On the calculation of electrostriction by DFT

D. S. P. Tanner[1,2] , and P-E. Janolin[2] , E. Bousquet[1]

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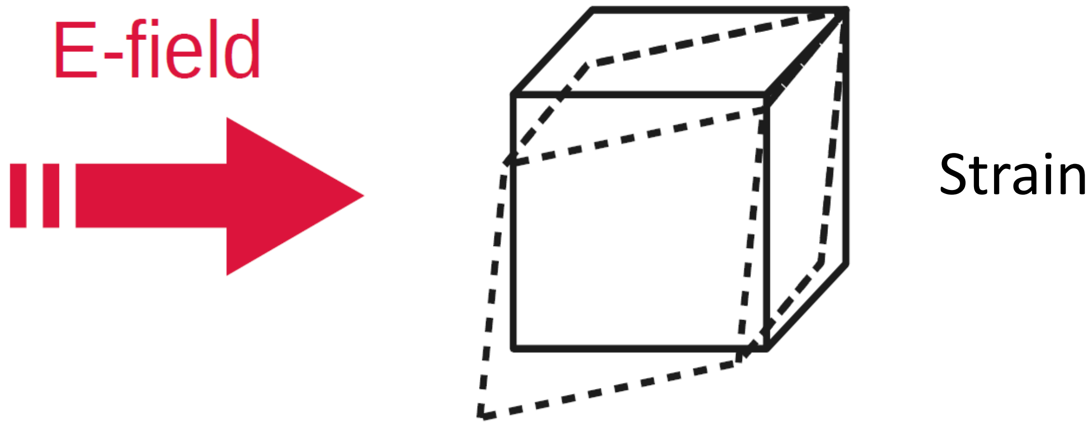
Project ANR-19-ASTR-0024, “MEGAEM”

Electromechanical coupling

- Crystal Mechanical response to $\boldsymbol{E}$ feld:



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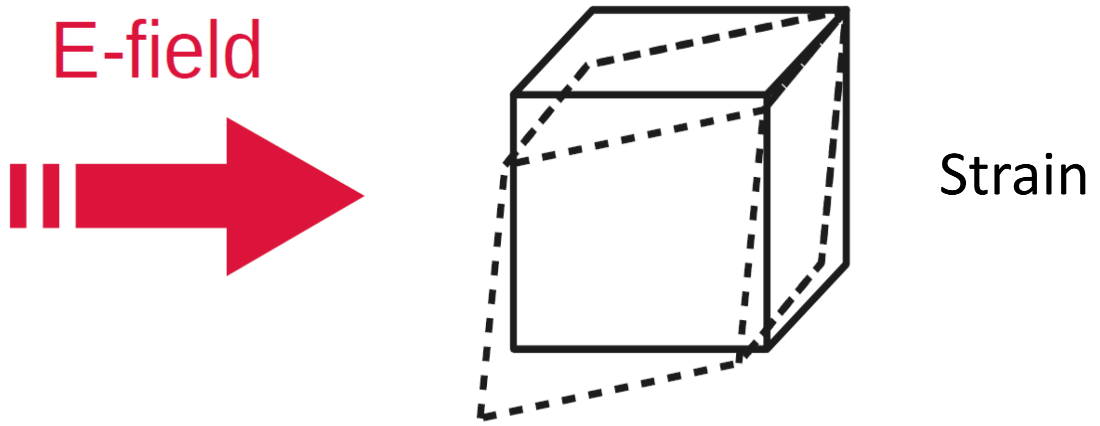
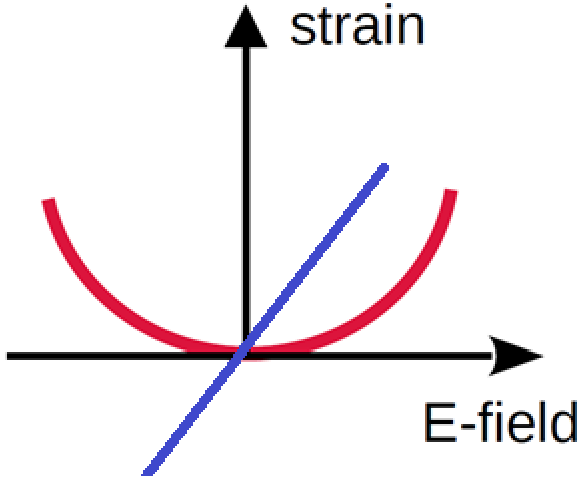


- **Electrostriction (all crystals)**, strain quadratic with $\vec{\boldsymbol{E}}$;
  Piezoelectricity (non-centric), strain linear with $\vec{\boldsymbol{E}}$

$$x_{ij} = \boldsymbol{d}_{\boldsymbol{ijm}} E_m + \boldsymbol{M}_{\boldsymbol{ijmn}} E_m E_n$$



Electromechanical coupling

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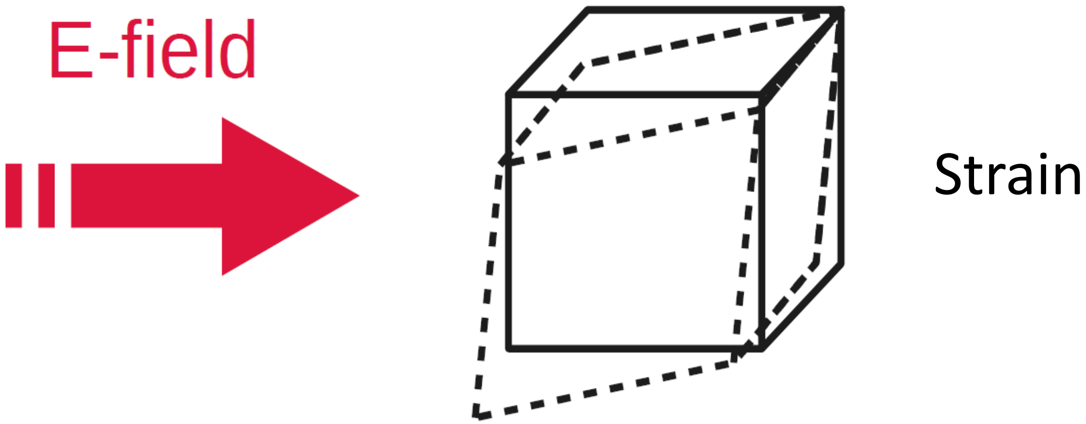

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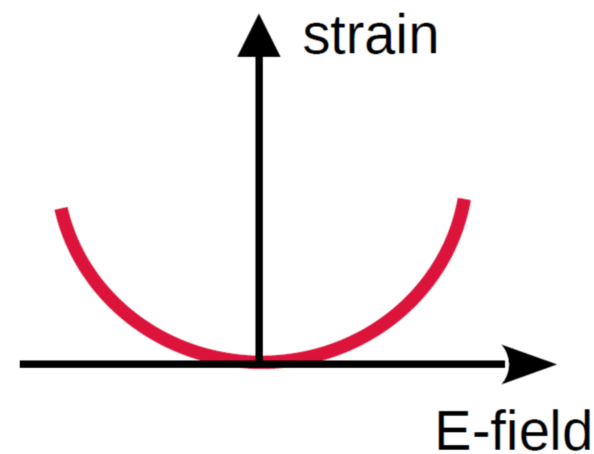

Electromechanical coupling

Electric Field $\vec{\boldsymbol{E}}$

Strain
($\boldsymbol{x}_{ij}$)

$$x_{ij} = \boldsymbol{M_{ijmn}} E_m E_n$$

Stress
(X_{ij})

$$X_{ij} = \boldsymbol{m_{ijmn}} E_m E_n$$

Electromechanical coupling

	Electric Field $\vec{\boldsymbol{E}}$	Polarisation Field $\vec{\boldsymbol{P}}$
Strain ($\boldsymbol{x}_{ij}$)	$x_{ij} = \boldsymbol{M_{ijmn}} E_m E_n$	$x_{ij} = \boldsymbol{Q_{ijmn}} P_m P_n$
Stress (X_{ij})	$X_{ij} = \boldsymbol{m_{ijmn}} E_m E_n$	$X_{ij} = \boldsymbol{q_{ijmn}} P_m P_n$

Electromechanical coupling

Electric Field $\vec{\boldsymbol{E}}$

Polarisation Field $\vec{\boldsymbol{P}}$

Strain $(\boldsymbol{x}_{ij})$

$x_{ij} = \boldsymbol{M_{ijmn}} E_m E_n$

$x_{ij} = \boldsymbol{Q_{ijmn}} P_m P_n$

Aim: Determine the best means by which to calculate electrostrictive properties using DFT

