Theory of Piezoelectricity

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Outline

1. Fundamentals & macroscopic (phenomenological) theory
2. Wurtzite structure
3. Textbooks' fallacies about polarization (induced & spontaneous)
4. A change of paradigm
5. Microscopic approach to piezoelectricity
6. A more difficult problem: flexoelectricity

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Gaussian units

- Conversion from SI units: $4\pi\varepsilon_0 \;\rightarrow\; 1$
- In vacuo $\mathbf{D} \equiv \mathbf{E}$
- Permittivity of free space $= 1$
- Coulomb interaction & Lorentz force:

$$V = \frac{Q_1 Q_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \; ; \qquad \mathbf{f} = Q\left(\mathbf{E} + \frac{1}{c}\mathbf{v}\times\mathbf{B}\right)$$

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Free energy per crystal cell $\mathcal{F}$ (at zero T)

- Independent variables:
  - Macroscopic **E** field
  - Macroscopic strain $\overleftrightarrow{\eta}$

- Conjugate variables:

$$\begin{aligned} \overleftrightarrow{\sigma}(\overleftrightarrow{\eta}, \mathbf{E}) &= -\frac{1}{V_{\text{cell}}} \frac{\partial \mathcal{F}}{\partial \overleftrightarrow{\eta}} && \text{macroscopic stress} \\ \mathbf{D}(\overleftrightarrow{\eta}, \mathbf{E}) &= -\frac{4\pi}{V_{\text{cell}}} \frac{\partial \mathcal{F}}{\partial \mathbf{E}} && \text{displacement field} \end{aligned}$$

- At equilibrium $\overleftrightarrow{\sigma} = 0$

Why using **E** (not **D**) as independent variable

- The **microscopic** field $\mathbf{E}^{(\mathrm{micro})}(\mathbf{r})$ is the only real electric field **inside the material**

- The **macroscopic** field **E** is the macroscopic average of $\mathbf{E}^{(\mathrm{micro})}(\mathbf{r})$ (see e.g. Jackson)

- For a crystalline material:
  macroscopic average = cell average

- **E** is sometimes called “internal screened field”

- **E** is actually controlled by the voltage at capacitor plates

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First order expansion

$$\begin{aligned}\mathcal{F}(\overleftrightarrow{\eta}, \mathbf{E}) &= \mathcal{F}_0 + \left.\frac{\partial \mathcal{F}}{\partial \overleftrightarrow{\eta}}\right|_0 \cdot \overleftrightarrow{\eta} + \left.\frac{\partial \mathcal{F}}{\partial \mathbf{E}}\right|_0 \cdot \mathbf{E} + \quad \ldots \\ &= \mathcal{F}_0 - V_{\mathrm{cell}} \overleftrightarrow{\sigma}_0 \cdot \overleftrightarrow{\eta} - \frac{V_{\mathrm{cell}}}{4\pi} \mathbf{D}_0 \cdot \mathbf{E} + \quad \ldots\end{aligned}$$

- We expand around “equilibrium”
- Our **choice** for “equilibrium”:
  the crystal structure having the lowest energy in **zero field**

- Macroscopic strain $\overleftrightarrow{\eta}$ is the tensor which measures the deviation from the equilibrium structure
- Macroscopic stress $\overleftrightarrow{\sigma}_0 = 0$
- What about $\mathbf{D}_0$?

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High symmetry vs. low symmetry crystals

$$\mathcal{F}(\overset{\leftrightarrow}{\eta}, \mathbf{E}) = \mathcal{F}_0 - \frac{V_{\mathrm{cell}}}{4\pi} \mathbf{D}_0 \cdot \mathbf{E} + \text{higher orders}$$

- From the general relationship $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ at $\mathbf{E} = 0$:

$$\mathcal{F}(\overset{\leftrightarrow}{\eta}, \mathbf{E}) = \mathcal{F}_0 - V_{\mathrm{cell}}\, \mathbf{P}_0 \cdot \mathbf{E} + \text{higher orders}$$

- Spontaneous polarization $\mathbf{P}_0$:
  - $\mathbf{P}_0 = 0$ in some high symmetry classes (e.g. GaAs)
  - $\mathbf{P}_0 \neq 0$ in low symmetry classes (e.g. GaN)
  - Both GaAs and GaN are piezoelectric
  - Only GaN is piezoelectric under isotropic pressure
- Free standing sample in zero **external** field:
  - Is $\mathbf{E} = 0$? Equivalently, is $\mathcal{F} = \mathcal{F}_0$?

