The Abdus Salam
International Centre
for Theoretical Physics

2440-4

16th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

10 - 12 January 2013

Field-lattice coupling in flexoelectrics and magnetoelectrics

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“Total Energy” Workshop, January 2013

Outline

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Phenomenological tensors (3rd & 4th rank)

$$P_\alpha = \eta_{\alpha\beta\gamma}\, \epsilon_{\beta\gamma}$$

Piezoelectricity
(needs **low** *symmetry)*

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

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

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

Outline

1. Strain induced polarization
   - Piezoelectricity

1972: Piezoelectricity as a bulk property

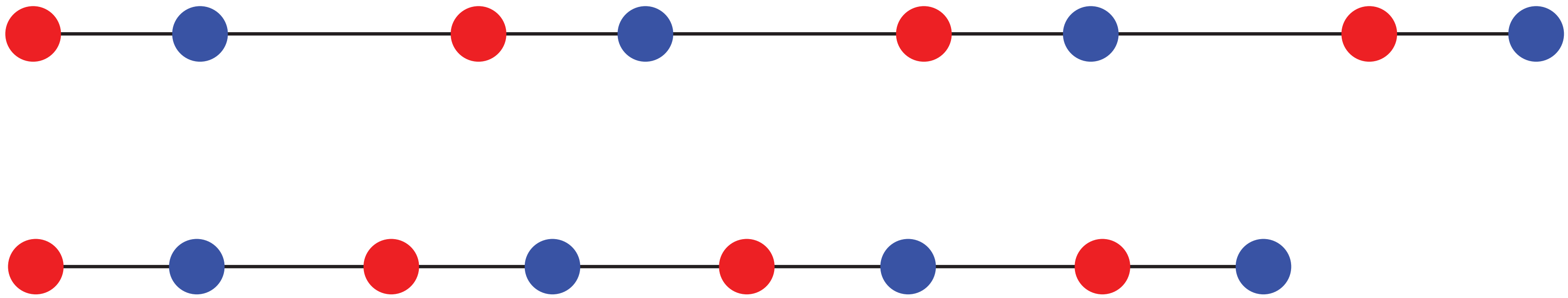
PHYSICAL REVIEW B VOLUME 5, NUMBER 4 15 FEBRUARY 1972

Piezoelectricity

Richard M. Martin
Xerox Palo Alto Research Center, Palo Alto, California 94304
(Received 19 July 1971; revised manuscript received 14 October 1971)

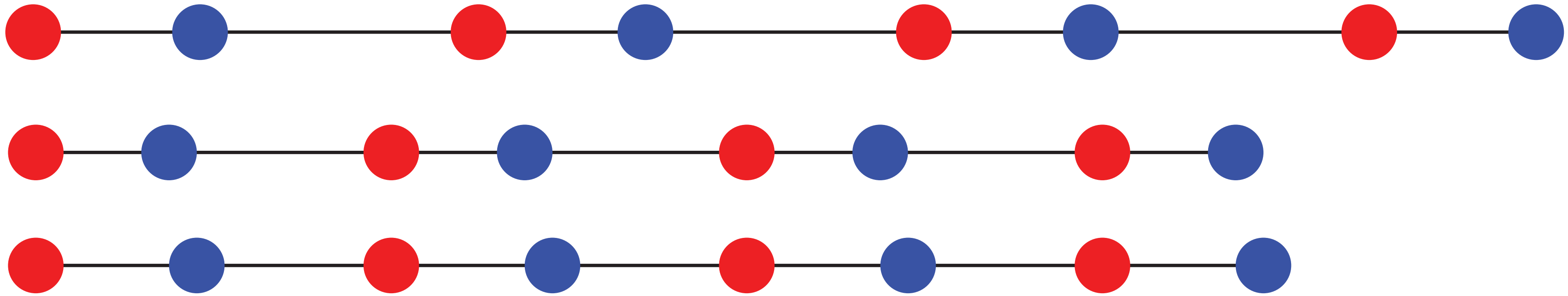
It is shown that piezoelectric effects can be easily derived from bulk properties and are expressible in terms of linear and *quadrupole* moments of variations in charge density induced by atomic displacements. The linear-moment contribution is determined by optic macroscopic effective charges and internal-strain 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.