Stress (X_{ij})

$X_{ij} = \boldsymbol{m_{ijmn}} E_m E_n$

$X_{ij} = \boldsymbol{q_{ijmn}} P_m P_n$

Outline

- Motivation
  - Why calculate electrostriction?
  - How best to calculate: Literature review
- DFPT Calculation of Electrostriction
  - Derivation and advantages
  - Validation/Comparison
- Application of method
- Summary and Outlook

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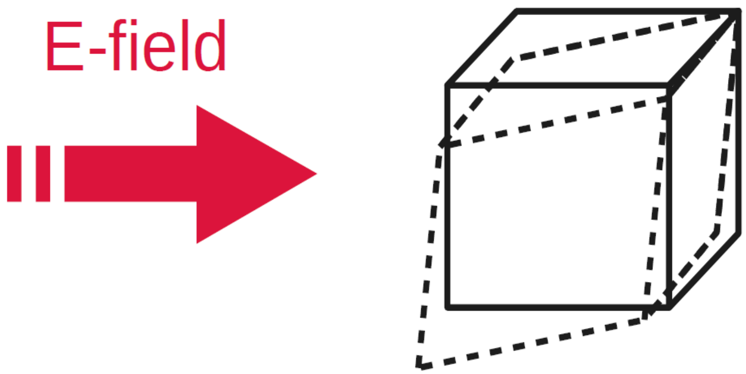
Motivation: Why calculate electrostriction?

- Electromechanical coupling:
  transducers – actuators, smart devices

- Electrostrictive strains too small
  ~10^{-8} %



Motivation: Why calculate electrostriction?

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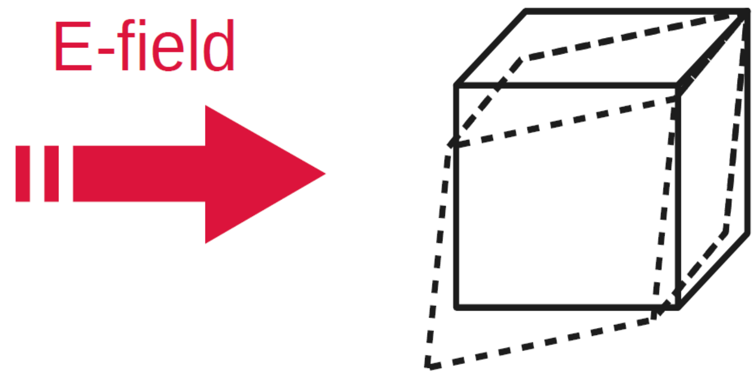
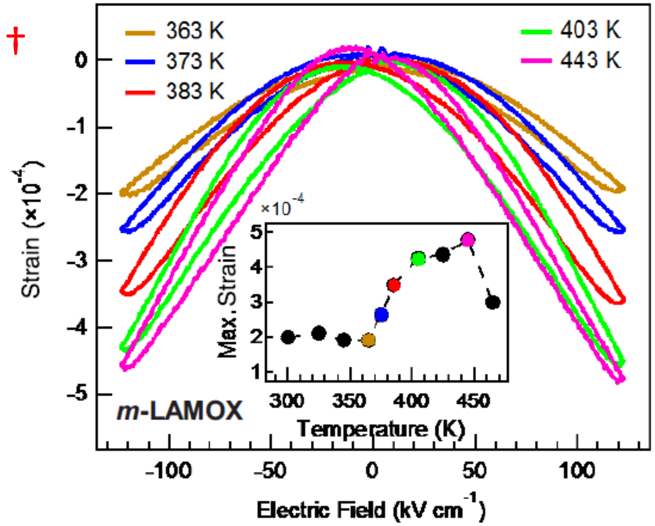


- Electrostrictive strains too small ~10^{-8} %
- **Giant** electrostrictors*: strains of ~0.6%

†



- Advantages over Piezo-transducers:
  - Temperature stability
  - Low hysteresis
  - Lead free

- **Find Giant Electrostrictors; Find origin of Giant Electrostriction**

* [R. Korobko *et al.* Adv. Mater. (2012), **24**, 5857] ; [N. Yavo *et al.* Acta Mater. (2018), **144**, 411]
† [Q. Li *et al.* Phys. Rev. Mat. (2018), **2**, 041403(R)]

Outline

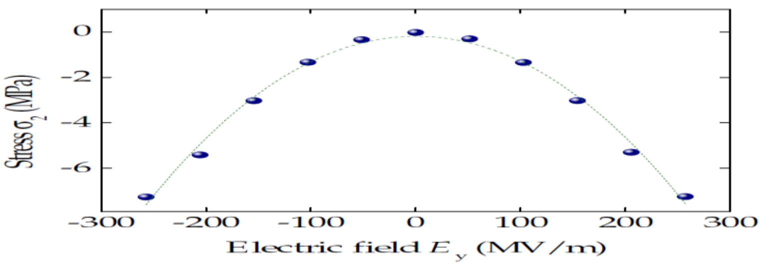
- **Motivation**
  - *Why calculate electrostriction*
  - ***How best to calculate*: *Literature review***
- Indirect Calculation of Electrostriction
  - Derivation and advantages
  - Example calculation: MgO
  - Comparison/validation against direct calculation
- Application
- Summary and Outlook

Motivation: How best to calculate electrostriction? - Literature review

AIP Conference Proceedings **1199**, 71 (2010)

Electrostriction Coefficients of GaN, AlN, MgO and ZnO in the Wurtzite Structure from First-Principles

I. Kornev*, M. Willatzen*, B. Lassen* and L. C. Lew Yan Voon†



. Finite **E** field methods

$$X_{ij} = \boldsymbol{m} E^2$$

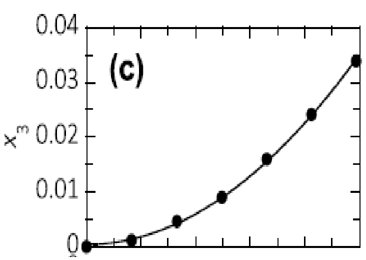
AIP ADVANCES **6**, 065122 (2016)

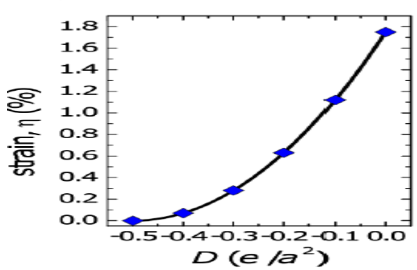
Electrostriction coefficient of ferroelectric materials from *ab initio* computation

Z. Jiang,[1,2] R. Zhang,[3] F. Li,[1] L. Jin,[1] N. Zhang,[1] D. Wang,[1,a] and C.-L. Jia[1,4]

Electrostriction at the $LaAlO_3/SrTiO_3$ Interface

C. Cancellieri,[1] D. Fontaine,[2] S. Gariglio,[1] N. Reyren,[1] A. D. Caviglia,[1] A. Fête,[1] S. J. Leake,[3] S. A. Pauli,[3] P. R. Willmott,[3] M. Stengel,[4] Ph. Ghosez,[2] and J.-M. Triscone[1,*]





. Finite **D** field methods

$$x_{ij} = \boldsymbol{Q_{ijmn}} P_m P_n$$

Motivation: How best to calculate electrostriction? - Literature review

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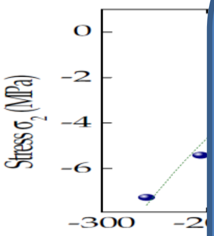
I. Kornev*, M.



