Electron Theory of Ferroelectrics

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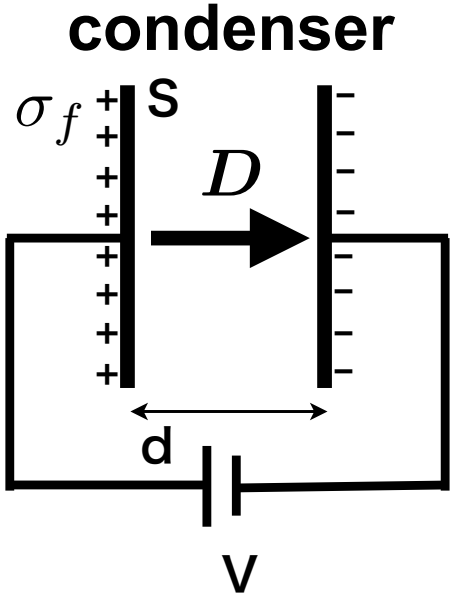
Electric Materials

- **Dielectrics: insulators**
- **Piezoelectrics: non-polar/polar w. applied stress/ strain**
- **Pyroelectrics: polar, spontaneous polarization, unswitchable**
- **Ferroelectrics: polar, switchable → FERAM**

Dielectric Constant and Polarization



Electric flux density

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} \qquad |\boldsymbol{D}| = \sigma_f$$

Surface charge density

$$(\mathrm{C/m^2})$$

Charge

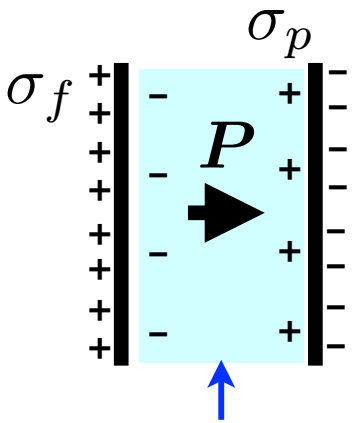
$$Q = \sigma_f S$$

Electric field

$$|\boldsymbol{E}| = \frac{V}{d} = \frac{\sigma_f}{\varepsilon_0}$$

Capacity

$$C = \frac{Q}{V} = \frac{\varepsilon_0 S}{d}$$



Electric polarization

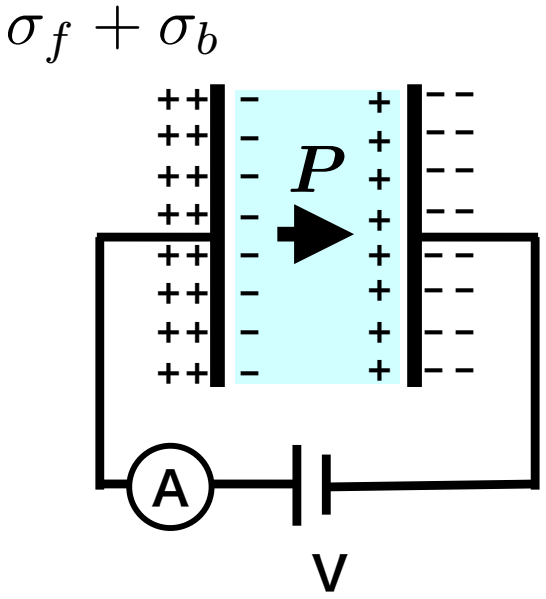
$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} = \varepsilon \varepsilon_0 \boldsymbol{E}$$

σ_f σ_p **relative permittivity**

$$\boldsymbol{P} = \varepsilon_0 \chi \boldsymbol{E}$$

Susceptibility

Dielectric Constant and Polarization



$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} = \varepsilon\varepsilon_0 \boldsymbol{E}$$

$$|\boldsymbol{D}| = \sigma_f + \sigma_b$$

$$|\boldsymbol{E}| = \frac{\sigma_f + \sigma_b}{\varepsilon\varepsilon_0} = \frac{\sigma_f}{\varepsilon_0}$$

$$C = \frac{\varepsilon\varepsilon_0 S}{d}$$

relative permittivity

$$\varepsilon = 1 + \chi = \frac{\sigma_f + \sigma_b}{\sigma_f}$$

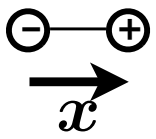
Dielectric constants and electric polarization can be obtained by measuring charge transfer (electric current).