Parsing linear piezoelectricity



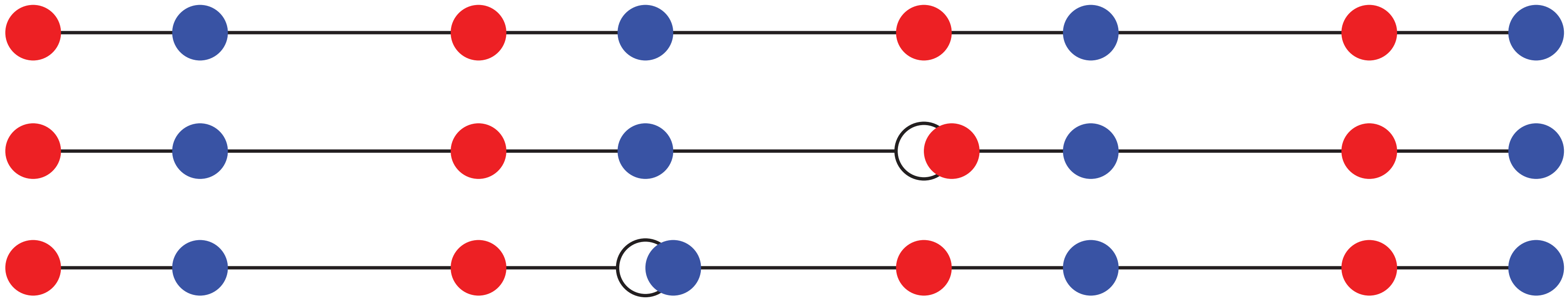
- Circles represent crystal planes

Parsing linear piezoelectricity



- Circles represent crystal planes
- First step: uniform strain **(difficult!)**
- Second step: internal strain **(easy: zone-center phonon)**

Uniform strain: the key idea



Moving only **one** plane in an otherwise unperturbed solid

- Monopoles: $= 0$
- Dipoles: Born effective charges (they sum to zero, **ASR**)
- Quadrupoles:
  They **don't** sum to zero, if symmetry is low enough

Bottom line (RMM 1972): sum of quadrupoles $\longrightarrow$ $\eta_{\alpha\beta\gamma}$

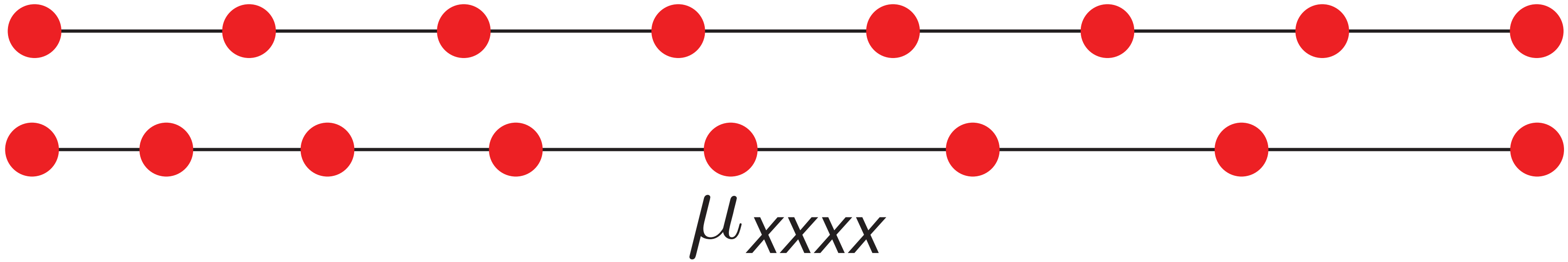
Outline

1. Strain induced polarization
   - Piezoelectricity
   - Flexoelectricity

Why a wave of interest in flexolectriciy?

- 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!

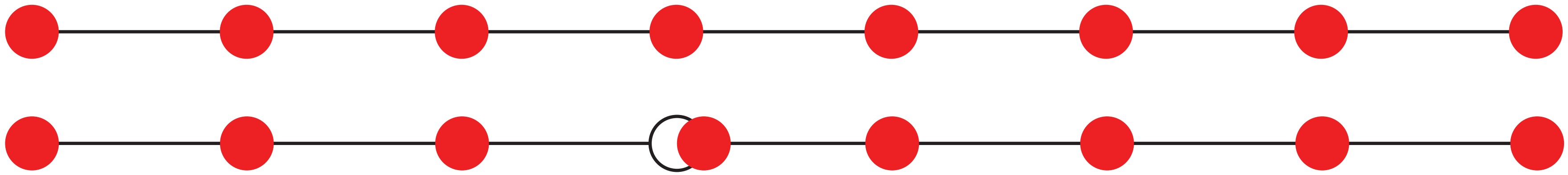
The simplest case: Elemental crystal, primitive lattice



Key steps the proof:

- $\mathbf{E}^{(\mathrm{macro})} = -4\pi\, \mathbf{P}^{(\mathrm{macro})}$ in this geometry
- Microscopic field $\mathbf{E}(\mathbf{r})$ well defined (nonperiodical)
- Macroscopic average of $\mathbf{E}(\mathbf{r})$ constant within the sample, and boundary independent

The main ingredient



Moving only **one** plane in an otherwise unperturbed solid

- Even multipoles: zero by symmetry
- Dipole: Born effective charge = 0 (ASR)
- Octupole: the leading order
- Bottom line: Octupole $\longrightarrow$ μ_{xxxx}

More useful crystals (polar)

