



Ab-initio study of the correlation between electric field gradients and electric polarization in ferroelectric oxides

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Outline

- Introduction: hyperfine interactions, ferroelectrics, motivation, previous work
 - Perovskite Tetragonal Structures
 - EFG(P), Tensor Direction
 - Correlation between EFG components
 - BaTiO₃ - Orthorhombic Structures
- Conclusion, future work

Hyperfine interactions

- **quadrupole interaction**

quadrupole nuclear moment interacts with

Electric Field Gradient (EFG):

second spacial derivatives of the electric potential, at the nuclear position

$$\Sigma V_{ii}(0) = 0$$

Definition: The traceless EFG is diagonalized

Diagonal components: $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$

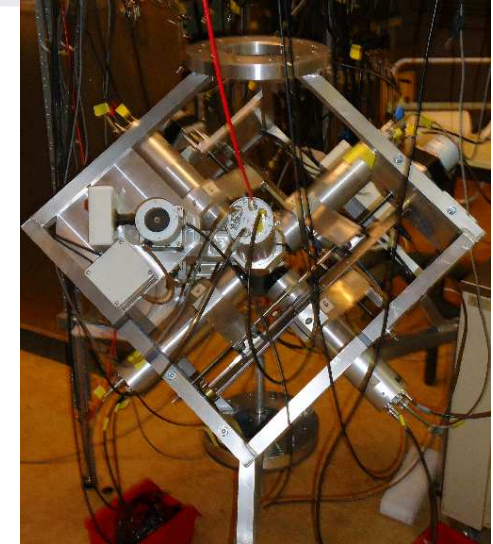
3 directions, for V_{xx} , V_{yy} , V_{zz}

$$V_{zz} \quad \eta = (V_{xx} - V_{yy})/V_{zz}$$

Hyperfine interactions techniques

Examples:

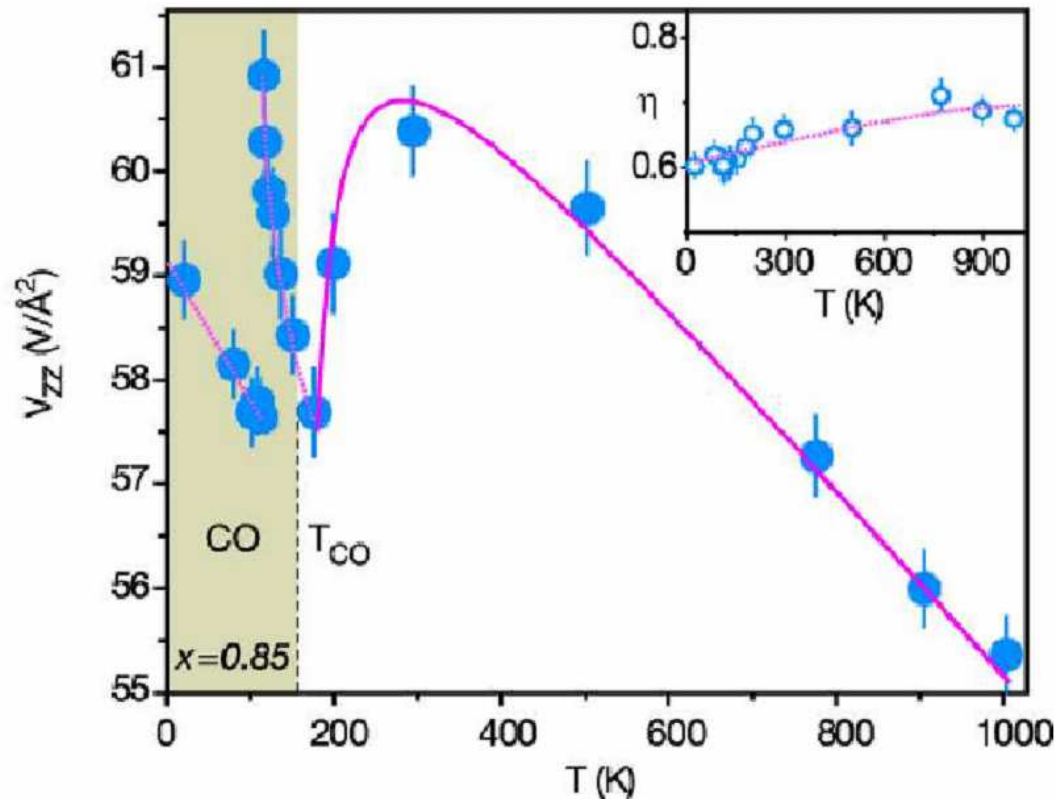
- **Perturbed Angular Correlation (PAC)**
- Mössbauer Spectroscopy
- Nuclear Magnetic Resonance (NMR) Spectroscopy
- Nuclear Quadrupole Resonance (NQR)



Previous work at ISOLDE with ferroelectrics

Manganites

Charge ordered manganites ($\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$,
 $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$)



– $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$
correlation between anomalous
behavior of the EFG and the
existence of ferroelectricity.

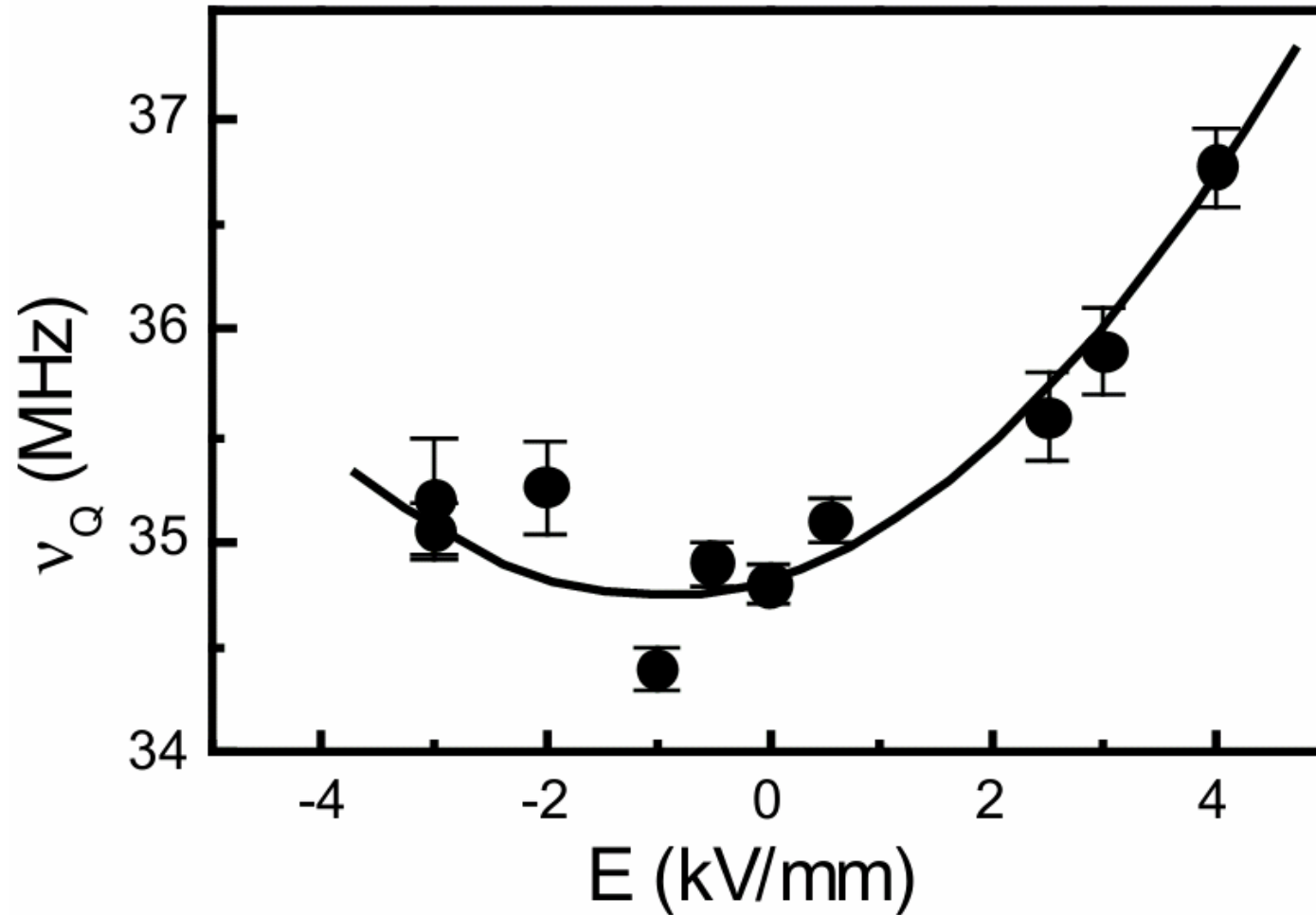
charge/orbital ordering

A. M. L. Lopes, J. P. Araújo, V. S. Amaral,
J. G. Correia, Y. Tokura, Y. Tomioka.
Phys. Rev. Lett. 2008;100(15)

G. Colizzi, A. Filippetti, V. Fiorentini.
*Multiferroicity and orbital ordering in
 $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ from first principles.* Phys.
Rev. B 2010;82(14):3-6.

