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SMR/1310 - 1

SPRING COLLEGE ON
NUMERICAL METHODS IN ELECTRONIC STRUCTURE THEORY

(7 - 25 May 2001)

"*Ab-initio* theory of ferroelectric perovskites"

presented by:

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Ab-Initio Theory of Ferroelectric Perovskites

David Vanderbilt
Rutgers University

Principle collaborators:
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W. Zhong
K. Rabe
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J. Padilla
L. Bellaiche
N. Marzari
B. Meyer
N. Sai

Spring College on Numerical Methods in Electronic Structure Theory
Trieste, Italy
May 8, 2001

OUTLINE

- Introduction: Ferroelectric Perovskites
- Ab-initio calculations
  - Ground state structures
  - Lattice dynamics
- Thermodynamics
  - Effective Hamiltonian approach
  - Phase transition sequences
  - Dielectric and piezoelectric properties
- Bridging length scales
  - 90° domain walls in $PbTiO_3$
- Local real-space investigations
  - Anomalous dynamical effective charges
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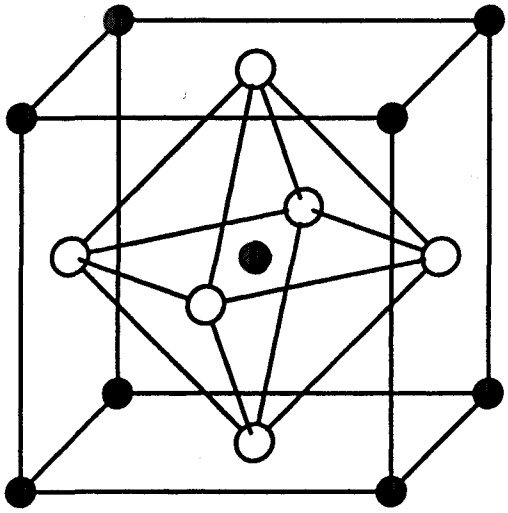
- Summary and Implications

Perovskite crystals

Structure of cubic perovskites:

ABO_3



A atom: K, Na, Ba, Sr, Pb, ...

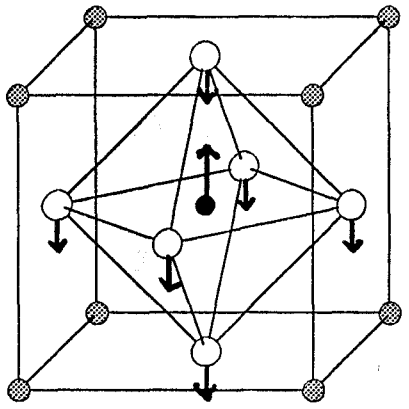
B atom: Nb, Ti, Zr

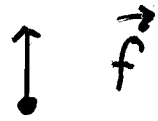
O: Oxygen

Examples: $BaTiO_3$, $BaZrO_3$, $PbTiO_3$, $PbZrO_3$, $KNbO_3$, $NaNbO_3$, ...

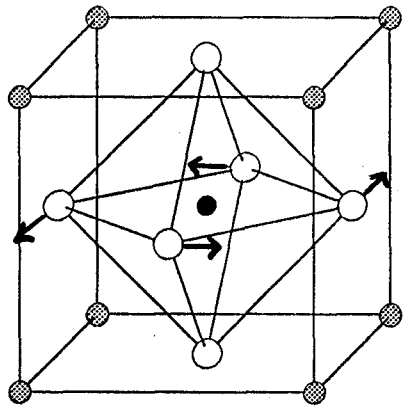
PZT = $PbXO_3$, where X is randomly Zr or Ti (~50%)

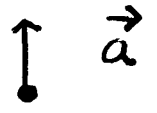
FE (FERRO ELECTRIC)





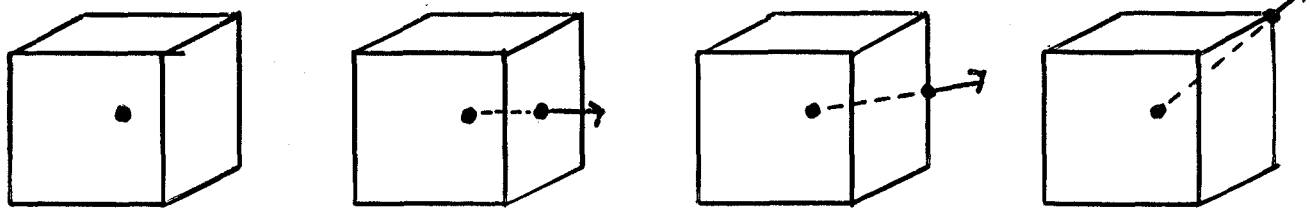
AFD (ANTI FERRO DISTORTIVE)





SYMMETRIES:

C T O R



$BaTiO_3$

- CUBIC
  ⇓ 120 °C.
- TETRAGONAL (FE)
  ⇓ 5 °C.
- ORTHORHOMBIC (FE)
  ⇓ -90 °C.
- RHOMBOHEDRAL (FE)

$PbTiO_3$

- CUBIC
  ⇓ 493 °C.
- TETRAGONAL (FE)

$SrTiO_3$

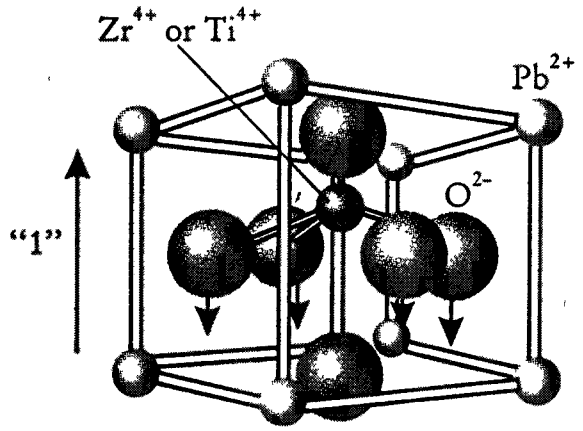
- CUBIC
  ⇓ 105 °K.
- TETRAGONAL (AFD) ⇒ QPE ?
  37 °K

PIEZOELECTRIC COEFF. :

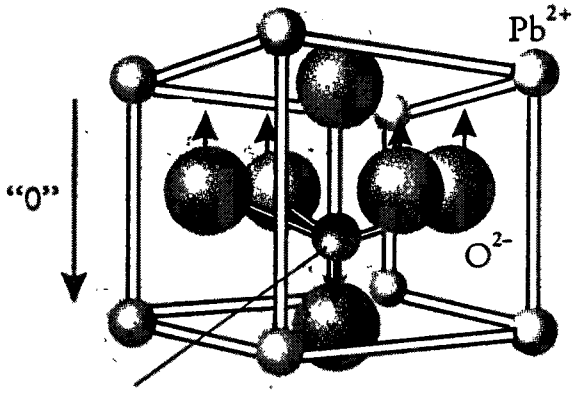
$$d_{ijk} = \frac{\partial P_i}{\partial \eta_{jk}}$$

$\vec{P}$ = POLARIZATION

$\overleftrightarrow{\eta}$ = STRAIN TENSOR



(i)



(ii)

"PZT"

$Pb(Zr_xTi_{1-x})\ O_3$
CUBIC PEROVSKITE

R. RAMESH

Ferroelectrics for Memories

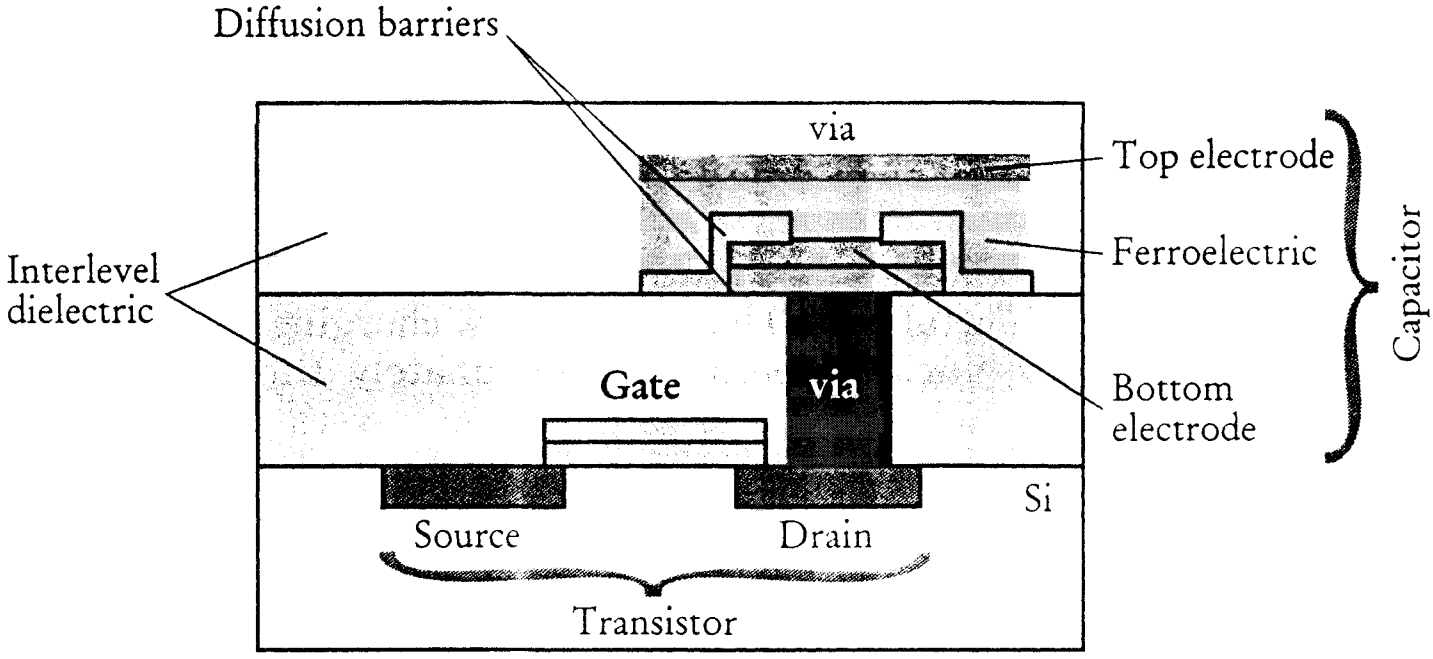
"Non-Volatile Memory"

Applications:

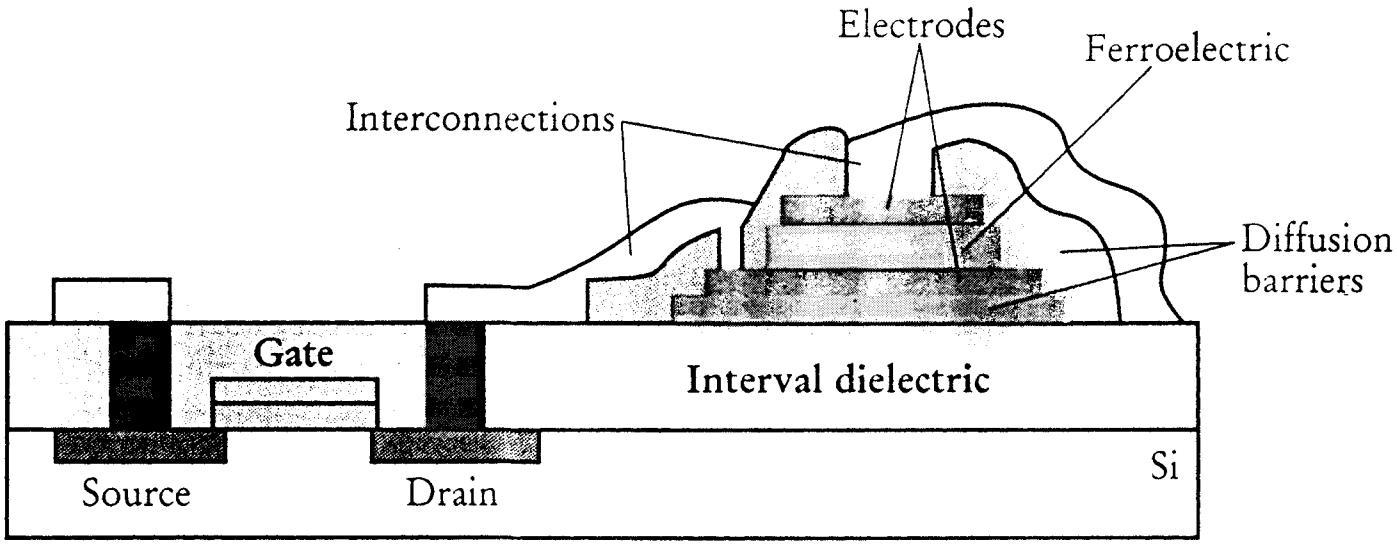
- Smart cards
- RF-ID cards
- Microprocessors
- Computer memory (RAM) !

Capacitor structures

- $Pt/SrBi_2Ta_2O_9/Pt$
- or
- $Pt/cond.oxide/Pb(Zr_xTi_{1-x})O_3/cond.oxide/Pt$



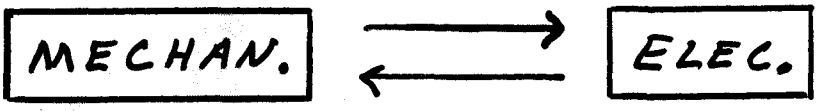
VERTICAL HIGH-DENSITY NVFRAM ARCHITECTURE



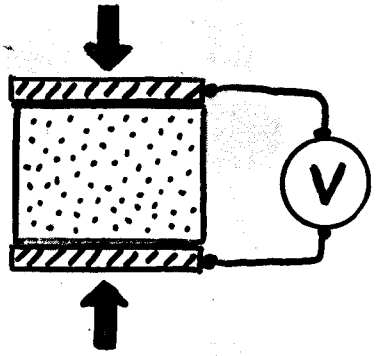
LATERAL LOW-DENSITY NVFRAM ARCHITECTURE

R. RAMESH

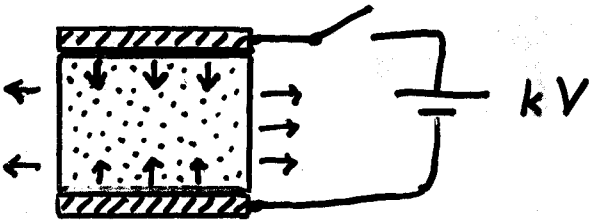
PIEZOELECTRIC EFFECTS



DIRECT EFFECT

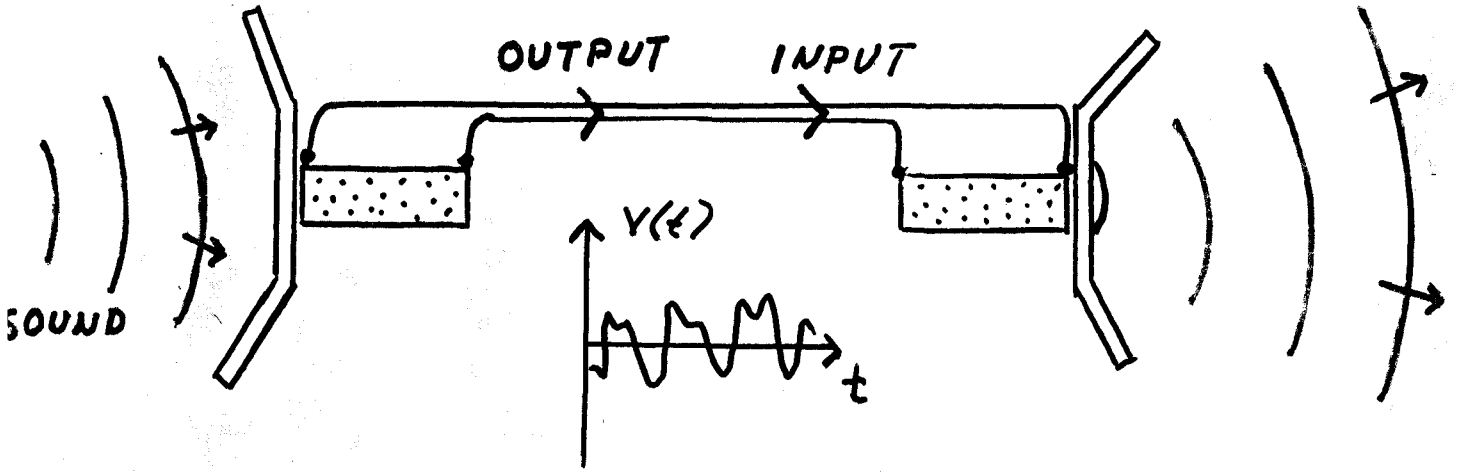


CONVERSE EFFECT



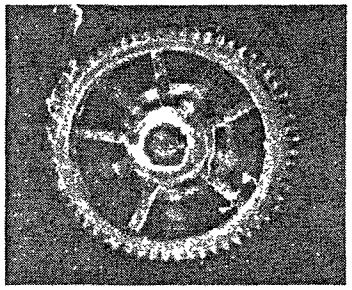
MICROPHONE

SPEAKER

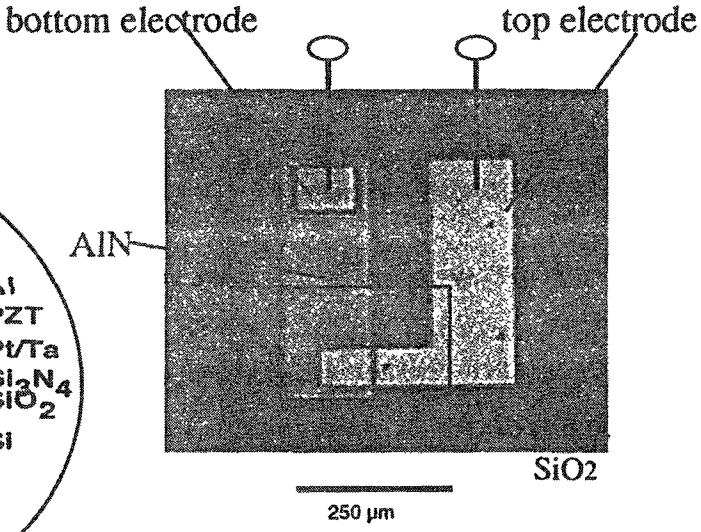


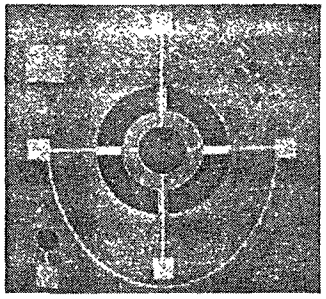
Ferroelectric films for MEMS applications

