The Polarization of Solids: a Historical Perspective

Raffaele Resta

Trieste, 2015

Manifesto

- In the early 1990s a **change of paradigm** occurred about what polarization really **is**
- Nowadays polarization is routinely computed according to the modern theory
- Very few textbooks have taken notice of the change of paradigm

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Outline

Breakthrough papers, listed by publication year:

1. The old paradigm
    - 1850
    - Textbooks

2. Computational physics and the new paradigm
    - 1979
    - 1983
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Pisa, Prato dei Miracoli

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Ottaviano Fabrizio Mossotti (1791-1863)

Professor at the University of Pisa since 1840
Chair: Meccanica celeste e fisica matematica

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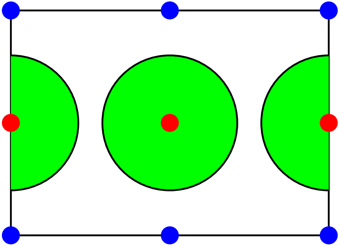
Clausius-Mossotti

O. F. Mossotti, Memorie di Matematica e di Fisica della Società Italiana delle Scienze Residente in Modena **24**, 49 (1850)



Material as an assembly of independently polarizable building bricks (electronic charges)

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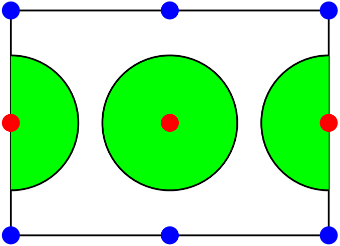

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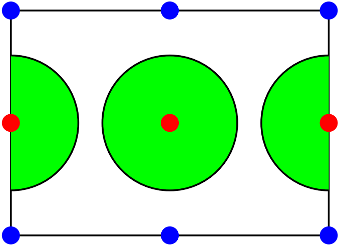
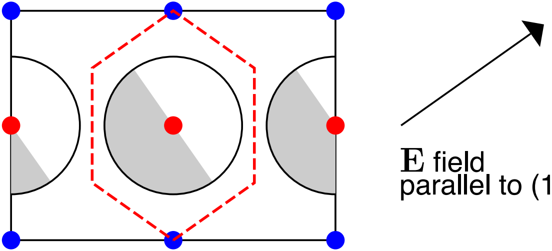
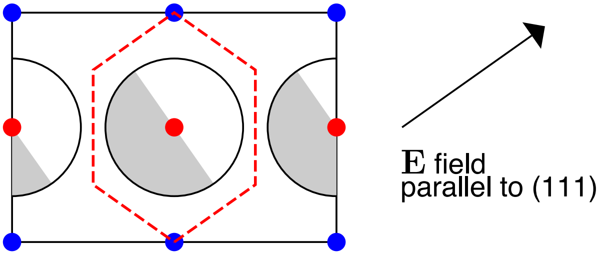




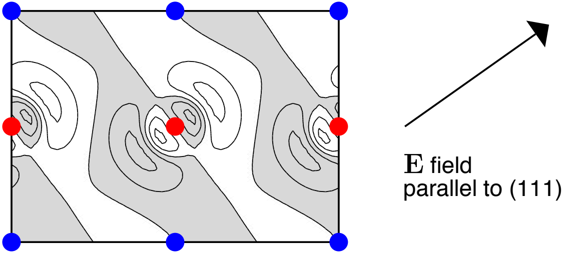
$\mathbf{E}$ field
parallel to (111)

Definition of macroscopic polarization **P**



Polarization = dipole / cell volume

With hindsight, as provided by computational physics

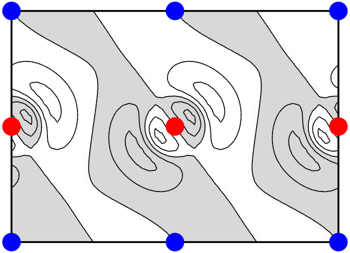


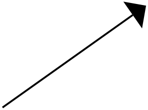
$\mathbf{E}$ field
parallel to (111)

- NaBr, induced (pseudo)charge density

- The polarization induced charge is **periodic**:
  How do we compute the induced **dipole per cell**?