Previous work at ISOLDE - BaTiO₃

- Electric field dependence of EFG



M. Dietrich *et al.*, CERN-OPEN-2001-072

Previous Studies

- **Rochelle salts [NaK(tartrate)4H₂O]:** EFG follows a **linear variation** relative to P

T. Oja, P. Casabella, PR ;177(2):830-838 1969

M. Fitzgerald, P. Casabella, PRB. 1970;2(5):1350-1354.

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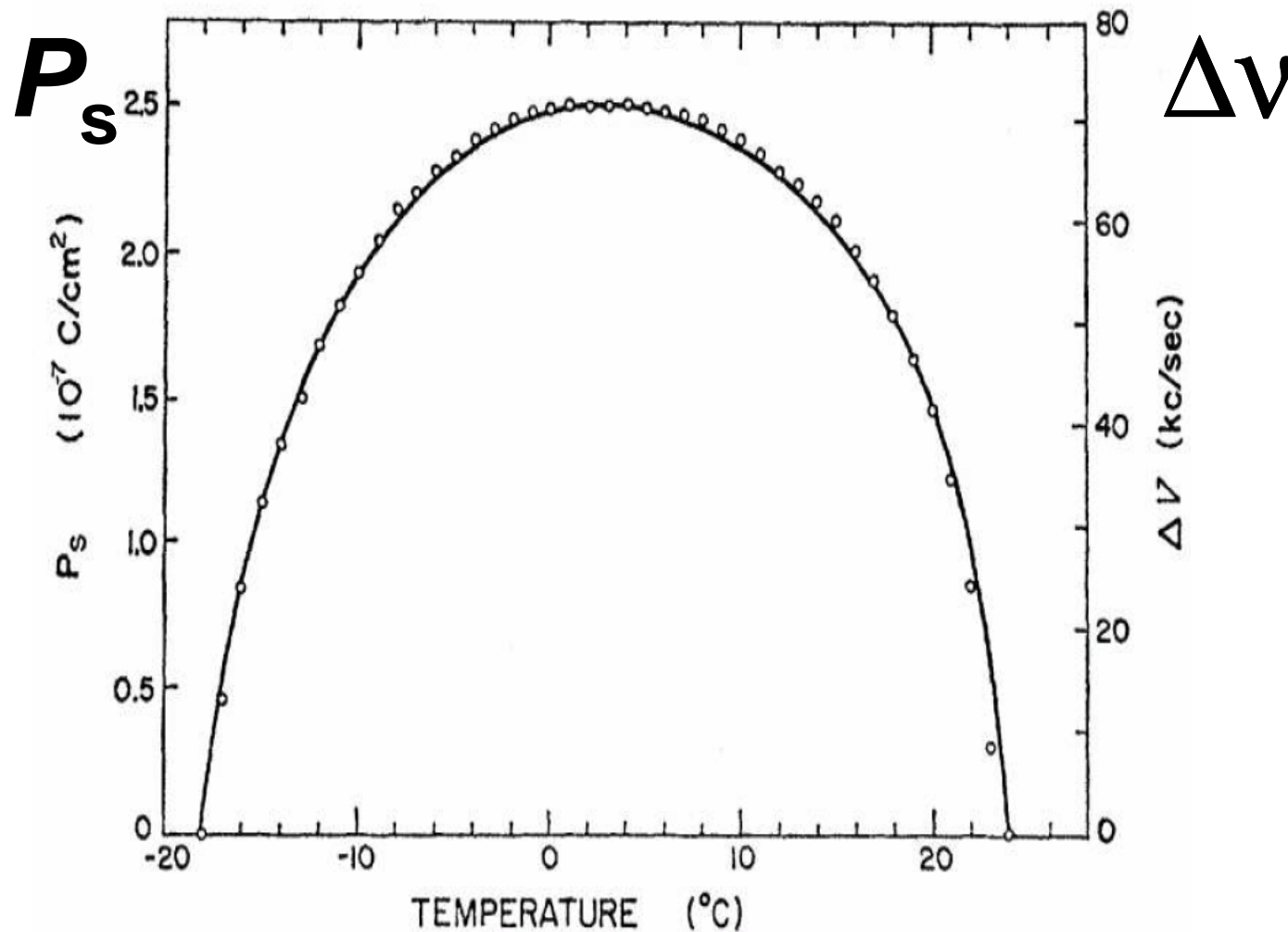
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Previous Studies

Experimental results

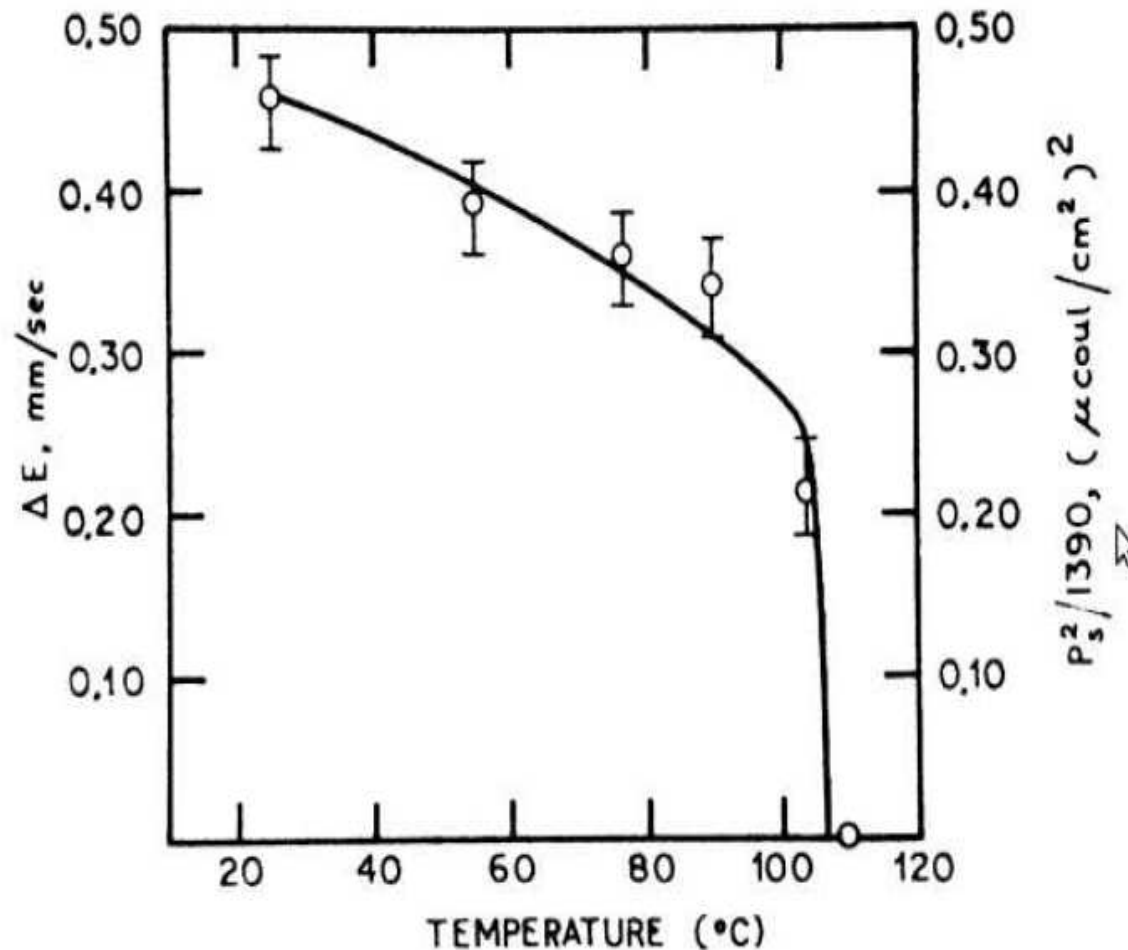
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Previous Studies

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V. Bhide, M. Multani., Phys. Rev. 1966;149(1):289-295.



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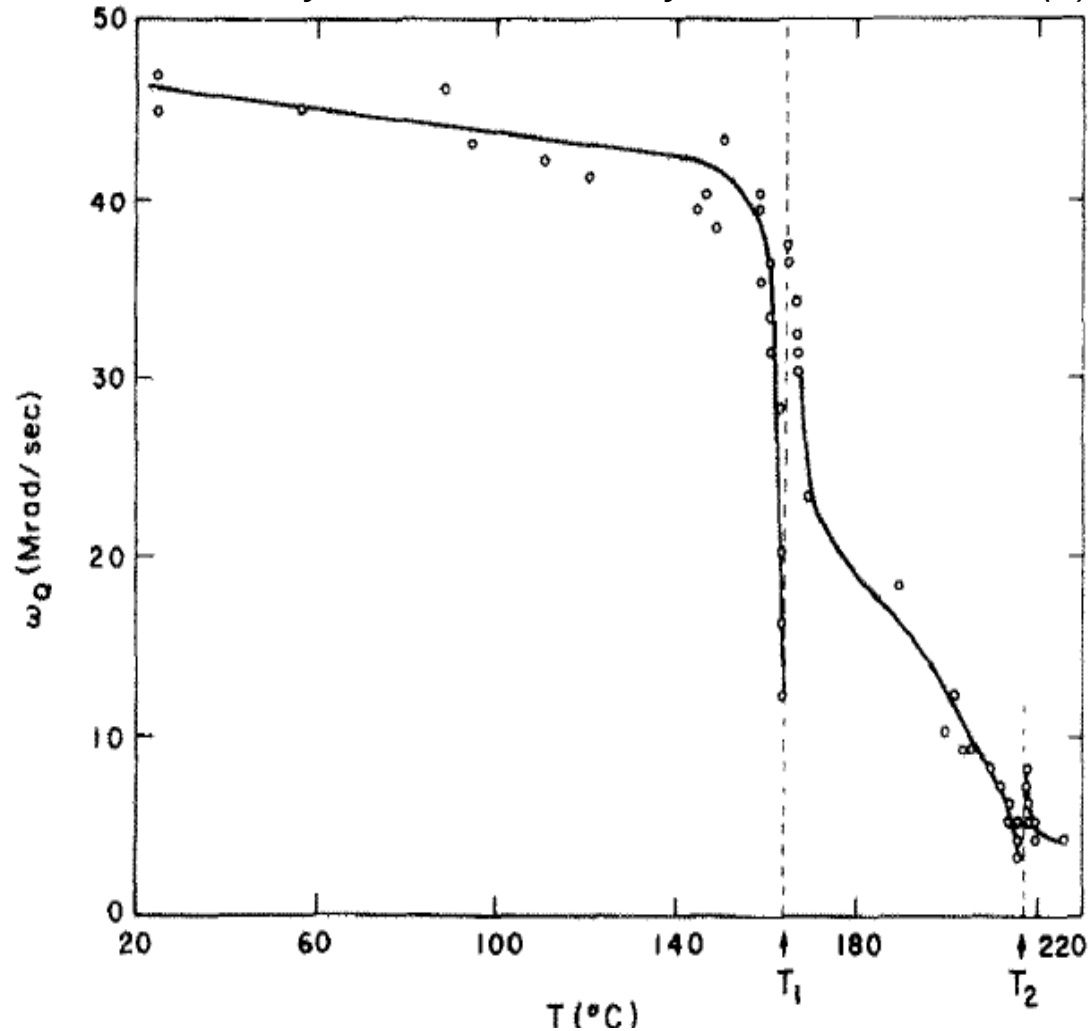
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- **PbHfO₃** - $V_{zz}(T)$ has a critical behavior near T_C
Y. Yeshurun, Journal of Physics and Chemistry of Solids. 1979;40(3):231-237.