- Polar crystal seem to present a **qualitatively** different challenge (work by Vanderbilt & coworkers)
- Flexoelectricity is essentially a mesoscopic phenomenon: thin films, superlattices, nanostructures (length scale?)
- **My conjecture:**
  - The full 4th rank tensor $\mu_{\alpha\beta\gamma\delta}$ is **not** a bulk material property
  - Only some components (or combinations thereof) are possibly bulk

Outline

2 Field-lattice coupling

Manifesto

- Polar dielectrics: **E** field coupled to the lattice:
  - $\varepsilon_\infty \neq \varepsilon_0$
  - Lyddane-Sachs-Teller relationship
  - Dynamical matrix nonanalytic ($\omega_{\mathrm{LO}} \neq \omega_{\mathrm{TO}}$)

- Magnetoelectrics: **E** and **H** fields coupled to the lattice:
  - ME response matrices at $\omega = 0$ and $\omega = \infty$ different
  - Generalized Lyddane-Sachs-Teller relationship
  - Dynamical matrix nonanalyticity

- Theory of field coupling needed **complete reformulation**
  - Achieved in two papers: PRL 2011 & PRB 2011

Linear magnetoelectric response (Gaussian units)

$$\begin{pmatrix} D \\ B \end{pmatrix} = \mathcal{R} \begin{pmatrix} E \\ H \end{pmatrix} \equiv \begin{pmatrix} \varepsilon & \alpha \\ \alpha & \mu \end{pmatrix} \begin{pmatrix} E \\ H \end{pmatrix}$$

Induced polarization & magnetization:

$$\begin{aligned} P &= \frac{D-E}{4\pi} = \frac{\varepsilon - 1}{4\pi} E + \frac{\alpha}{4\pi} H \\ M &= \frac{B-H}{4\pi} = \frac{\mu - 1}{4\pi} H + \frac{\alpha}{4\pi} E \end{aligned} \tag{1}$$

$\alpha \neq 0$ requires absence of **both**
inversion symmetry and time-reversal symmetry:
Paradigmatic material Cr_2O_3

Revival of the magnetoelectric effect ($\gtrapprox$ 2005)

The chase for the **giant magnetoelectric effect** is ongoing

- $\varepsilon \gg 1$ near a ferroelectric transition
- $\mu \gg 1$ near a ferromagnetic transition
- What about a large α ?

Candidates:

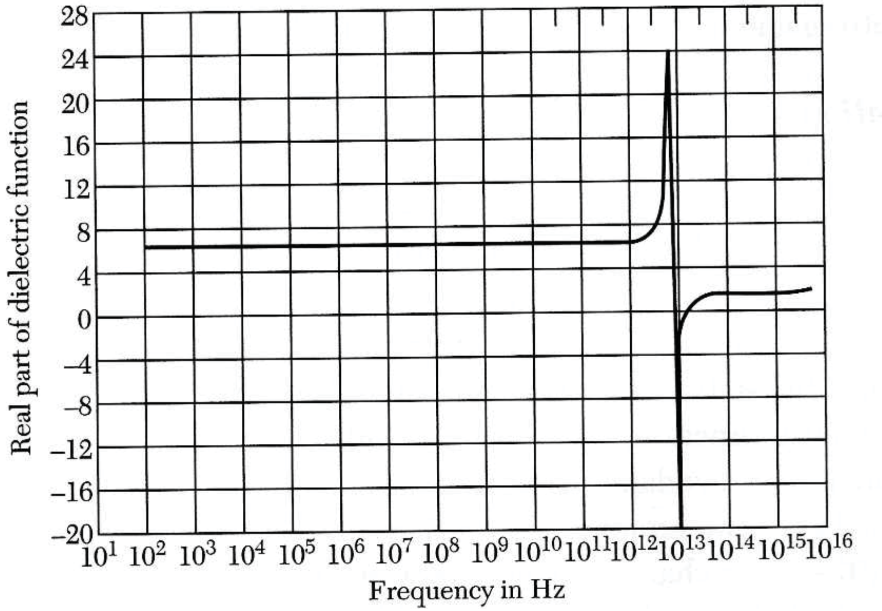
- Multiferroics? (prototype: $BiFeO_3$)
- Thin films?
- Anisotropic strain?
- Heterogenous composites ?
  (particulate, nanostructured, laminated....)