Electric Dipole and Polarization

Electric dipole

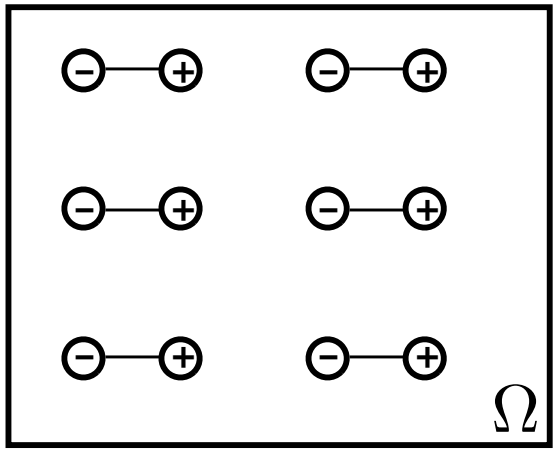
$$\boldsymbol{p} = q\boldsymbol{x}$$

$-q \quad +q$



Polarization: dipole density

$$\boldsymbol{P} = \frac{1}{\Omega}\sum_i \boldsymbol{p}_i \quad (\mathrm{C/m^2})$$



Localized ion model with point charges

$$\boldsymbol{P} = \frac{e}{\Omega}\sum_n Z_n^* \boldsymbol{R}_n$$

↑

effective charge

inversion operation

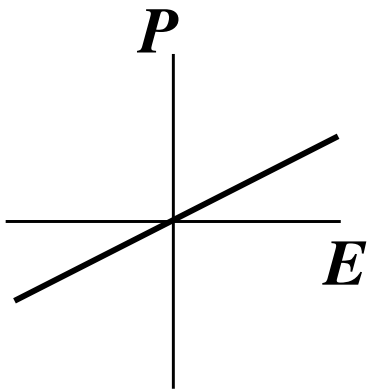
$$\boldsymbol{r} \rightarrow -\boldsymbol{r} \Rightarrow \boldsymbol{P} \rightarrow -\boldsymbol{P}$$