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Harmonic expansion

$$\mathcal{F}(\overset{\leftrightarrow}{\eta}, \mathbf{E}) \simeq \mathcal{F}_0 - V_{\text{cell}}\, \mathbf{P}_0 \cdot \mathbf{E} + \frac{1}{2} \left. \frac{\partial^2 \mathcal{F}}{\partial \overset{\leftrightarrow}{\eta}\, \partial \overset{\leftrightarrow}{\eta}'} \right|_0 \overset{\leftrightarrow}{\eta}\, \overset{\leftrightarrow}{\eta}' + \left. \frac{\partial^2 \mathcal{F}}{\partial \overset{\leftrightarrow}{\eta}\, \partial \mathbf{E}} \right|_0 \overset{\leftrightarrow}{\eta}\, \mathbf{E} + \frac{1}{2} \left. \frac{\partial^2 \mathcal{F}}{\partial \mathbf{E}\, \partial \mathbf{E}'} \right|_0 \mathbf{E}\, \mathbf{E}'$$

- $\frac{1}{V_{\text{cell}}} \left. \frac{\partial^2 \mathcal{F}}{\partial \overset{\leftrightarrow}{\eta} \partial \overset{\leftrightarrow}{\eta}'} \right|_0 = \hat{C}$ elastic constants (4th rank tensor)
- $-\frac{1}{V_{\text{cell}}} \left. \frac{\partial^2 \mathcal{F}}{\partial \overset{\leftrightarrow}{\eta} \partial \mathbf{E}} \right|_0 = \hat{e}$ piezoelectric constants (3rd rank tensor)
- $-\frac{4\pi}{V_{\text{cell}}} \left. \frac{\partial^2 \mathcal{F}}{\partial \mathbf{E}\, \partial \mathbf{E}'} \right|_0 = \hat{\varepsilon}$ dielectric tensor (2nd rank tensor)
- All constants defined at $\overset{\leftrightarrow}{\eta} = 0$ and $\mathbf{E} = 0$

Conjugate variables, to harmonic order

$$\begin{aligned}
\mathcal{F}(\overset{\leftrightarrow}{\eta},\mathbf{E}) &\simeq \mathcal{F}_0 - V_{\text{cell}}\,\mathbf{P}_0\cdot\mathbf{E} \\
&+ \frac{1}{2}\hat{C}\;\overset{\leftrightarrow}{\eta}\,\overset{\leftrightarrow}{\eta}' - \hat{e}\;\overset{\leftrightarrow}{\eta}\;\mathbf{E} - \frac{1}{2}\hat{\varepsilon}\,\mathbf{E}\,\mathbf{E}'
\end{aligned}$$

$$\begin{aligned}
\sigma &= -\hat{C}\;\overset{\leftrightarrow}{\eta} + \hat{e}\,\mathbf{E} \\
\mathbf{D} &= \hat{e}\;\overset{\leftrightarrow}{\eta} + \hat{\varepsilon}\,\mathbf{E} + \mathbf{D}_0
\end{aligned}$$

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\end{aligned}$$

- Piezoelectric tensor $\hat{e}$:
    - Stress linearly induced by a unit $\mathbf{E}$ at $\overset{\leftrightarrow}{\eta} = 0$
    - Polarization linearly induced by a unit strain $\overset{\leftrightarrow}{\eta}$ at $\mathbf{E} = 0$

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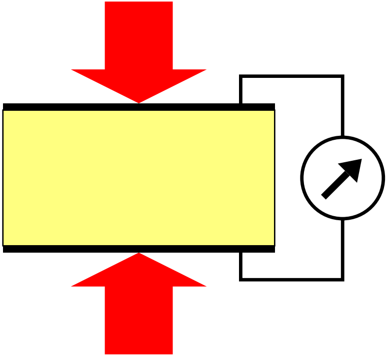
Measurement in zero **E** field

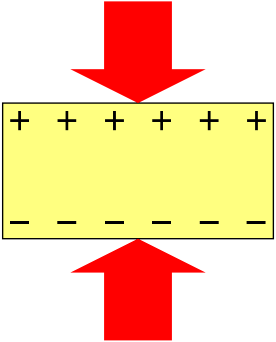
Sample between shorted metallic electrodes



Measurement via the transient current: $\Delta \mathbf{P} = \hat{e} \overleftrightarrow{\eta} = \int_0^{\Delta t} \mathbf{j}(t)dt$

Measurement in zero **D** field

Insulating surfaces, sample in zero **external** field: $\mathbf{E} \neq 0$



Simple case $\mathbf{P}_0 = 0$:

$$\Delta \mathbf{P} = \hat{e} \overset{\leftrightarrow}{\eta} + \frac{1}{4\pi}(\hat{\varepsilon} - \hat{1})\,\mathbf{E} \qquad \longrightarrow \qquad \mathbf{P} = \hat{\varepsilon}^{-1}\hat{e} \overset{\leftrightarrow}{\eta}$$

Free standing sample in zero **external** field

- A finite macroscopic sample at zero stress σ
- Field $\mathbf{E}(\mathbf{r}) = 0$ in vacuo far away from the sample

- Is the internal field $\mathbf{E} = 0$?
- Is the strain $\overset{\leftrightarrow}{\eta} = 0$?

- **Answer:** Yes and No!
  - **Yes**, for a material with **no spontaneous polarization** (e.g. GaAs)
  - **No**, for a material with **spontaneous polarization** (e.g. GaN): both $\mathbf{E}$ and $\overset{\leftrightarrow}{\eta}$ depend on the **shape** of the sample.