Outline

2 Field-lattice coupling

- Ordinary dielectrics

From: C. Kittel, Introduction to Solid State Physics

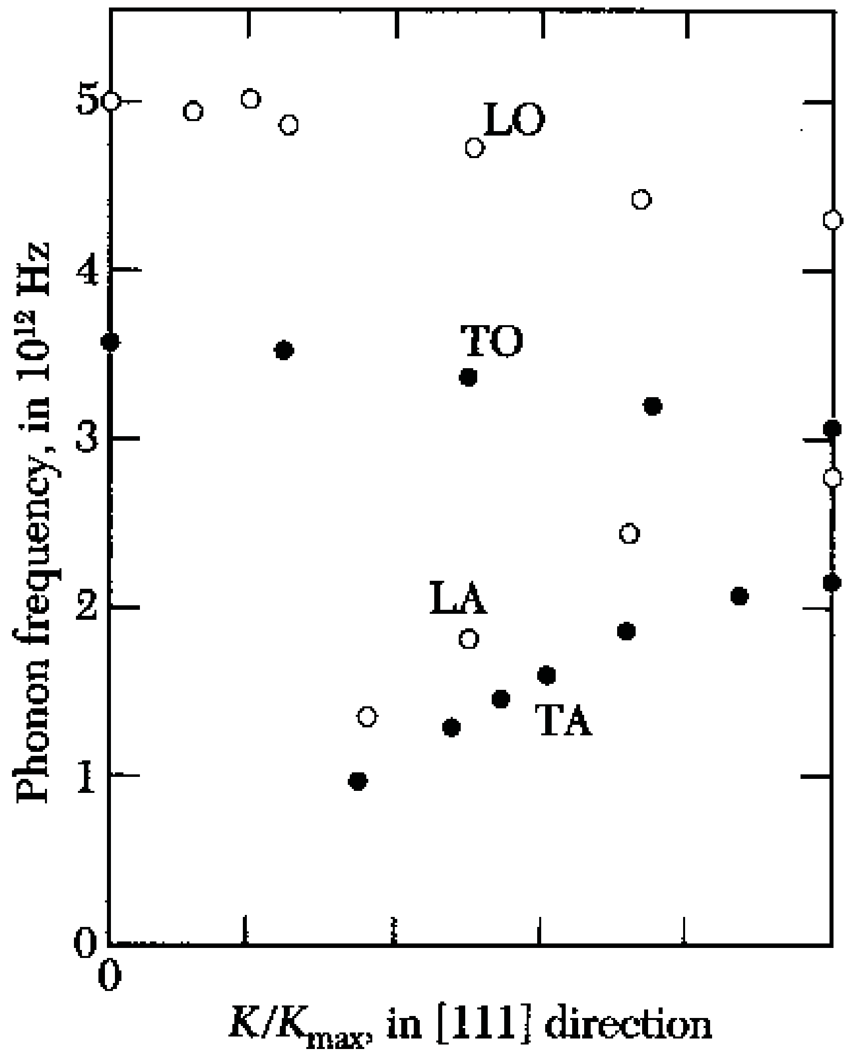


$\varepsilon(\omega)$ for SrF_2 (real part)

Two regimes:

- $\varepsilon(\omega) \longrightarrow \varepsilon_0$: static
- $\varepsilon(\omega) \longrightarrow \varepsilon_\infty$: “static high frequency”
  a.k.a. clamped-ion, a.k.a. electronic

From: C. Kittel, Introduction to Solid State Physics



Inelastic neutron scattering in KBr

Dynamical matrix **nonanalytic** at the zone center

Ordinary dielectric, cubic binary

Three **phenomenological** material constants:

- $M\omega^2_{\mathrm{TO}}$ = analytic force constant (M reduced mass)
- ε_∞ = electronic dielectric constant
- Z^* = Born effective charge

Nowadays routinely computed by first principles

Other measurable quantities

- Static dielectric constant:

$$\varepsilon_0 = \varepsilon_\infty + \frac{4\pi e^2 (Z^*)^2}{V_\mathrm{c} M \omega_\mathrm{TO}^2}$$

- Zone-center LO frequency:

$$\omega_\mathrm{LO}^2 = \omega_\mathrm{TO}^2 + \frac{4\pi e^2 (Z^*)^2}{\varepsilon_\infty V_\mathrm{c} M}$$

- Lyddane-Sachs-Teller (1941):

$$\frac{\omega_\mathrm{LO}^2}{\omega_\mathrm{TO}^2} = \frac{\varepsilon_0}{\varepsilon_\infty}$$

- All relationships **exact** within the harmonic approximation

Coupling to which field?

- In cubic binary crystals:
  - $\omega^2_{\rm TO}$ is computed within the ordinary periodic boundary conditions (routinely via DFPT, but possibly even via “frozen phonons”)
  - Z^*, ε_∞ are computed by a linear-response code (most popular: `quantum-espresso`, `abinit`)
  - In both cases the **E** field is the computational control parameter
- In low symmetry crystals:
  - The corresponding (tensorial) quantities are routinely computed

- What about magnetoelectrics?