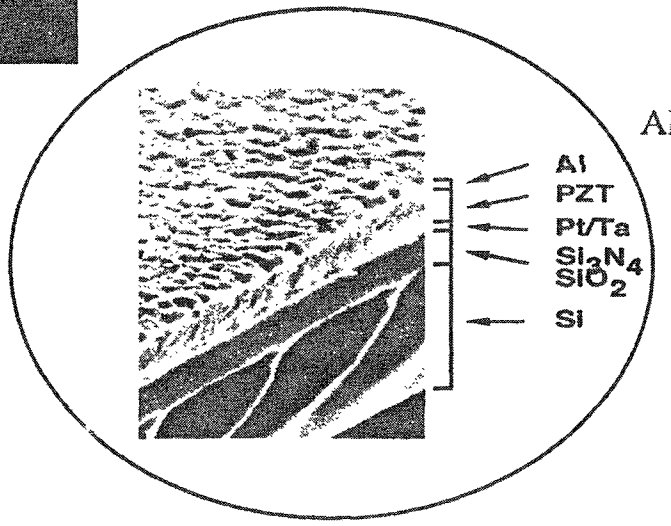
Ultrasonic micromotor



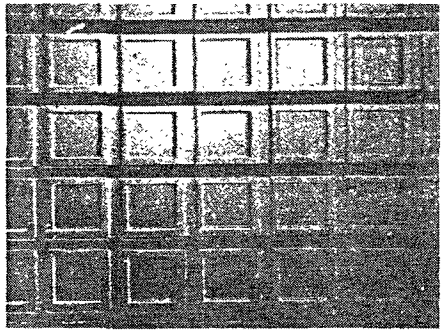
Top view on realized BAW structure



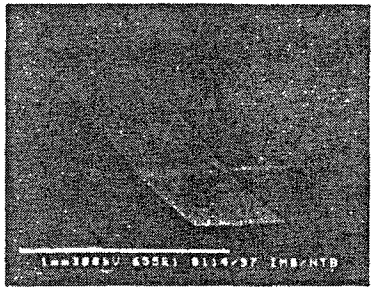




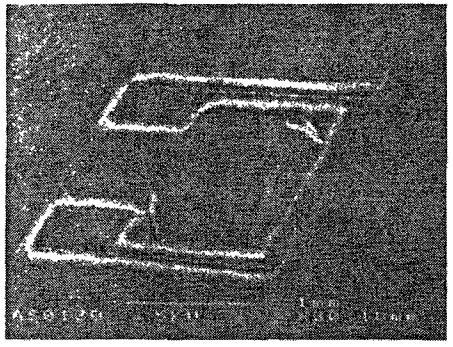
Pressure sensor array



Active micro mirror



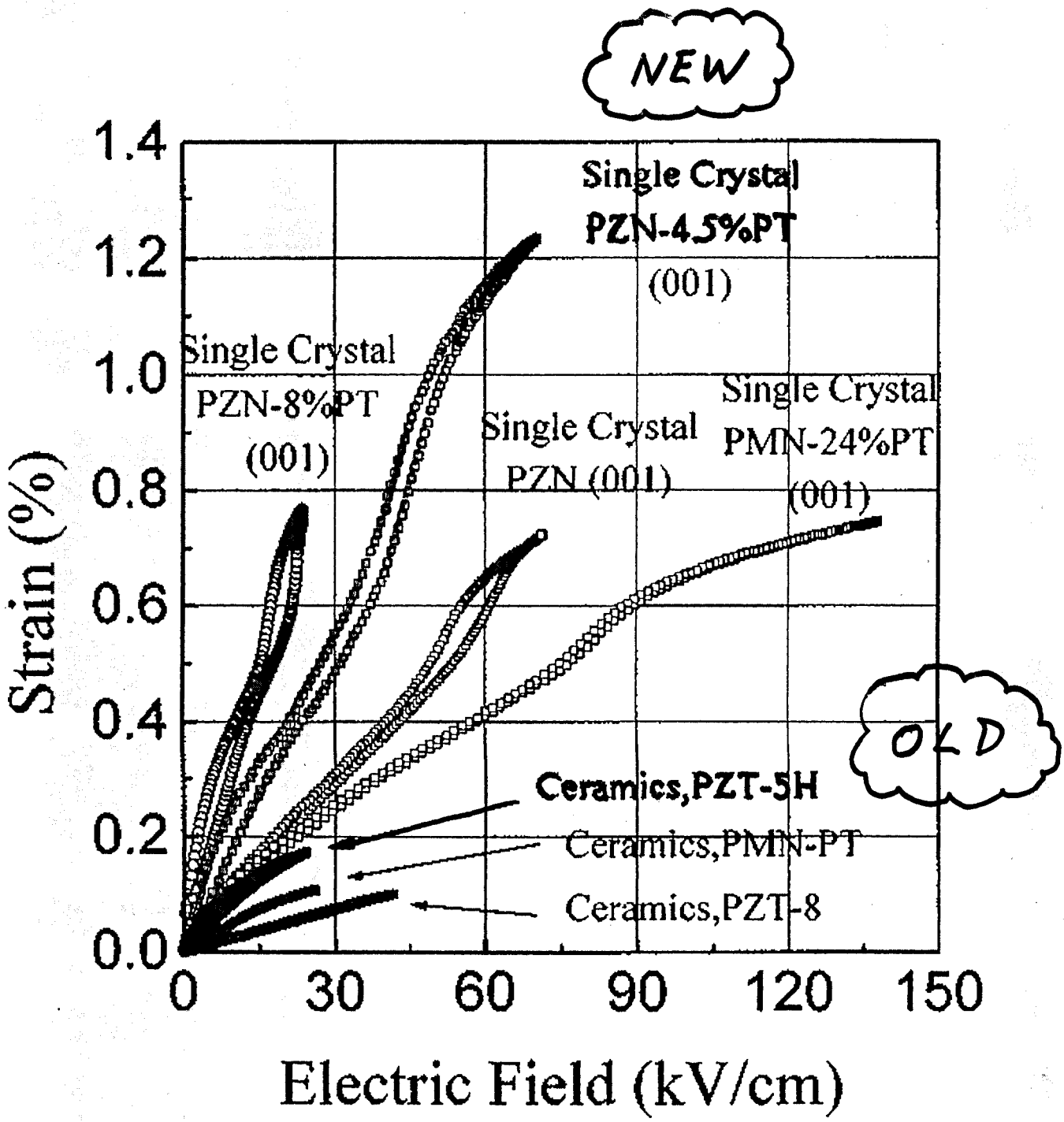
Accelerometer



N. SETTER

LC EPFL

$Pb(Zn_{0.32}Nb_{0.64}Ti_{0.04})O_3$



PARK & SHROUT, 1997

(PENN STATE U.)

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AB-INITIO THEORY

- Density-Functional Theory (DFT)
  with Local-Density Approximation (LDA)
- Plane-wave basis
- Conjugate-gradient minimization
- Ultra-soft pseudopotential
  - Low plane-wave cutoff
  - Excellent transferability
  - Semi-core states included
- $4, 4, 4$ or $6, 6, 6$ k-point sets
- Polarization (*King-Smith & Vanderbilt*) for LO modes
- Doubled supercell for zone-boundary phonons

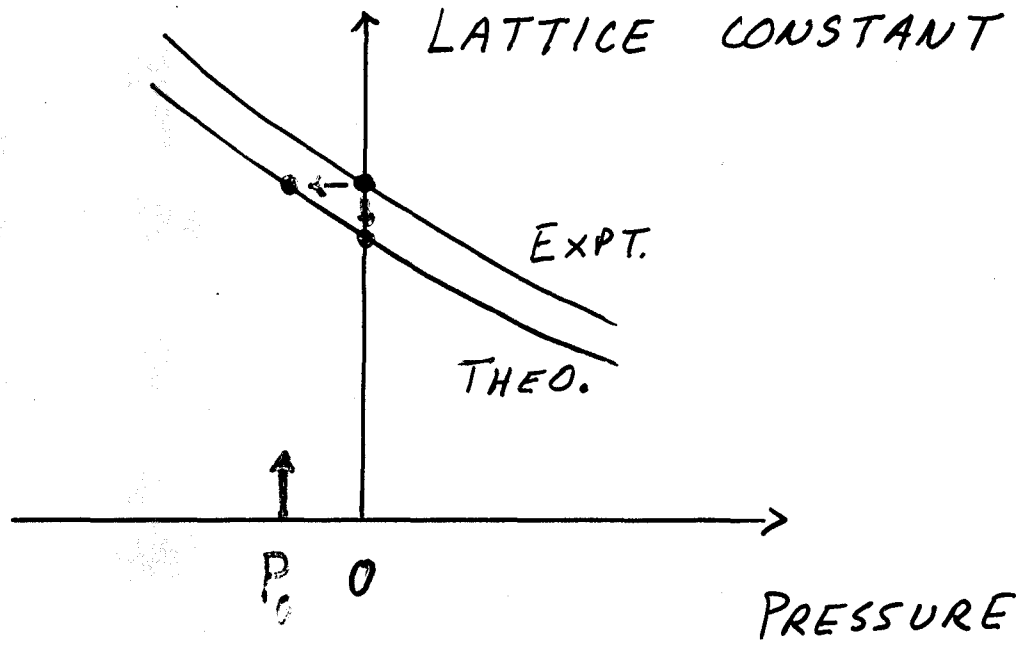
Lattice constants (a.u.)

	Pseudo *	LAPW *	Exper *
$BaTiO_3$	7.456	7.45	7.58
$KNbO_3$	7.472	7.488	7.58
$PbTiO_3$	7.350	7.35	7.50
$SrTiO_3$	7.303		7.38
$KTaO_3$		7.48	7.53
$PbZrO_3$	7.770	7.786	7.81
$CaTiO_3$	7.192		7.25

* KING-SMITH & VANDERBILT

* COHEN & KRAKAUER ; SINGH & BOYER ; SINGH

* LANDOLT BORNSTEIN


LATTICE CONSTANT
EXPT.
THEO.
P
0
PRESSURE

Ground State Structure ($T = 0$)

	Theory			Experiment		
	Symm	Type	Atoms	Symm	Type	Atoms
$BaTiO_3$	R	FE	5	R	FE	5
$KNbO_3$	R	FE	5	R	FE	5
$PbTiO_3$	T	FE	5	T	FE	5
$SrTiO_3$	T	AFD + FE	10	T	AFD	10
(q fluct)	T	AFD	10			
$KTaO_3$*	C	Para	5	C	Para	5
$PbZrO_3$		??		O	AFD + (A)FE	40
$CaTiO_3$	R	AFD	10	O	AFD + AFE	20

* SINGH

TABLE IV. Structural parameters of $PbTiO_3$.

	Theory I	Theory II	Experiment
a (a.u.)	7.380 *	7.298	7.380
c/a	1.063 *	1.054	1.063
z(Ti)	0.549	0.537	0.540
z(O_1,O_2)	0.630	0.611	0.612
z(O_3)	0.125	0.100	0.112

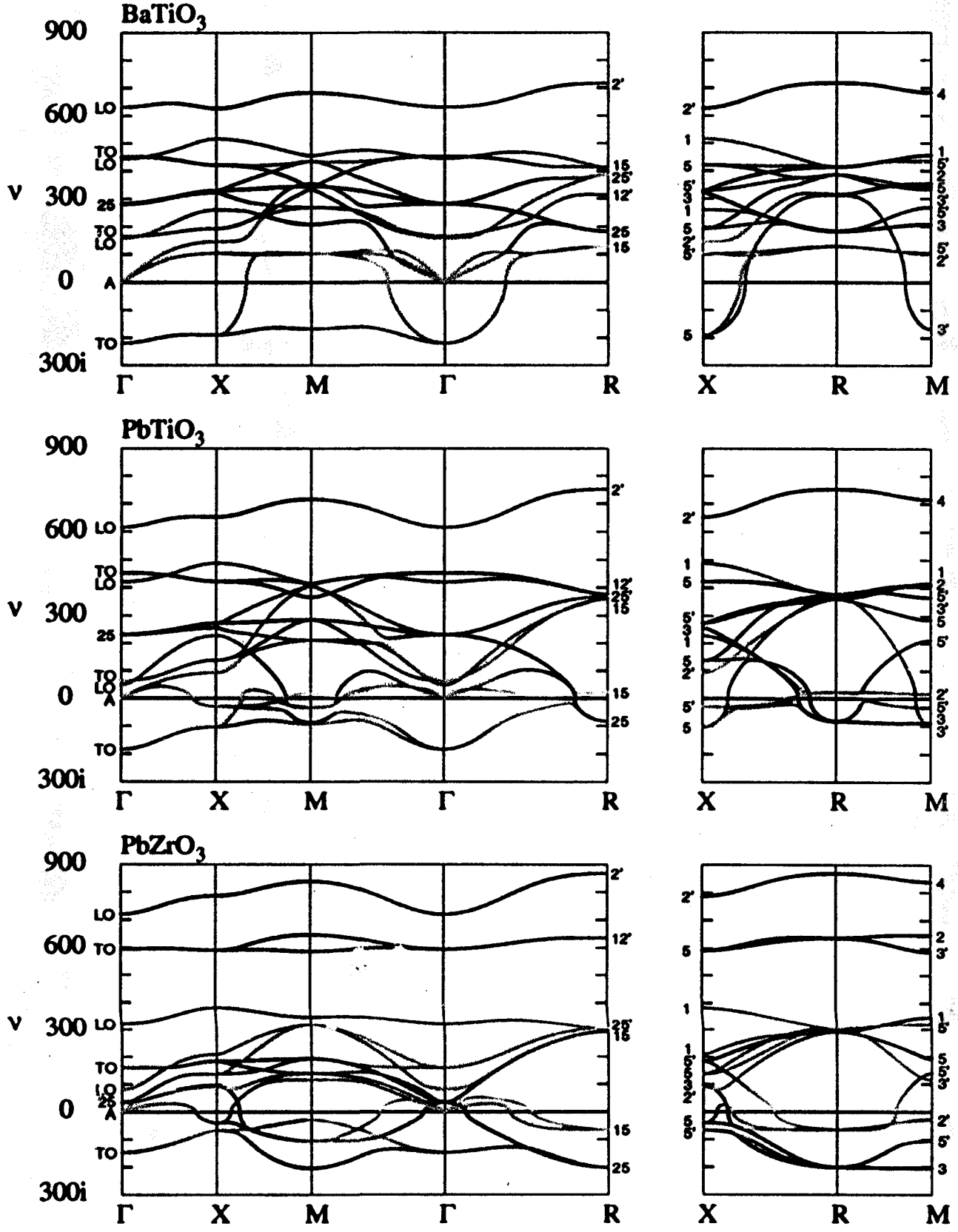
* FIXED

Pb Ti O_3

TABLE V. Frequencies of optical modes at Γ in cm^{-1}. Infrared-active modes exhibit LO-TO splitting. Experimental values as compiled in by J.D. Freire and R.S. Katiyar.

	Theory	Experiment
A_1(TO)	151	147
A_1(TO)	355	359
A_1(TO)	645	646
E(TO)	81	88
E(TO)	183	220
E(TO)	268	289
E(TO)	464	505
B_1	285	289
A_1(LO)	187	189
A_1(LO)	449	465
A_1(LO)	826	796
E(LO)	114	128
E(LO)	267	289
E(LO)	435	436
E(LO)	625	723

GARCIA & VANDERBILT, 1996



GHOSEZ, COCKAYNE, WAGHMARE, & RABE
PRB 60, 836 (1999).

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How to study phase transitions?

E.G. Cubic $\longleftrightarrow$ Tetrag. FE

130°C $BaTiO_3$

- **Ab-Initio MD?**

LDA: Can afford 5-10 cells

(25-50 atoms)

But $\xi_{FE} \cong$ 5-10 lattice consts.!

$\Rightarrow$ 100's of cells!

- **Introduce H_{eff}** Rabe + JDJ

  - Choose degrees of freedom
  - Expand H in Taylor series
  - Determine expansion parameters

Yes!