With hindsight, as provided by computational physics





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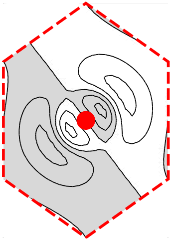

- Dipole of a Wigner-Seitz cell

- According to Clausius-Mossotti, **P** $= \mathrm{d}/V_{\mathrm{cell}}$
- In our computer experiment $\mathrm{d}/V_{\mathrm{cell}}$ is about **one half** of the right **P** value
- Even in the extreme ionic case, macroscopic polarization **is not** a function of the periodic polarization charge

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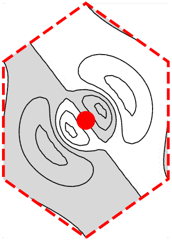

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Feynman Lectures on Physics, Vol. 2

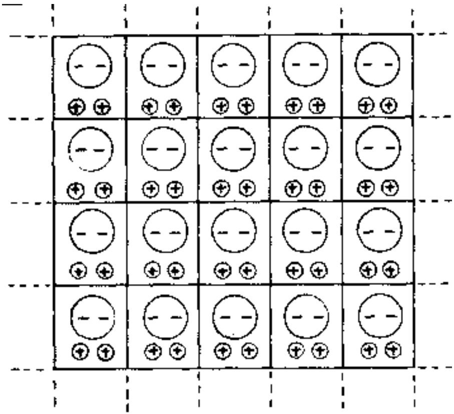
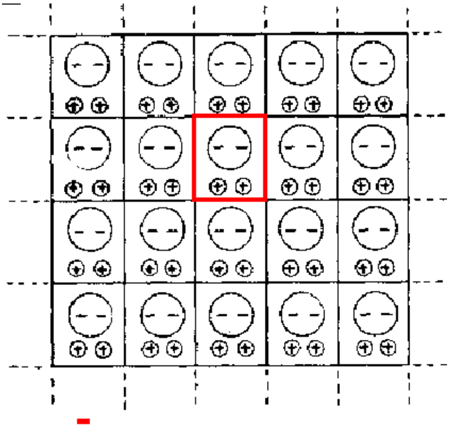


Fig. 11–8. A complex crystal lattice can have a permanent intrinsic polarization P.

Feynman Lectures on Physics, Vol. 2



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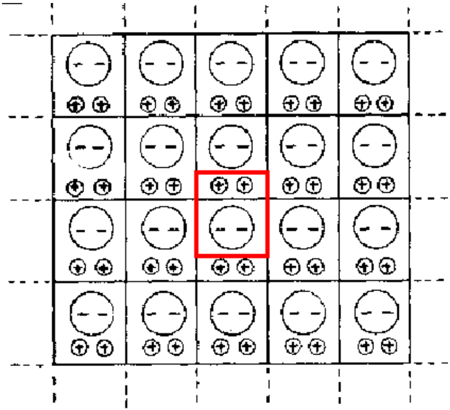

Fig. 11–8. A complex crystal lattice can have a permanent intrinsic polarization P.

Other textbooks

- **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

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

- Focus invariably on the **charge density**

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Outline

Electronic structure as a microscope

A. Baldereschi, R. Car, & E. Tosatti, Solid State Commun. **32**, 757 (1979)

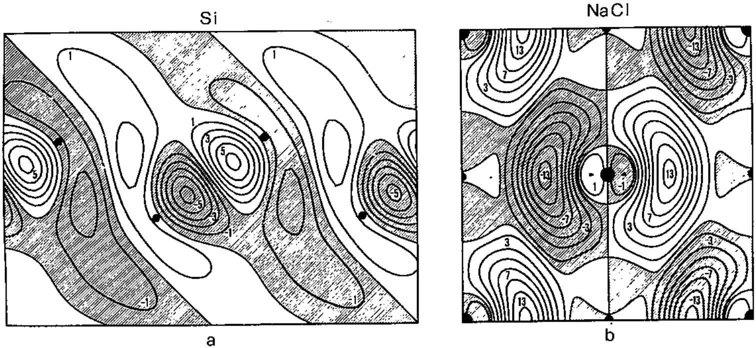
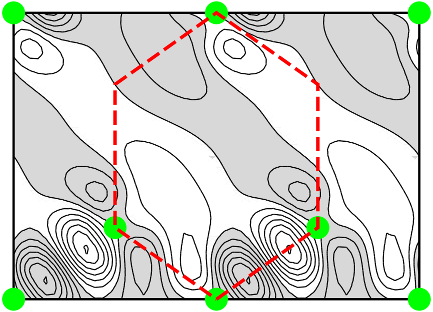
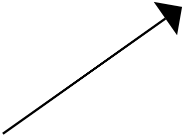


Fig. 2. Polarization charge density in units of electrons/cell induced by a constant displacement $D = 1$ a.u. $\mathbf{D} \parallel (111)$ in Si and $\mathbf{D} \parallel (100)$ in NaCl. The contour maps are represented in the (110) and (100) planes for Si and NaCl respectively. Shaded areas indicate negative charges.