Electrostricti from *ab initio*

Z. Jiang,[1,2] P

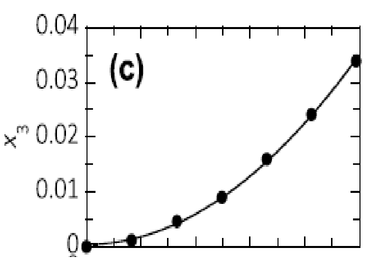
Elec

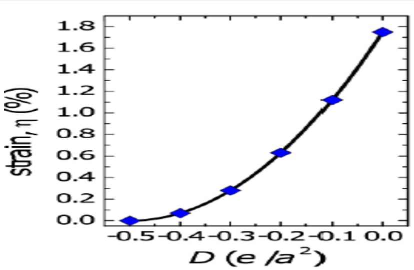
C. Cancellieri,[1] D. Fontaine,[2] S

P.R. Willmott,

- All **direct** Electrostritive effect
- Not all methods represented
- **methodological study required**

$$x_{ij} = Q_{ijmn} P_m P_n$$





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Indirect Calculation of Electrostriction

Thermodynamical derivation for M_{ijkl}

Gibbs free energy

$$G = u - T.S - E.P - x.X$$

$$dG = -S.dT - x_{kl}dX_{kl} - P_i dE_i$$

First derivatives

$$\frac{\partial G}{\partial X_{kl}} = -x_{kl}\ ; \qquad x_{kl} = M_{klij}E_iE_j$$

$$\frac{\partial G}{\partial E_i} = -P_i\ ; \qquad P_i = \chi_{ij}E_j$$

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Third derivatives

Differentiate by E_i, then E_j

$$\frac{\partial^3 G}{\partial E_j \partial E_i \partial X_{kl}} = -\frac{\partial x_{kl}}{\partial E_j \partial E_i} = -2M_{klij}$$

Differentiate by E_j, then by X_{kl}

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Differentiate by E_j, then by X_{kl}

$$\frac{\partial^3 G}{\partial X_{kl} \partial E_j \partial E_i} = -\frac{\partial \chi_{ij}}{\partial X_{kl}}$$

New Expression

$$M_{klij} = \frac{1}{2}\frac{\partial^2 x_{kl}}{\partial E_j E_i} = \frac{1}{2}\frac{\partial \chi_{ij}}{\partial X_{kl}}$$

Electromechanical coupling

	Electric Field $\vec{\boldsymbol{E}}$	Polarisation Field $\vec{\boldsymbol{P}}$
Strain ($\boldsymbol{x}_{ij}$)	$x_{ij} = \boldsymbol{M_{ijmn}} E_m E_n$	$x_{ij} = \boldsymbol{Q_{ijmn}} P_m P_n$
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A-Priori Methodological Advantages

Indirect method

$$\frac{\Delta\chi/\Delta\eta}{\Delta X/\Delta x}$$

Direct method

$$\frac{\Delta x/\Delta X}{\Delta E/\Delta P}$$

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✓ Hydrostatic strain/pressure

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X Always Unidirectional field.

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- ✓ Well established (1990): excellent infrastructure

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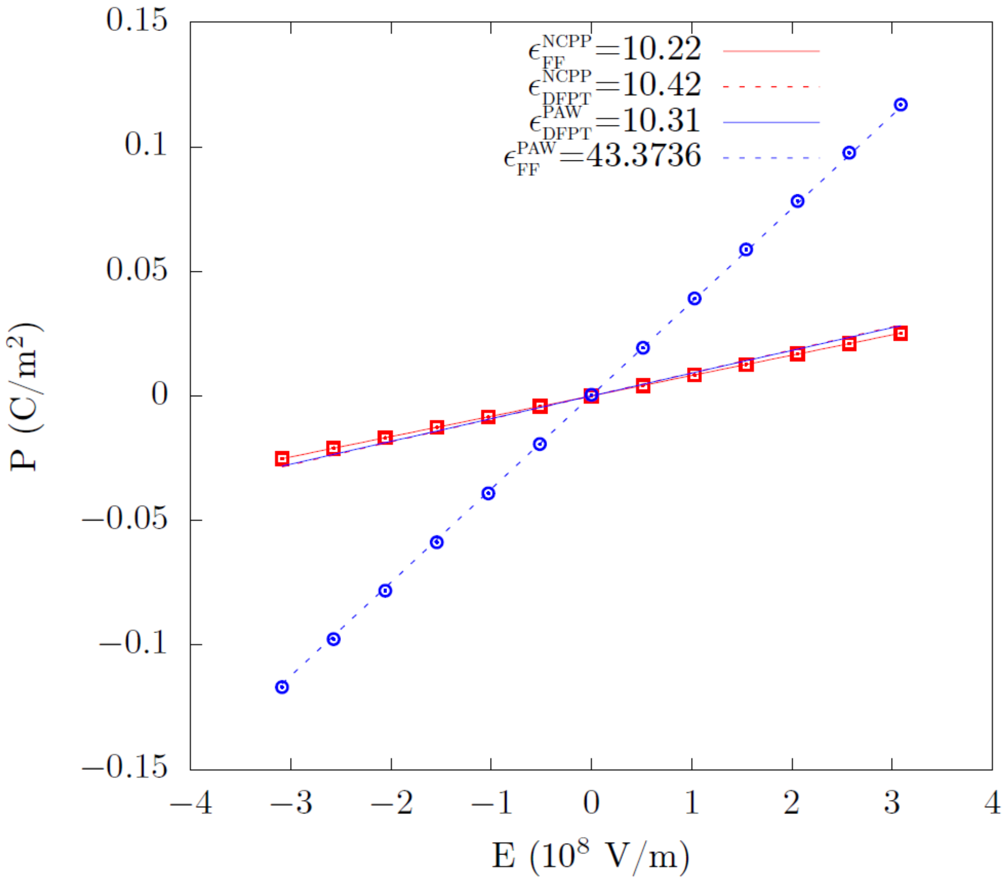
- X No easy decomposition of tensor
- X New (2009):
  - No parallelism for **D**
  - PAW erroneous results

Finite Field and PAW in ABINIT



- P Vs E by DFPT and finite field with both PAW and NCPP
- PAW finite field: incorrect behaviour, permitivity
- => Incorrect electrsotrictive coefficients
- DFPT works with PAW – can use current method with PAW for large unit cells/supercells

A-Priori Methodological Advantages

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Indirect method more robust, more efficient, easier to implement.

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  - *How to calculate*: *Literature review*
- **Indirect Calculation of Electrostriction**
  - Introduction and advantages
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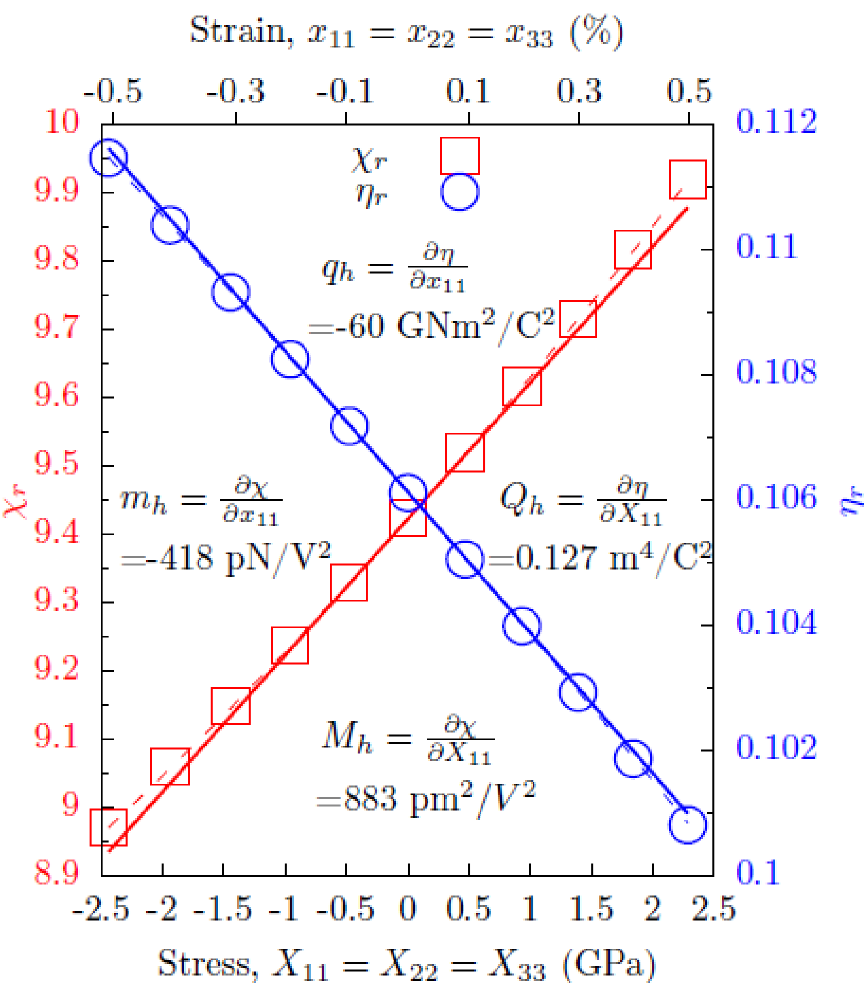
Indirect Calculation of Electrostriction