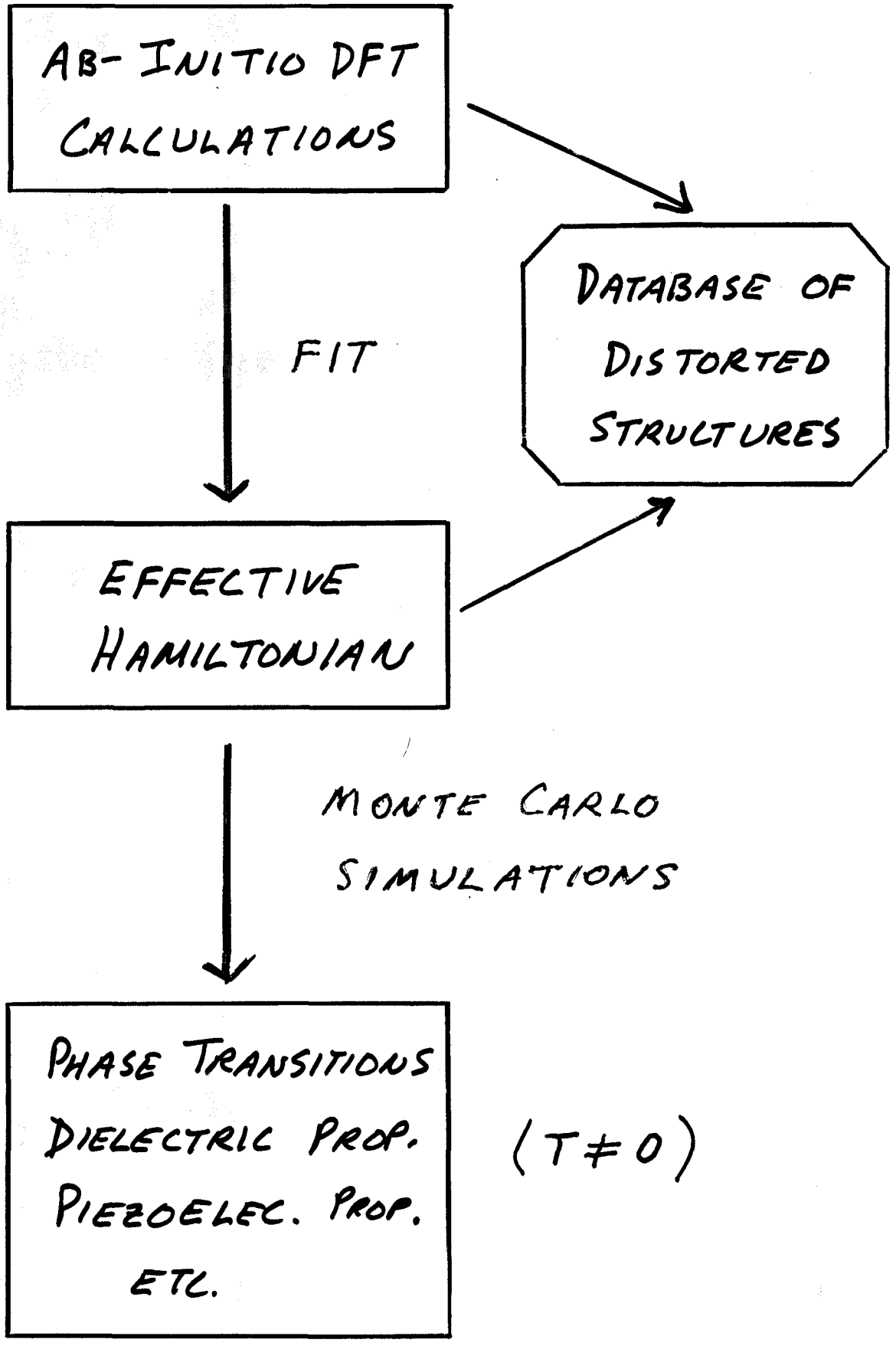
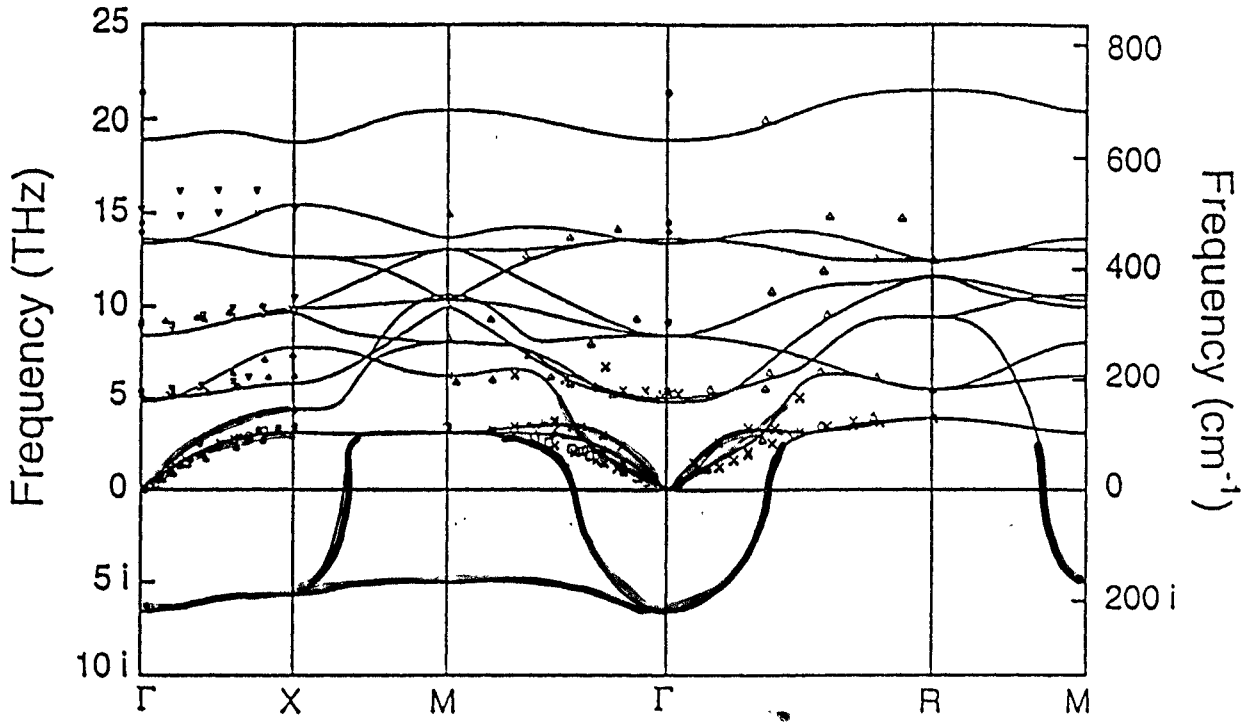

AB-INITIO DFT CALCULATIONS
DATABASE OF DISTORTED STRUCTURES
FIT
EFFECTIVE HAMILTONIAN
MONTE CARLO SIMULATIONS
PHASE TRANSITIONS
DIELECTRIC PROP.
PIEZOELEC. PROP.
ETC.
(T≠0)

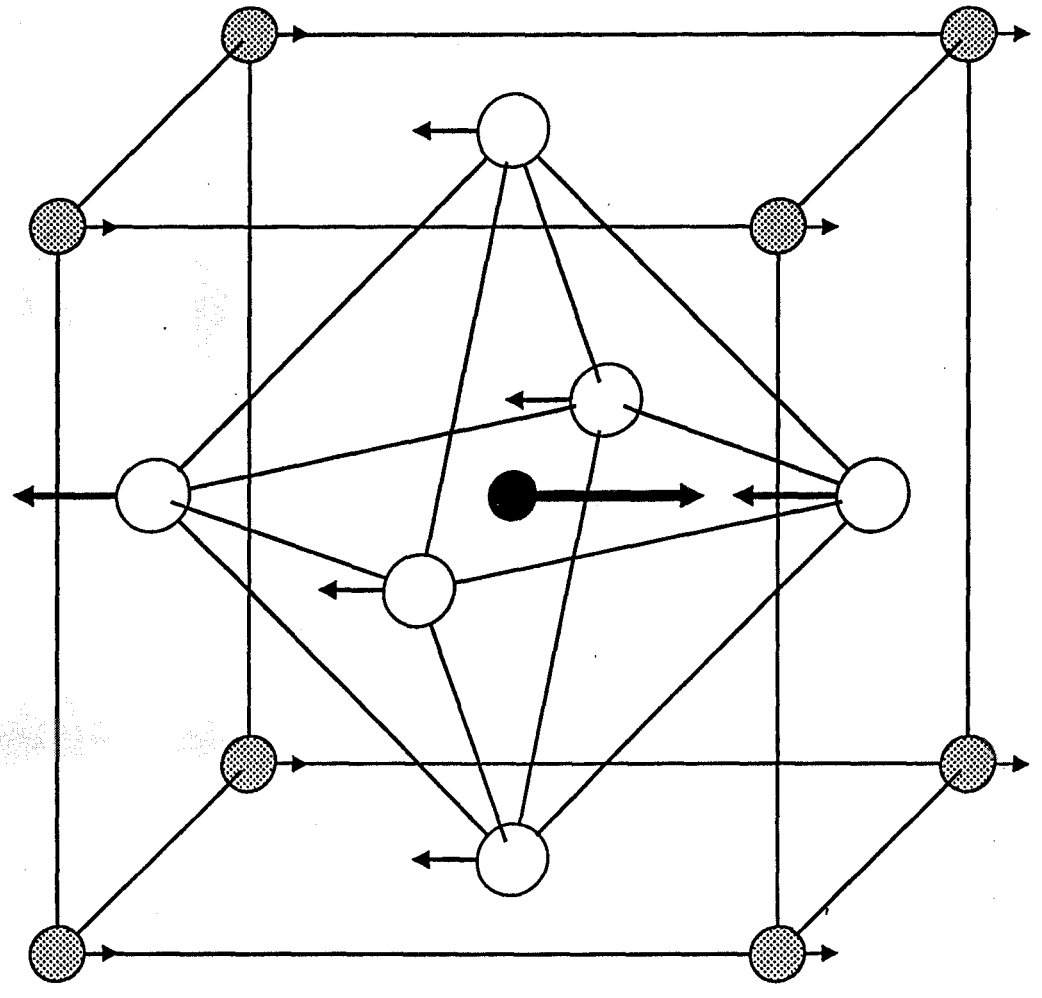
Figure 7.4: *Calculated phonon dispersion curves of cubic $BaTiO_3$ at the experimental lattice constant. The theoretical result shows a reasonable agreement with the experimental data: (•) Ref. [3], (○) Ref. [6], (+) Ref. [7], (□) Ref. [8], (×) Ref. [9], (▽) Ref. [10], (△) Ref. [11].*

T = 0



THESIS OF PH. GHOSEZ, 1997

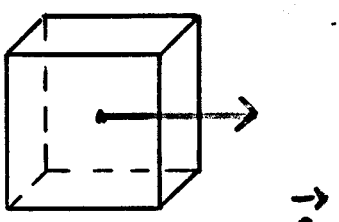
$Ba\ Ti\ O_3$



FE LOCAL MODE

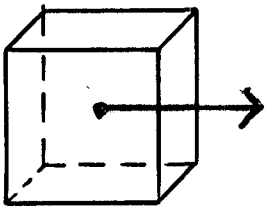
$\vec{f}_l$

DEGREES OF FREEDOM :



"FE"

$\vec{f}_\ell$



"STRAIN"

$\vec{u}_\ell \Rightarrow \overleftrightarrow{\eta}_\ell$

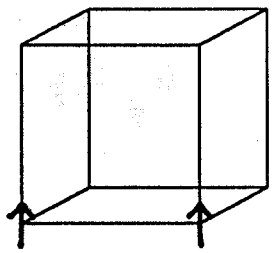
EFFECTIVE HAMILTONIAN :

$H_{on\text{-}site}$:

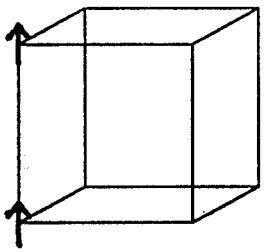
- $\mathcal{O}(f_\ell^4)$ FE DOUBLE-WELL POT.
- $\mathcal{O}(\eta_\ell^2)$ ELASTIC - HARMONIC
- $\mathcal{O}(f_\ell^2 \eta_\ell)$ GRUNEISEN COUPLING

$H_{intersite}$:

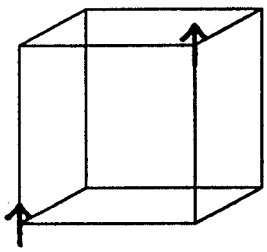
- $\dfrac{Z^* f_\ell f_{\ell'}}{\epsilon_\infty |\ell - \ell'|^3}$ TO ∞ RANGE.
- $\mathcal{O}(f_\ell f_{\ell'})$ CORRECTIONS TO 3RD NEIGH.



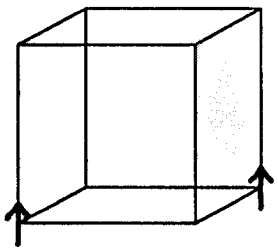
j_1



j_2



j_3



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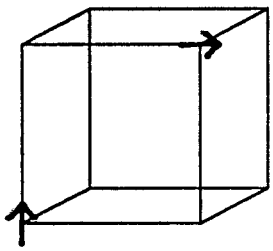
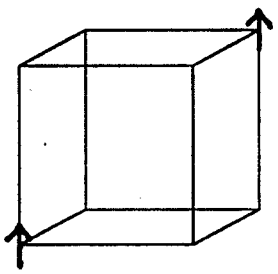
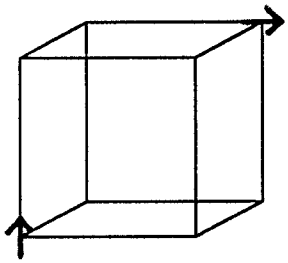


j_5

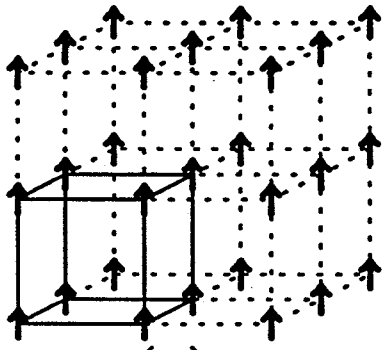


j_6

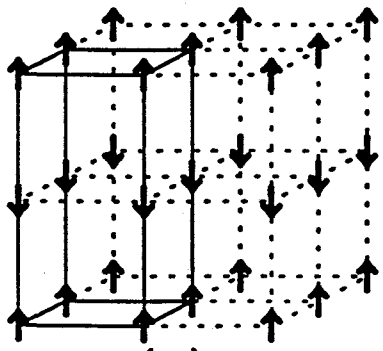


j_7

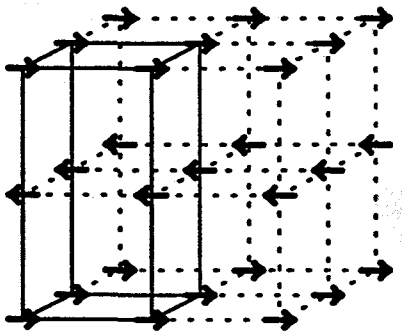
LDA CALCULATIONS NEEDED



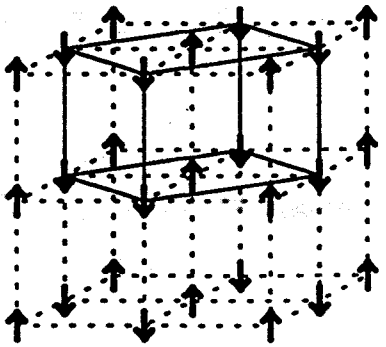
(a)



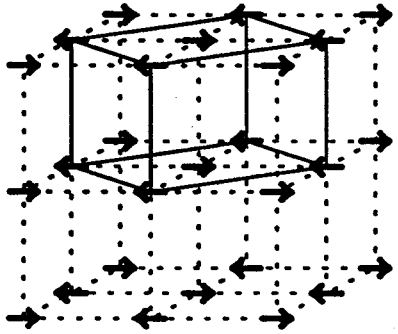
(b)



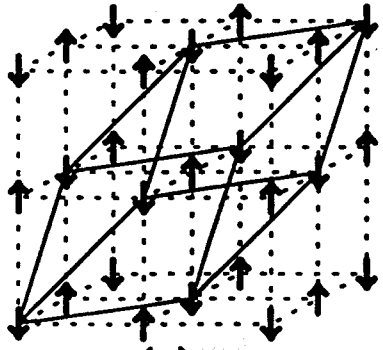
(c)



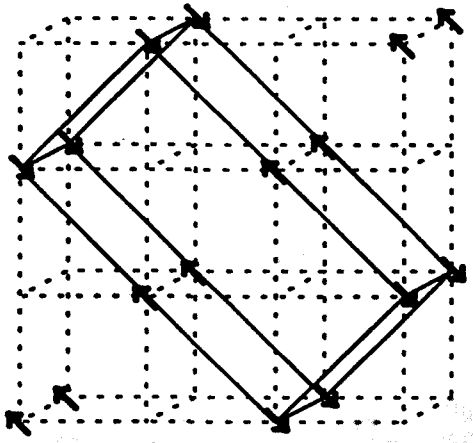
(d)



(e)



(f)



(g)

Expansion parameters of the Hamiltonian for $BaTiO_3$. Energies are in Hartrees.