The dipole of a cell





$\mathbf{E}$ field
parallel to (111)

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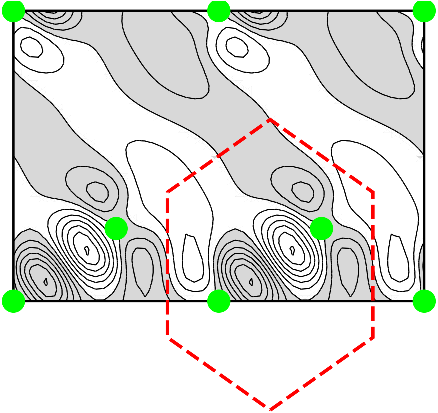

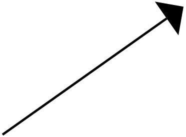

E field
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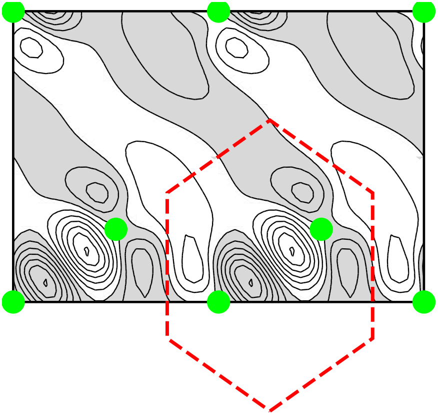
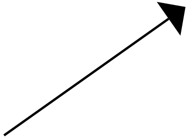




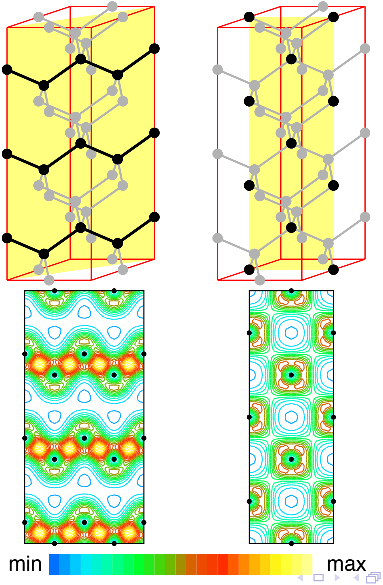
E field
parallel to (111)

With hindsight:

- Dipole disturbingly nonunique
- Dipole by far too small

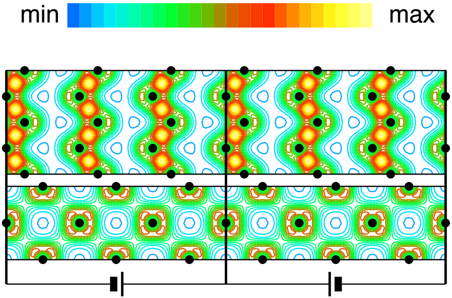
Outline

Silicon (pseudo)charge density, unperturbed



Dielectric inside a capacitor

K. Kunc & R. Resta, Phys. Rev. Lett. **51**, 686 (1983)



Dielectric inside a capacitor
Silicon induced charge density
(technically: a supercell calculation)