Simulation Details

- DFPT ABINIT;
- Ecut=50 Ha;
- 8x8x8 monkorst pack-grid;
- Pseudodojo NCPP;
- PBEsol;
- Rocksalt MgO

Indirect Calculation of Electrostriction

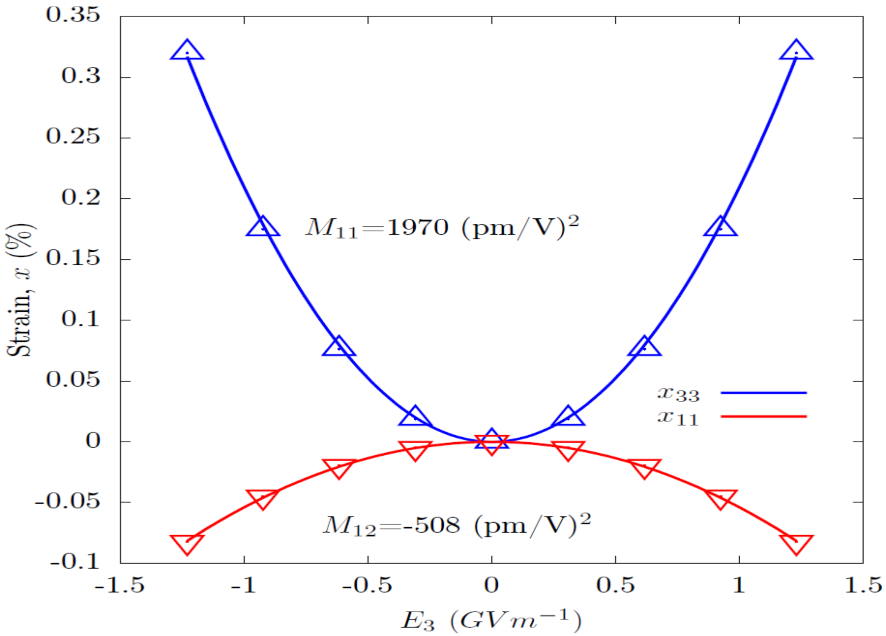
Pressure derivative of χ_{ij} and η_{ij} in MgO

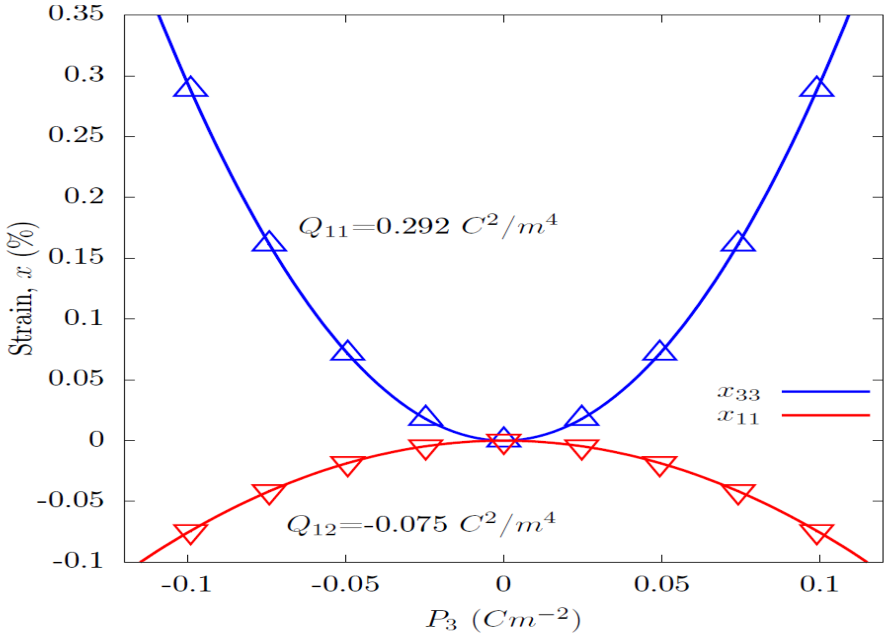


- Strain (x_{ij}) between ±0.5%; calculate stress X_{ij}, susceptibility χ, and inverse susceptibility η.
- Fit χ and η vs X_{ij}/x_{ij} for electrostrictive coefficients.
- Q_h, M_h, m_h and q_h obtained in same calculation

Direct Calculation of Electrostriction

Electric/Displacement Field Response - Strain

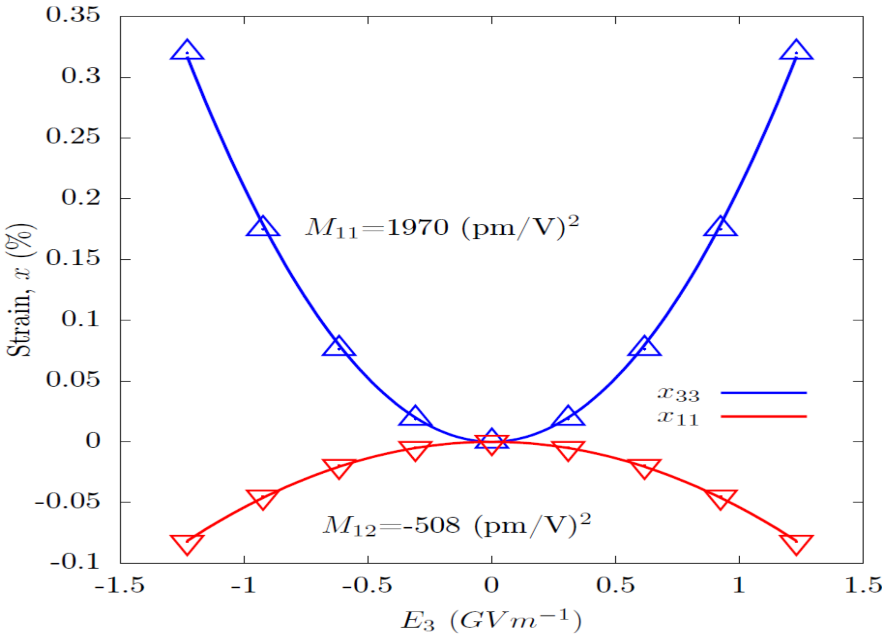


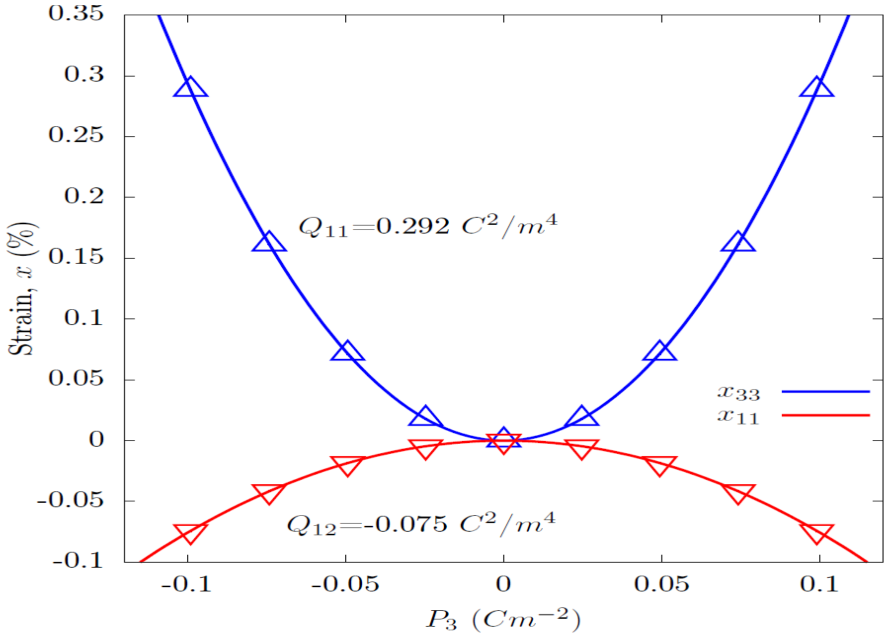


- Full energy minimisation under fixed E_z, D_z
- Longitudinal expansion; Transverse contraction.