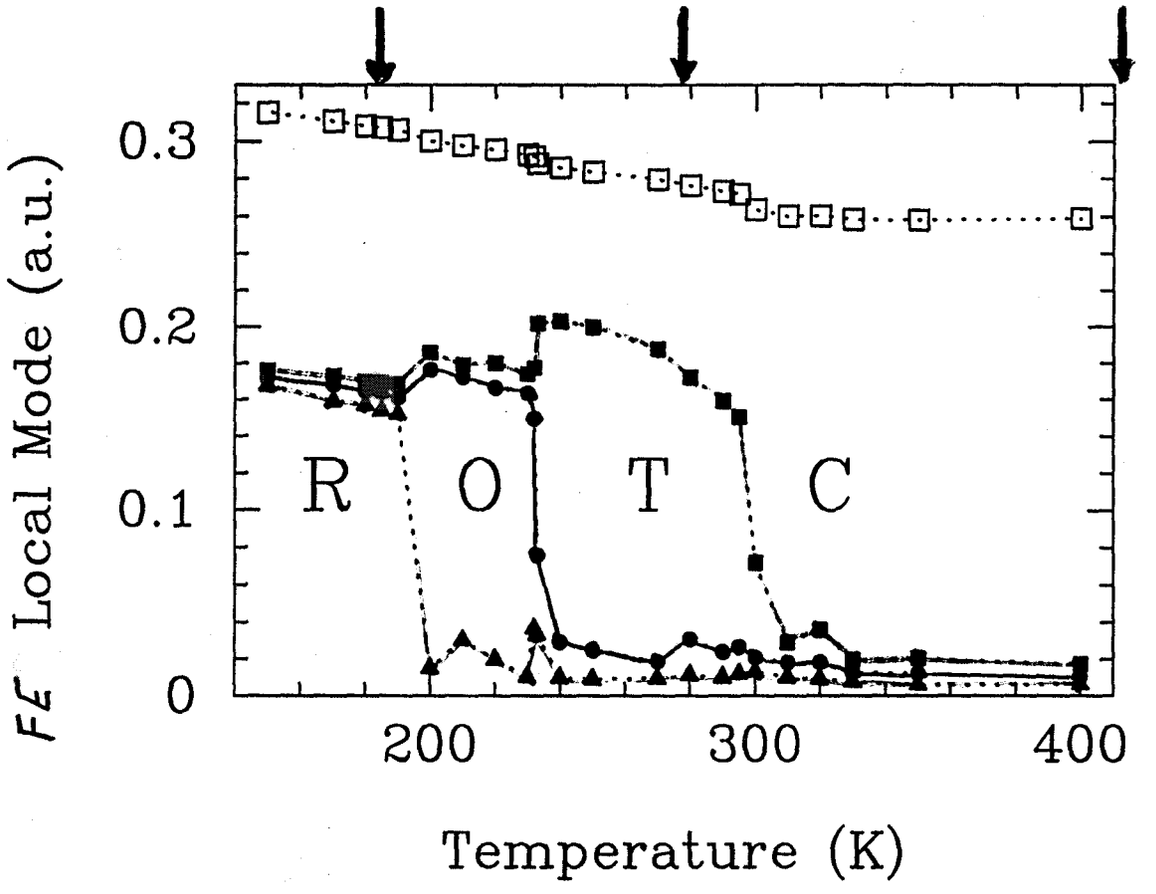
On-site	κ_2	0.0568	α	0.320	γ	−0.473
Intersite	j_1 j_3 j_6	−0.02734 0.00927 0.00370	j_2 j_4 j_7	0.04020 −0.00815 0.00185	j_5	0.00580
Elastic	B_{11}	4.64	B_{12}	1.65	B_{44}	1.85
Coupling	B_{1xx}	−2.18	B_{1yy}	−0.20	B_{4yz}	−0.08
Dipole	Z^*	9.956	ϵ_∞	5.24		

ZHONG, VANDERBILT & RABE
1995

ZHONG, VANDERBILT & RABE, 1994

$BaTiO_3$ AT EXPER. LATT. CONST.

$12 \times 12 \times 12$



■ $|\langle f_x \rangle|$

● $|\langle f_y \rangle|$

▲ $|\langle f_z \rangle|$

□ $\langle f^2 \rangle^{1/2}$

Material	Transition	T_c Theory	T_c Expt
$BaTiO_3$ (1)	C–T	290	403
	T–O	230	278
	O–R	197	183
$KNbO_3$ (2)	C–T	370	710
	T–O	260	488
	O–R	210	210
$PbTiO_3$ (3)	C–T	660	763

(1) Zhong, Vanderbilt, and Rabe

(2) Krakauer, Yu, Wang, and LaSota

(3) Waghmare and Rabe

Response coefficients

$$\underline{\Phi} = \underline{\Phi}(T, \sigma, E)$$

Dielectric susceptibility:

$$\chi_{ij} = \frac{1}{\varepsilon_0}\left(\frac{\partial P_i}{\partial E_j}\right)_{\sigma,T} \qquad (1)$$

Piezoelectric coefficients:

$$d_{i\nu} = \left(\frac{\partial \eta_\nu}{\partial E_i}\right)_\sigma = \left(\frac{\partial P_i}{\partial \sigma_\nu}\right)_E \qquad (2)$$

Elastic constants:

$$s_{\nu\mu} = \left(\frac{\partial \eta_\nu}{\partial \sigma_\mu}\right)_E \qquad (3)$$

WITH A. GARCIA

Behavior as a function of temperature

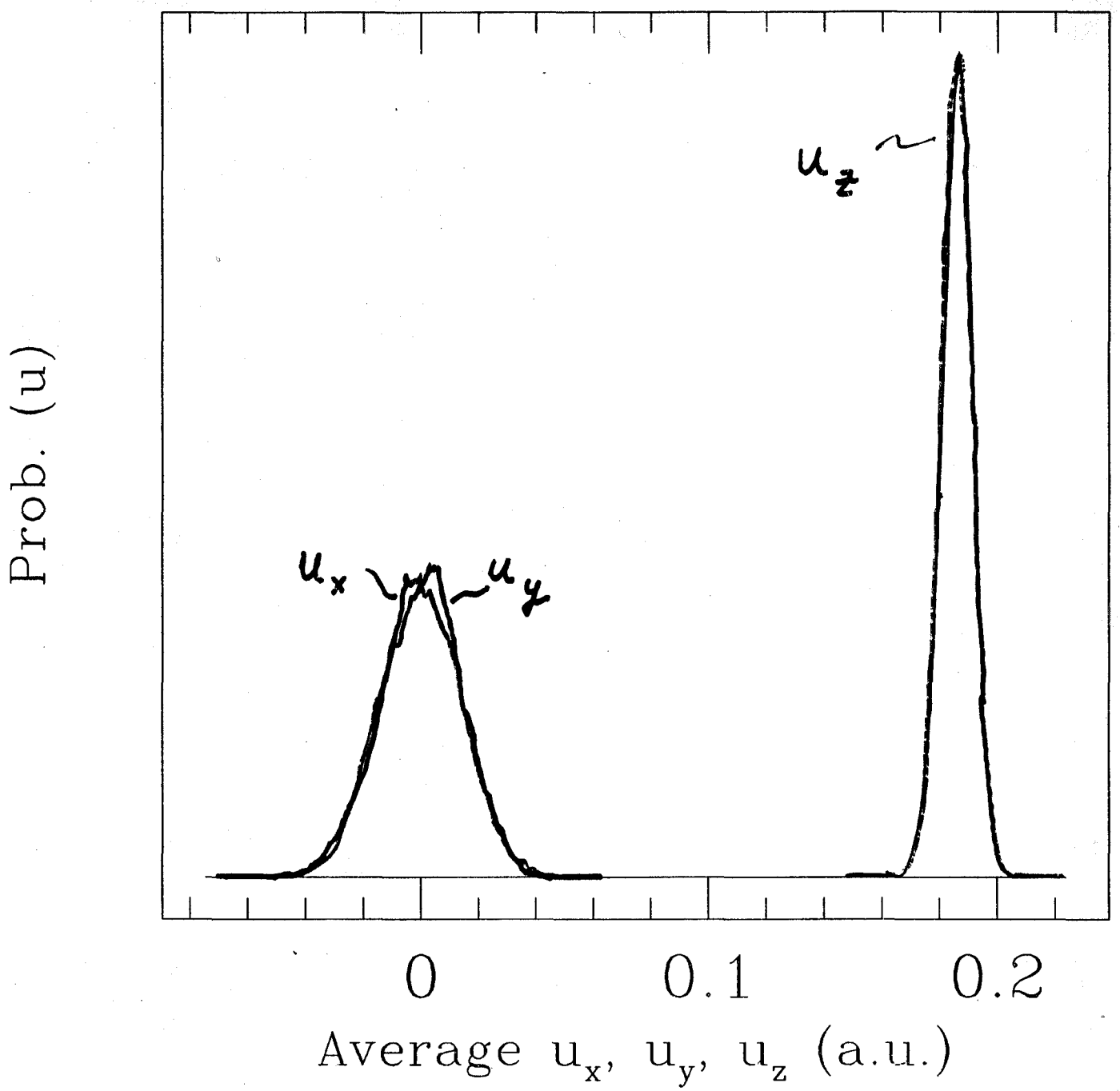
- MC simulations using same H_{eff}
- At fixed σ, E, T
- Direct calculation by finite differences

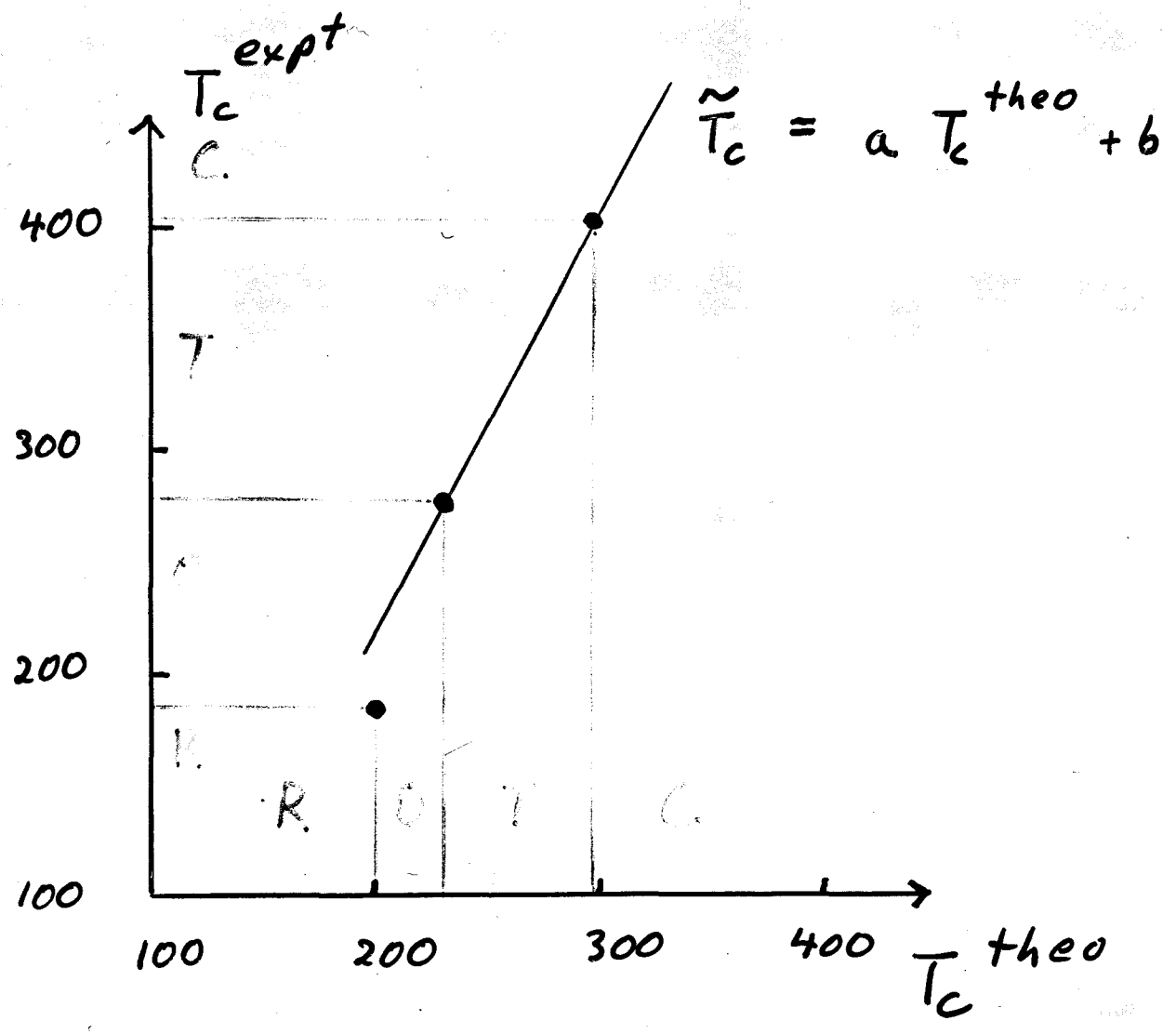
e.g., $$\varepsilon_0 \chi_{ij} = \frac{1}{\Delta E_j} [\, P_i(E + \Delta E_j) - P_i(E) \,]$$

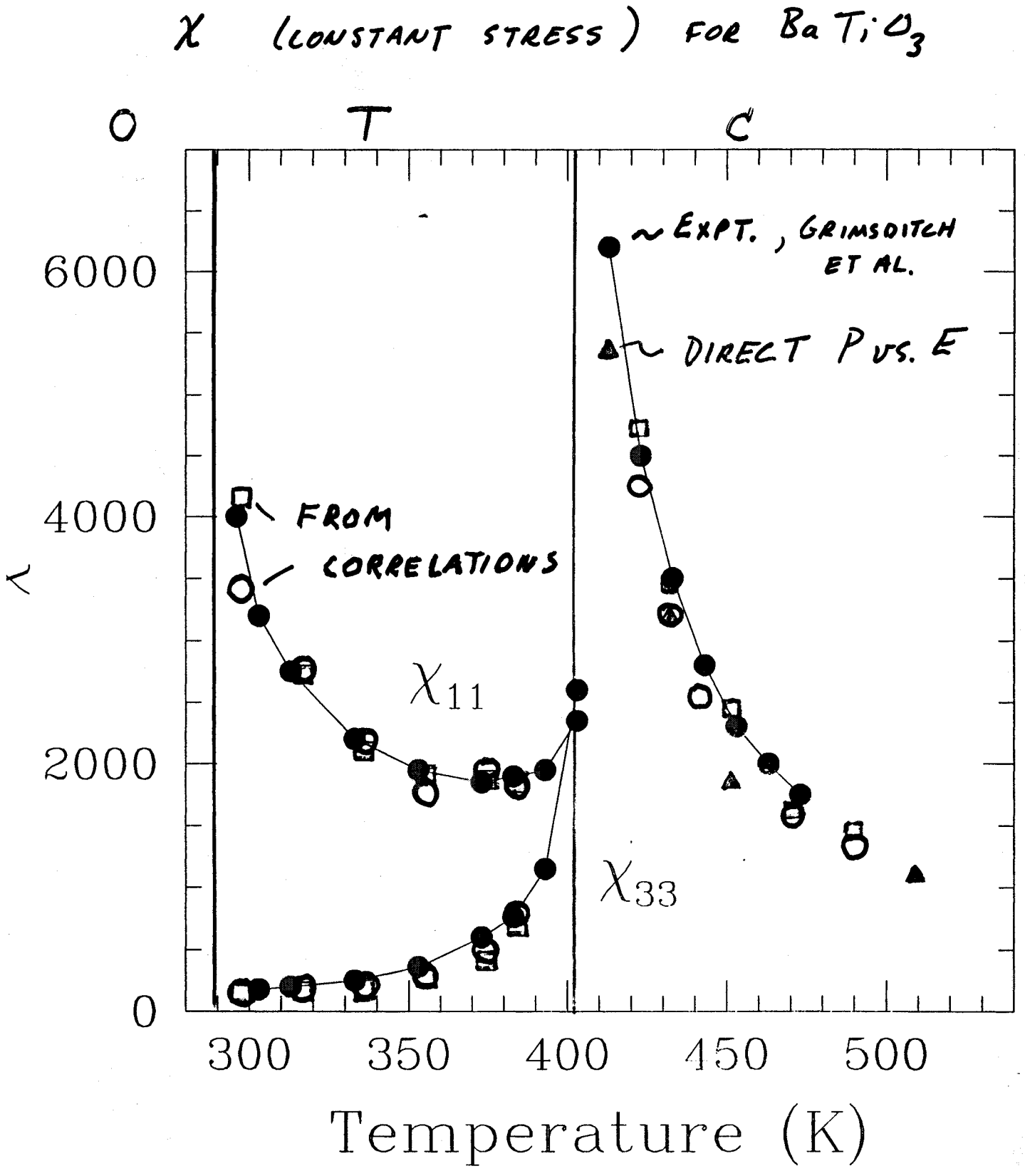
- Or, using correlation analysis

e.g., $$\varepsilon_0 \chi_{ij} = \beta V_0 [\, \langle P_i P_j \rangle - \langle P_i \rangle \langle P_j \rangle \,]$$

$BaTiO_3$ $\tilde{T} = 355K$ (TETRAGONAL)