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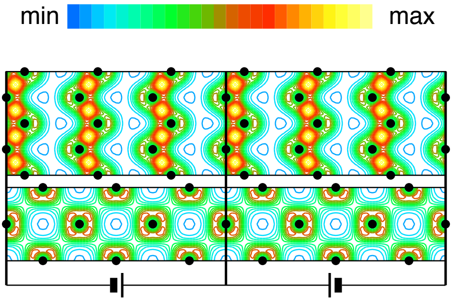
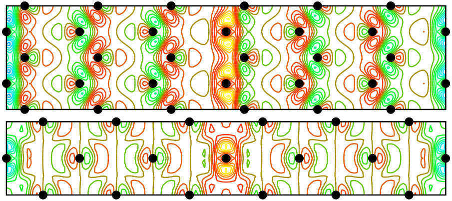
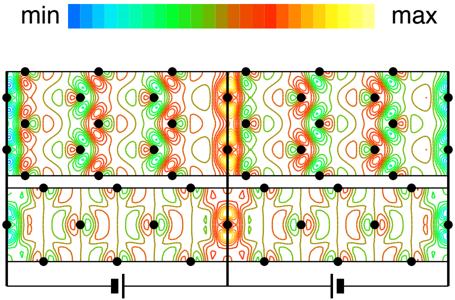


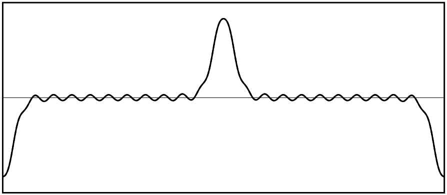
polarization density (times 50)



How is polarization retrieved?



planar average



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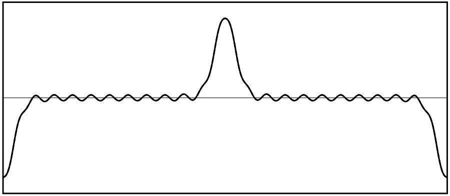

- The induced charge on the capacitor plates, divided by the applied voltage, provides the value of the dielectric constant.
- The (periodical) induced charge in the bulk of a uniformly polarized dielectric **cannot** tell the value of the dielectric constant
- What we really have measured is only the **polarization difference** between two slabs of the same material (polarized in opposite directions)

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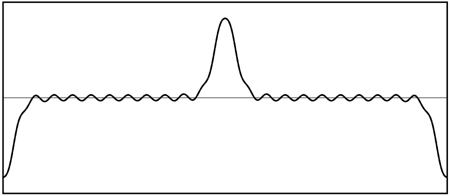

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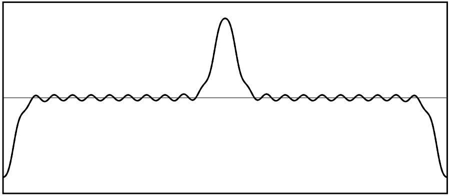

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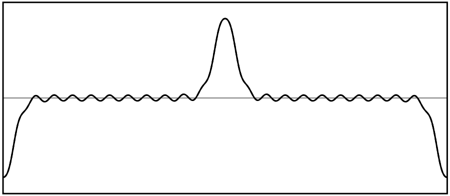
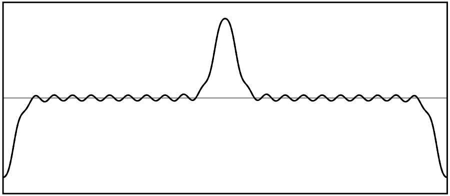
With (much) hindsight......



- The charge in a uniformly polarized dielectric **has nothing to do** with macroscopic polarization **P**.
- The charge is the **square modulus** of the wavefunction.
- From charge to current......
- So far: induced polarization. What about **spontaneous polarization** in zero **E** field?

With (much) hindsight......



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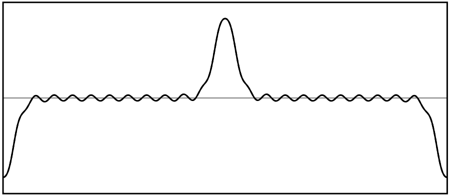

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Spontaneous polarization

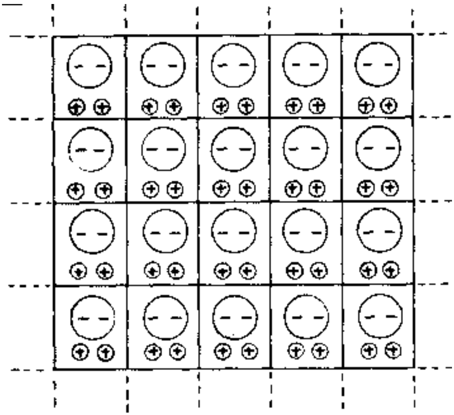
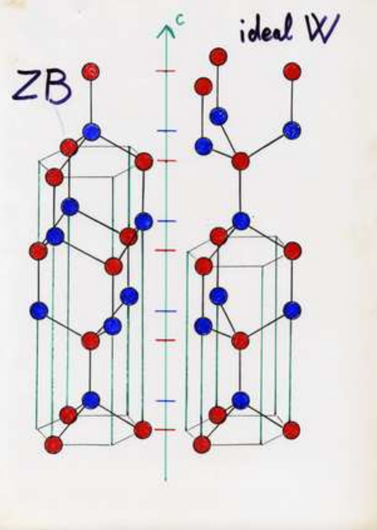


Fig. 11–8. A complex crystal lattice can have a permanent intrinsic polarization *P*.