Previous Studies

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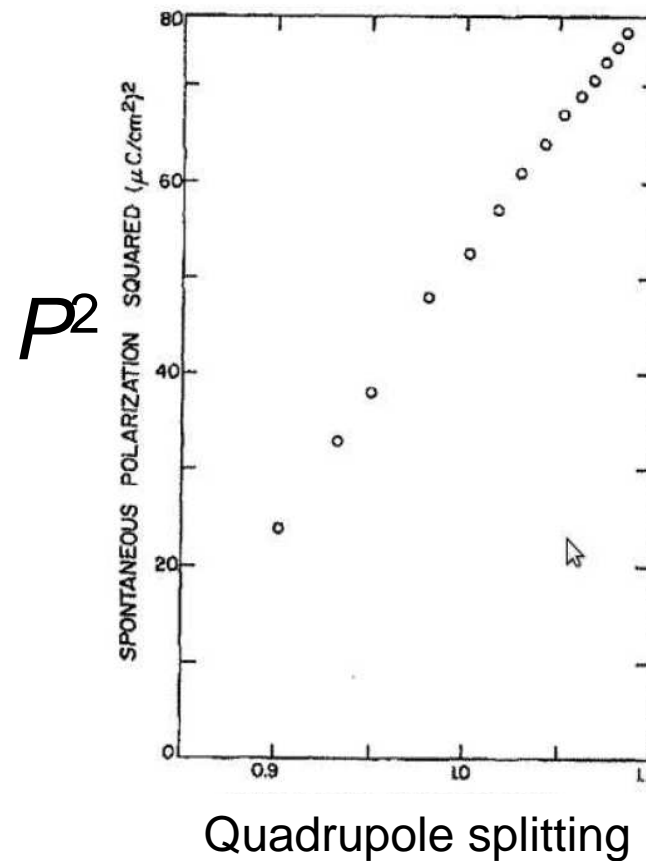
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- ²³Na at **NaNO₂** - V_{zz} follows linearly P^2
D. Dening, Journal of Magnetic Resonance (1969). 1980;38(2):277-282.

Previous Studies

- ^{23}Na at NaNO_2 - V_{zz} follows linearly P_2 .
D. Dening, Journal of Magnetic Resonance (1969). 1980;38(2):277-282.



Previous Studies

- It is clear from previous experimental studies that a relationship between EFGs and ferroelectric properties (spontaneous polarization, electric susceptibility) exists
- **What about Models?**

EFG-polarization: previous models

D. Dening, Journal of Magnetic Resonance (1969). 1980;38(2):277-282.

Y. Yeshurun, S. Havlin and Y. Schlesinger, Solid State communications (1978) 27:181-184

- Taylor expansion of V_{zz} around the nuclear position (valid in the limit of small displacements and small changes in V_{zz} , *i.e.* small changes in electronic density).

$$V_{zz} = V_{zz}^0 + \sum_i \frac{\partial V_{zz}}{\partial r_i} \delta r_i + \sum_i \frac{\partial^2 V_{zz}}{\partial r_i^2} \delta r_i^2 + \dots$$

With inversion symmetry this term is zero, but **without** inversion symmetry should be **dominant** (Na@Rochelle salts)

Dominant term with inversion symmetry.

The susceptibility is found to be proportional to V_{zz} .

$$\bar{V}_{zz} = aP_s^2 + bT \sum_q \chi_q$$

Y. Yeshurun et al.

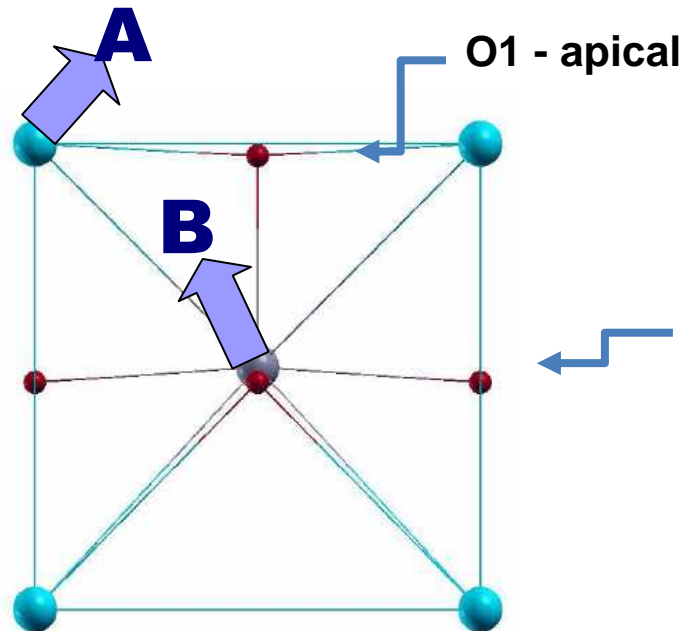
Considering the displacements are small, the polarization is expected to be a linear function of them. It follows that $V_{zz}(P)$ is linear in sites without inversion symmetry, but quadratic in sites with inversion symmetry.

Previous Studies

- It is clear from previous experimental studies that a relationship between EFGs and ferroelectric properties (spontaneous polarization, electric susceptibility) exists
- There are also simple models that relate these properties.
- However, there are not yet calculations from first-principles relating these properties.

Calculation Details

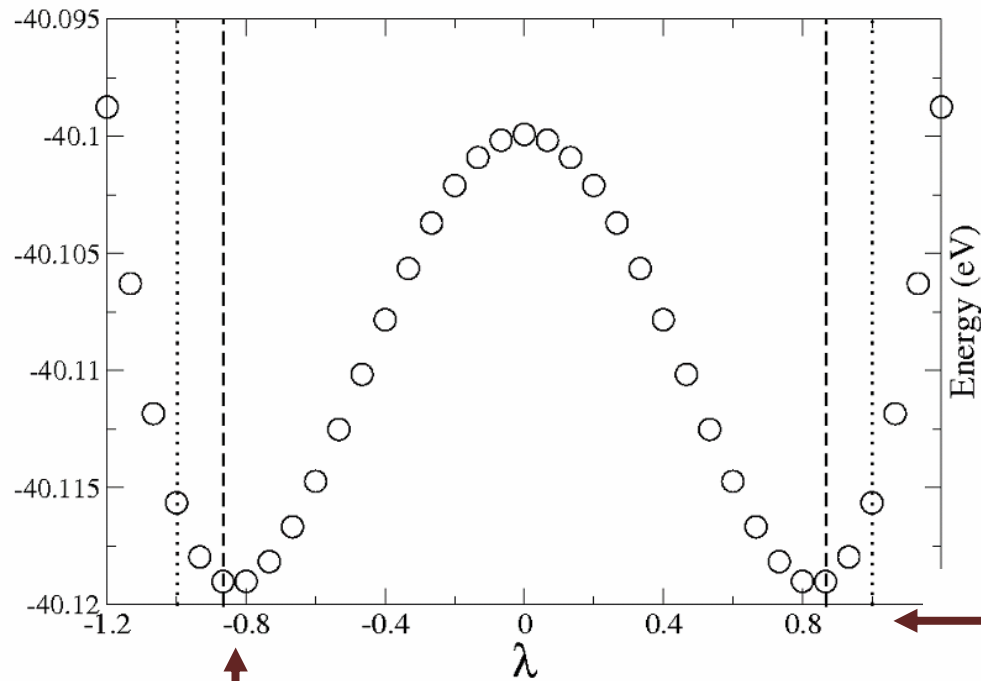
- Density Functional Theory (DFT)
 - Approximation for the exchange-correlation potential: PBE-GGA
 - PAW – Projector Augmented-Wave method. VASP code.
- Following some of the first *ab-initio* investigations of ferroelectricity (King-Smith, Vanderbilt), we considered a series of perovskites in our calculations.