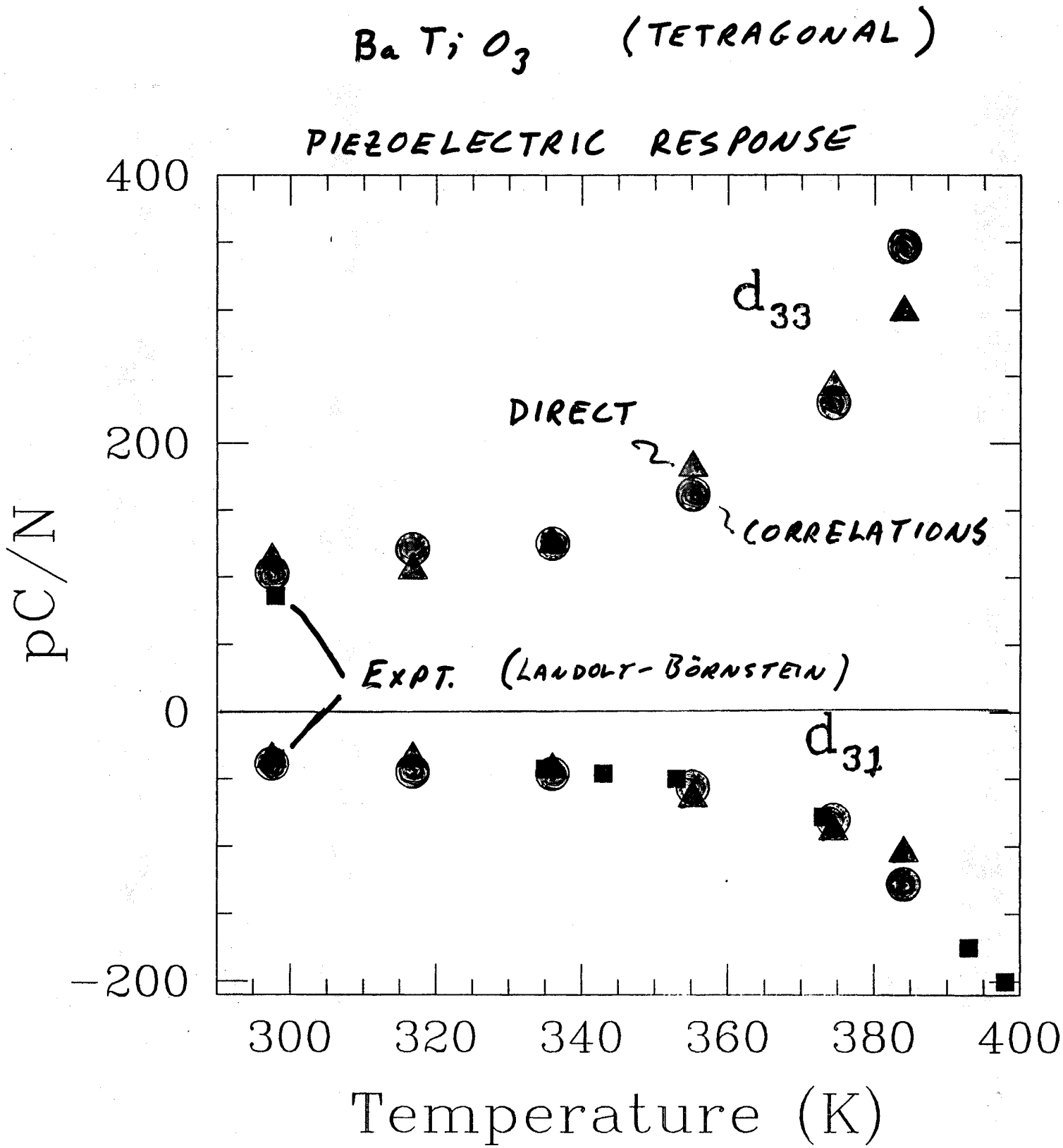



T_c^{expt}
$\tilde{T}_c = a\, T_c^{theo} + b$
400
300
200
100
100
200
300
400
T_c^{theo}

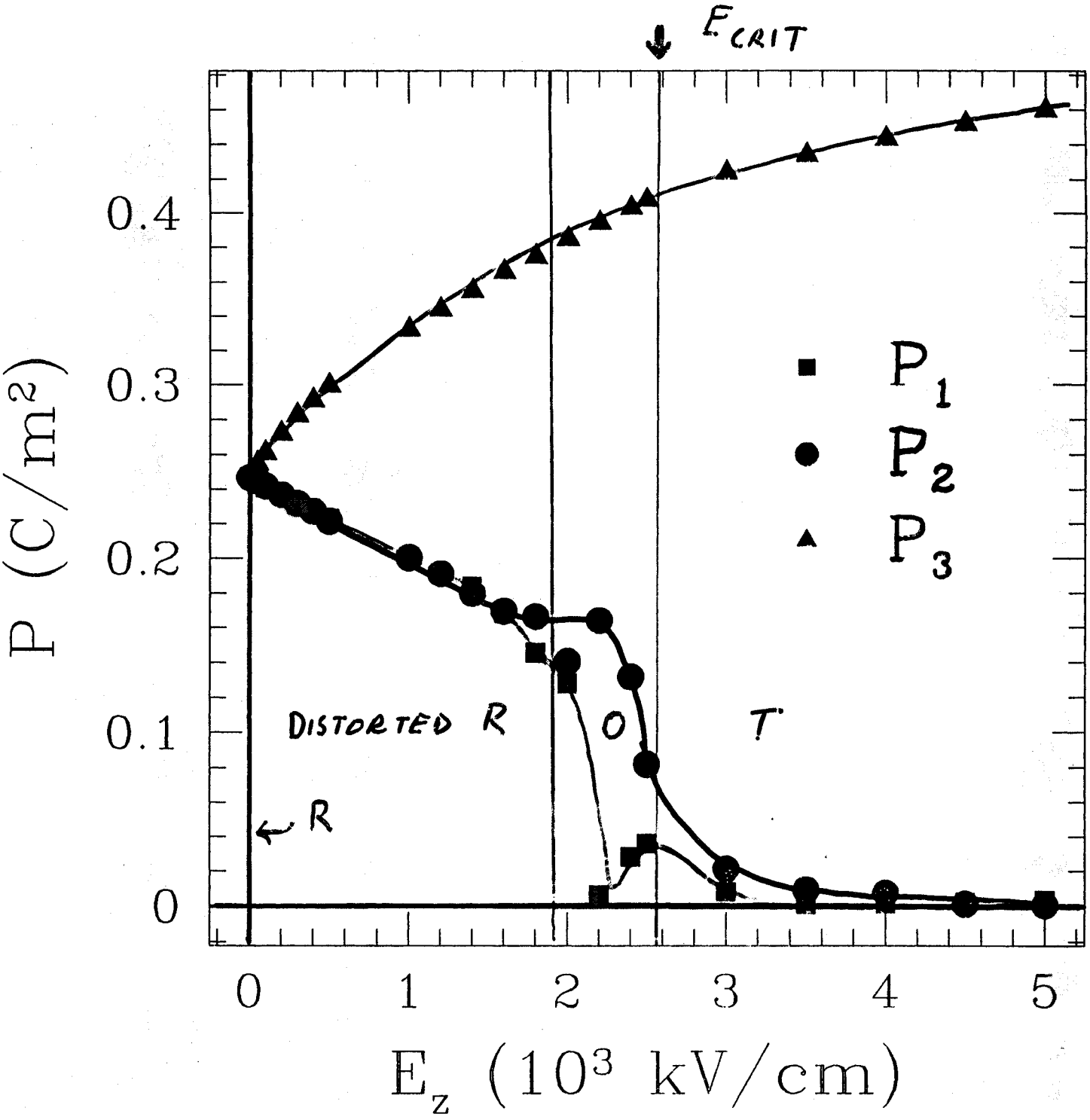

χ (CONSTANT STRESS) FOR $BaTiO_3$
O
T
C
~ EXPT., GRIMSDITCH ET AL.
~ DIRECT P VS. E
FROM CORRELATIONS
χ_{11}
χ_{33}
χ
6000
4000
2000
0
300
350
400
450
500
Temperature (K)

□ L = 14

○ L = 12


BaTiO3 (TETRAGONAL)
PIEZOELECTRIC RESPONSE
400
200
0
−200
pC/N
d33
DIRECT
CORRELATIONS
EXPT. (LANDOLT-BÖRNSTEIN)
d31
300
320
340
360
380
400
Temperature (K)

$BaTiO_3$ $\tilde{T} = 100K$ (RHOMB.)



COMPARE PARK & SHROUT:

$E_{CRIT} \cong 40$ kV/cm

OUTLINE

- Introduction: Ferroelectric Perovskites
- Ab-initio calculations
  - Ground state structures
  - Lattice dynamics
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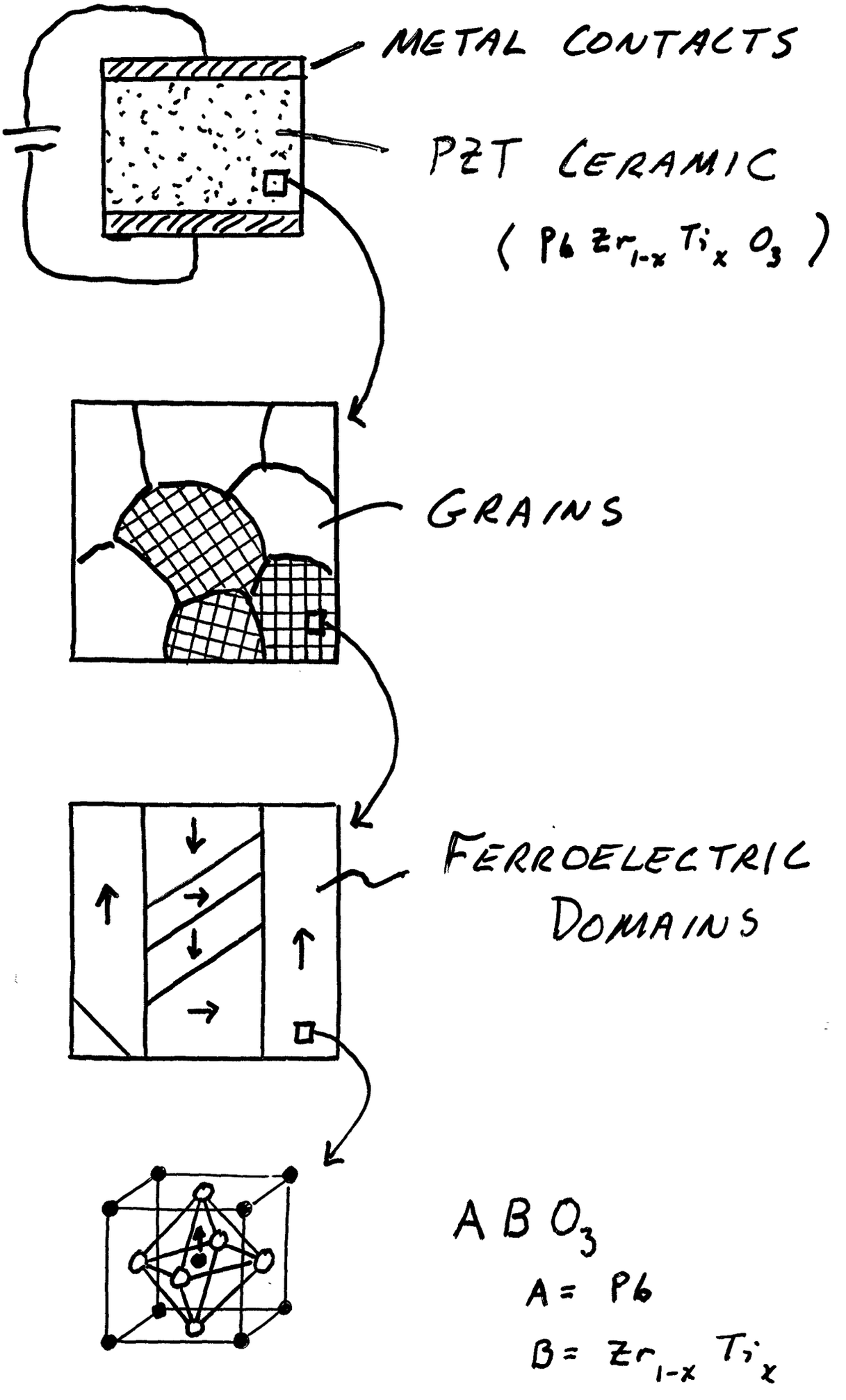
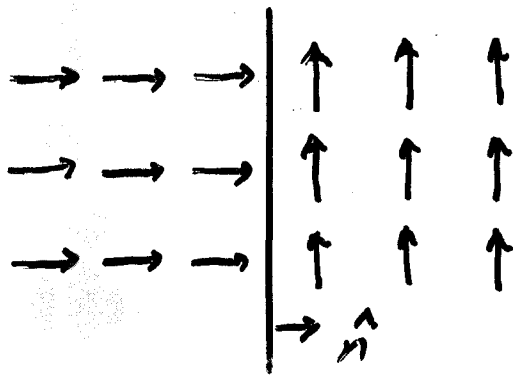
  - Effective Hamiltonian approach
  - Phase transition sequences
  - Dielectric and piezoelectric properties
- → Bridging length scales
  - 90° domain walls in $PbTiO_3$
- Local real-space investigations
  - Anomalous dynamical effective charges
  - Interpretation in terms of Wannier functions
- Summary and Implications


METAL CONTACTS
PZT CERAMIC
($Pb\,Zr_{1-x}\,Ti_x\,O_3$)
GRAINS
FERROELECTRIC DOMAINS
ABO_3
A = Pb
B = $Zr_{1-x}\,Ti_x$

COMPATIBILITY CONDITIONS

(1) ELECTRICAL: $\vec{P}_1 \cdot \hat{n} = \vec{P}_2 \cdot \hat{n}$

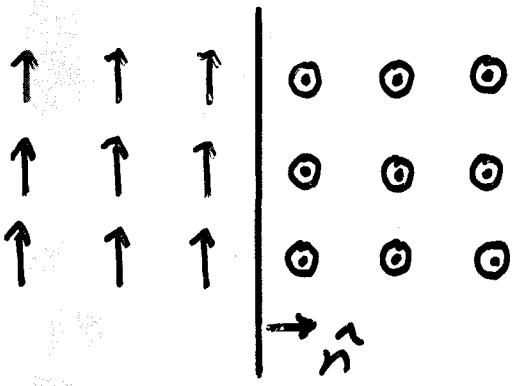
E.G.,



IS FORBIDDEN

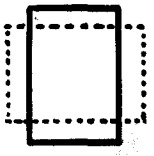
(2) STRAIN: PROJECTED $\eta_1^{2D} = \eta_2^{2D}$

E.G.,



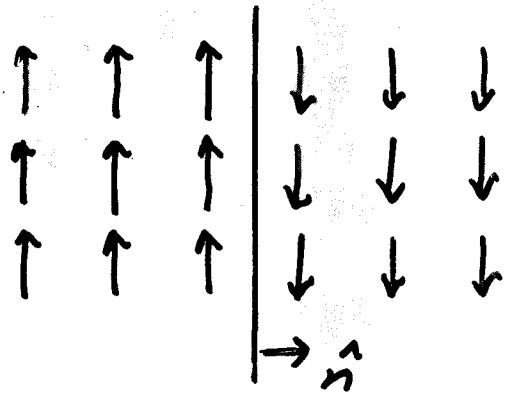
IS FORBIDDEN

SIDE VIEW:

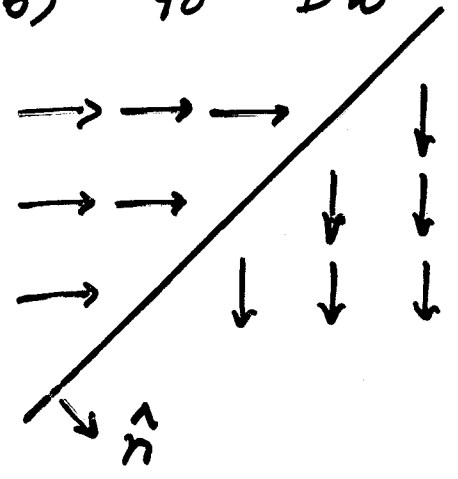


TWO ALLOWED CONFIGURATIONS:

(a) "180° DW"



(b) "90° DW"



Summary: 180° domain walls

- Even small supercells are metastable
- DW located at symmetry position: PbO plane
- DW width: $\sim$ 1 lattice constant
- DW barrier energy: $\sim$ 30% of DW creation energy