Wurtzite vs. zincblende

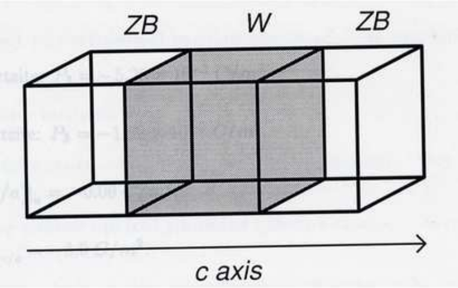


Zincblende:
Cubic, hence no vector property, such as **P**, is allowed

Wurtzite:
The simplest crystal structure where a vector property is allowed

The basic idea

M. Posternak, A. Baldereschi, A. Catellani, and R. Resta, Phys Rev Lett 1990

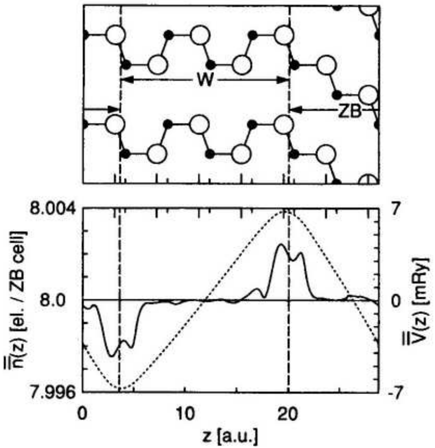


- The basic equation $\nabla \cdot \mathbf{P} = -\rho$ implies $\Delta\mathbf{P} \cdot \mathbf{n} = -\sigma$

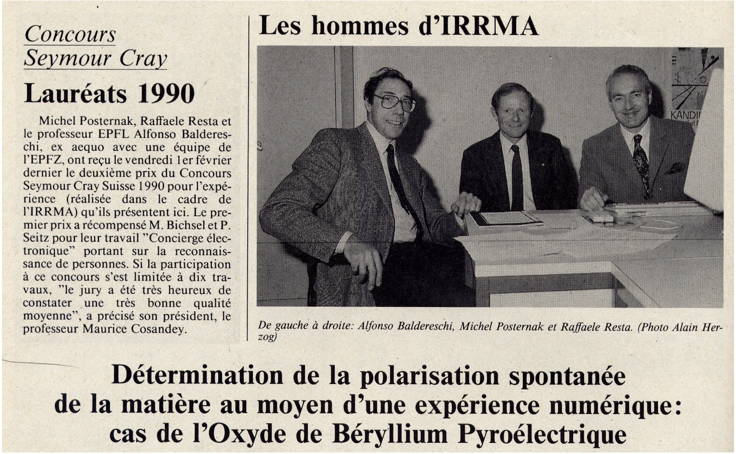
- Since **P**(ZB) is zero, by measuring σ we infer the value of **P**(W)

The first calculation ever of spontaneous polarization

M. Posternak, A. Baldereschi, A. Catellani, and R. Resta, Phys Rev Lett 1990



Seymour Cray Prize (Switzerland) 1990



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.