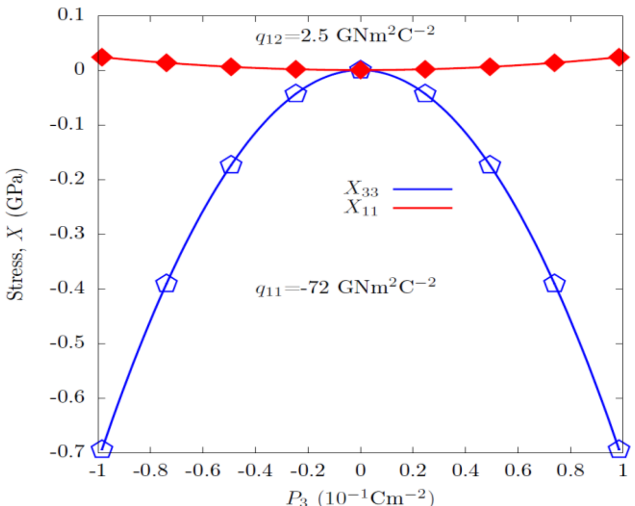
Direct Calculation of Electrostriction

Electric/Displacement Field Response - Strain



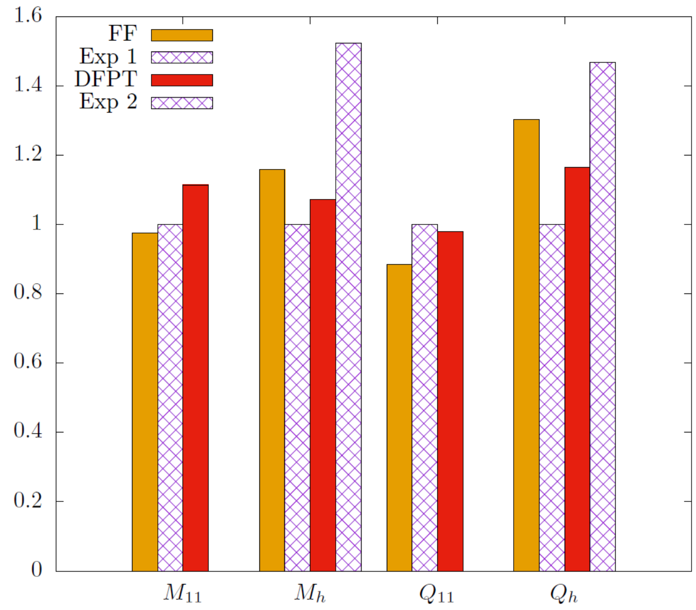


- Full energy minimisation under fixed E_z, D_z
- Longitudinal expansion; Transverse contraction.
- Stress coefficients m, q: Relax *only* internal positions under fixed E_z, D_z; calculate stress.



Comparison between Direct and Indirect methods

- Agreement between methods and exp: Coefficients normalised to Exp 1 in bar chart.



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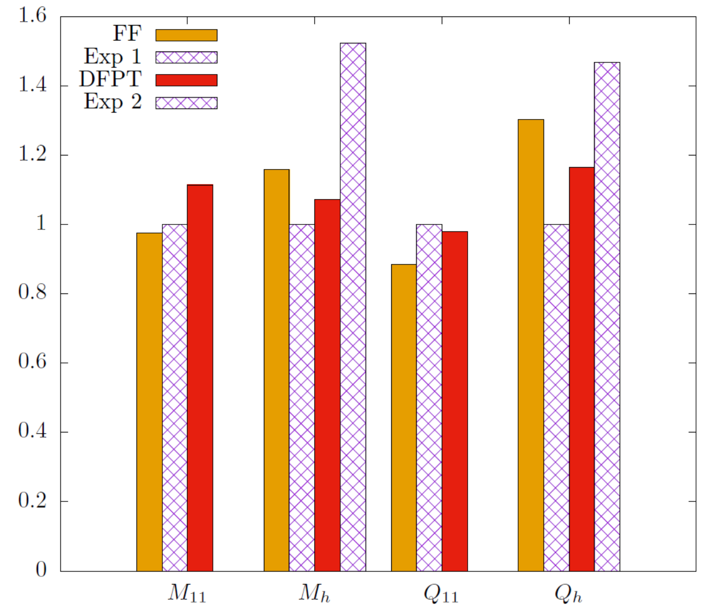
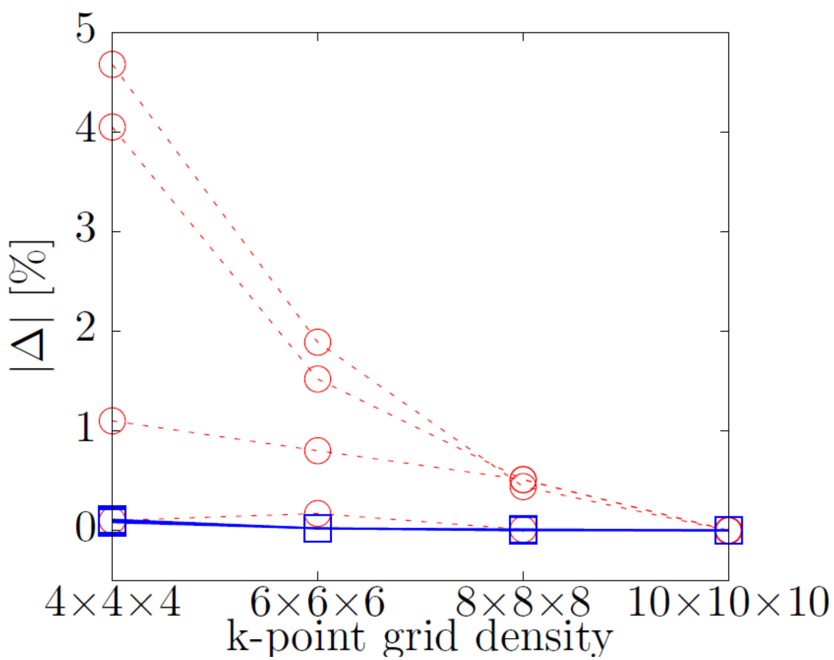
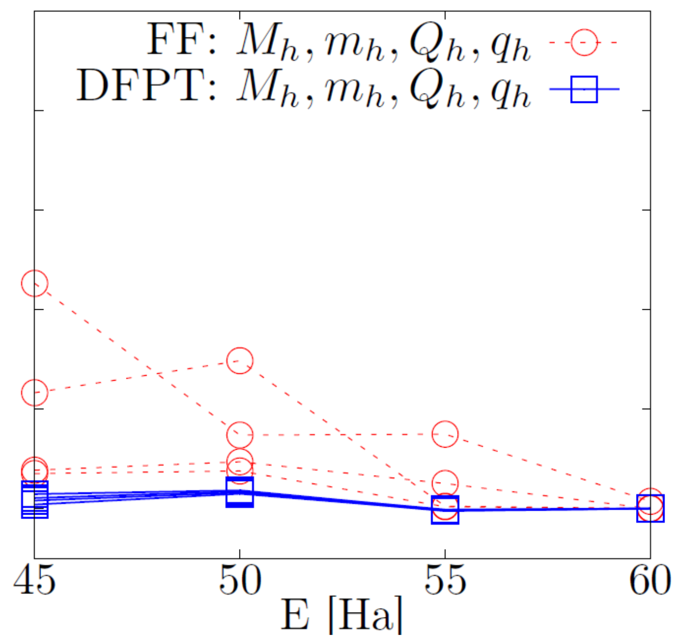


- Faster convergence with k-points and cut-off energy.
- **8 times faster** for given k-point density, cutoff energy.