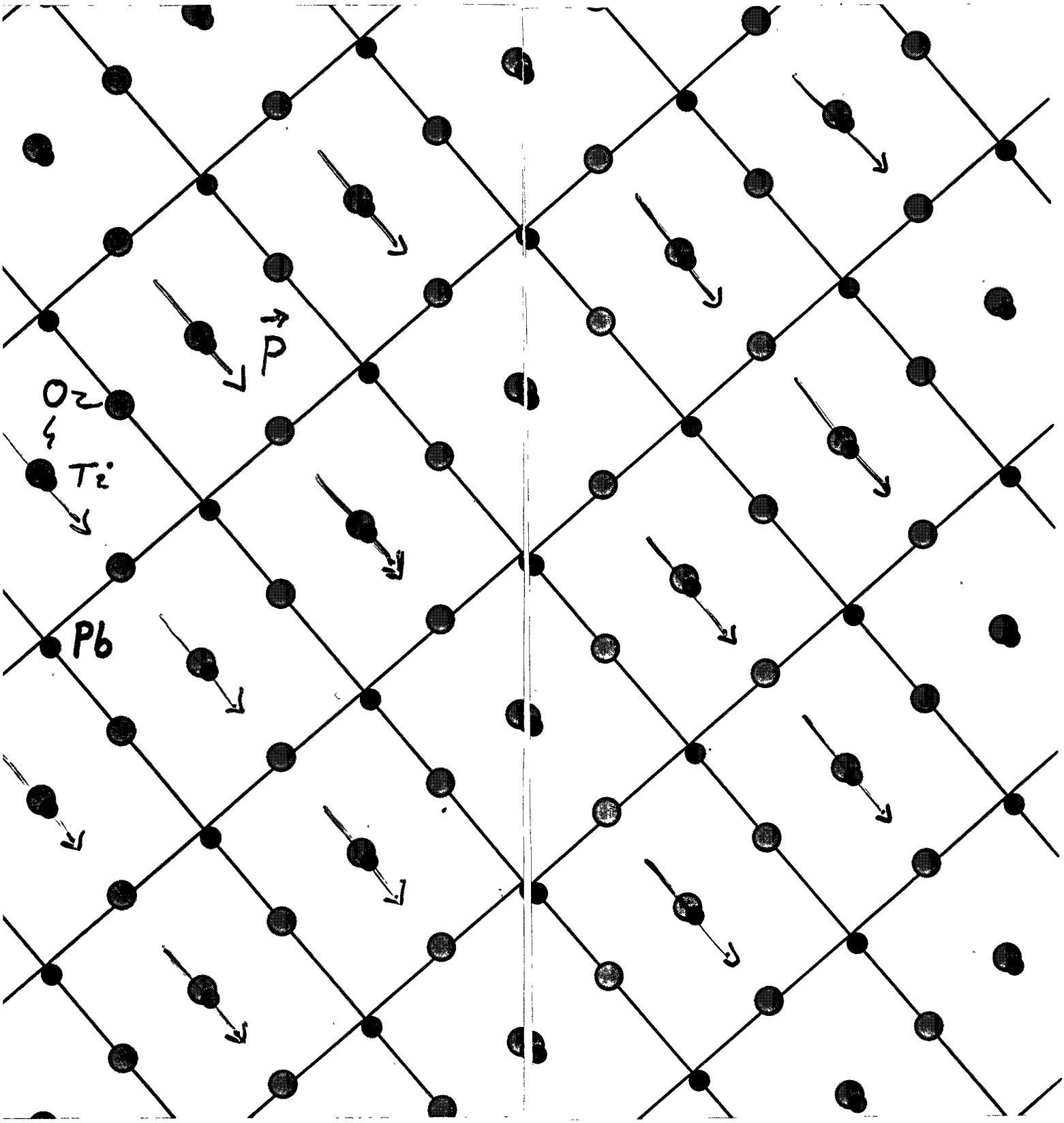
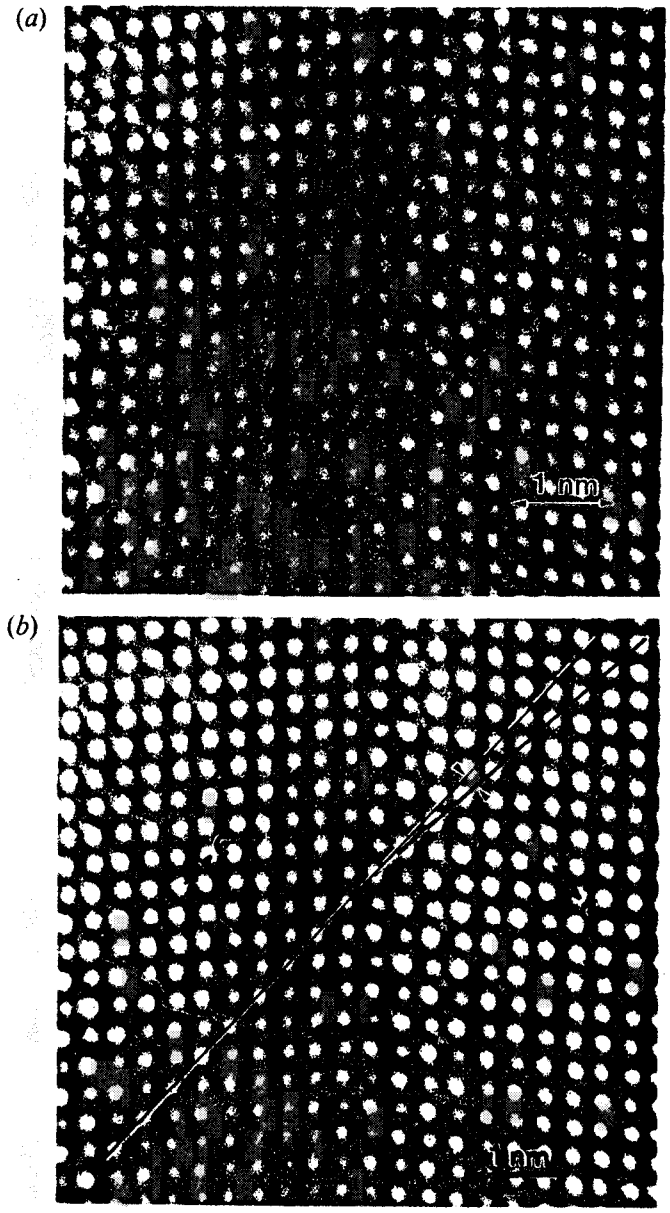
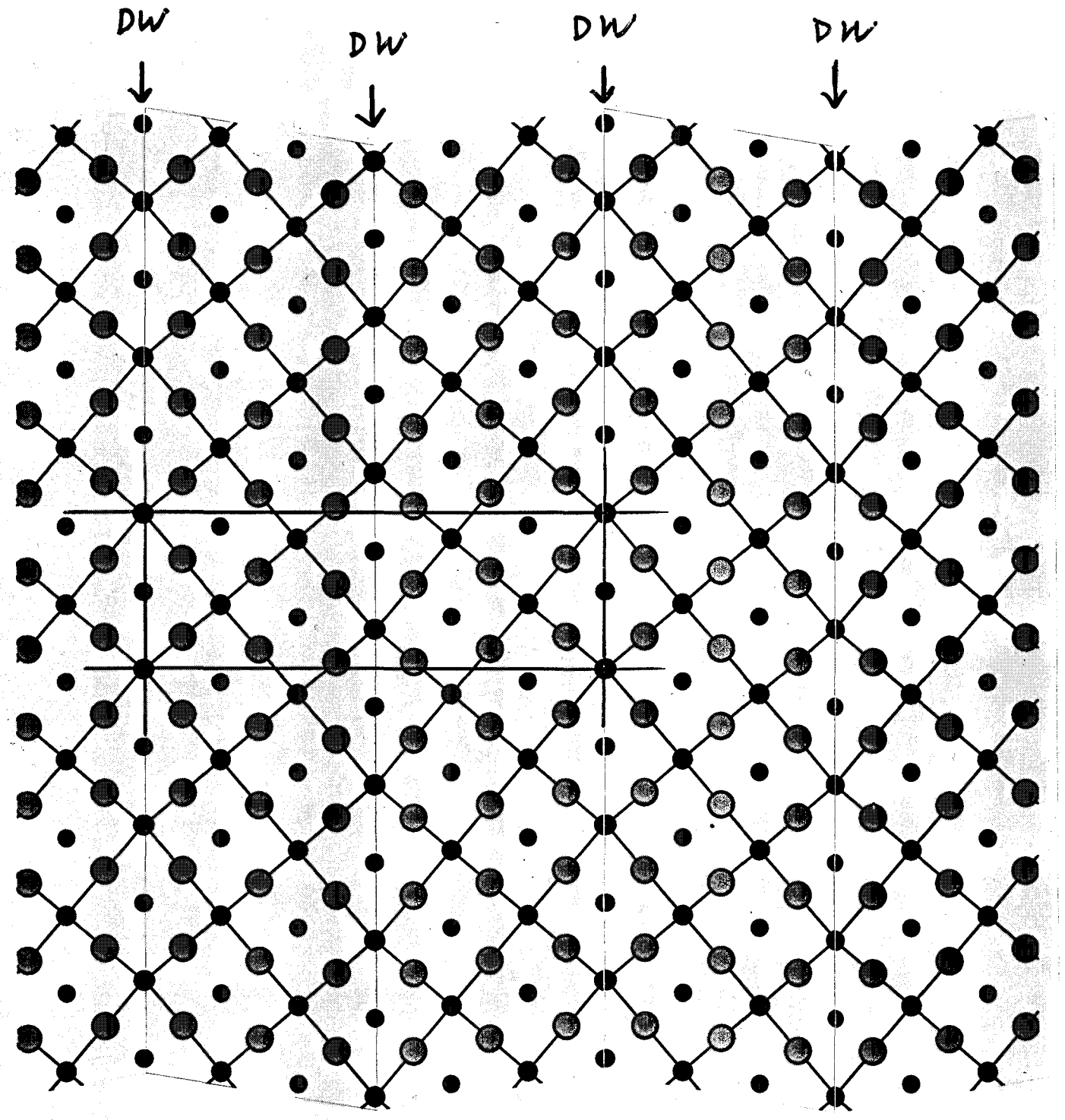

P
O
Ti
Pb

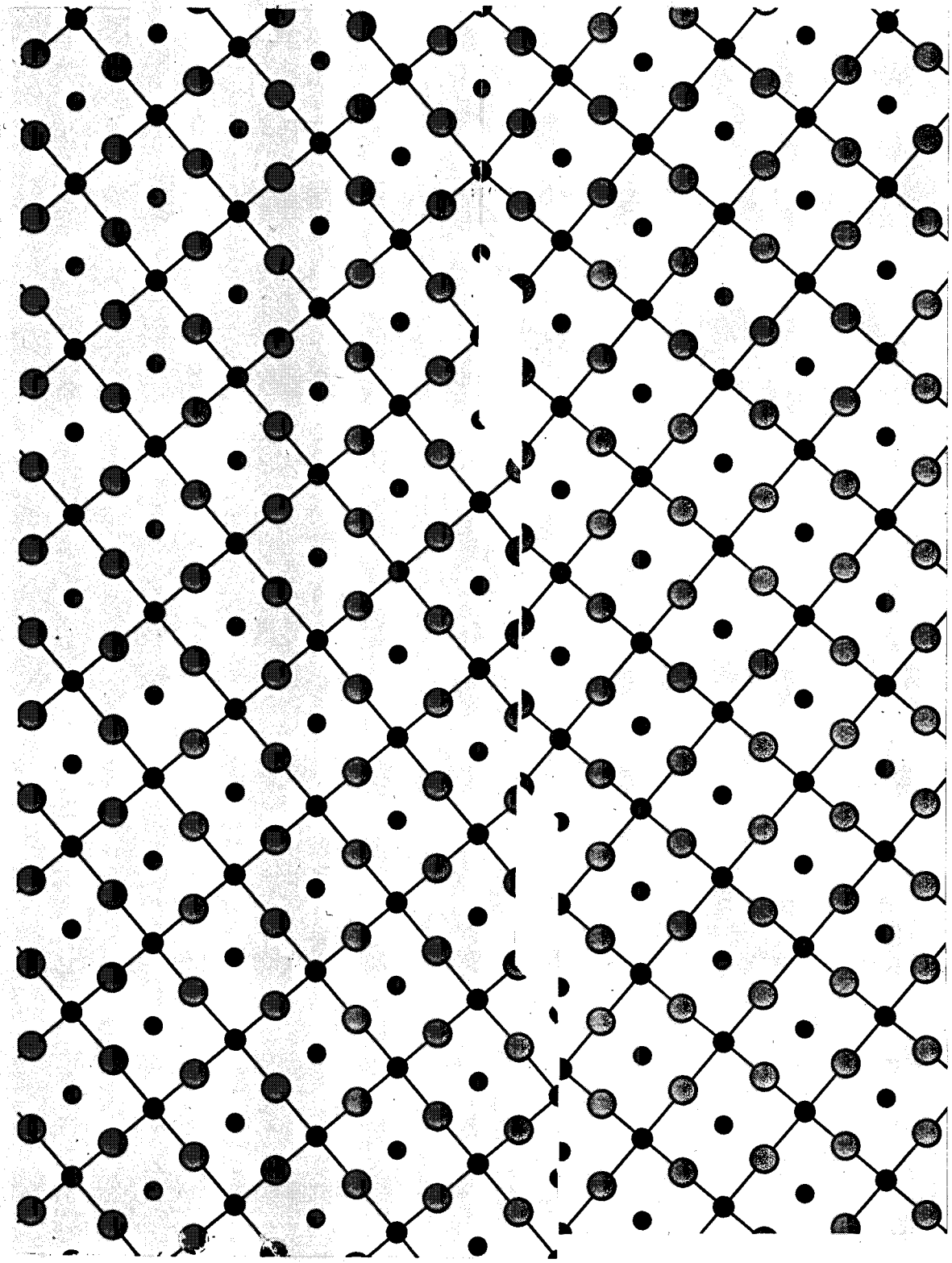
Fig. 2



(*a*) Cross-sectional HRTEM image of an *a*|*c* domain wall in $PbTiO_3$; (*b*) after adaptive Fourier filtering.

Strictly speaking, because only differences between atom positions are needed to extract lattice parameters, all that this method requires is that the intensity maxima across the image remain in the same position relative to the atomic columns. Exact coincidence is not necessary. In order to estimate the possible error introduced by this assumption, we simulated the HRTEM image of the structure model obtained from the variation of the local lattice parameters for the *a*|*c* domain wall. (The structure model is discussed shortly.) Cross-correlation of the simulated image with a single-


DW
DW
DW
DW

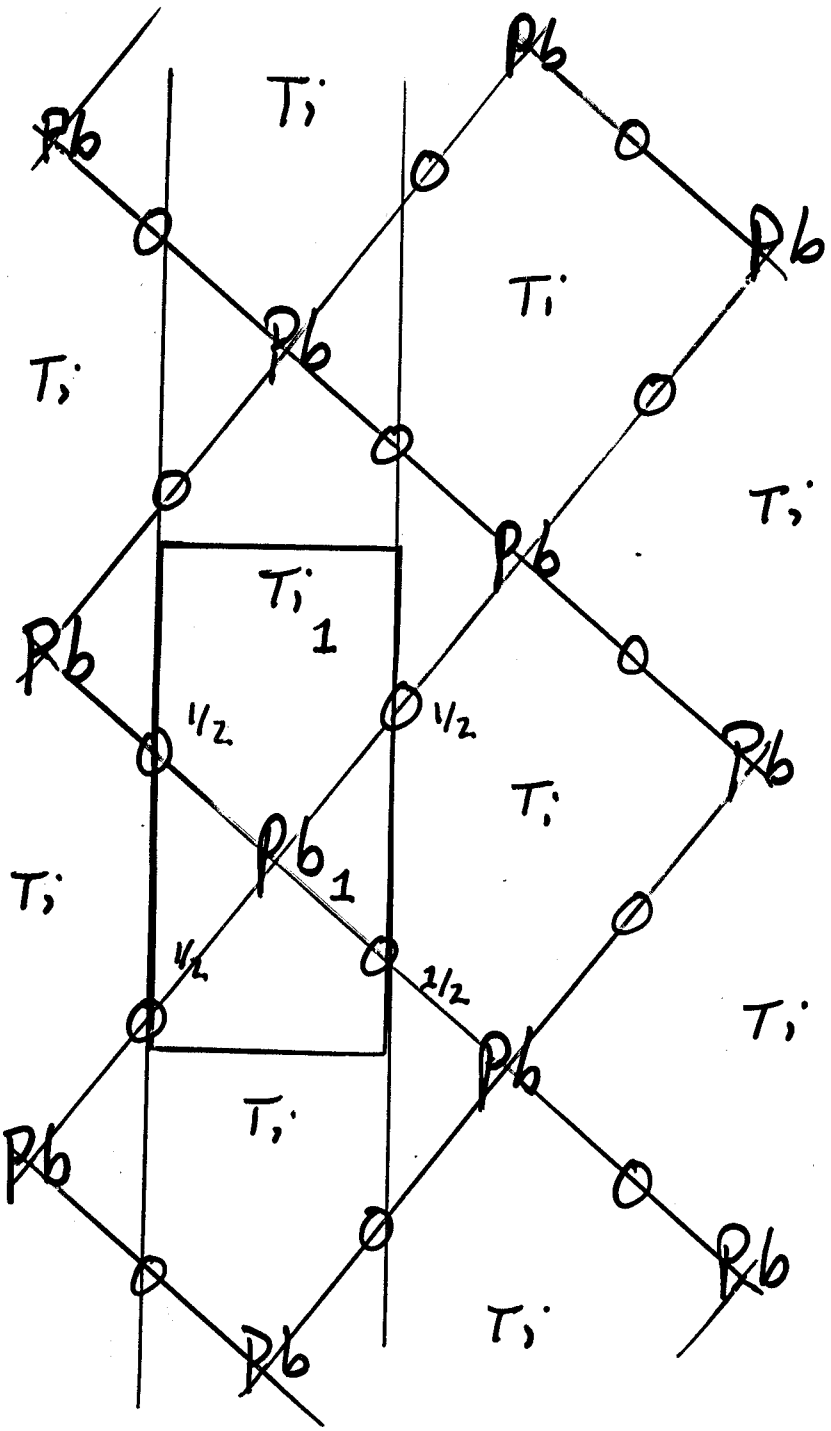


$PbTiO_3$ Domain Walls

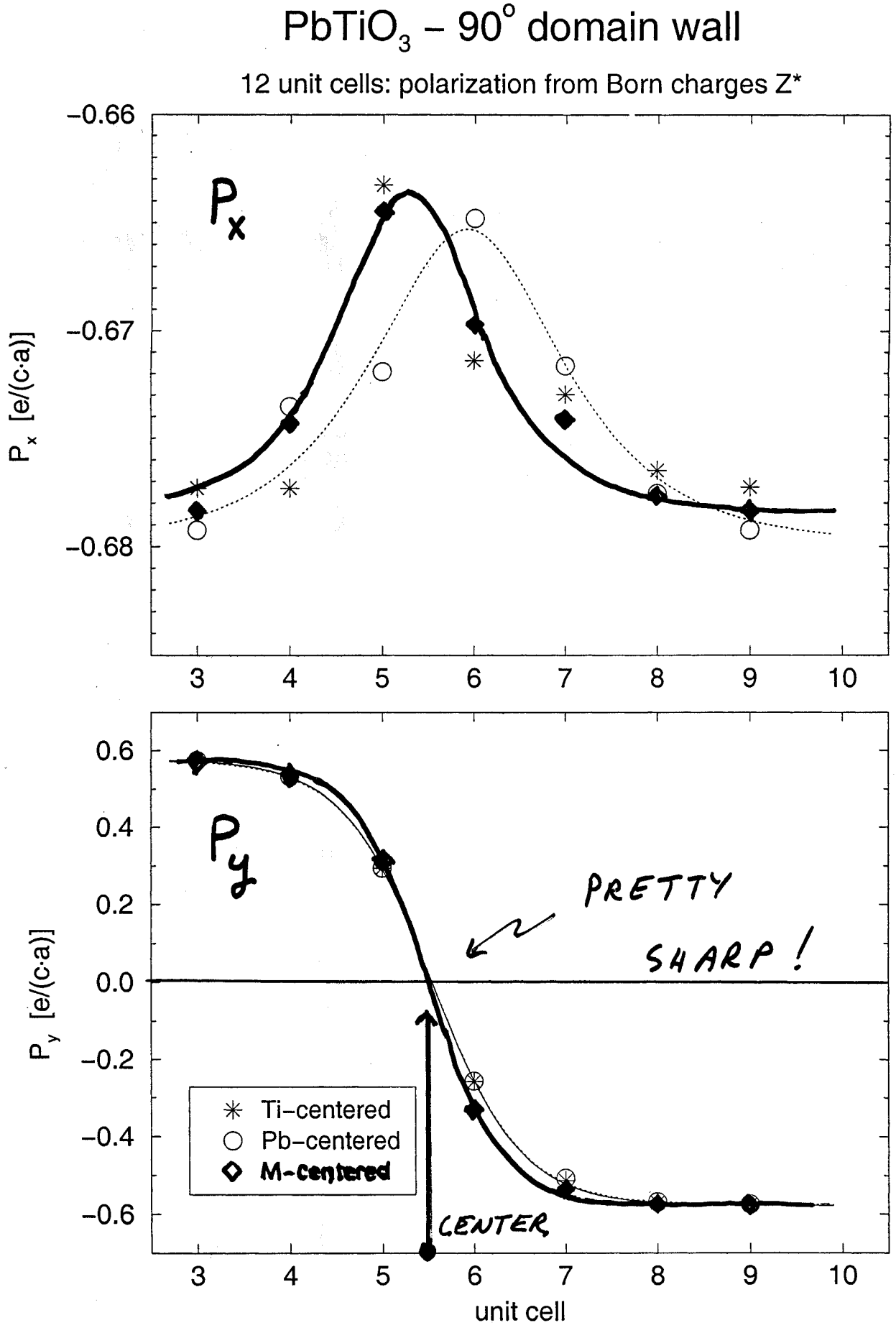
		DW Energy (mJ/m^2)	
180°	Pb-Centered	132.2	
	Ti-Centered	169.5	
	Barrier	37.3	←
90°	Min-Energy	35.0 **	Compare !
	Max-Energy	36.5	
	Barrier	1.5	←