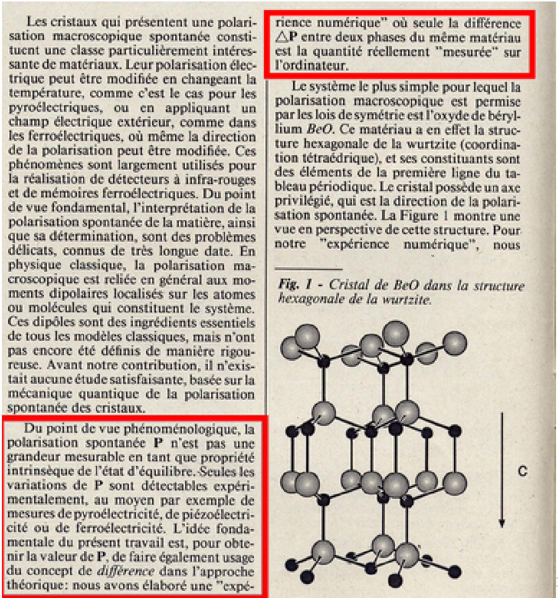
Les hommes d'IRRMA

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

Flash (EPFL weekly journal), February 12th, 1991

A change of paradigm



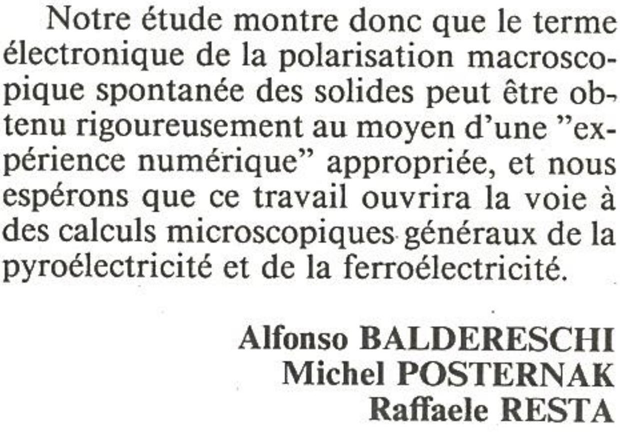
Les cristaux qui présentent une polarisation macroscopique spontanée constituent une classe particulièrement intéressante de matériaux. Leur polarisation électrique peut être modifiée en changeant la température, comme c'est le cas pour les pyroélectriques, ou en appliquant un champ électrique extérieur, 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 Δ**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.

Prophetic conclusion



Notre étude montre donc que le terme électronique de la polarisation macroscopique spontanée des solides peut être obtenu rigoureusement au moyen d’une ”expérience numérique” appropriée, et nous espérons que ce travail ouvrira la voie à des calculs microscopiques généraux de la pyroélectricité et de la ferroélectricité.

Alfonso BALDERESCHI
Michel POSTERNAK
Raffaele RESTA

What about the experiments?

- We have **not** computed the “absolute” polarization of the W material; instead, we have computed a polarization **difference**: W minus ZB.
- It is only an **additional symmetry argument** which allows us to infer the value of **P** 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.
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1. The old paradigm
   - 1850
   - Textbooks

2. Computational physics and the new paradigm
   - 1979
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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.
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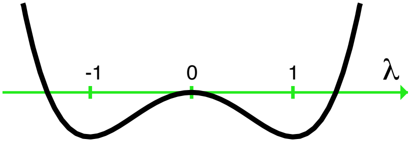
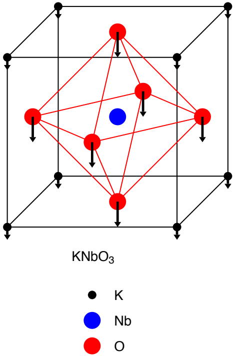
A prototypical material: $KNbO_3$





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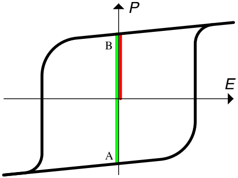

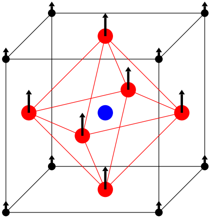

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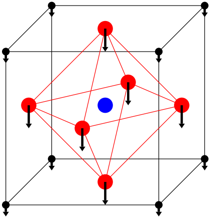

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$$\mathbf{P}_s = \int_0^{\Delta t} \mathbf{j}(t)\,dt$$

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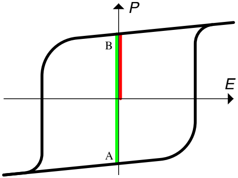

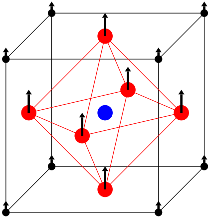

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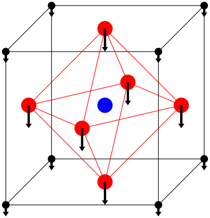

