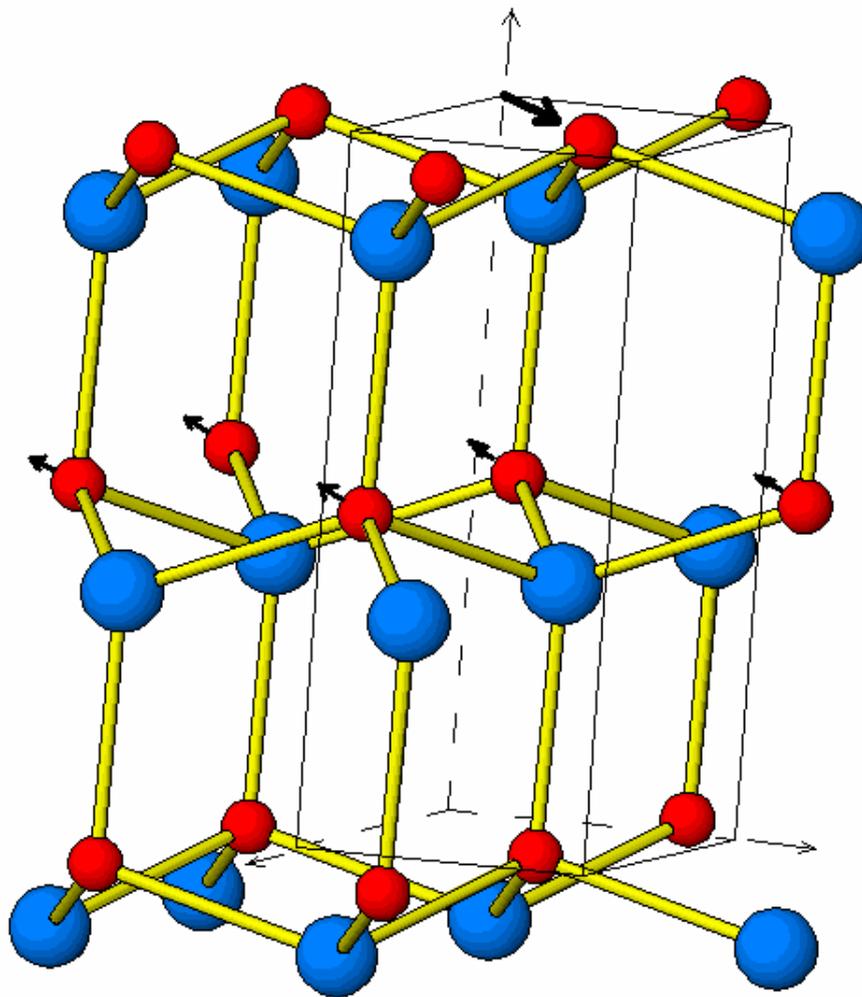# ZnO/ZnS hexagonal • $\varepsilon_1 = \varepsilon_2$ strain • $e_{31} < 0$
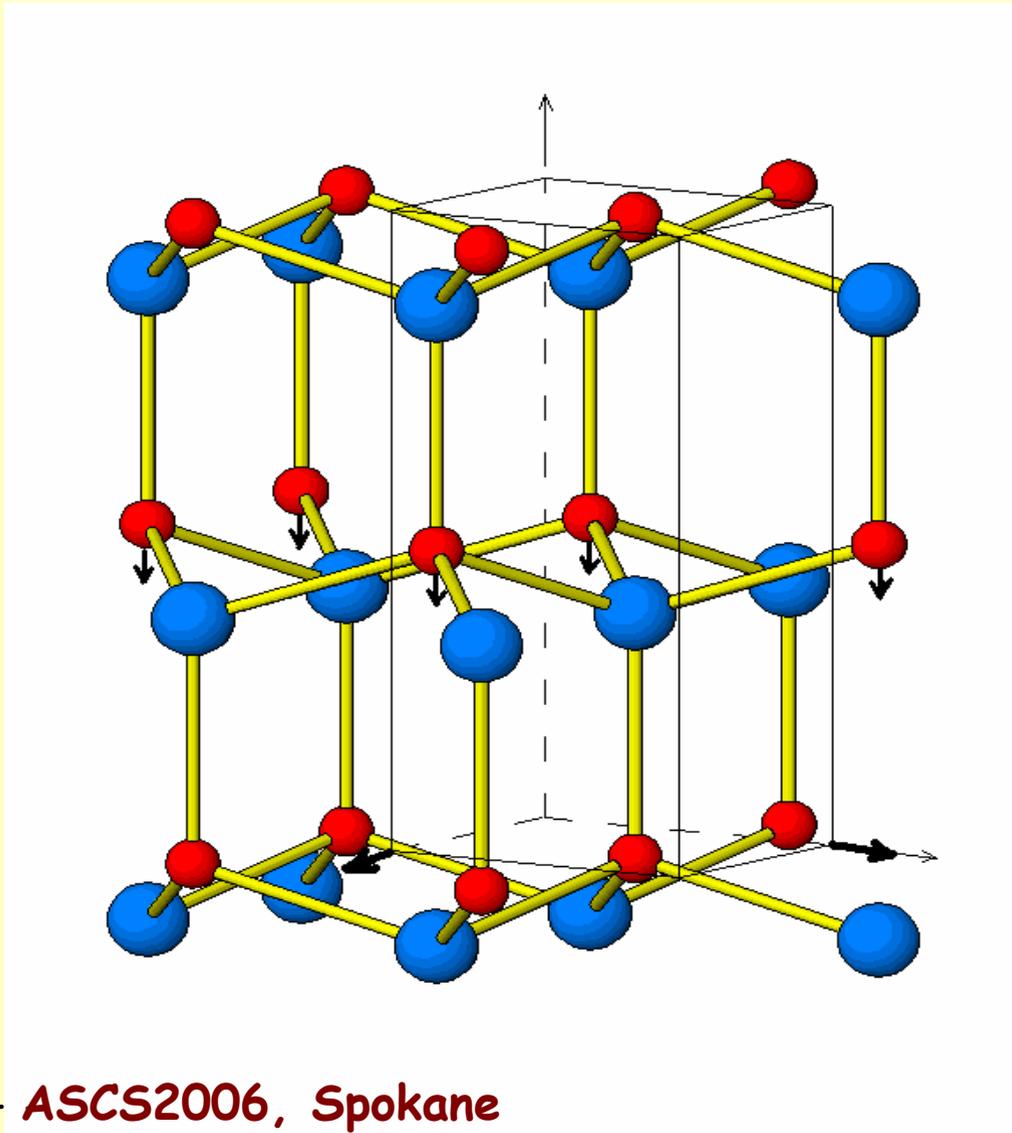
- Internal-strain effect:

    - major source of piezoelectric response

    - quantum-mechanical results are similar to those by classical RI model   based on *ab initio* values of $\partial u / \partial \varepsilon$ relaxation terms
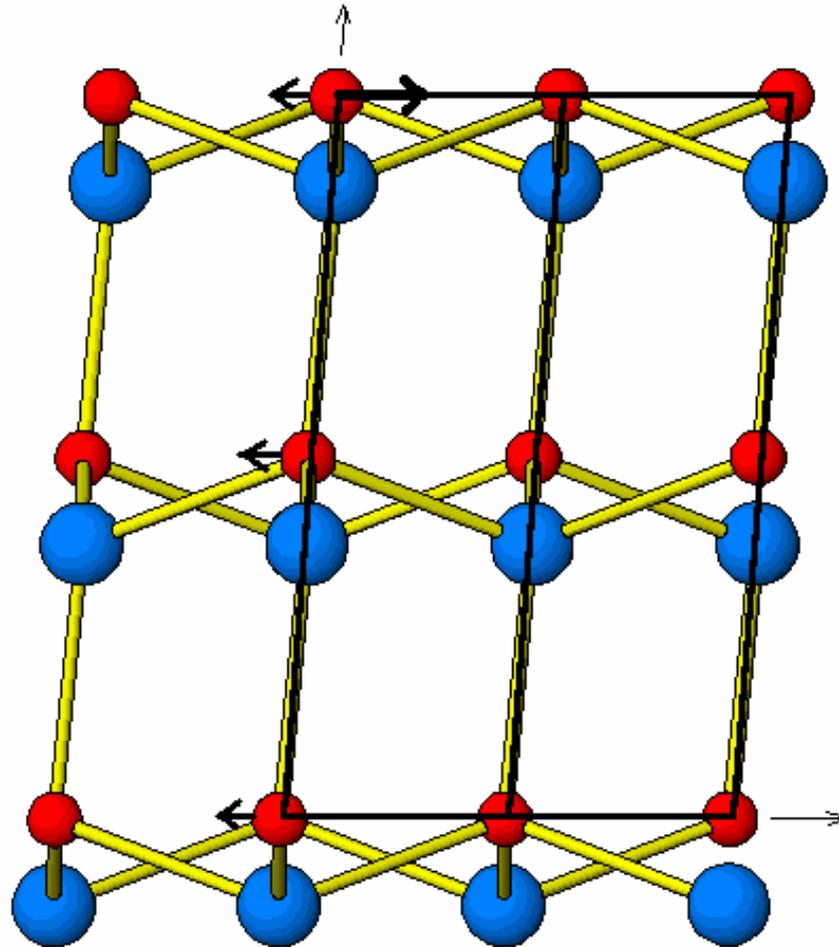
- Clamped-ion effect:

    reduces the piezoelectric response, and corresponds to effects of electronic polarization opposing the ionic polarization caused by structural relaxation
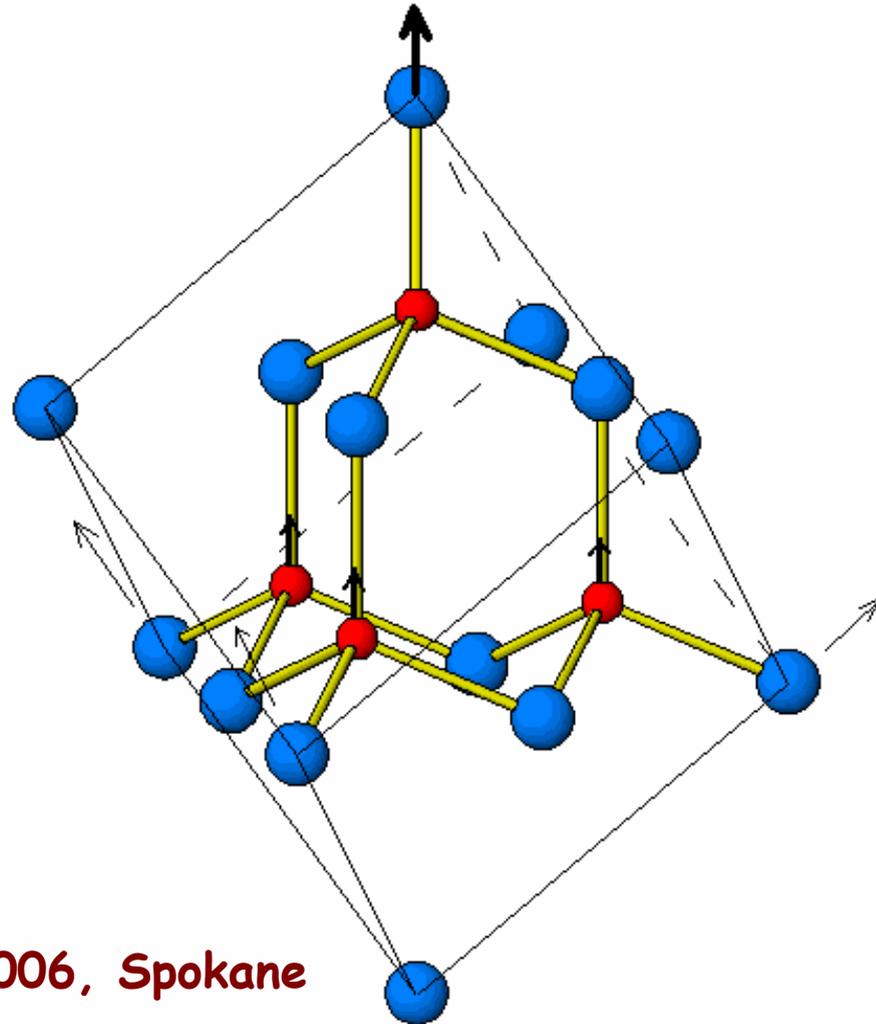
ZnO/ZnS hexagonal • $\varepsilon_4 = \varepsilon_5$ strain • $e_{15} < 0$

ZnO/ZnS hexagonal • $\varepsilon_4 = \varepsilon_5$ strain • $e_{15} < 0$

SUMMARY

♦ Elastic and piezoelectric constants can be computed reliably for any crystal by periodic quantum-mechanical methods

♦ Complexity of the crystal structure and/or low symmetry may increase the computational cost, because of the full structural relaxation needed

♦ Two goals can be achieved:
  - prediction of elastic and piezoelectric properties not yet measured or not measurable
  - physical insight into the microscopic origin of elastic and piezoelectric behaviour of crystals

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