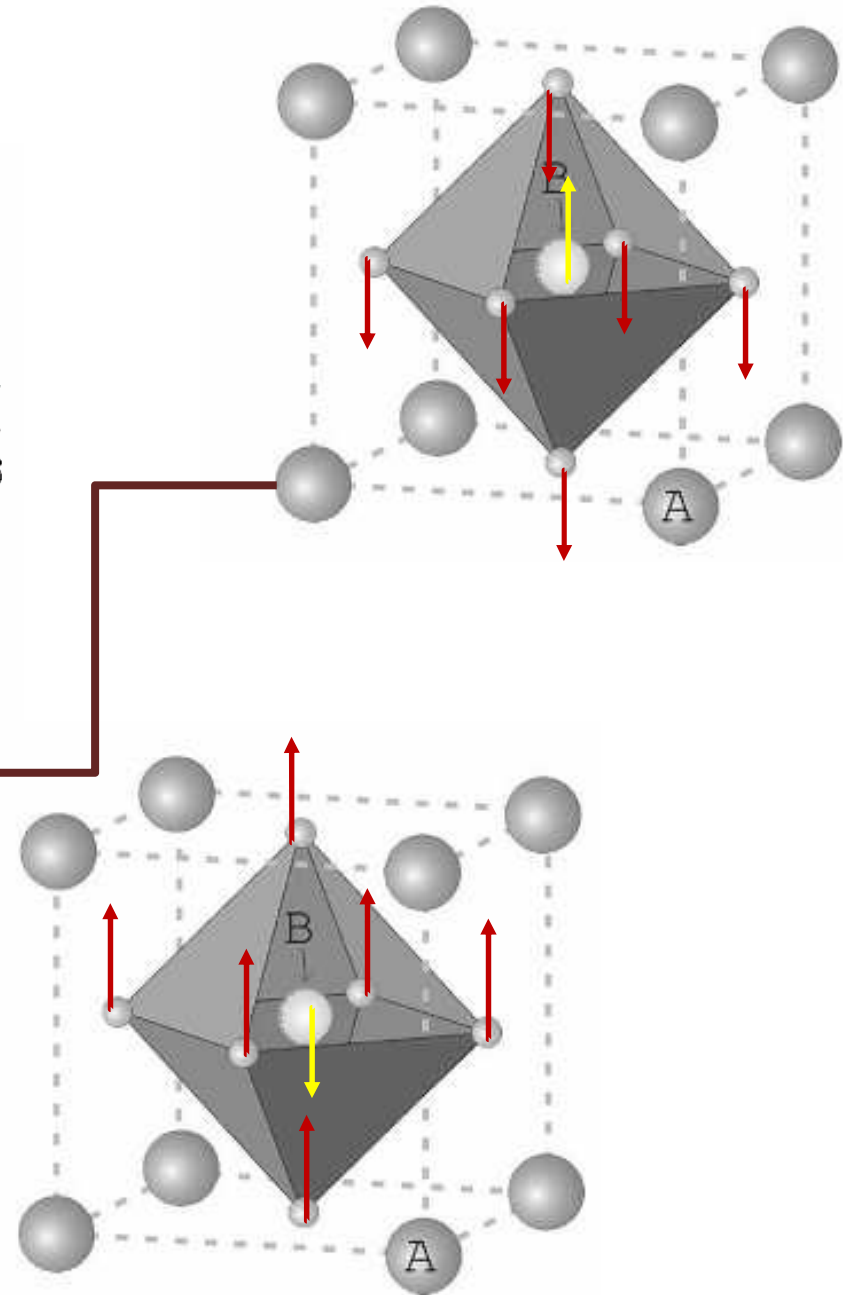
Lattice parameters are kept constant at the experimental values of the tetragonal phase ($a=b \neq c$).

Distortions in the z direction:

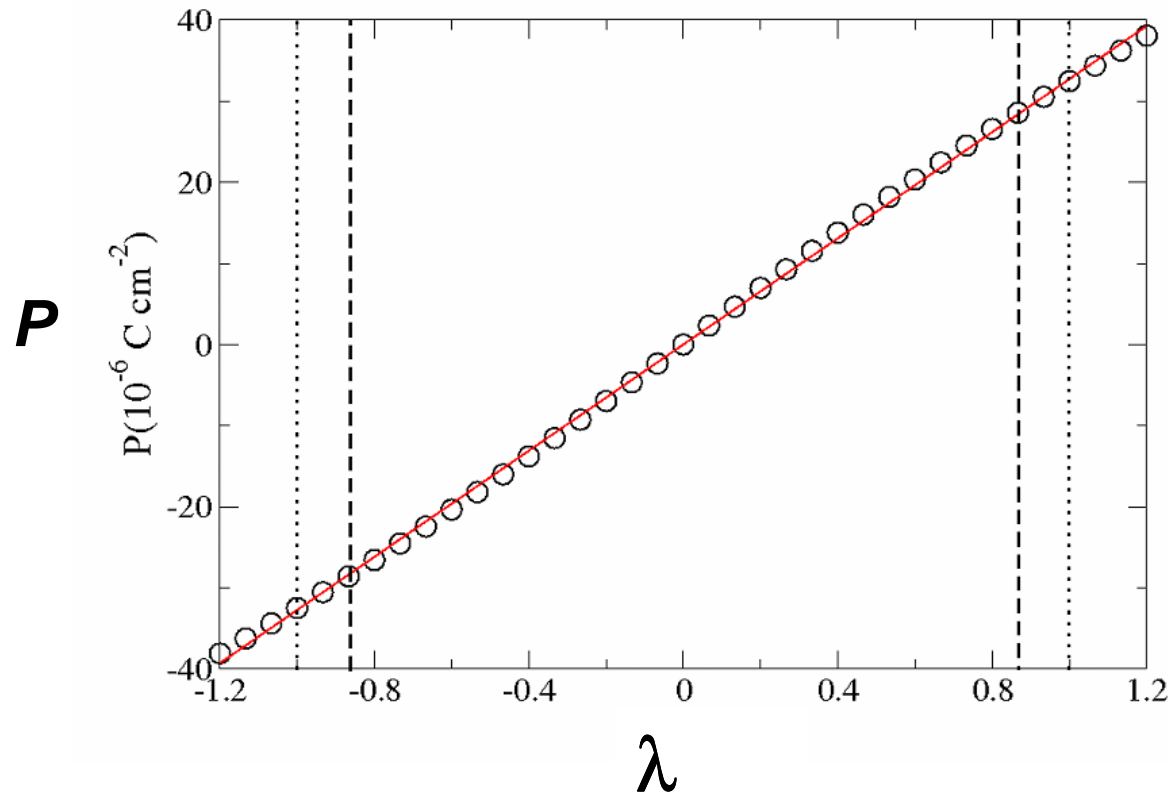
Compound	δ_A	δ_B	δ_{O1}	$\delta(O2)$
BaTiO ₃		0.018	-0.0265	-0.012
PbTiO ₃		0.0377	0.1118	0.1174
KNbO ₃	0.023		0.04	0.042

Results – BaTiO₃

λ represents the fraction of the experimental displacements relative to the paraelectric phase.



Results – BaTiO₃

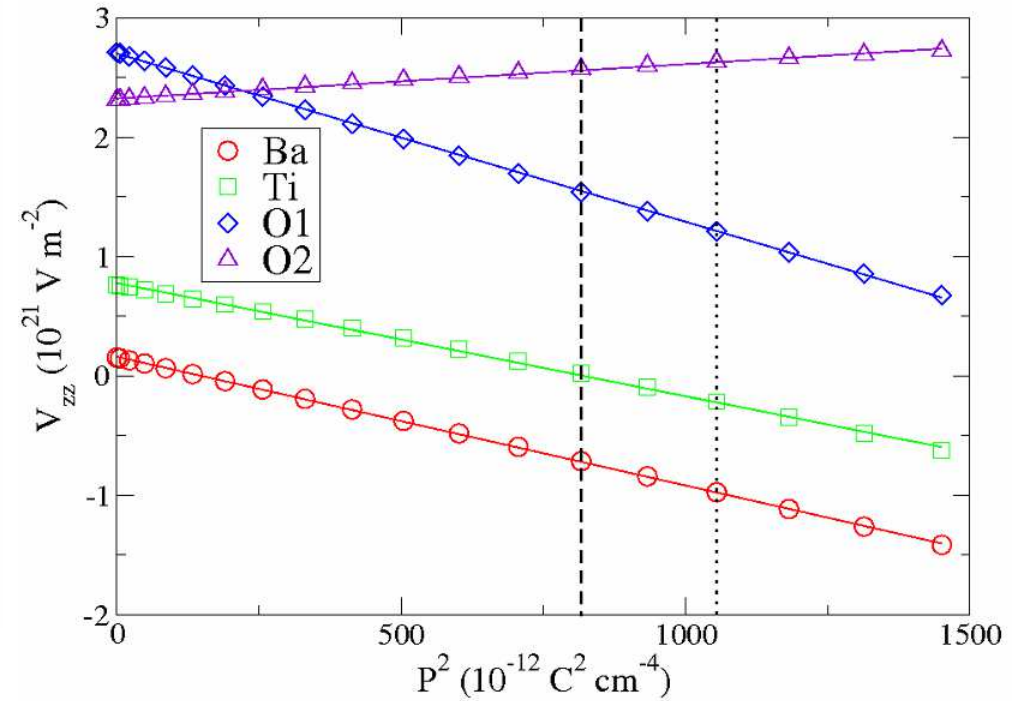
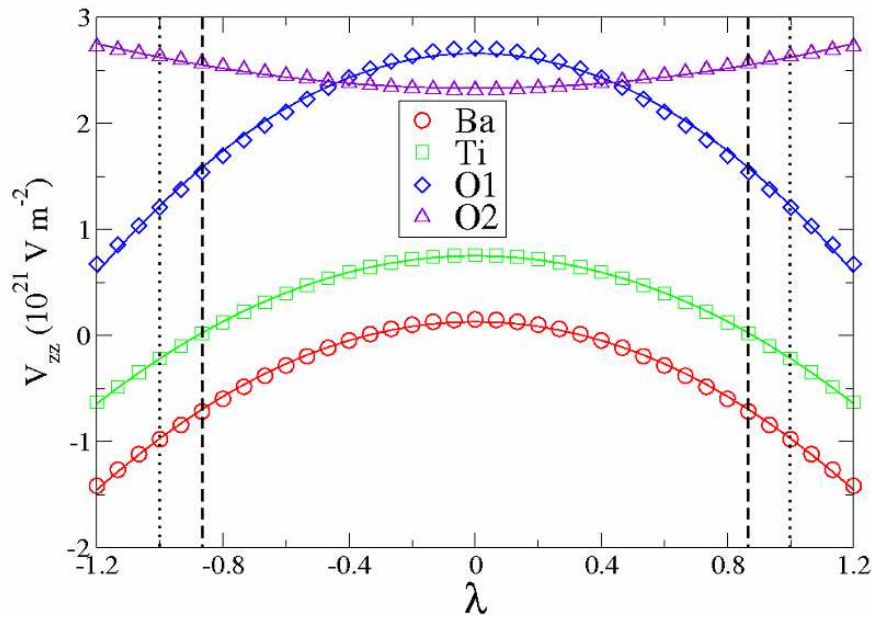


Polarization is linear with distortion.