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Free standing sample in zero external field: The trivial case ($\mathbf{P}_0 = 0$)

- If $\mathbf{E}^{(\mathrm{ext})} = 0$ then $\mathbf{E} = 0$ and $\mathbf{D} = 0$ inside the material
- The main equations at zero stress σ

$$\begin{aligned} \sigma &= -\hat{C} \overset{\leftrightarrow}{\eta} + \hat{e}\,\mathbf{E} \\ \mathbf{D} &= \hat{e} \overset{\leftrightarrow}{\eta} + \hat{\varepsilon}\,\mathbf{E} \end{aligned}$$

  imply zero strain η

Free standing sample in zero **external** field: The nontrivial case ($\mathbf{P}_0 \neq 0$)

- Even if $\mathbf{E}^{(\mathrm{ext})} = 0$, the internal field $\mathbf{E} \neq 0$
  - The internal field is constant if and only if the sample is **ellipsoidal**
  - The slab and the cylinder are limiting cases of ellipsoids
  - $\mathbf{E}$ is called **depolarization field**
  - The $\mathbf{E}$ value is governed by the **depolarization coefficients**

- Simplest geometry: a slab
  - If $\mathbf{P}$ is normal to the slab, then $\mathbf{E} = -4\pi\mathbf{P}$
  - If $\mathbf{P}$ is parallel to the slab, then $\mathbf{E} = 0$

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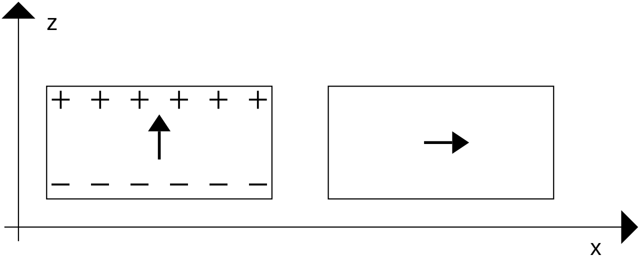


Macroscopic polarization **P** in a slab normal to *z*, for a vanishing external field $\mathbf{E}^{(\mathrm{ext})}$

- When **P** is normal to the slab, a depolarizing field $\mathbf{E} = -4\pi\mathbf{P}$ is present inside the slab, and charges at its surface, with areal density $\sigma_{\mathrm{surface}} = \mathbf{P} \cdot \mathbf{n}$
- When **P** is parallel to the slab, no depolarizing field and no surface charge is present

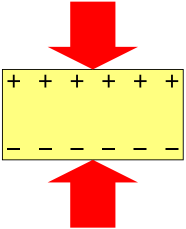
Free standing sample in zero **external** field

The main equations:

$$\begin{aligned} \sigma &= -\hat{C} \overset{\leftrightarrow}{\eta} + \hat{e}\,\mathbf{E} \\ \mathbf{P} &= \hat{e} \overset{\leftrightarrow}{\eta} + \frac{1}{4\pi}(\hat{\varepsilon} - \hat{1})\,\mathbf{E} + \mathbf{P}_0 \end{aligned}$$

- For $\mathbf{P}_0$ **parallel** to the slab:
  at zero stress $\mathbf{E} = 0, \overset{\leftrightarrow}{\eta} = 0, \mathbf{P} = \mathbf{P}_0$
- For $\mathbf{P}_0$ **normal** to the slab:
  at zero stress $\mathbf{E} = -4\pi\mathbf{P}, \overset{\leftrightarrow}{\eta} \neq 0, \mathbf{P} \neq \mathbf{P}_0$

Piezoelectric response of a slab (open circuit)



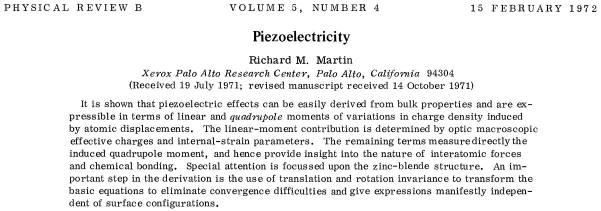
$$\mathbf{P} = \hat{e}\ \overset{\leftrightarrow}{\eta} + \frac{1}{4\pi}(\hat{\varepsilon} - \hat{1})\,\mathbf{E} + \mathbf{P}_0$$

$$\mathbf{E} = -4\pi\mathbf{P} \qquad \longrightarrow \qquad \mathbf{P} = \hat{\varepsilon}^{-1}(\hat{e}\ \overset{\leftrightarrow}{\eta} + \mathbf{P}_0)$$

Open/closed circuit measurements yield **very different** results!
In GaN $\varepsilon_0 = 8.9, \varepsilon_\infty = 5.35$

Is piezoelectricity really a bulk material property?

- So far, we have assumed phenomenologically that piezoelectricity **is** a bulk material property.
- What about microscopics?



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Piezoelectricity

Richard M. Martin
Xerox Palo Alto Research Center, Palo Alto, California 94304

(Received 19 July 1971; revised manuscript received 14 October 1971)

It is shown that piezoelectric effects can be easily derived from bulk properties and are expressible in terms of linear and *quadrupole* moments of variations in charge density induced by atomic displacements. The linear-moment contribution is determined by optic macroscopic effective charges and internal-strain parameters. The remaining terms measure directly the induced quadrupole moment, and hence provide insight into the nature of interatomic forces and chemical bonding. Special attention is focussed upon the zinc-blende structure. An important step in the derivation is the use of translation and rotation invariance to transform the basic equations to eliminate convergence difficulties and give expressions manifestly independent of surface configurations.