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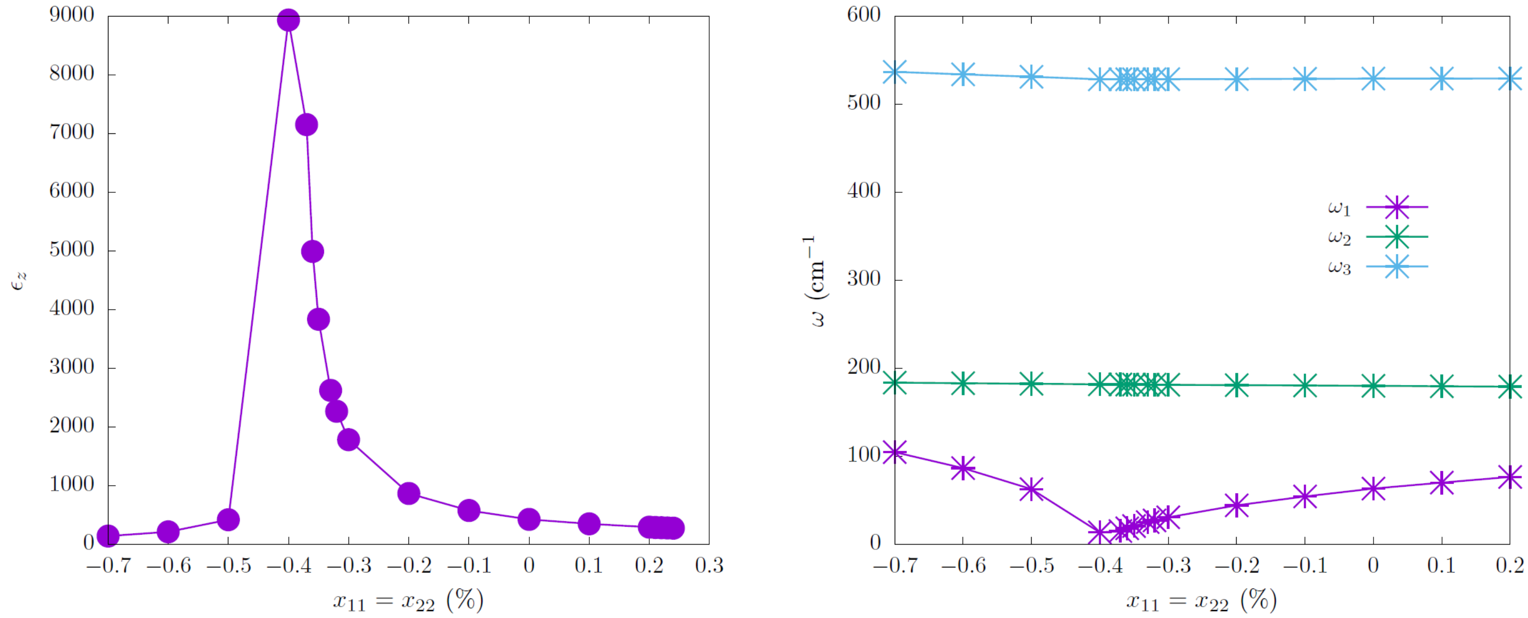
Application

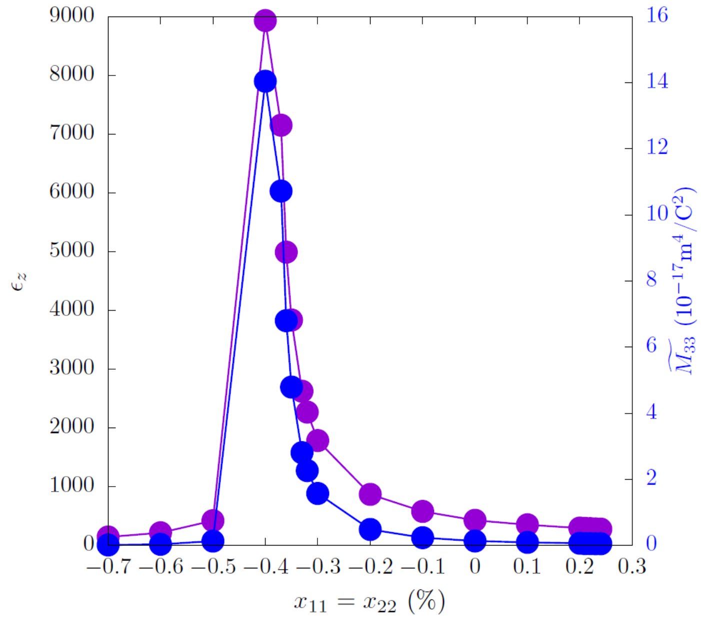
Electrostriction at ferroelectric phase transition: KTaO3

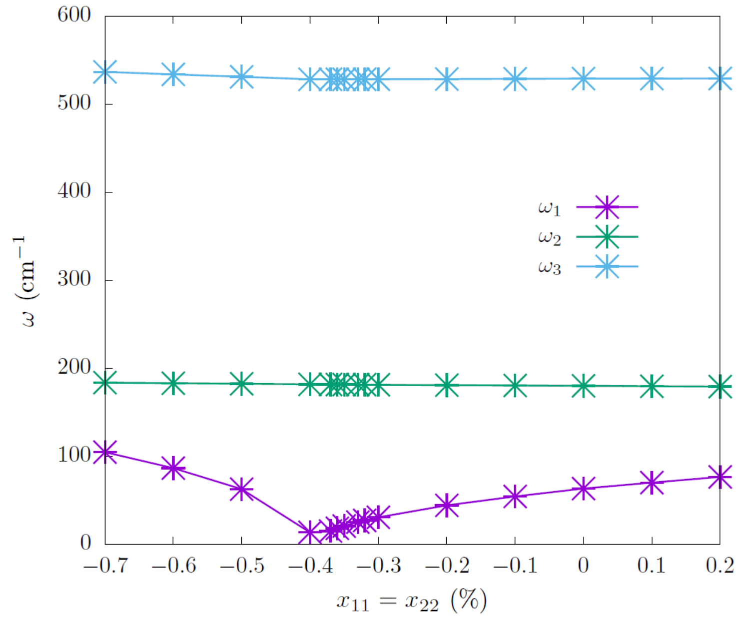


- Compressive strain induced phase transition: ϵ_z diverges
- Transition driven z-polar soft mode

Application

Electrostriction at ferroelectric phase transition: KTaO3





- Compressive strain induced phase transition: ϵ_z diverges
- Transition driven by z-polar soft mode
- M_{33} also diverges
- Reaches $1x10^{-15}$: d_{33}^{eff} = 60 000 pm/V; compare 162 pm/V for PZT

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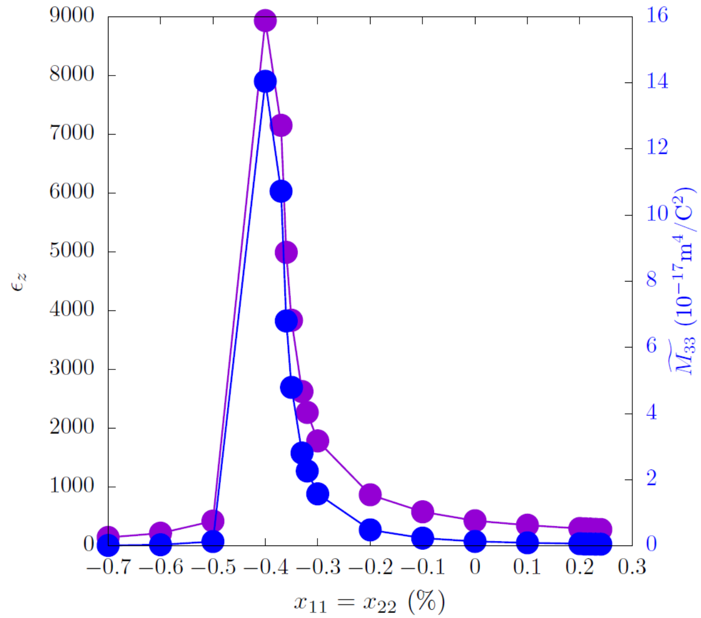