This appears to be a general feature of perovskite ferroelectric oxides, as found in previous calculations (KNbO₃).

R. Resta, M. Posternak, A. Baldereschi. Phys. Rev. Lett. 1993;70(7):1010-1013.

Results – BaTiO₃



Lines are quadratic fits.

For a given site.

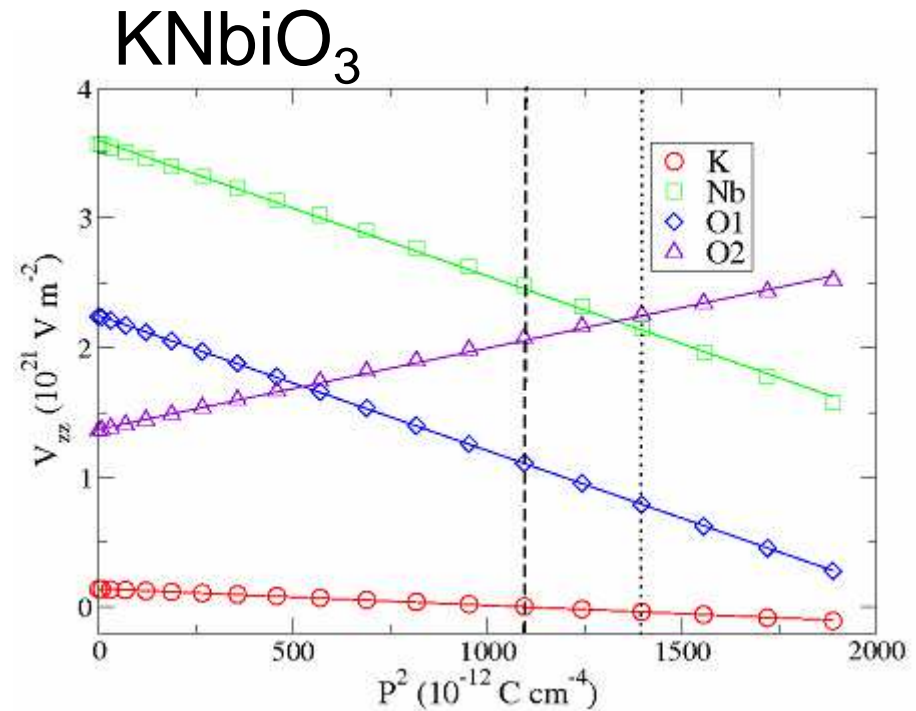
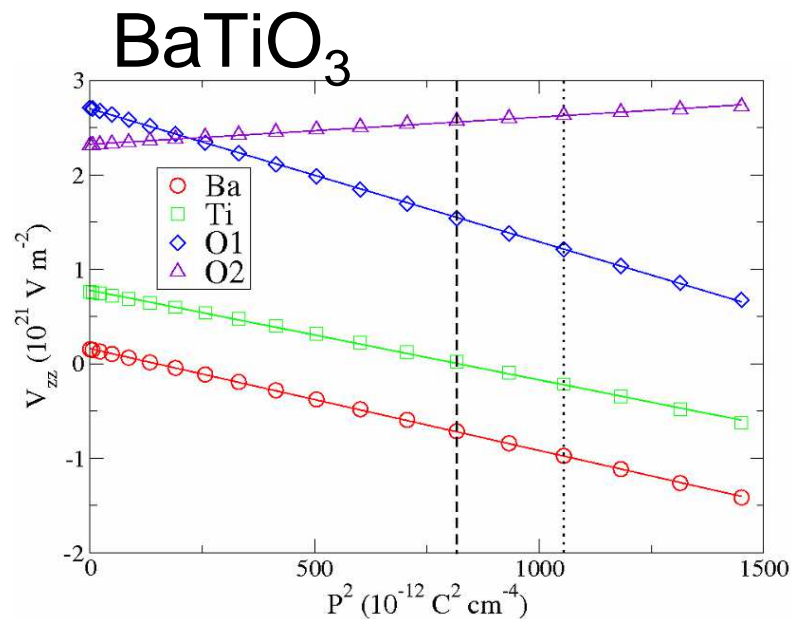
$$V_{zz}(P) = V_{zz}(0) + a * P^2$$

$$V_{zz}(P^2)$$

Where a is constant that depends on the site.

Results – KNbO₃

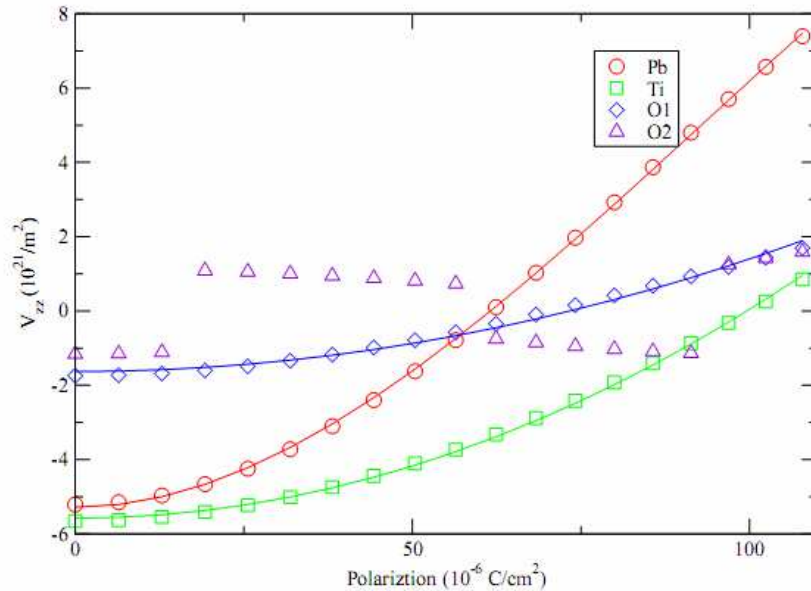
Phases with increasing T: rhombohedral, orthorhombic, tetragonal- similar to BaTiO₃



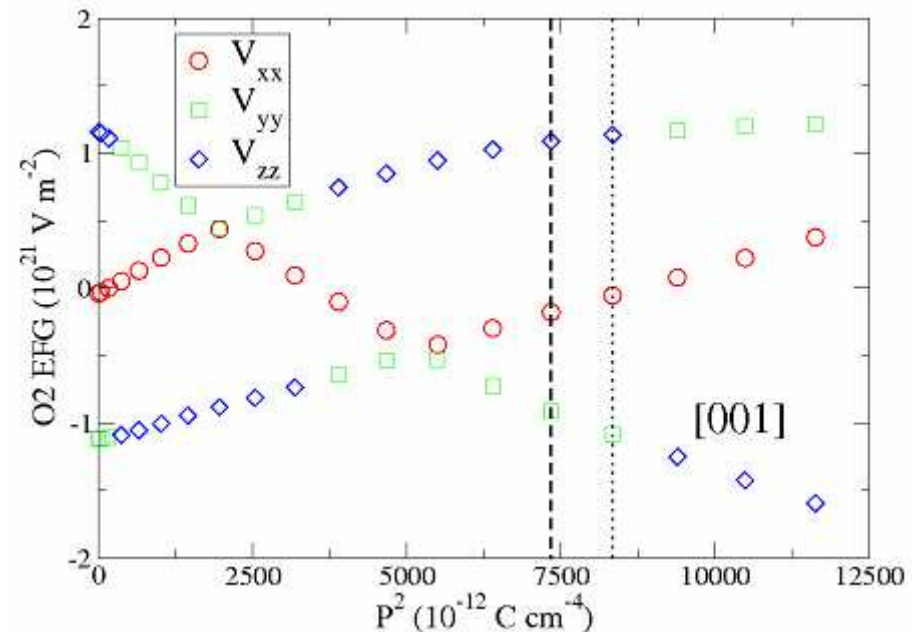
V_{zz} follows here similarly a quadratic dependence of polarization, but the coefficients, as expected, are not the same as in BaTiO₃. a depends on the site and the compound.

Results – PbTiO₃

- V_{zz} at Pb does not have a quadratic variation. For the higher polarization values in this compound, V_{zz} at the A site as an approximately linear behavior. A cubic term is needed for a correct fit.
- At the O2 site, V_{zz} (O2) EFG components of the tensor are interchanged in the distortion path.