- Bulklike nature of piezoelectricity challenged until the mid 1980s.
- First calculation ever of piezoelectricity in 1989 (**not** based on Martin's theory).

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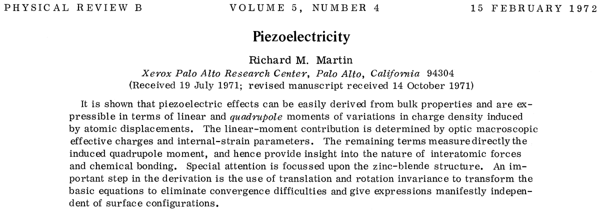

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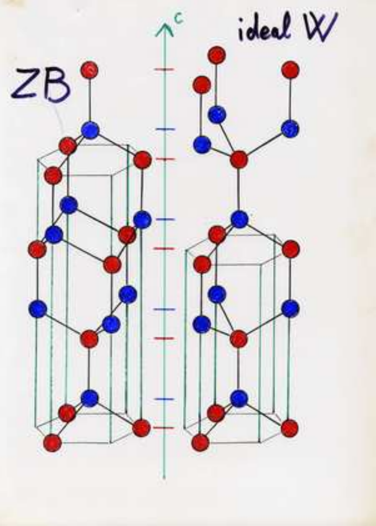
Zincblende vs. Wurtzite

Zincblende: III-V's (not nitrides)
Wurtzite: Nitrides & many II-VI's

Ideal W: $c_0/a_0 = 1.6333$

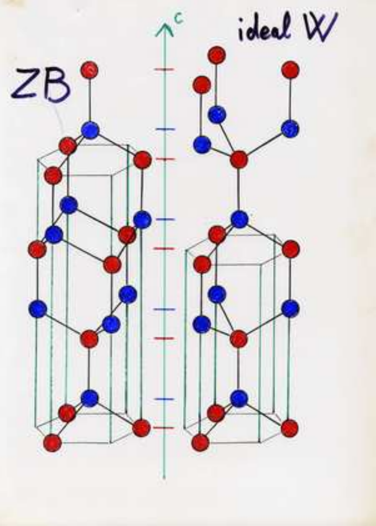
AlN	1.6008
GaN	1.6263
InN	1.6119
ZnO	1.602
ZnS	1.638



Zincblende vs. Wurtzite

Wurtzite:
Highest symmetry where $\mathbf{P}_0 \neq 0$
Piezoelectric tensor has independent components e_{33}, e_{31}, e_{15}

Zincblende:
Tetrahedral symmetry: $\mathbf{P}_0 = 0$
Piezoelectric tensor has one component

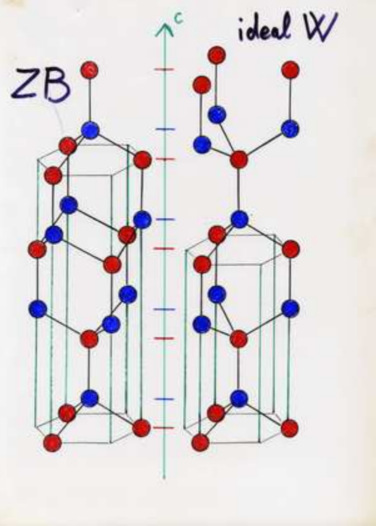


Simple piezoelectric strain

Voigt notations:

- strain along the c axis
  $\eta_3 = (c - c_0)/c_0$
- isotropic in-plane strain
  $\eta_1 = \eta_2 = (a - a_0)/a_0$

- piezoelectric polarization:
  $\mathbf{P} - \mathbf{P}_0 = e_{33}\eta_3 + e_{31}(\eta_2 + \eta_3)$
  in zero field!



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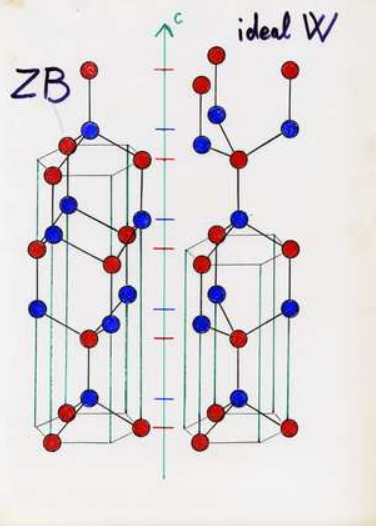

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What the popular textbooks **wrongly** say

- **Kittel,** *Introduction to Solid State Physics*:

  A ferroelectric crystal exhibits an electric dipole moment even in the absence of an external electric field. In the ferroelectric state the **center of positive charge** does not coincide with the **center of negative charge**.

- **Ashcroft & Mermin,** *Solid State Physics*:

  Crystal whose **natural primitive cells** have a nonvanishing **dipole moment** $\mathbf{p}_0$ are called pyroelectric.