no polarization with inversion

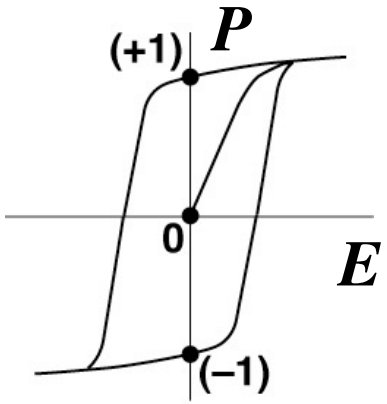
Paraelectrics and Ferroelectrics

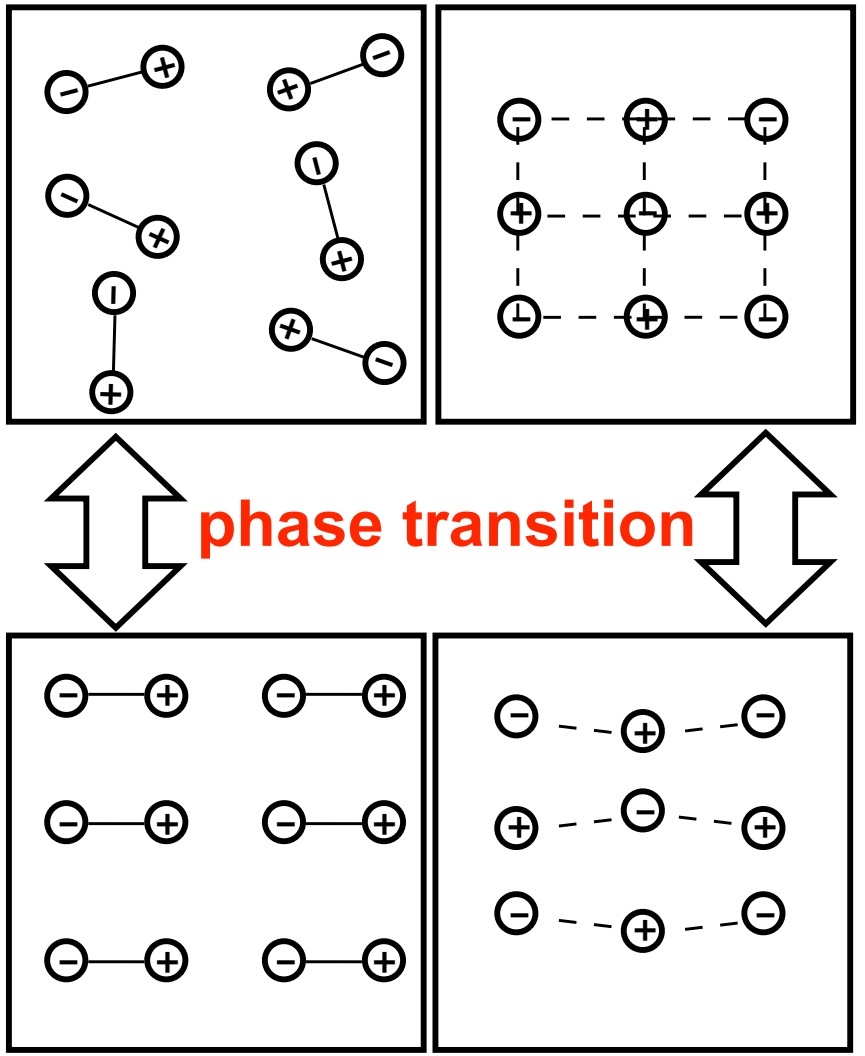
- **Paraelectric phase**

$$\boldsymbol{P} = \varepsilon_0 \chi \boldsymbol{E}$$



- **Ferroelectric phase**
  - **Spontaneous polarization**
  - **Non-volatile memory**





order-disorder displace

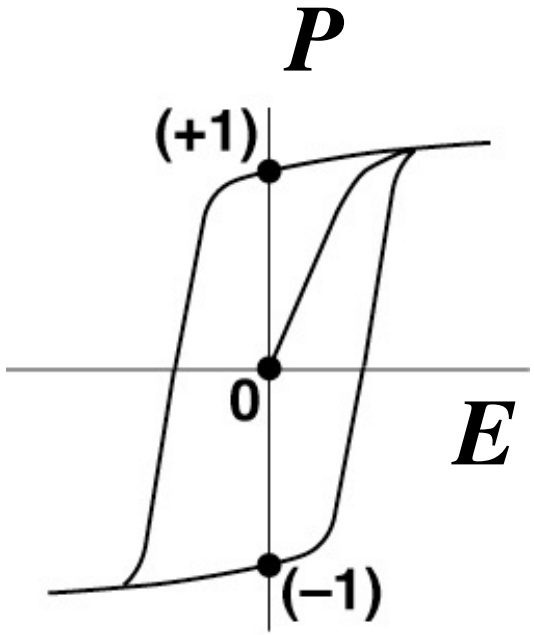
Electron Theory of Ferroelectrics

Ferroelectrics

Spontaneous polarization

traditional interpretation:

polarization of ionic charges



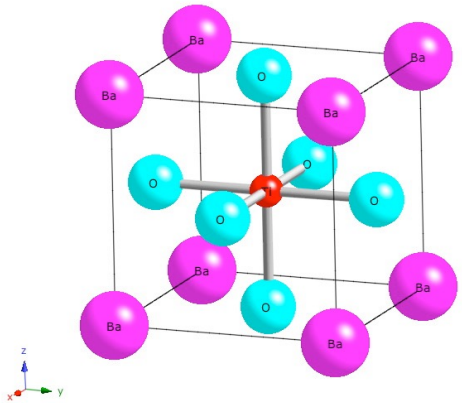
Crucial Factors → Necessity of electron theory