Outline

2 Field-lattice coupling

- Ordinary dielectrics
- Magnetoelectrics

Free energy in linear magnetoelectrics: $\mathcal{F}(\{\mathbf{u}_s\}, \mathbf{E}, \mathbf{H})$

Harmonic equation of motion:

$$\mathbf{f}_s = -\frac{\partial \mathcal{F}}{\partial \mathbf{u}_s} = -\sum_{s'} C^{(\text{analytic})}_{ss'} \mathbf{u}_{s'} + Z^{*\dagger}_s \mathbf{E} + \zeta^{*\dagger}_s \mathbf{H}$$

$$\mathbf{D} = -\frac{4\pi}{V_c}\frac{\partial \mathcal{F}}{\partial \mathbf{E}} = \varepsilon_\infty \mathbf{E} + \alpha_\infty \mathbf{H} + \frac{4\pi}{V_c}\sum_s Z^*_s \mathbf{u}_s$$

$$\mathbf{B} = -\frac{4\pi}{V_c}\frac{\partial \mathcal{F}}{\partial \mathbf{H}} = \alpha^\dagger_\infty \mathbf{E} + \mu_\infty \mathbf{H} + \frac{4\pi}{V_c}\sum_s \zeta^*_s \mathbf{u}_s$$

All Cartesian indices α, β **implicit**

- $\varepsilon_\infty, \mu_\infty$ symmetric Cartesian tensors
- α_∞ electronic ME coupling: nonsymmetric tensor
- Z^*_s Born charge: nonsymmetric Cartesian tensor
- ζ^*_s Ìñiguez charge (2008, Born's magnetic analog)

Free energy in linear magnetoelectrics: $\mathcal{F}(\{\mathbf{u}_s\}, \mathbf{E}, \mathbf{H})$

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Harmonic equation of motion:

$$\begin{aligned}
\mathbf{f}_s &= -\frac{\partial \mathcal{F}}{\partial \mathbf{u}_s} = && -\sum_{s'} C_{ss'}^{(\text{analytic})} \mathbf{u}_{s'} + Z_s^{*\dagger} \mathbf{E} + \zeta_s^{*\dagger} \mathbf{H} \\
\mathbf{D} &= -\frac{4\pi}{V_c} \frac{\partial \mathcal{F}}{\partial \mathbf{E}} = && \varepsilon_\infty \mathbf{E} + \alpha_\infty \mathbf{H} + \frac{4\pi}{V_c} \sum_s Z_s^* \mathbf{u}_s \\
\mathbf{B} &= -\frac{4\pi}{V_c} \frac{\partial \mathcal{F}}{\partial \mathbf{H}} = && \alpha_\infty^\dagger \mathbf{E} + \mu_\infty \mathbf{H} + \frac{4\pi}{V_c} \sum_s \zeta_s^* \mathbf{u}_s
\end{aligned}$$

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- $\varepsilon_\infty, \mu_\infty$ symmetric Cartesian tensors
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Response matrix

- Electronic ("clamped nuclei") response

$$\begin{pmatrix} \mathbf{D} \\ \mathbf{B} \end{pmatrix} = \begin{pmatrix} \varepsilon_\infty & \alpha_\infty \\ \alpha^\dagger_\infty & \mu_\infty \end{pmatrix} \begin{pmatrix} \mathbf{E} \\ \mathbf{H} \end{pmatrix} \equiv \mathcal{R}_\infty \begin{pmatrix} \mathbf{E} \\ \mathbf{H} \end{pmatrix}$$

- Static response (including lattice contribution)

$$\mathcal{R}_0 \neq \mathcal{R}_\infty$$

- The difference is a function of the $C_{ss'}^{(\mathrm{analytic})}$, Z_s^*, ζ_s^*

High symmetry (all tensors simultaneously diagonal)

- In ordinary dielectrics, along a principal axis:

$$\frac{\omega_{\mathrm{LO}}^2}{\omega_{\mathrm{TO}}^2} = \frac{\varepsilon_0}{\varepsilon_\infty} \qquad \text{Lyddane-Sachs-Teller (1941)}$$