The reference book about ferroelectrics in the 1980s

- **Lines & Glass,** *Principles and Applications of Ferroelectrics and Related Materials (1977)*:

  If and when good **electron-density maps** become available for ferroelectrics, expressing charge density $\rho(\mathbf{r})$ as a function of position vector $\mathbf{r}$ throughout the unit cell, more quantitative estimates of spontaneous polarization might be envisaged as

$$\mathbf{P}_\mathrm{s} = \frac{1}{V} \int_V \mathbf{r}\,\rho(\mathbf{r})\; d\mathbf{r}. \qquad (6.1.19)$$

- Focus invariably on the **charge density**

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Where the problem is (after Feynman, Vol. 2)

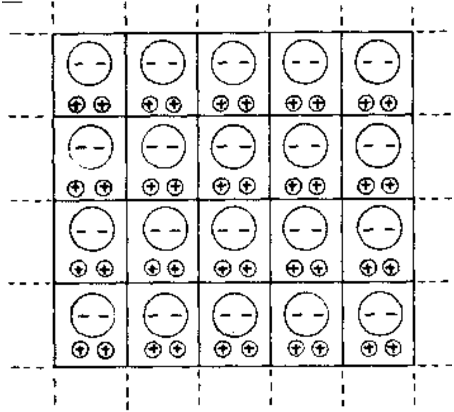

Fig. 11–8. A complex crystal lattice can have a permanent intrinsic polarization P.

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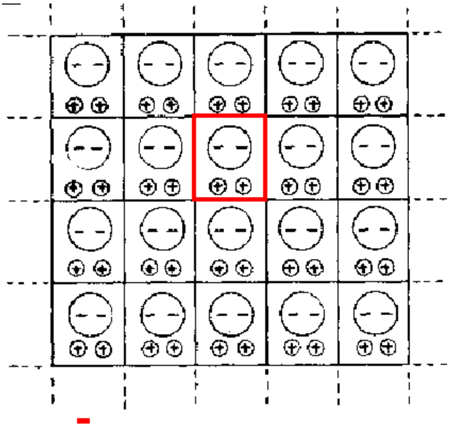

Fig. 11–8. A complex crystal lattice can have a permanent intrinsic polarization P.

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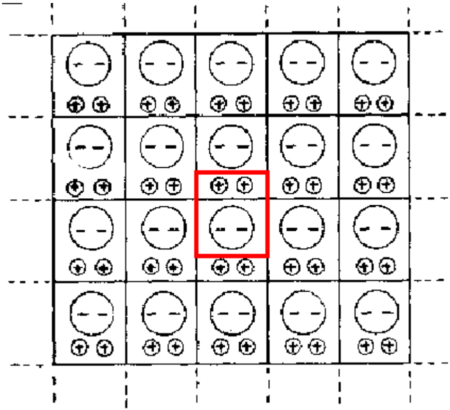

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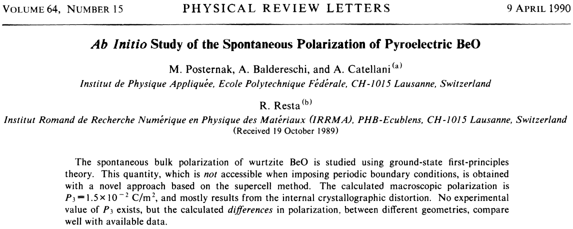
Spontaneous polarization: the “new” paradigm (1990)



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Ab Initio Study of the Spontaneous Polarization of Pyroelectric BeO

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(Received 19 October 1989)

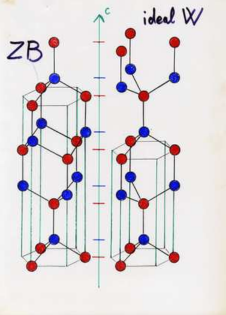
The spontaneous bulk polarization of wurtzite BeO is studied using ground-state first-principles theory. This quantity, which is *not* accessible when imposing periodic boundary conditions, is obtained with a novel approach based on the supercell method. The calculated macroscopic polarization is $P_3 = 1.5\times10^{-2}$ C/m^2, and mostly results from the internal crystallographic distortion. No experimental value of P_3 exists, but the calculated *differences* in polarization, between different geometries, compare well with available data.

Zincblende:

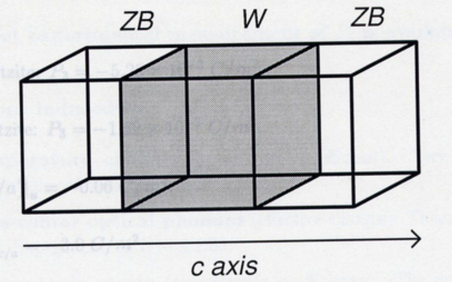
$\mathbf{P}_0 = 0$ by symmetry

Wurtzite:

Simplest crystal structure where $\mathbf{P}_0 \neq 0$



The basic idea



- The basic equation $\nabla \cdot \mathbf{P} = -\rho$

  implies $\Delta \mathbf{P} \cdot \mathbf{n} = -\sigma$
- Since $\mathbf{P}_0 = 0$ in the zincblende slab
  by measuring σ we infer the value of $\mathbf{P}_0$ in the wurtzite slab
- Actually, $\Delta \mathbf{P} = \mathbf{P}_0 / \varepsilon$ (longitudinal!)