$$V_{zz} (P)$$



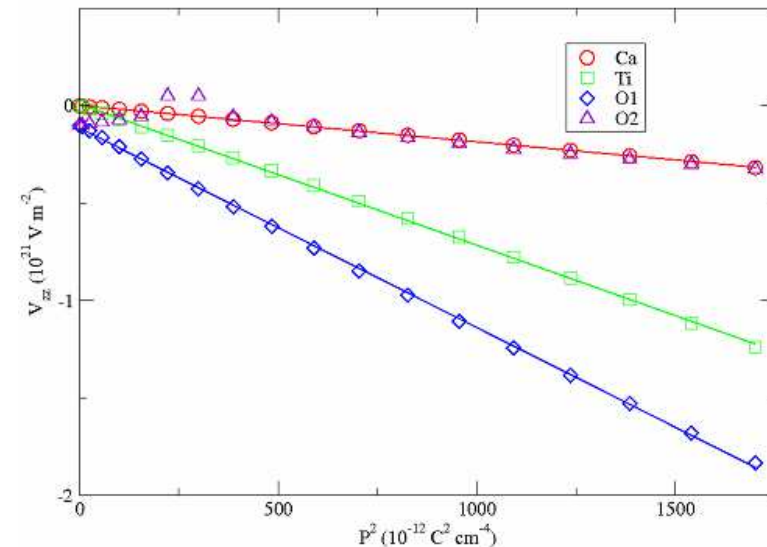
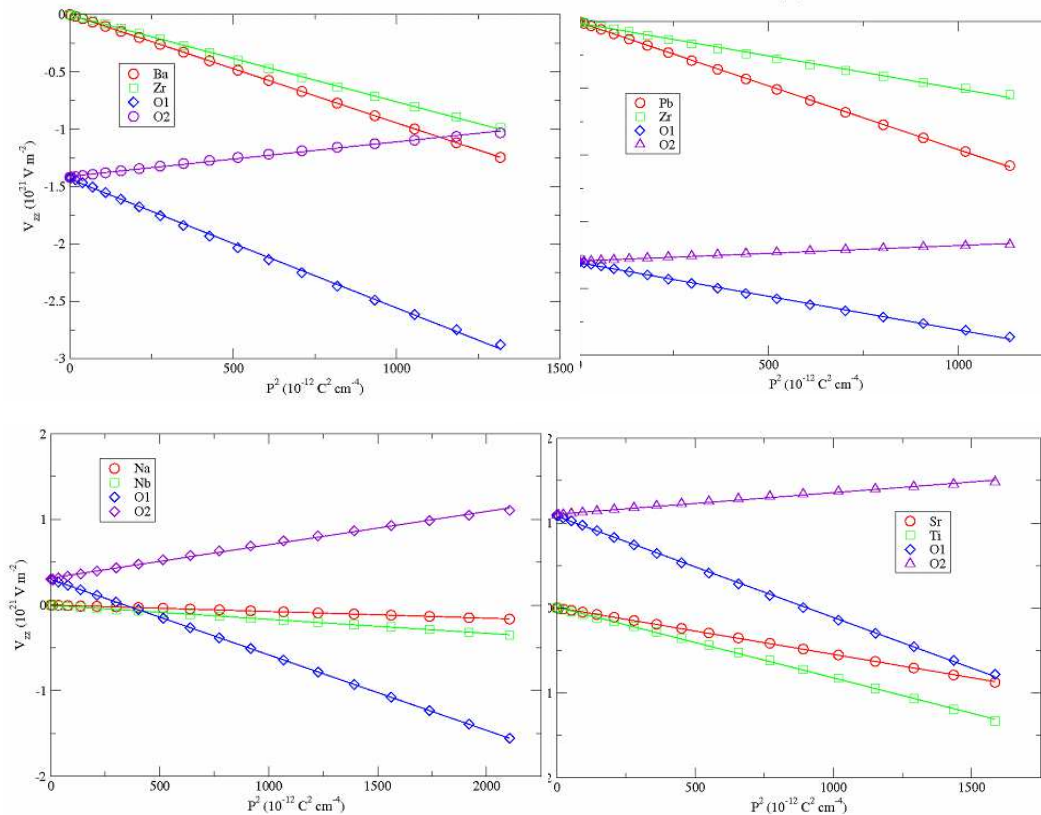
$$V_{xx}, V_{yy}, V_{zz} \text{ at the O2 site}$$

Other perovskites

BaZrO₃, PbZrO₃, CaTiO₃, SrTiO₃, NaNbO₃,...

These materials are not ferroelectric in normal conditions, or have complicated ferroelectric ground states. To simplify we calculated cubic structures (exp. Lattice parameters of the cubic phase, with the same atomic distortions as in BaTiO₃)

$$V_{zz} = V_{zz}(0) + a \cdot P^2$$



V_{zz} of O2 at CaTiO₃ does not follow a regular variation.

Other components of the EFG tensor?

For the A, B, O1 atoms in the tetragonal perovskite, $\eta=0$

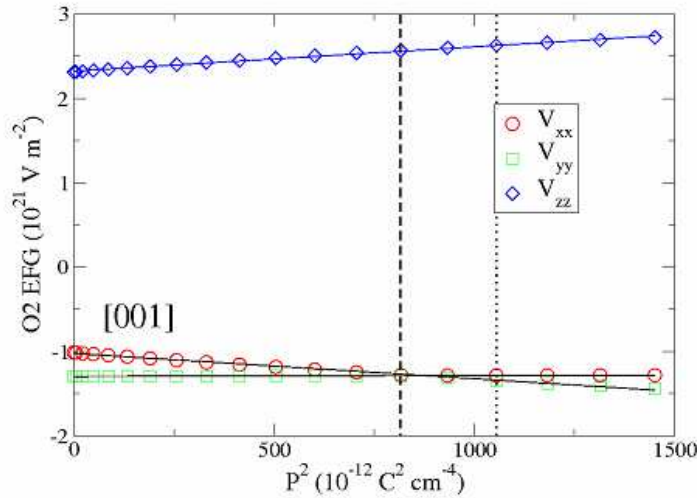
If $\eta=0$, $V_{xx}=V_{yy}=-1/2V_{zz}$ and $a_{xx}=a_{yy}=-1/2a_{zz}$

$$\Delta V_{zz} \times \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \Delta P^2 \times a \times \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

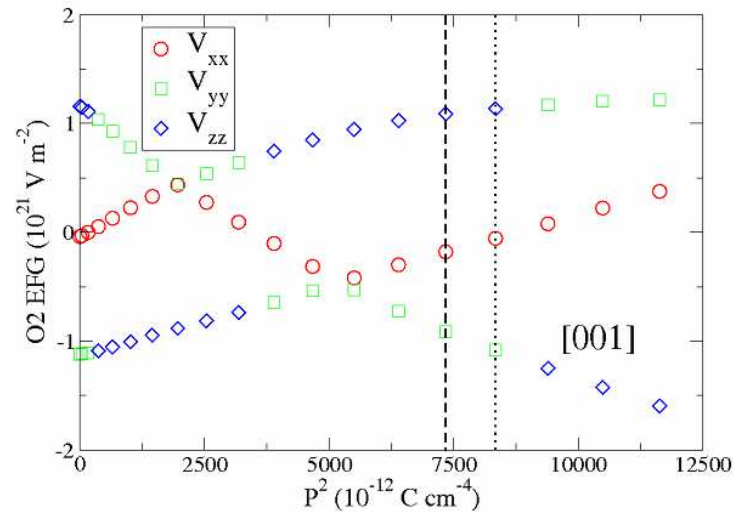
$$\begin{pmatrix} \Delta V_{xx} & 0 & 0 \\ 0 & \Delta V_{yy} & 0 \\ 0 & 0 & \Delta V_{zz} \end{pmatrix} = \Delta P^2 \times \begin{pmatrix} a_{xx} & 0 & 0 \\ 0 & a_{yy} & 0 \\ 0 & 0 & a_{zz} \end{pmatrix}$$

For the cases where $\eta \neq 0$, this relation is not followed.

Other components of the EFG tensor?



EFG at O2 vs P2
BaTiO3



EFG at O2 vs distortion
PbTiO3

V_{xx}
 V_{yy}
 V_{zz}

At the EFGO2 tensor of BaTiO₃, PbTiO₃ and CaTiO₃ there are interchanges of the tensor components due to the convention $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$