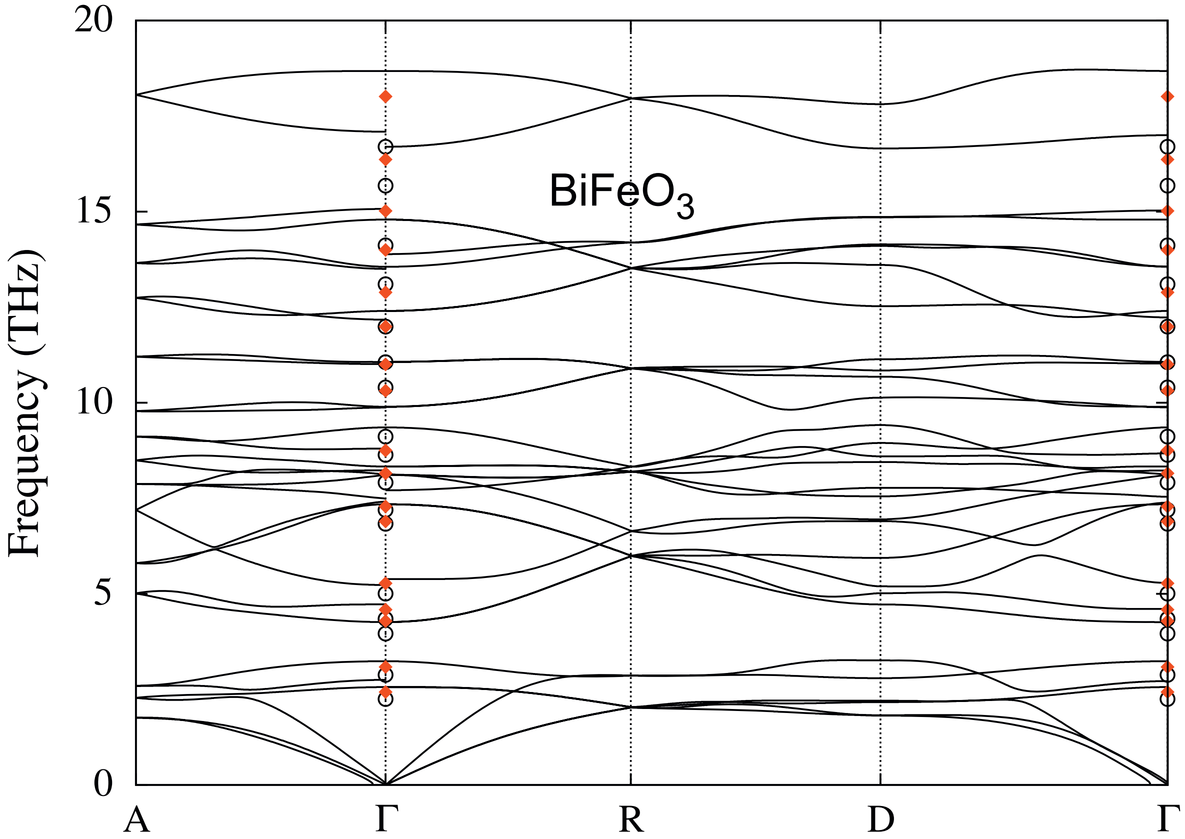
$$\equiv \frac{\varepsilon_\infty^{-1}\varepsilon_0 - 1}{1 - \varepsilon_0^{-1}\varepsilon_\infty}$$

- In magnetoelectrics $\mathcal{R}_0$, $\mathcal{R}_\infty$ 2×2 matrices

$$\frac{\omega_{\mathrm{LO}}^2}{\omega_{\mathrm{TO}}^2} = \text{a scalar function of } \mathcal{R}_0 \text{ and } \mathcal{R}_\infty$$

$$= \frac{\mathrm{tr}\,\{\mathcal{R}_\infty^{-1}\mathcal{R}_0 - \mathbb{I}\}}{\mathrm{tr}\,\{\mathbb{I} - \mathcal{R}_0^{-1}\mathcal{R}_\infty\}} \qquad \text{generalized LST (2011)}$$

A low-symmetry dielectric: Phonon spectrum



- Nonanalytic at the zone center
- Homogeneous of degree **zero** in **q**

Nonanalytic force constants (ordinary dielectric)

- Cubic binary crystal (Cartesian indices α, β implicit)

$$\mathbf{f}_s(\mathbf{q}) = -\sum_{s'=1}^{2} \left[C_{ss'}^{(\mathrm{analytic})} + \frac{4\pi e^2}{V_\mathrm{c}} \frac{(Z^*)^2 \delta_{ss'}}{\varepsilon_\infty} \mathcal{P}(\hat{\mathbf{q}}) \right] \mathbf{u}_{s'}(\mathbf{q})$$

  - $C_{ss'}^{(\mathrm{analytic})}$: scalar times the 3×3 identity
  - Z^*, ε_∞: scalar quantities
  - $\mathcal{P}(\hat{\mathbf{q}}) = \frac{q_\alpha q_\beta}{q^2}$ projector in the **q** direction (nonanalytic)

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  - $\mathcal{P}(\hat{\mathbf{q}}) = \frac{q_\alpha q_\beta}{q^2}$ projector in the **q** direction (nonanalytic)

- Low symmetry crystal (Cochran & Cowley, 1962):

$$\mathbf{f}_s(\mathbf{q}) = -\sum_{s'}\left[C_{ss'}^{\text{(analytic)}} + \frac{4\pi e^2}{V_\mathrm{c}}\frac{Z_s^{*\dagger}\mathcal{P}(\hat{\mathbf{q}})\,Z_{s'}^*}{\hat{\mathbf{q}}^\dagger\varepsilon_\infty\hat{\mathbf{q}}}\right]\mathbf{u}_{s'}(\mathbf{q})$$

  - All Cartesian matrices 3×3: $C_{ss'}^{\text{(analytic)}}, Z_s^*, Z_s^{*\dagger}, \varepsilon_\infty, \mathcal{P}(\hat{\mathbf{q}})$

Nonanalytic force constants (ordinary dielectric)

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  - All Cartesian matrices 3×3: $C_{ss'}^{(\mathrm{analytic})}, Z_s^*, Z_s^{*\dagger}, \varepsilon_\infty, \mathcal{P}(\hat{\mathbf{q}})$