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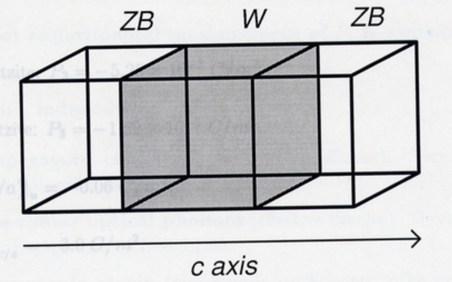

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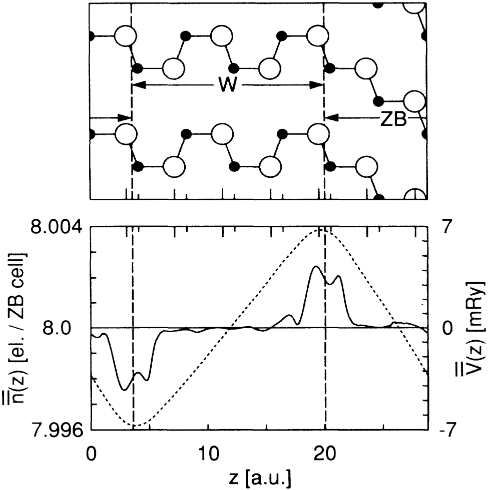
The computer experiment



The paradigm change

Concours
Seymour Cray

Lauréats 1990

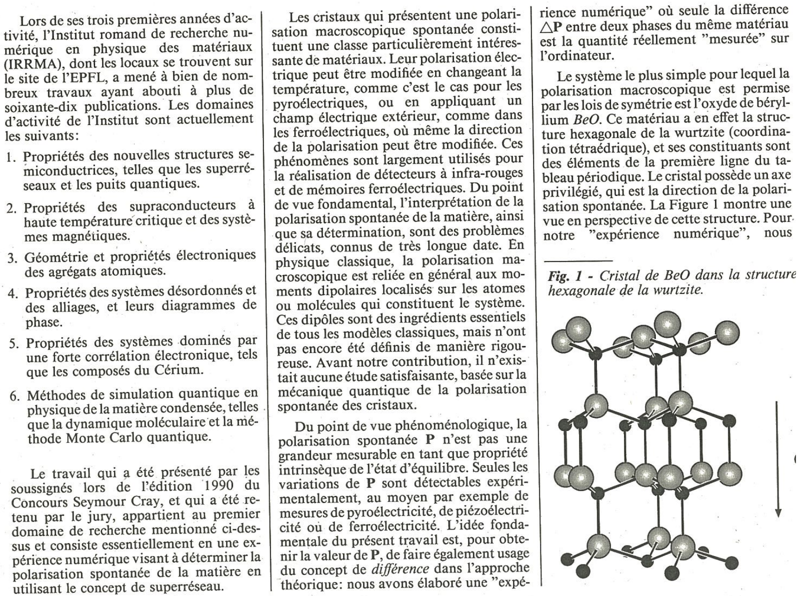
Michel Posternak, Raffaele Resta et le professeur EPFL Alfonso Baldereschi, ex aequo avec une équipe de l'EPFZ, ont reçu le vendredi 1er février dernier le deuxième prix du Concours Seymour Cray Suisse 1990 pour l'expérience (réalisée dans le cadre de l'IRRMA) qu'ils présentent ici. Le premier prix a récompensé M. Bichsel et P. Seitz pour leur travail "Concierge électronique" portant sur la reconnaissance de personnes. Si la participation à ce concours s'est limitée à dix travaux, "le jury a été très heureux de constater une très bonne qualité moyenne", a précisé son président, le professeur Maurice Cosandey.

Les hommes d'IRRMA

De gauche à droite: Alfonso Baldereschi, Michel Posternak et Raffaele Resta. (Photo Alain Herzog)

Détermination de la polarisation spontanée de la matière au moyen d'une expérience numérique: cas de l'Oxyde de Béryllium Pyroélectrique

The paradigm change



Lors de ses trois premières années d'activité, l'Institut romand de recherche numérique en physique des matériaux (IRRMA), dont les locaux se trouvent sur le site de l'EPFL, a mené à bien de nombreux travaux ayant abouti à plus de soixante-dix publications. Les domaines d'activité de l'Institut sont actuellement les suivants:

1. Propriétés des nouvelles structures semiconductrices, telles que les superréseaux et les puits quantiques.
2. Propriétés des supraconducteurs à haute température critique et des systèmes magnétiques.
3. Géométrie et propriétés électroniques des agrégats atomiques.
4. Propriétés des systèmes désordonnés et des alliages, et leurs diagrammes de phase.
5. Propriétés des systèmes dominés par une forte corrélation électronique, tels que les composés du Cérium.
6. Méthodes de simulation quantique en physique de la matière condensée, telles que la dynamique moléculaire et la méthode Monte Carlo quantique.

Le travail qui a été présenté par les soussignés lors de l'édition 1990 du Concours Seymour Cray, et qui a été retenu par le jury, appartient au premier domaine de recherche mentionné ci-dessus et consiste essentiellement en une expérience numérique visant à déterminer la polarisation spontanée de la matière en utilisant le concept de superréseau.