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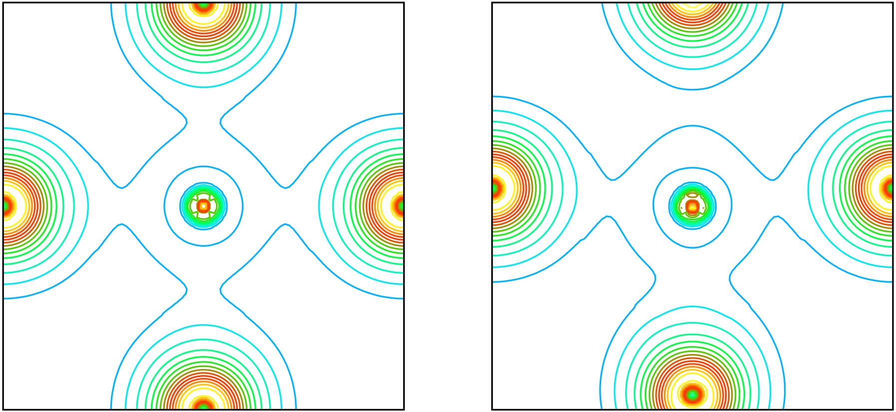
What must be computed?

Valence charge density in $KNbO_3$



centrosymmetric

broken-symmetry (ferroelectric)

Main message

Macroscopic polarization has nothing to do with the periodic charge of a polarized dielectric

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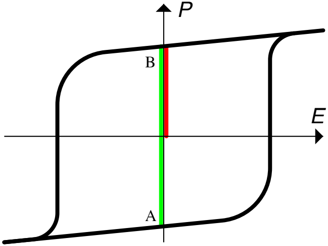

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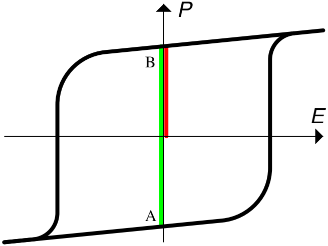

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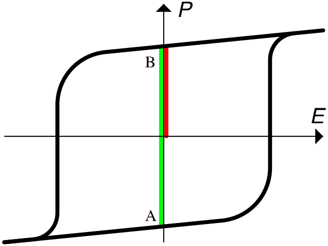

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The (by now famous) King-Smith & Vanderbilt formula.

Electronic term only, one dimension, one band:

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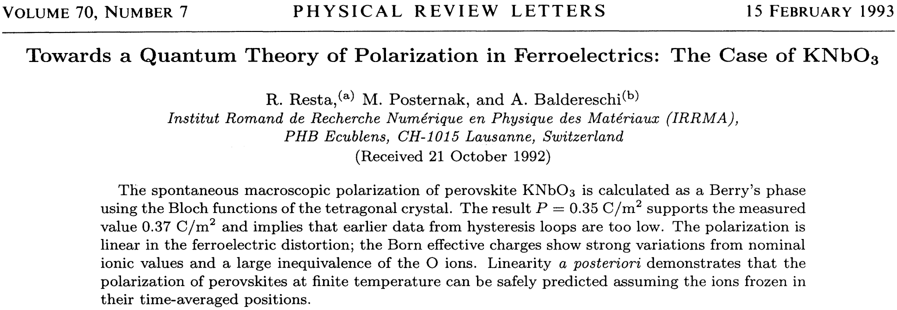

VOLUME 70, NUMBER 7 PHYSICAL REVIEW LETTERS 15 FEBRUARY 1993

Towards a Quantum Theory of Polarization in Ferroelectrics: The Case of $KNbO_3$

R. Resta,(a) M. Posternak, and A. Baldereschi(b)
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PHB Ecublens, CH-1015 Lausanne, Switzerland

(Received 21 October 1992)

The spontaneous macroscopic polarization of perovskite $KNbO_3$ is calculated as a Berry's phase using the Bloch functions of the tetragonal crystal. The result $P = 0.35\ \mathrm{C/m^2}$ supports the measured value $0.37\ \mathrm{C/m^2}$ and implies that earlier data from hysteresis loops are too low. The polarization is linear in the ferroelectric distortion; the Born effective charges show strong variations from nominal ionic values and a large inequivalence of the O ions. Linearity *a posteriori* demonstrates that the polarization of perovskites at finite temperature can be safely predicted assuming the ions frozen in their time-averaged positions.