Nonanalytic force constants

- Ordinary dielectric (Cochran & Cowley, 1962):

$$\mathbf{f}_s(\mathbf{q}) = -\sum_{s'} \left[C_{ss'}^{(\mathrm{analytic})} + \frac{4\pi e^2}{V_\mathrm{c}} \frac{Z_s^{*\dagger} \mathcal{P}(\hat{\mathbf{q}})\, Z_{s'}^*}{\hat{\mathbf{q}}^\dagger \varepsilon_\infty \hat{\mathbf{q}}} \right] \mathbf{u}_{s'}(\mathbf{q})$$

  - All Cartesian matrices 3×3: $C_{ss'}^{(\mathrm{analytic})}, Z_s^*, Z_s^{*\dagger}, \varepsilon_\infty, \mathcal{P}(\hat{\mathbf{q}})$

- Magnetoelectric

$$\mathbf{f}_s(\mathbf{q}) = -\sum_{s'} \left[C_{ss'}^{(\mathrm{analytic})} + \frac{4\pi e^2}{V_\mathrm{c}}\, \mathcal{Z}_s^\dagger \mathcal{M}^{-1}(\hat{\mathbf{q}}) \mathcal{P}(\hat{\mathbf{q}})\, \mathcal{Z}_{s'} \right] \mathbf{u}_{s'}(\mathbf{q})$$

  - $C_{ss',3\times3}^{(\mathrm{analytic})}, \quad \mathcal{Z}_{s,3\times6}^\dagger, \quad \mathcal{M}_{6\times6}^{-1}(\hat{\mathbf{q}}), \quad \mathcal{P}_{6\times6}(\hat{\mathbf{q}}), \quad \mathcal{Z}_{s,6\times3}$

Ingredients

- $C^{(\mathrm{analytic})}_{ss',3\times3}$ calculated at $\mathbf{E} = 0$ and $\mathbf{H} = 0$
- $\mathcal{Z}^{\dagger}_{s,3\times6} \equiv (\ Z^{*\dagger}_{s}, \zeta^{*\dagger}_{s}\ )$ electric & magnetic lattice couplings
- $\mathcal{Z}_{s,6\times3}$
- $\mathcal{P}_{6\times6}(\hat{\mathbf{q}})$ diagonal on the field indices:

$$\mathcal{P}(\hat{\mathbf{q}}) = \frac{q_\alpha q_\beta}{q^2}$$

- $\mathcal{M}^{-1}_{6\times6}(\hat{\mathbf{q}})$ diagonal on the Cartesian indices, inverse of

$$\mathcal{M}(\hat{\mathbf{q}}) = \begin{pmatrix} \hat{\mathbf{q}}^{\dagger}\varepsilon_\infty\hat{\mathbf{q}} & \hat{\mathbf{q}}^{\dagger}\alpha_\infty\hat{\mathbf{q}} \\ \hat{\mathbf{q}}^{\dagger}\alpha^{\dagger}_\infty\hat{\mathbf{q}} & \hat{\mathbf{q}}^{\dagger}\mu_\infty\hat{\mathbf{q}} \end{pmatrix}$$

Outline

Outline

3 Additional topics

- First-principle calculations: **H** vs. **B**

Which macroscopic fields?

- **In dealing with lattice coupling:**
  E and **H** play the major role
  - **E** and **H** longitudinal (**D** and **B** transverse).

- **In running first-principle calculations:**
  E and **B** play the major role
  - A standard (e.g. "frozen phonon") calculation means **E** $=$ **B** $= 0$ (**not** **H** $= 0$)
  - Linear response to **E**: implemented, standard DFPT
  - Linear response to **B**: algorithm known (Essin et al. 2010)

- **Ergo:**
  - A standard calculation **would not** provide $C_{ss'}^{(\mathrm{analytic})}$
  - A linear-response calculation does **not** provide $Z_s^{*\dagger},\ \varepsilon_\infty,\ \alpha_\infty,\ \zeta_s^{*\dagger}\ ,\mu_\infty,$

The analytic term

- We run one of the existing linear-response codes (`quantum-espresso`, `abinit`) at $\mathbf{E} = \mathbf{B} = 0$

- Output for a magnetoelectric crystal: force constants

$$\tilde{C}_{ss'} \neq C^{(\mathrm{analytic})}_{ss'}$$

- At $\mathbf{B} = 0$ in general $\mathbf{H} \neq 0$: the spurious $\mathbf{H}$ contribution must be discounted:

$$C^{(\mathrm{analytic})}_{ss'} = \tilde{C}_{ss'} - \frac{4\pi}{V_{\mathrm{c}}} \zeta^{*\dagger}_{s} \mu^{-1}_{\infty} \zeta^{*}_{s'}$$