EFG component	V(0)	a
V ₁	1.310	-0.0192
V ₂	1.030	0.2965
V ₃	-2.341	-0.2773

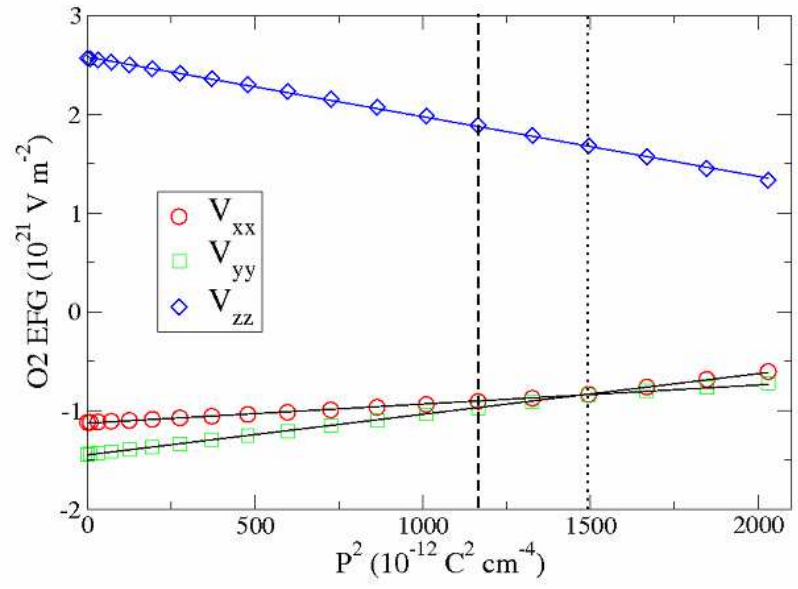
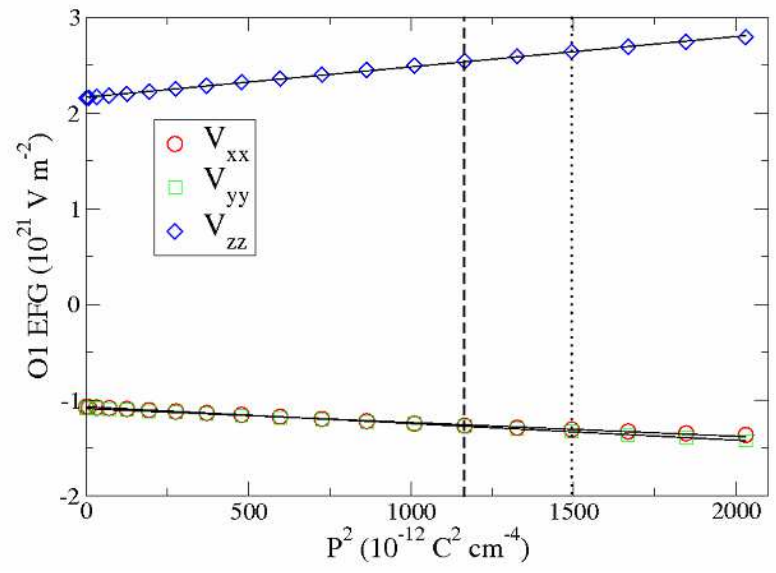
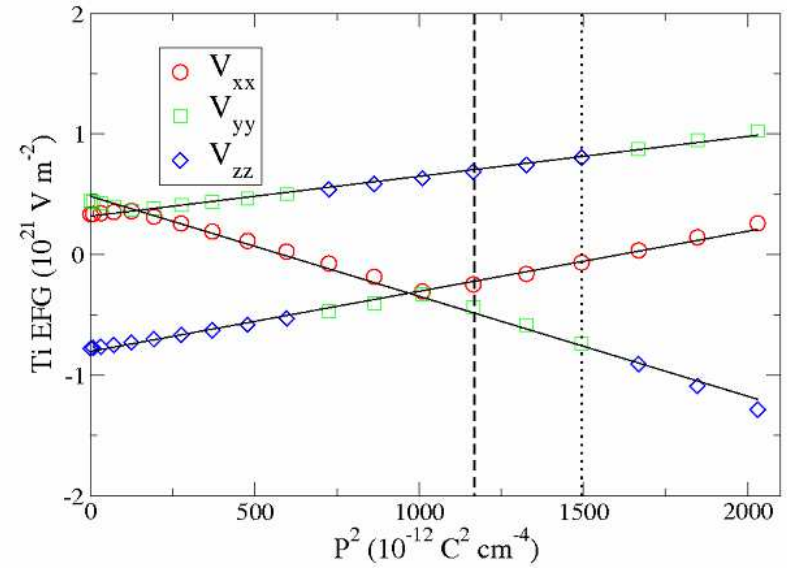
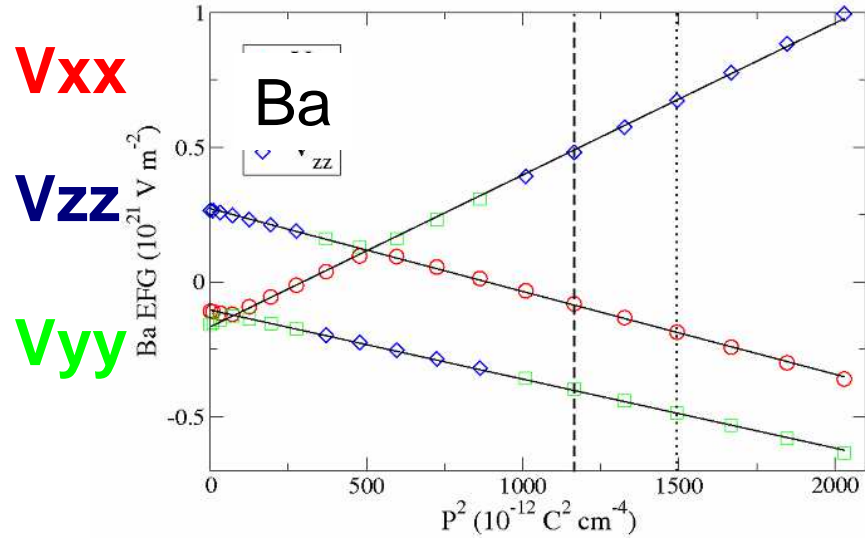
Ignoring the interchanges the variation is still usually quadratic but there is not a simple proportionality with the undistorted V_{zz} , as in the $\eta=0$ case.

$$V_{zz}(P) = V_{zz}(0) + a \times P^2$$

Compound	Atom	$V_{zz}(0)$	a
BaTiO ₃	Ba	-0.1608	1.0967
	Ti	-0.7838	0.9171
	O1	-2.7274	1.3959
	O2	-2.3401	-0.2779
PbTiO ₃	Pb	-5.2829	1.7874
	Ti	-5.5772	0.5623
	O1	-1.6310	0.3033
	O2	–	–
KNbO ₃	K	-0.1424	0.1283
	Nb	-3.5980	1.04493
	O1	-2.2481	1.04137
	O2	-1.3718	-0.6259

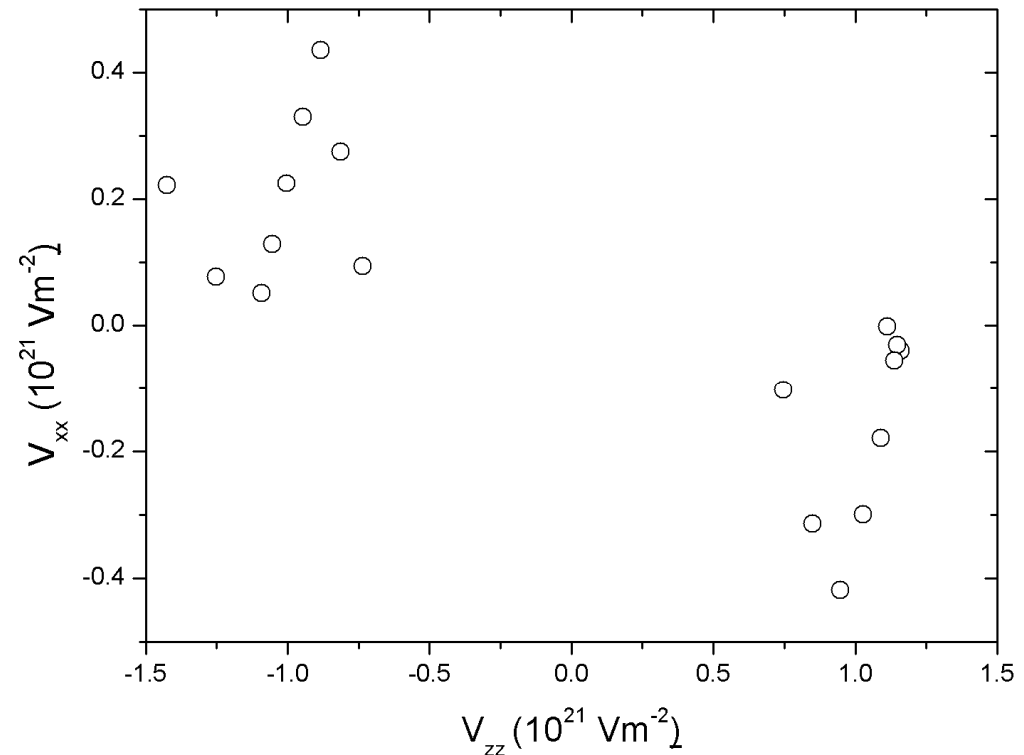
All the materials studies follow this relation except: $V_{zz}(\text{Pb})$ in PbTiO₃ which needs a cubic term for a good fit

BaTiO₃ - Orthorhombic Phase



Correlation between EFG tensor components

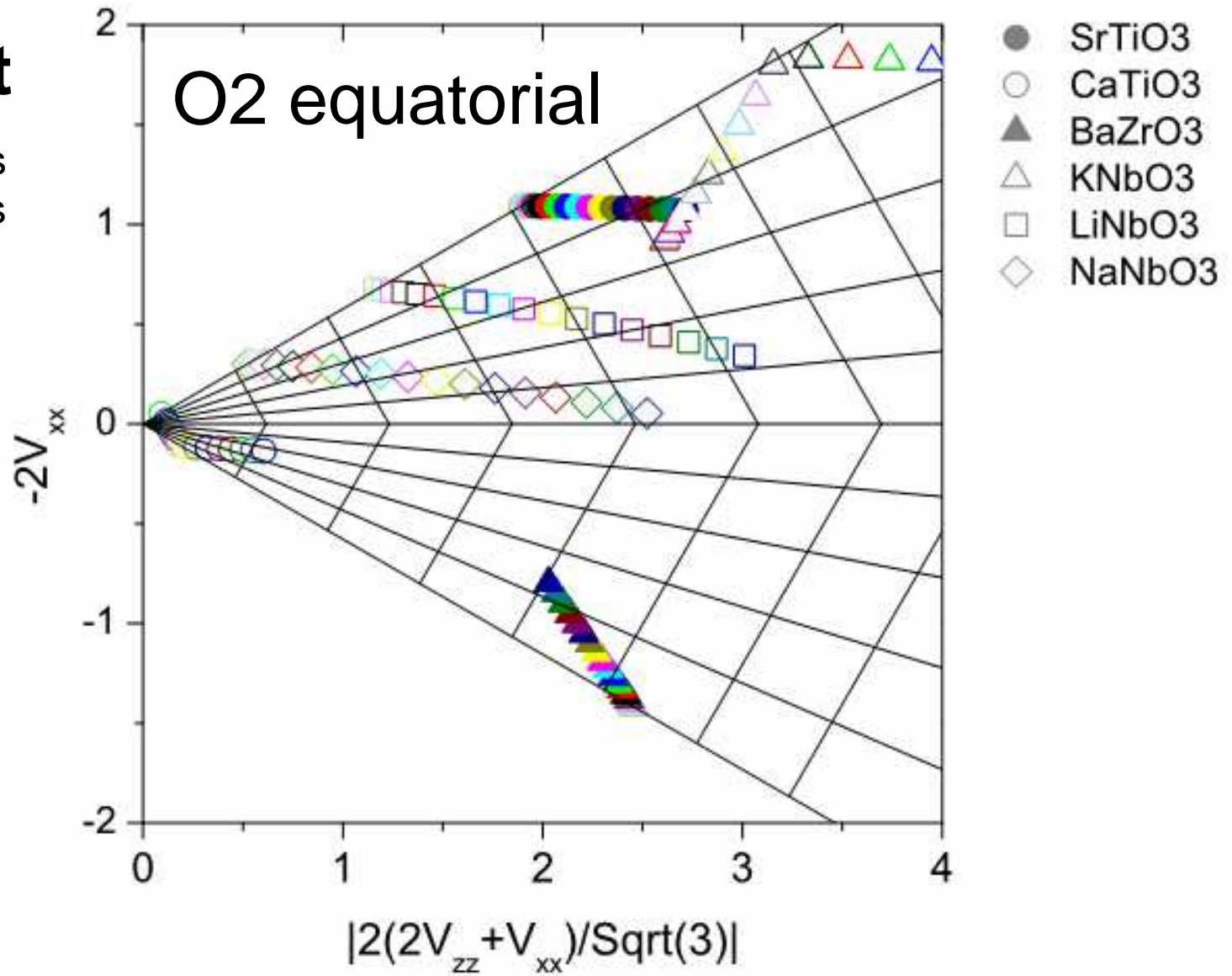
- At the A, B, or O1 sites $\eta = 0$ and the correlation is trivial ($V_{zz} = -1/2V_{xx} = -1/2V_{yy}$)
- What about at the O2 sites, where η is not zero and changes with the distortion?
 - A plot of one component against the other is needed.
 - $V_{zz}(V_{xx})$: when the EFG passes by $\eta = 1$ (V_{zz} changes sign) the trajectory is not connected. A better plot is the Czjzek plot.