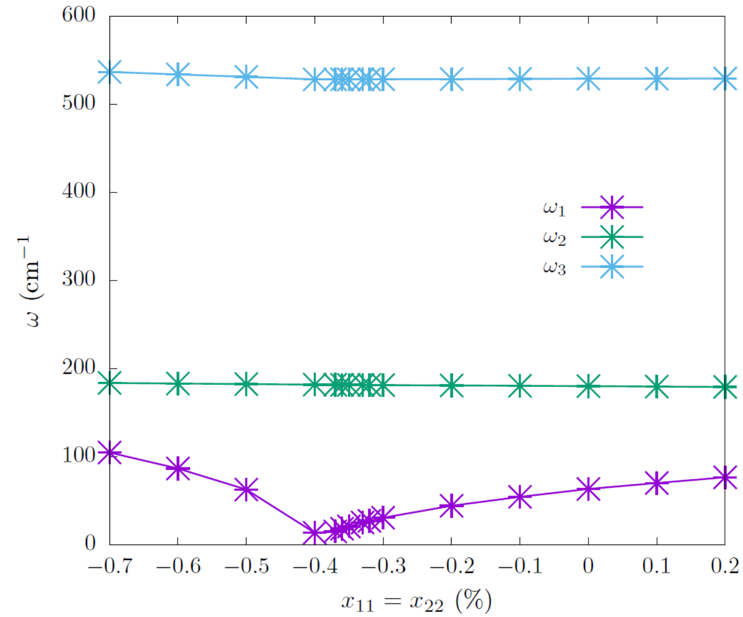

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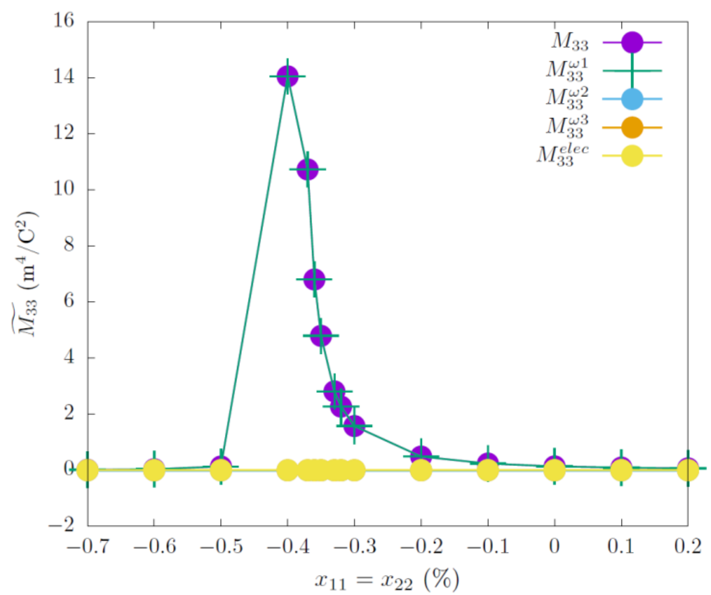
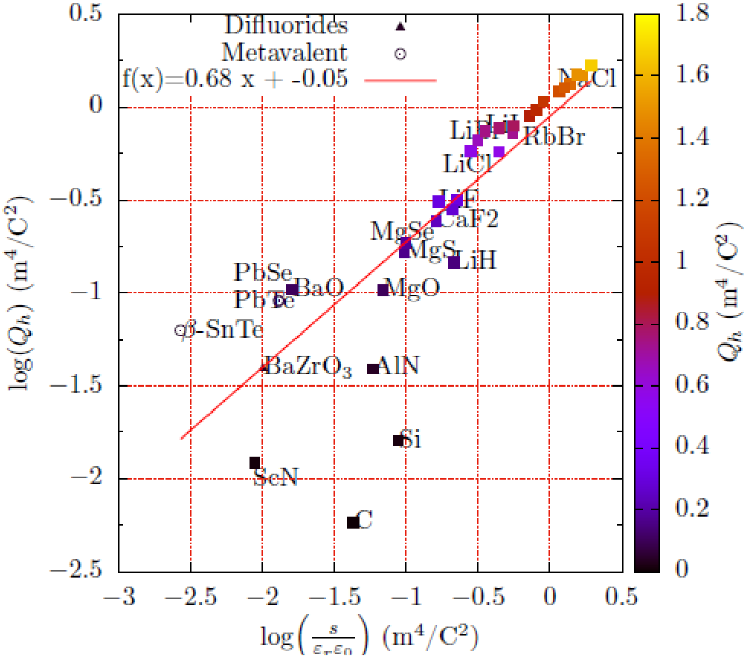
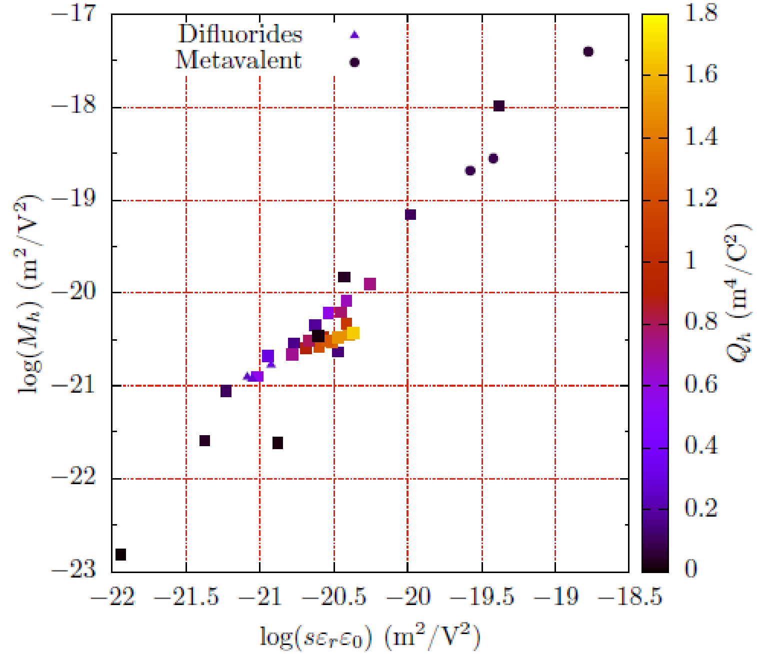
- decomposition shows soft polar mode responsable



Application

Correlation between M_h and Q_h





Materials with large Q_h do not necessarily have large M_h

⟹ Large strain in response to E field does not mean large strain in response to P field

Outline

- Motivation
  - *Why calculate electrostriction*
  - *How best to calculate*: *Literature review*
- Indirect Calculation of Electrostriction
  - Introduction and advantages
  - Validation/Comparison
- Application
- **Summary**

Summary

- Stress/strain dependence of permitivity best way to compute Electrostriction.
- Validated method against finite field calculation and experiment
- Advantages: Fewer calculations; Faster convergence; **8** times faster computation; Decomposition of tensors
- Applications:

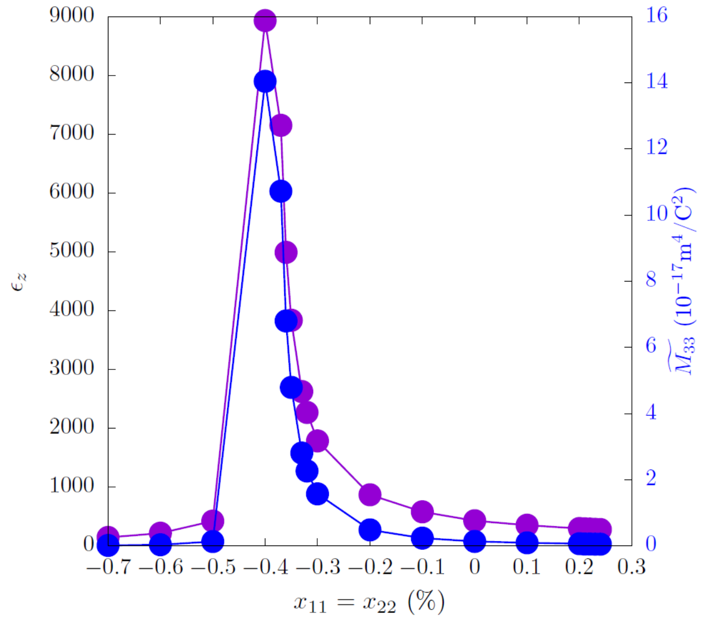
  - Analysed electrostriction at ferroelectric phase transition

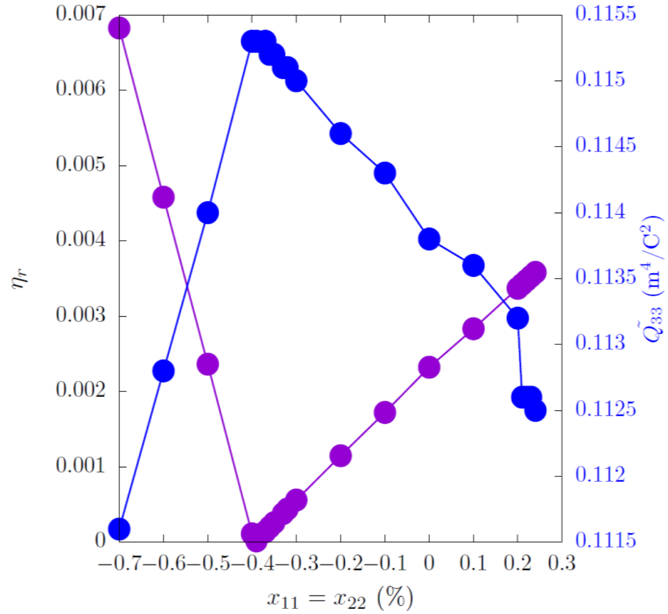
  - Demonstrated M_h and Q_h are uncorrelated