* Atoms/Cell	E (mJ/m^2)
30	29.2
40	32.3
50	34.4
60	34.4
70	35.0

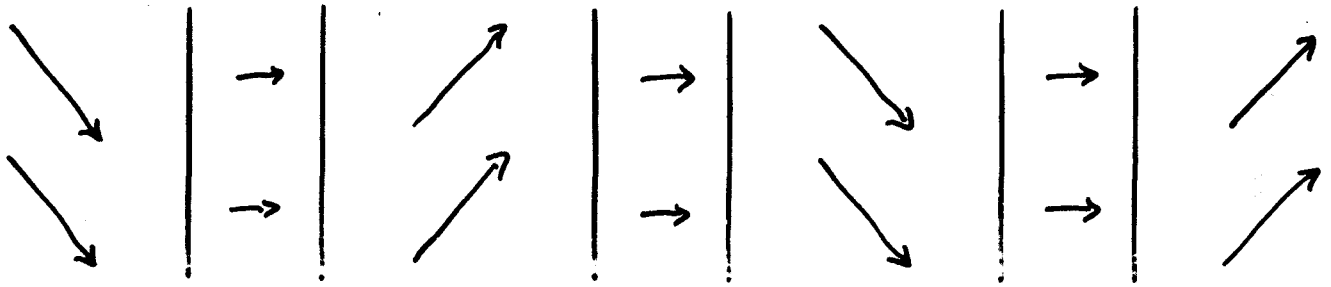
* "Expt." ~ 50 mJ/m^2



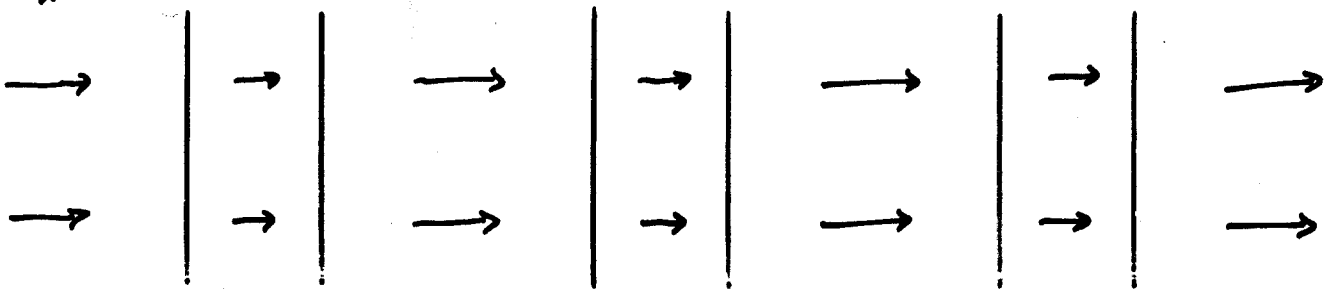
$$\vec{P}_{CELL\ i} = \frac{e}{\Omega} \sum_j w_j \overleftrightarrow{z}^*_j \cdot \vec{u}_j$$


PbTiO3 – 90° domain wall
12 unit cells: polarization from Born charges Z*
Px
Py
Px [e/(c·a)]
Py [e/(c·a)]
−0.66
−0.67
−0.68
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
3
4
5
6
7
8
9
10
unit cell
PRETTY SHARP !
CENTER
Ti-centered
Pb-centered
M-centered

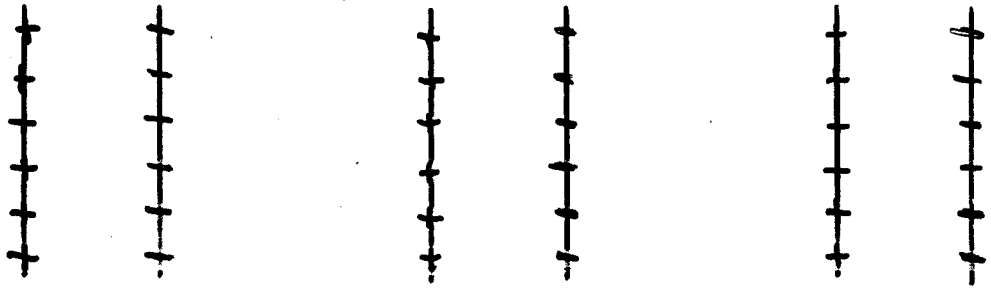
$\vec{p}$:



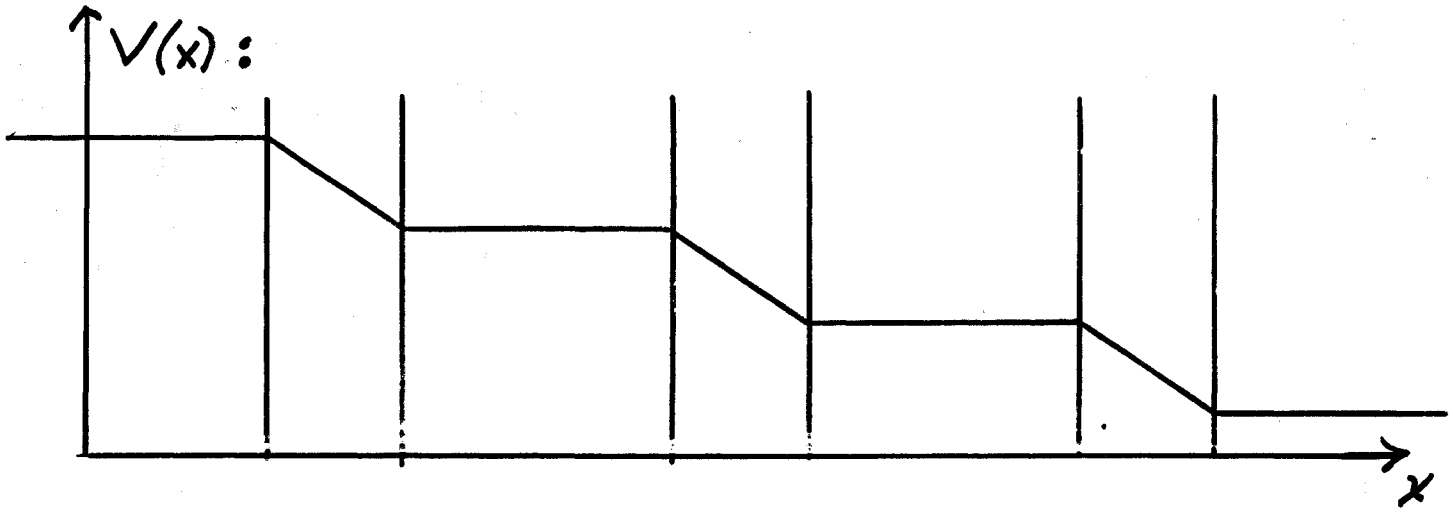
p_x :

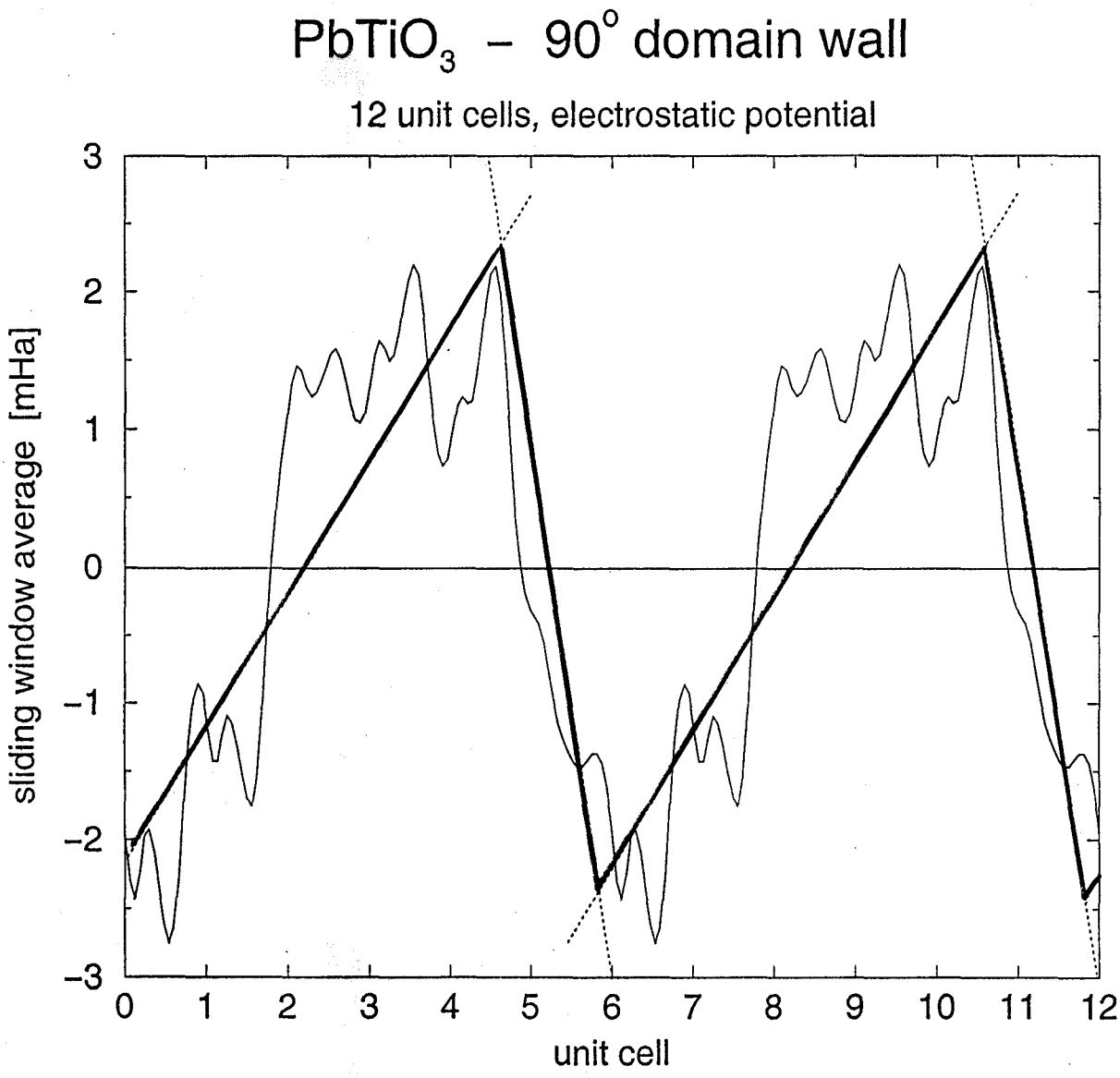


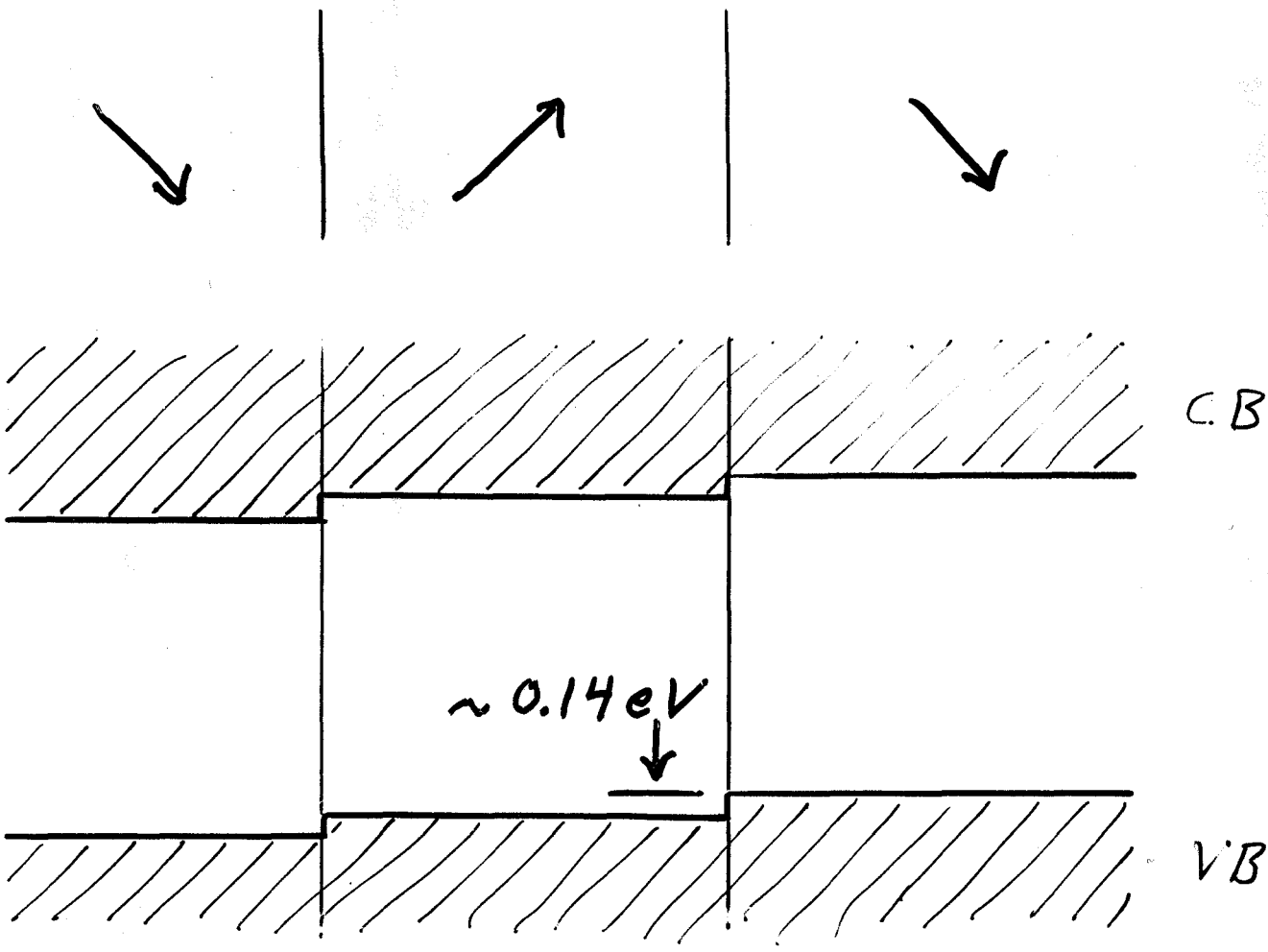
$\sigma = \Delta \vec{p} \cdot \hat{n} = \Delta p_x$:



$V(x)$:




PbTiO3 – 90° domain wall
12 unit cells, electrostatic potential
sliding window average [mHa]
unit cell
3
2
1
0
−1
−2
−3
0
1
2
3
4
5
6
7
8
9
10
11
12



" BAND OFFSET "

(RECTIFICATION OF e^-, h^+ ?)

Summary: 90° domain walls

- Even small supercells are metastable !
- DW location: Symmetry plays no role !
  - Rougly, halfway between Pb–Ti planes
- DW width: $\sim$ 1 lattice constant
- DW barrier energy: $\sim$ 4% of DW creation energy !
- Predict existence of band offset of $\sim$0.14 eV !