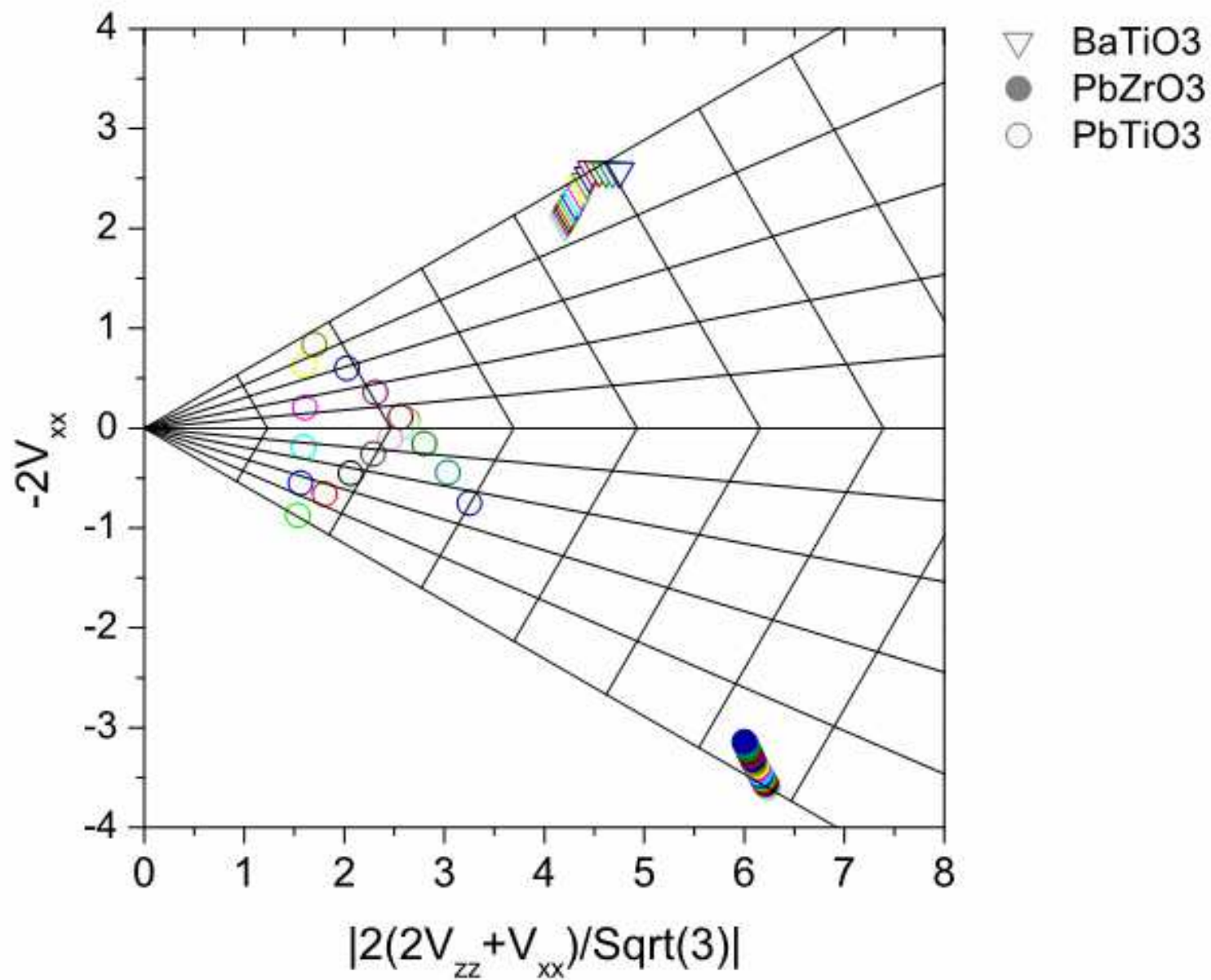
$V_{zz}(V_{xx})$ for PbTiO_3 , $0 \leq \lambda \leq 1.2$

Czjzek Plot

- All EFG trajectories are connected in this plot
- Constant $V_{zz} =$ “herringbone lines”
- Constant $\eta =$ horizontal/diagonal lines

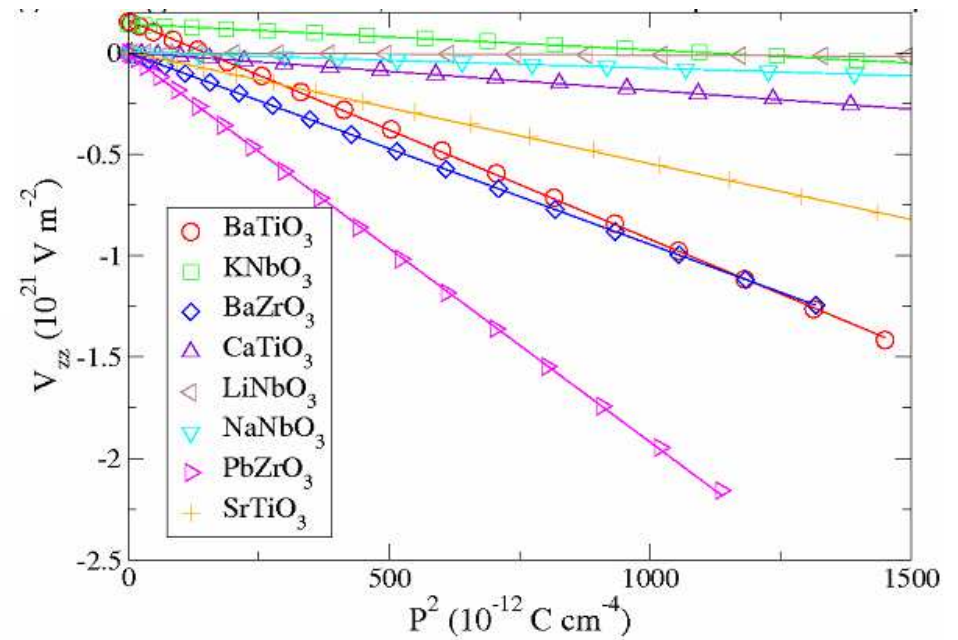
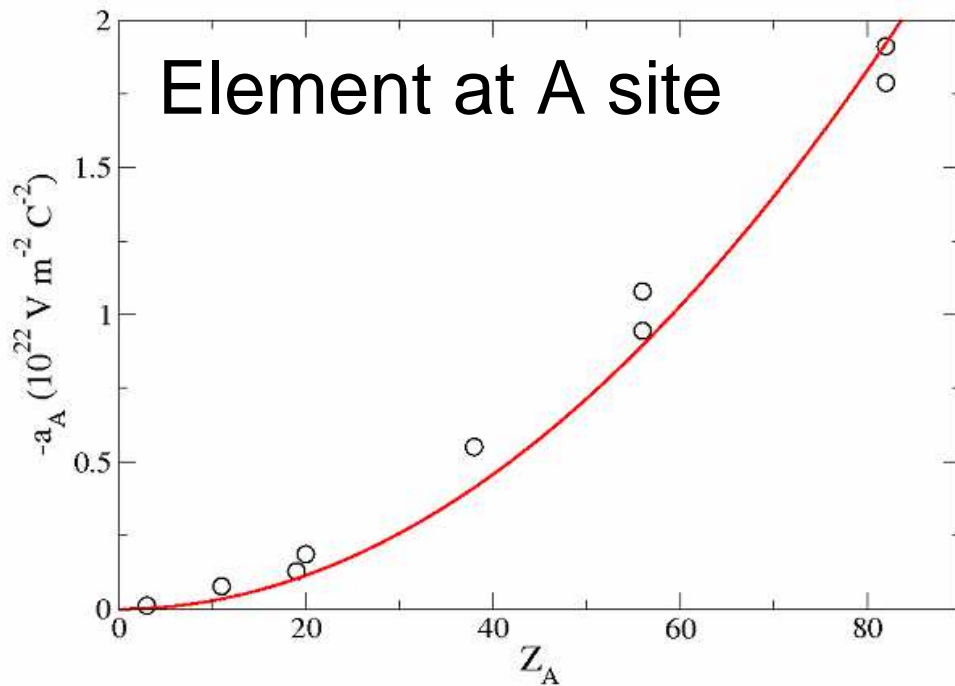


Straight trajectories = Linear correlation



One final observation: Comparison of different materials, with V_{zz} at the A site.

$$V_{zz}(P) = V_{zz}(0) + a \times P^2$$



Coefficient a approximately proportional to atomic number Z_A^2

Conclusion

- Correlation of EFG variation at all the atomic sites with P variation.
EFG is a *local analogue* of P .
- *Very similar behavior* in all the *perovskites*.
- Concluding:
This work aims to explore the richness of experimental information which can be obtained with the EFG.

Due to its local atomic character, it is an observable with great potential. Their measurement and interpretation is possible today due to the combination of experimental techniques and simulation.

In the future:

- Is there an “universal relationship” for the various perovskites?
- Comparison of the EFG of different phases in charge-ordered systems, or orbital-ordered systems.
- Calculations to understand $V_{zz}(P)$ in other systems: e. g. HoMnO_3 , where changes in the orientation of spins are responsible for the polarization.

- Thank you for your attention