Project ANR-19-ASTR-0024, “MEGAEM”

Electrostriction at ferroelectric phase transition of $KTaO3$

Q coefficients

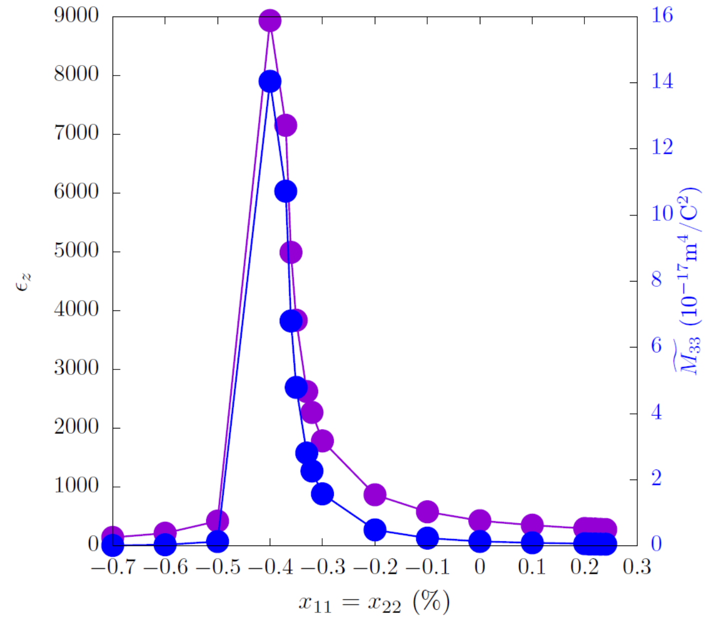


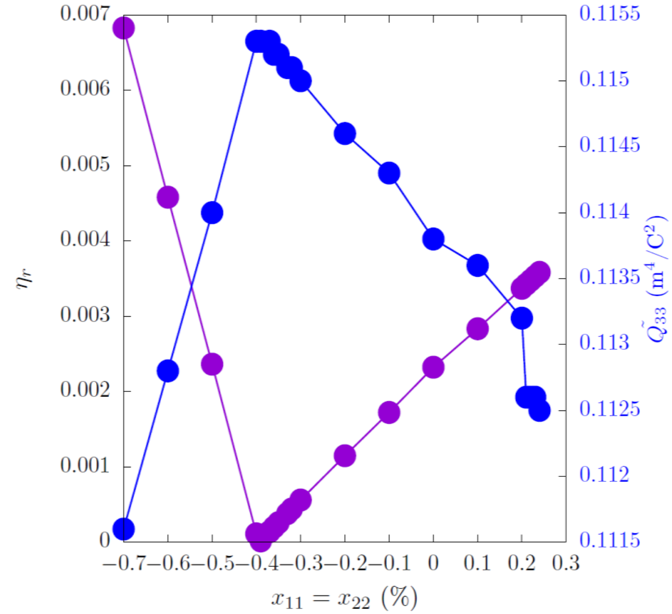


- Q33 does vary at the phase transition, but only by ≈4%

Electrostriction at ferroelectric phase transition of KTaO3

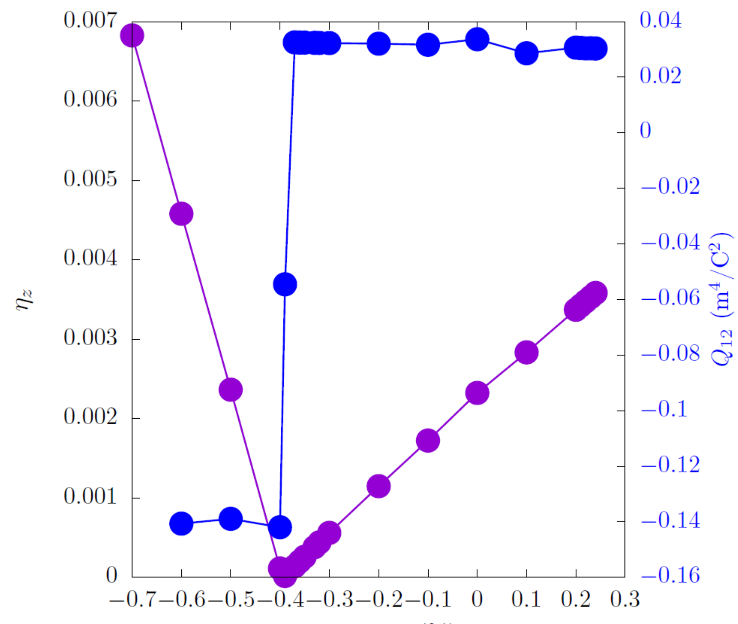
Q coefficients





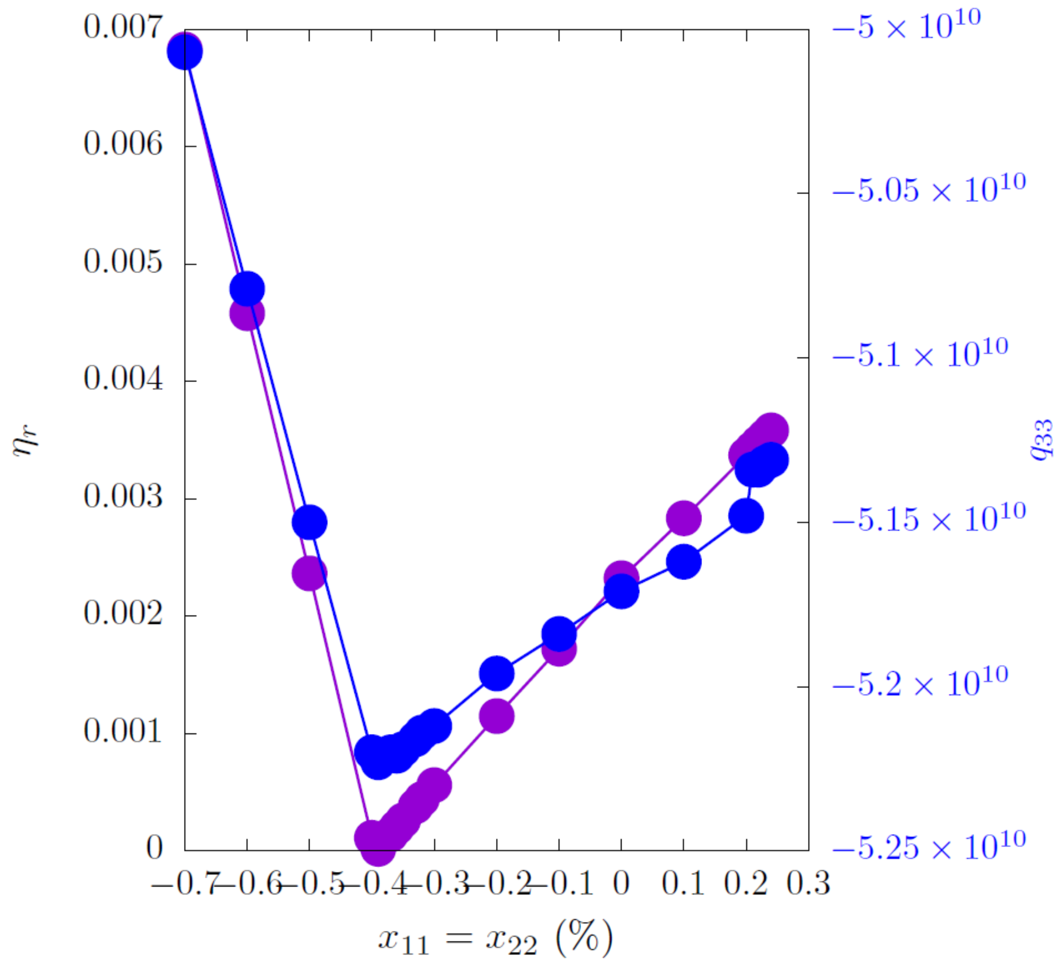
- Q33 does vary at the phase transition, but only by ≈4%

- Q12 changes sign



Electrostriction at ferroelectric phase transition of KTaO3

Q coefficients



- q33 less complicated behaviour

Application

Decomposition of BaZrO3 Mh

- Permitivity has electronic contribution, but electrostriction does not
- Softest polar mode, with largest polarity contributes most
- 4 coefficients m_h, M_h, q_h , and Q_h have same composition