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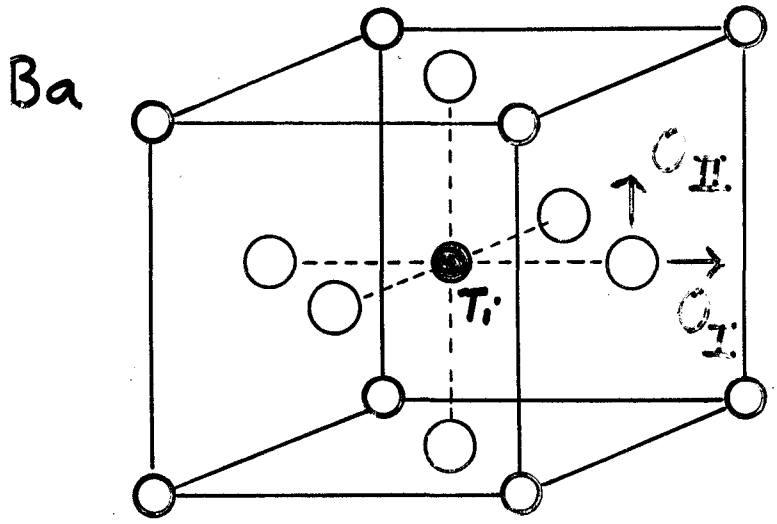
LOCAL REAL-SPACE DECOMPOSITIONS

- $E_{TOT} = \int d^3r \; e(\vec{r})$ — CHETTY & MARTIN, 1992.
- $\sigma_{\alpha\beta} = \int d^3r \; \sigma_{\alpha\beta}(\vec{r})$ — FILIPPETTI & FIORENTINI, 2000; ROGERS & KAPPE, 2001
- $J_\alpha = \int d^3r \; j_\alpha(\vec{r})$ — RESTA ET. AL., 2001
- $\sum_n \int d^3k \, \langle \psi_{nk} | \hat{A} | \psi_{nk} \rangle = \sum_{nR} \langle w_{nR} | \hat{A} | w_{nR} \rangle$

  KOHN, 1959
  KING-SMITH & VANDERBILT, 1993
  MARZARI & VANDERBILT, 1997
- LINEAR SCALING METHODS
- LOCAL HARONESS, ELF, ETC.

DYNAMICAL EFFECTIVE CHARGES



$Ba^{[+2]}\ Ti^{[+4]}\ O_3^{[-2]}$

$$P_\alpha = \sum_{i\beta} Z^{*(i)}_{\alpha\beta}\, u_{i\beta} + \dots$$

$Z^*(Ba) = +2.75\ e$

$Z^*(Ti) = +7.16\ e$

$Z^*(O_I) = -5.69\ e$

$Z^*(O_{II}) = -2.11\ e$

W. ZHONG

How to compute Z^* ?

(1) Linear response methods

de Gironcoli, Baroni, & Resta, 1989.

(2) ΔP_{el} from Berry-phase approach

King-Smith & Vanderbilt, 1993

$$P_{el} = \frac{(-2e)}{2\pi} \sum_n^{occ} \int_{BZ} dk \, \langle u_{nk} | -i \frac{d}{dk} | u_{nk} \rangle$$

(3) ΔP_{el} from Wannier centers

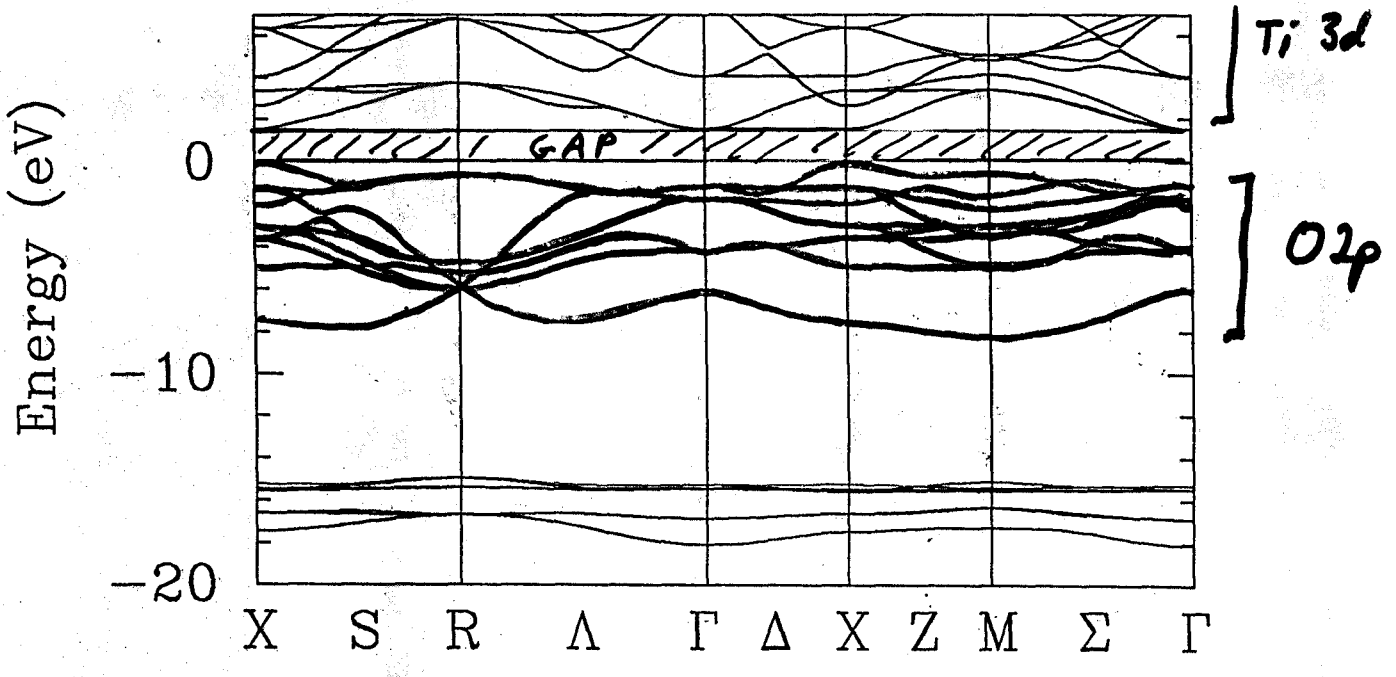
Marzari & Vanderbilt, 1997

$$P_{el} = (-2e) \sum_n^{occ} \langle w_n | \hat{x} | w_n \rangle$$

$|w_n\rangle$ = Wannier function of band n

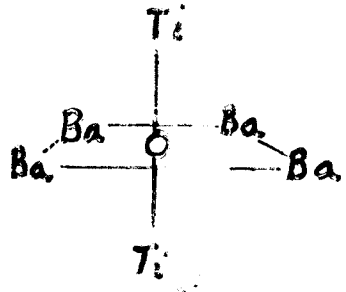
$$= \frac{a}{2\pi} \int_{BZ} dk \, | \psi_{nk} \rangle$$

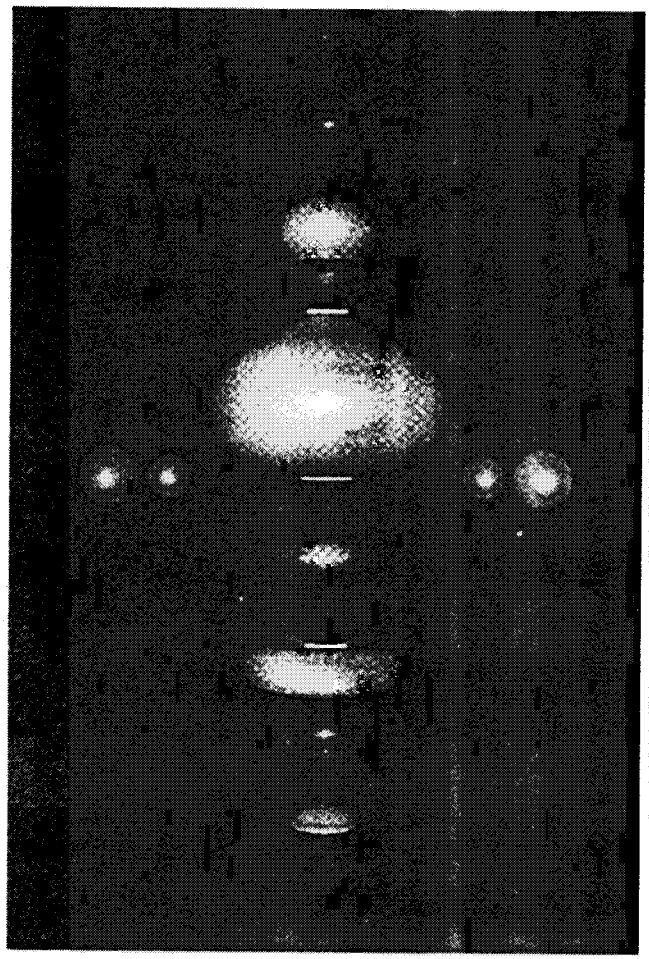
$BaTiO_3$ BANDSTRUCTURE

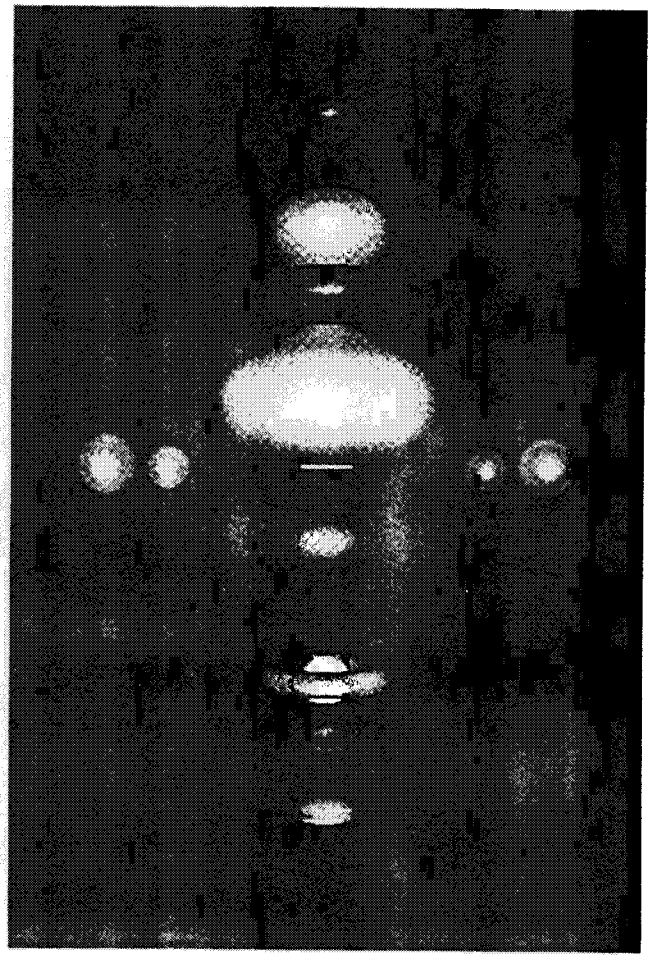


R.D. King-Smith and D. Vanderbilt, Fig. 5

$BaTiO_3$





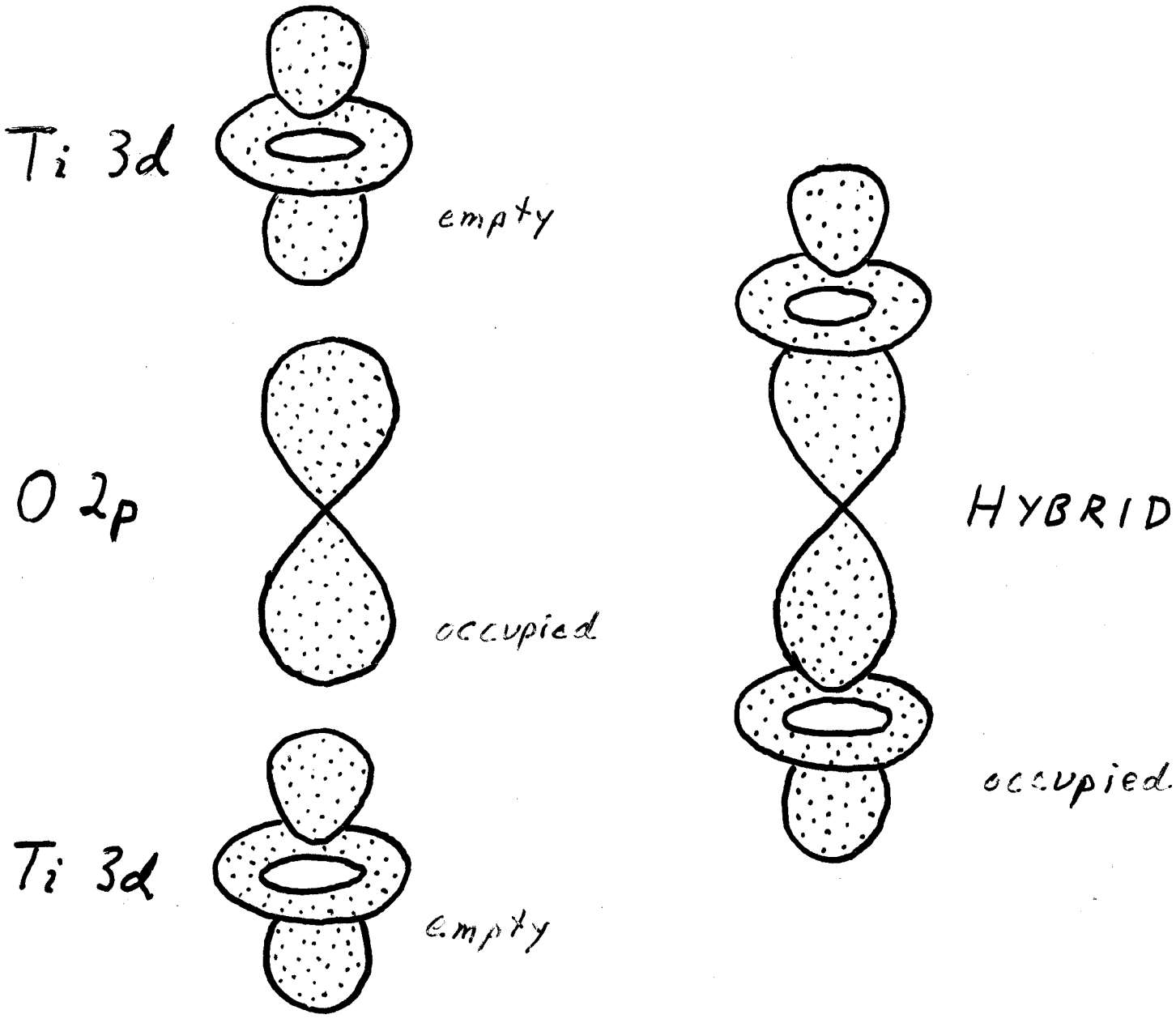


SYMMETRIC

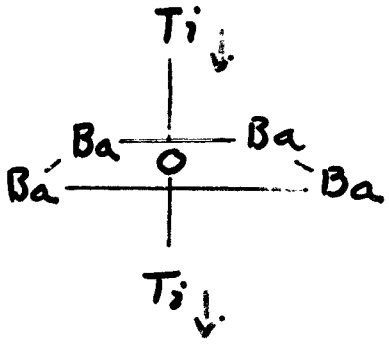
DISPLACED 0.3 Å

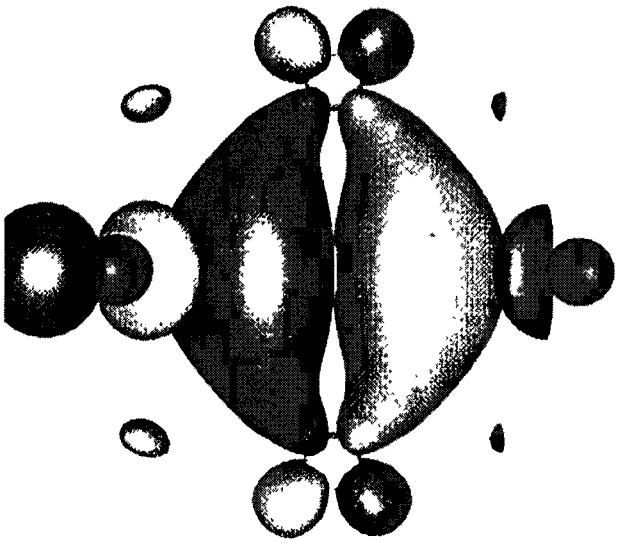
CONTRIB. TO Z^* = 0.81 e

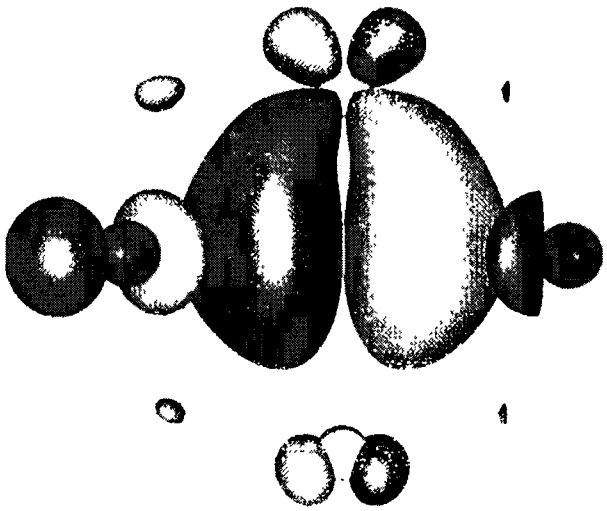
COVALENT p-d BOND



$BaTiO_3$







SYMMETRIC

Ti DISPLACED

CONTRIB. TO $z^* = 1.78\,e$

WANNIER ANALYSIS: $Z^*(Ti)$ IN $BaTiO_3$

NOMINAL Ti CORE	4.00
$[Ti-O-Ti]_\sigma$ WF	0.81
$[Ti-O-Ti]_\pi$ WFs	1.78 × 2
OTHER WFs	-1.04
TOTAL	7.33

SUMMARY

- Introduction: Ferroelectric Perovskites
- Ab-initio calculations
  - Ground state structures
  - Lattice dynamics
- Thermodynamics
  - Effective Hamiltonian approach
  - Phase transition sequences
  - Dielectric and piezoelectric properties
- Bridging length scales
  - 90° domain walls in $PbTiO_3$
- Local real-space investigations
  - Anomalous dynamical effective charges
  - Interpretation in terms of Wannier functions