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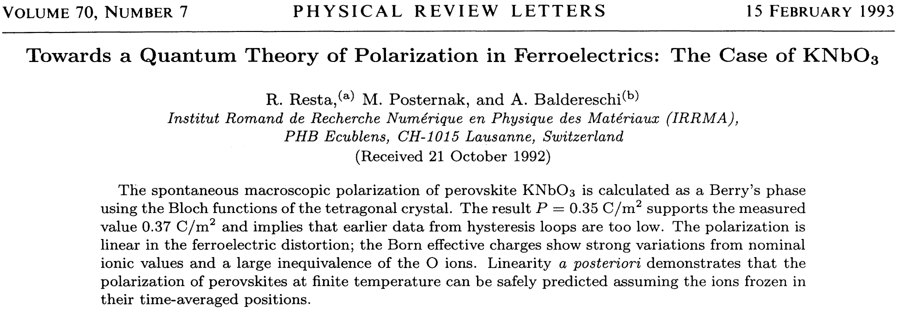

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2006 Aneesur Rahman APS Prize for Computational Physics

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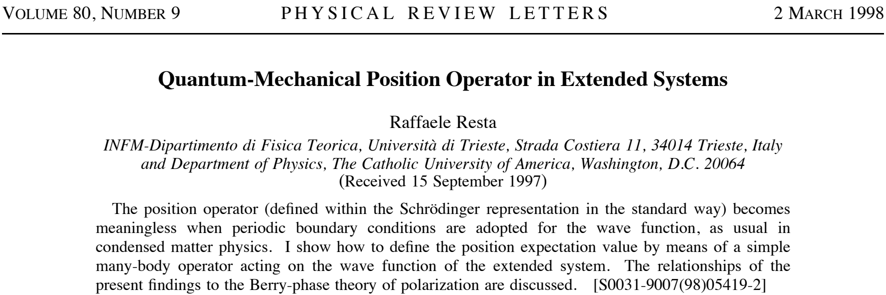

VOLUME 80, NUMBER 9 PHYSICAL REVIEW LETTERS 2 MARCH 1998

Quantum-Mechanical Position Operator in Extended Systems

Raffaele Resta
INFM-Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, 34014 Trieste, Italy
and Department of Physics, The Catholic University of America, Washington, D.C. 20064

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The position operator (defined within the Schrödinger representation in the standard way) becomes meaningless when periodic boundary conditions are adopted for the wave function, as usual in condensed matter physics. I show how to define the position expectation value by means of a simple many-body operator acting on the wave function of the extended system. The relationships of the present findings to the Berry-phase theory of polarization are discussed. [S0031-9007(98)05419-2]

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- Routinely implemented for liquid & amorphous systems

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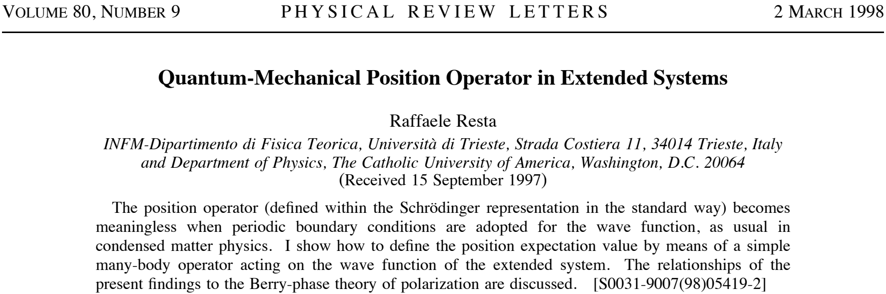

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- It is the simple multiplicative operator which maps (1d): $\psi(x) \rightarrow x\,\psi(x)$
- Its expectation value is: $\langle x \rangle = \int dx\; x\,|\psi(x)|^2$
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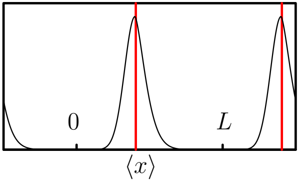

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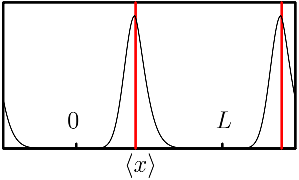

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- Analytical formulas and “theorems” discovered **after** the computations
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