Les cristaux qui présentent une polarisation macroscopique spontanée constituent une classe particulièrement intéressante de matériaux. Leur polarisation électrique peut être modifiée en changeant la température, comme c'est le cas pour les pyroélectriques, ou en appliquant un champ électrique extérieur, comme dans les ferroélectriques, où même la direction de la polarisation peut être modifiée. Ces phénomènes sont largement utilisés pour la réalisation de détecteurs à infra-rouges et de mémoires ferroélectriques. Du point de vue fondamental, l'interprétation de la polarisation spontanée de la matière, ainsi que sa détermination, sont des problèmes délicats, connus de très longue date. En physique classique, la polarisation macroscopique est reliée en général aux moments dipolaires localisés sur les atomes ou molécules qui constituent le système. Ces dipôles sont des ingrédients essentiels de tous les modèles classiques, mais n'ont pas encore été définis de manière rigoureuse. Avant notre contribution, il n'existait aucune étude satisfaisante, basée sur la mécanique quantique de la polarisation spontanée des cristaux.

Du point de vue phénoménologique, la polarisation spontanée **P** n'est pas une grandeur mesurable en tant que propriété intrinsèque de l'état d'équilibre. Seules les variations de **P** sont détectables expérimentalement, au moyen par exemple de mesures de pyroélectricité, de piézoélectricité ou de ferroélectricité. L'idée fondamentale du présent travail est, pour obtenir la valeur de **P**, de faire également usage du concept de *différence* dans l'approche théorique: nous avons élaboré une "expérience numérique" où seule la différence $\Delta\mathbf{P}$ entre deux phases du même matériau est la quantité réellement "mesurée" sur l'ordinateur.

Le système le plus simple pour lequel la polarisation macroscopique est permise par les lois de symétrie est l'oxyde de béryllium *BeO*. Ce matériau a en effet la structure hexagonale de la wurtzite (coordination tétraédrique), et ses constituants sont des éléments de la première ligne du tableau périodique. Le cristal possède un axe privilégié, qui est la direction de la polarisation spontanée. La Figure 1 montre une vue en perspective de cette structure. Pour notre "expérience numérique", nous

Fig. 1 - Cristal de BeO dans la structure hexagonale de la wurtzite.

The paradigm change

- We have not computed the absolute polarization of the W material; instead, we have computed a polarization **difference**: Wurtzite minus Zincblende.
- It is only an additional symmetry argument which allows us to infer the value of $\mathbf{P}_0$ from the calculation.
- In our material (wurtzite BeO) how is spontaneous polarization measured?
- We discovered (after our computer experiment) that it is not really measured! Reading the experimental literature we only found some **estimates** of the spontaneous polarization in BeO.
- Slowly, we came to the idea that the concept of “polarization itself” doesnt make sense, and we must content ourselves of addressing polarization **differences** (or derivatives).

How is polarization measured?

- Infrared charges, a.k.a. Born effective charges for lattice dynamics:
  Derivatives of **P** with respect to zone-center phonon amplitudes
- Permittivity, a.k.a. macroscopic dielectric constant (or tensor):
  Derivative of **P** with respect to an external applied field.
- Piezoelectricity:
  Derivative of **P** with respect to macroscopic strain.
- Pyroelectricity:
  Derivative of **P** with respect to temperature.
- **“Spontaneous” P** in ferroelectrics:
  What is actually measured?

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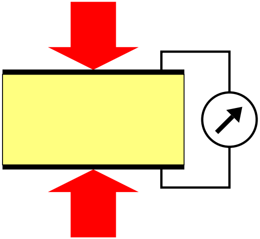
Main message revisited

- Macroscopic polarization has nothing to do with the periodic charge of a polarized dielectric
- Instead, the polarization **difference** is an integrated transient current



$$\Delta \mathbf{P} = \int_0^{\Delta t} \mathbf{j}(t)dt$$

The Berry phase formula (1992-93)

- In quantum mechanics the current is mostly related to the **phase** of the wavefunction
  (**not** to the square modulus!)
- The by now famous King-Smith & Vanderbilt formula (electronic term only, one dimension, one band):

$$P(1) - P(0) = \int_0^1 \frac{dP}{d\lambda}\, d\lambda = -\frac{e}{\pi}[\gamma(1) - \gamma(0)]$$

- The Berry phase:

$$\gamma = i \int_{\mathrm{BZ}} \langle u_k | \frac{d}{dk} u_k \rangle \, dk$$

$u_k(x) = \mathrm{e}^{-ikx}\psi_k(x)$ is the periodic part of the Bloch function

20 years on........

- Most electronic-structure computer codes on the market implement the Berry phase as a standard option: `CRYSTAL, QUANTUM-ESPRESSO, ABINIT, VASP, SIESTA, CPMD...`
- Textbooks are slow to catch: most of them give a flawed **definition** of what polarization is

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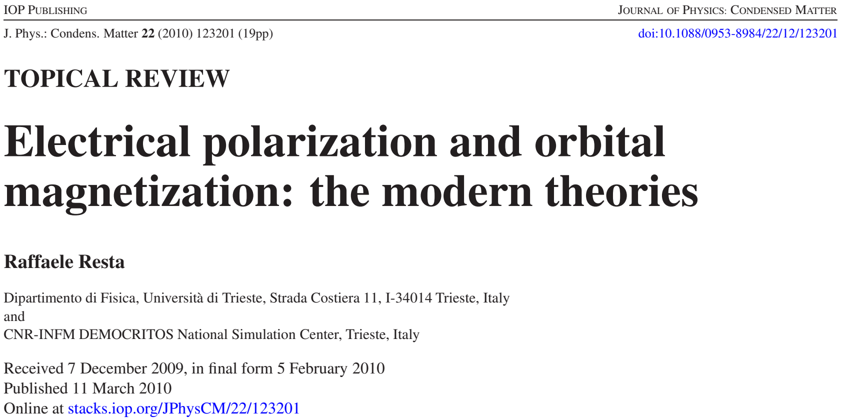
Everything you always wanted to know about polarization & magnetization but were afraid to ask:



IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

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TOPICAL REVIEW

Electrical polarization and orbital magnetization: the modern theories

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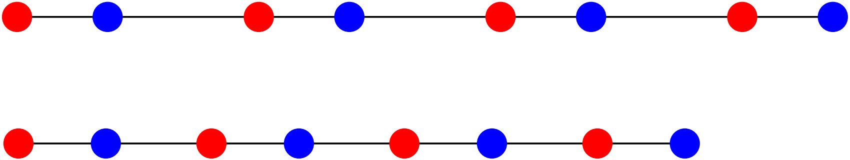
Outline

1. Fundamentals & macroscopic (phenomenological) theory
2. Wurtzite structure
3. Textbooks' fallacies about polarization (induced & spontaneous)
4. A change of paradigm
5. **Microscopic approach to piezoelectricity**
6. A more difficult problem: flexoelectricity

Milestones

- Bulklike nature of piezoelectricity established in 1972 by R.M. Martin , but challenged until the mid 1980s
- First calculation ever of piezoelectricity in 1989 by us: Zincblende III-V's, using linear response theory
- Most modern calculations, routinely:
  Numerical differentiation using the Berry phase theory
  (Wurtzite ZnO by us in 1994)

Parsing linear piezoelectricity



- Circles represent crystal planes (normal to the wurtzite *c* axis)
- First step: uniform strain (a.k.a. clamped ion) (difficult!)
- Second step: internal strain (easy: zone-center phonon)

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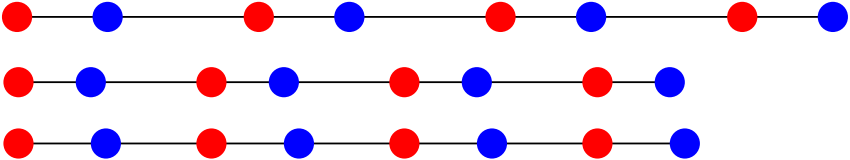

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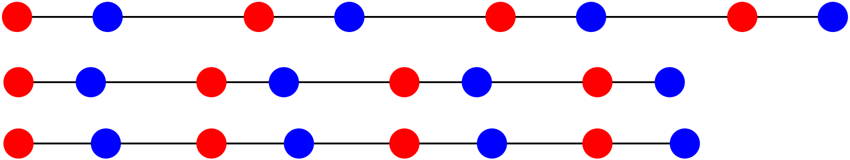

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Calculations for the wurtzite materials

(Bernardini, Fiorentini,& Vanderbilt 1997, 2011)

	$e_{33}^{(0)}$	e_{33}
AlN	-0.47	1.46
GaN	-0.84	0.73
InN	-0.88	0.97
ZnO	-0.66	0.89

- $e_{33}^{(0)}$: “clamped ion” term
- e_{33}: sum of the two terms

Trends:

- The two terms are different in sign and compete
- Balance is opposite in zincblende III-V’s
- Absolute values rather large, not far from ferroelectrics

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Phenomenological tensors (3rd & 4th rank)

$$P_\alpha = e_{\alpha\beta\gamma}\ \eta_{\beta\gamma}$$

Piezoelectricity

(needs **low** *symmetry)*

$$P_\alpha = \mu_{\alpha\beta\gamma\delta}\ \nabla_\beta \eta_{\gamma\delta}$$

Flexoelectricity

(nonzero in **any** *symmetry)*

- Are $e_{\alpha\beta\gamma}$ and $\mu_{\alpha\beta\gamma\delta}$ **bulk properties**?
- Can they be computed using **periodic boundary conditions**?
- Does such tensors make any sense?

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Why a wave of interest in flexoelectricity?

- Effect negligible at macroscopic length scales, possibly very strong at the nanoscale
- It looks very promising for electromechanical coupling using **nonpiezoelectric** materials
- Actual devices have been realized (e.g. at Penn State)
- It is not at all clear whether the $\mu_{\alpha\beta\gamma\delta}$ are genuine **bulk material properties**
- The distorted crystal lacks any **lattice periodicity**: This makes the problem difficult for us theorists!

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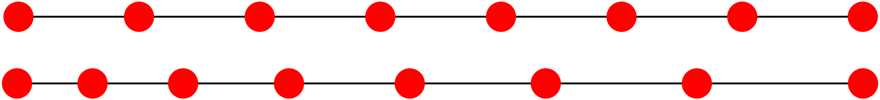
The simplest case: Elemental crystal, primitive lattice



$$\mu_{xxxx}$$

- μ_{xxxx} is a well defined bulk property in elemental crystals (R. Resta, PRL 2010)
- Work for nonprimitive lattices in progress:
  M. Stengel, `http://arxiv.org/abs/1306.4240`,
  posted **last week!**