Ingredients for the non analytic term

- The present codes provide the linear response to **E**
  - In **ordinary dielectrics**

$$Z_s^{*\dagger} = \frac{\partial \mathbf{f}_s}{\partial \mathbf{E}}, \qquad \varepsilon_\infty = 1 + 4\pi \frac{\partial \mathbf{P}}{\partial \mathbf{E}}$$

  - In **MEs** even these standard formulas require a correction

- Future codes will provide the linear response to **E** and **B**:

$$\frac{\partial \mathbf{f}_s}{\partial \mathbf{E}}, \quad \frac{\partial \mathbf{P}}{\partial \mathbf{E}}, \quad \frac{\partial \mathbf{M}}{\partial \mathbf{E}}, \quad \frac{\partial \mathbf{f}_s}{\partial \mathbf{B}}, \quad \frac{\partial \mathbf{P}}{\partial \mathbf{B}}, \quad \frac{\partial \mathbf{M}}{\partial \mathbf{B}}$$

- These uniquely define the linear response to **E** and **H**:

$$Z_s^{*\dagger}, \ \varepsilon_\infty, \ \alpha_\infty, \ \zeta_s^{*\dagger}, \mu_\infty,$$

Outline

3 Additional topics

- First-principle calculations: **H** vs. **B**
- Microscopic origin of the magnetic lattice coupling

$\mathbf{E}$ field: macroscopic vs. microscopic

$\mathbf{E}^{(\text{micro})}(\mathbf{r})$ is the "real" electric field inside the material:

$$\mathbf{f}_s = eZ_s\,\mathbf{E}^{(\text{micro})}(\mathbf{r}_s) \qquad eZ_s \text{ bare nuclear charge}$$

$$\mathbf{f}_s = eZ_s^{*\dagger}\mathbf{E} \qquad \text{force induced by } \textbf{macroscopic } \mathbf{E} \text{ field } (\mathbf{u}_s = 0)$$

$$Z_s^{*\dagger} = \frac{\mathbf{E}^{(\text{micro})}(\mathbf{r}_s)}{\mathbf{E}}\,Z_s$$

$$Z^*_{\text{cation}} > 0 \qquad\qquad Z^*_{\text{anion}} < 0$$

CAVEAT: No pseudopotentials here!

The magnetic (Ìñiguez)“effective charge”

$$Z_s^* = -\frac{1}{e}\frac{\partial^2 \mathcal{F}}{\partial \mathbf{E} \partial \mathbf{u}_s} \qquad \zeta_s^* = -\frac{1}{e}\frac{\partial^2 \mathcal{F}}{\partial \mathbf{H} \partial \mathbf{u}_s}$$

$$\mathbf{M} = \frac{e}{V_c}\zeta_s^* \mathbf{u}_s$$ magnetization induced by $\mathbf{u}_s$ ($\mathbf{E} = \mathbf{H} = 0$)

$$\mathbf{f}_s = e\,\zeta_s^{*\dagger}\,\mathbf{H}$$ force induced by **macroscopic** **H** field ($\mathbf{u}_s = 0$)

$$\mathbf{f}_s = e\,\zeta_s^{*\dagger}\frac{\partial \mathbf{H}}{\partial \mathbf{B}}\mathbf{B} = e\frac{\zeta_s^{*\dagger}}{\mu_\infty}\mathbf{B}$$

What about **microscopics**?

$$\mathbf{f}_s = e\,Z_s\,\mathbf{E}^{(\mathrm{micro})}(\mathbf{r}_s) \qquad \mathbf{f}_s \overset{?}{\propto} \mathbf{B}^{(\mathrm{micro})}(\mathbf{r}_s)$$

Microscopic forces

$\mathbf{f}_s$ has nothing to do with $\mathbf{B}^{(\mathrm{micro})}(\mathbf{r}_s)$

$$\mathbf{f}_s = e Z_s \mathbf{E}^{(\mathrm{micro})}(\mathbf{r}_s)$$ even in the magnetoelectric case!

- **Ordinary dielectrics**:
  $\mathbf{E}^{(\mathrm{micro})}(\mathbf{r}_s)$ is a linear function of **E** (or **D**)

- **Magnetoelectrics**:
  $\mathbf{E}^{(\mathrm{micro})}(\mathbf{r}_s)$ is a linear function of **both** **E** and **H** (or **B**)
  it may be nonzero even when $\mathbf{E} = 0$ and $\mathbf{H} \neq 0$

Conclusions (magnetoelectrics)

- The fields **E** and **H** are coupled to the lattice on the same footing (formally)

- Fields coupling affects:
  - Magnetoelectric response
  - Lyddane-Sachs-Teller relationship
  - Nonanalytic term in the zone-center dynamical matrix
  - Theory **exact** at the harmonic level

- The fields **E** and **B** (not **H**) are the control parameters in first-principle calculations. How to cope with this

- Microscopic origin of the magnetic lattice coupling

Thank you for your attention!

Total Energy 1999, Poster Session