- **Broken inversion symmetry**
- **Detailed response of electrons**

$BaTiO_3$

Paraelectric phase

$Pm\bar{3}m$

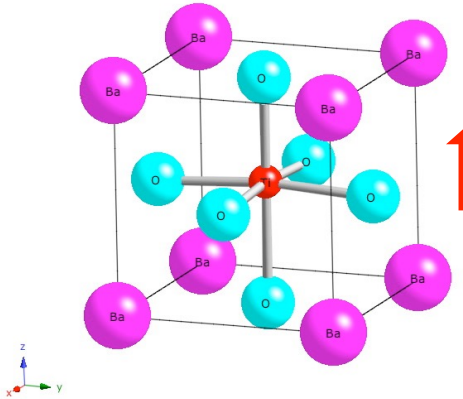


$c/a = 1.00$

403K

Ferroelectric phase

$P4mm$



P_s

polarization

$c/a \sim 1.01$

displacements

$u(\mathrm{Ti}) = 0.054$Å

$u(\mathrm{O1}) = -0.097$Å

$u(\mathrm{O2}) = -0.061$Å

Ferroelectric Instability

Broken Inversion

Why？

Born-Oppenheimer Potential

- **BO Approximation**
  - **Nucleic system**

$$\left[-\sum_n \frac{\hbar^2}{2M_n}\nabla_n^2 + \sum_{n>n'} \frac{Z_n Z_{n'} e^2}{|\boldsymbol{R}_n - \boldsymbol{R}_{n'}|} + E_e(\{\boldsymbol{R}_n\})\right] \phi(\{\boldsymbol{R}_n\}) = \mathcal{E}\phi(\{\boldsymbol{R}_n\})$$

BO potential

  - **Electron system**

$$\mathcal{H}_e \Psi(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_n\}) = E_e(\{\boldsymbol{R}_n\})\Psi(\{\boldsymbol{r}_i\};\{\boldsymbol{R}_n\})$$

$$\mathcal{H}_e = -\sum_i \frac{\hbar^2}{2m}\nabla_i^2 + \sum_{i>j} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{i,n} \frac{Z_n e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_n|}$$

external field by nuclei

- **Density Functional Theory**
  - **One-electron problem in an effective field**

Born-Oppenheimer Potential

- **BO Potential (Total Energy)**

$$E(\{\boldsymbol{R}_n\}) = + \sum_{n>n'} \frac{Z_n Z_{n'} e^2}{|\boldsymbol{R}_n - \boldsymbol{R}_{n'}|} + E_e(\{\boldsymbol{R}_n\})$$

- **Atomic Forces → Structure Optimization, MD**

$$\boldsymbol{F}_n(\{\boldsymbol{R}_n\}) = -\nabla_n E(\{\boldsymbol{R}_n\})$$

- **Force Constants → Phonon, Structure Stability**

$$k_{n\alpha,n'\beta}(\{\boldsymbol{R}_n\}) = \frac{\partial^2}{\partial R_{n\alpha} \partial R_{n'\beta}} E(\{\boldsymbol{R}_n\})$$

Phonon Calculation

- **Atomic Coordinates**

$$\boldsymbol{R}_n = \boldsymbol{R}_{l\nu} = \underline{\boldsymbol{R}_l} + \underline{\boldsymbol{\tau}_\nu}$$

lattice vector coordinates in cell

- **Atomic Displacements**

$$\boldsymbol{u}_{l\nu} = \boldsymbol{R}_{l\nu} - \underline{\boldsymbol{R}^{(0)}_{l\nu}}$$

equilibrium positions

- **Harmonic Approximation with wave vector Q and angular frequency ω**

$$\boldsymbol{u}_{l\nu} = \boldsymbol{u}_\nu e^{i(\boldsymbol{Q}\cdot\boldsymbol{R}_l - \omega t)}$$

- **Bloch Theorem**

$$\boldsymbol{u}_{l'\nu} = \boldsymbol{u}_{l\nu} e^{i\boldsymbol{Q}\cdot(\boldsymbol{R}_{l'} - \boldsymbol{R}_l)}$$

Phonon Calculation

- **Atomic Forces**

$$F_{l\nu\alpha} = -\sum_{l'\nu'\beta} k_{l\nu\alpha,l'\nu\beta} u_{l'\nu'\beta}$$

$$= -\sum_{\nu'\beta} \bar{k}_{\nu\alpha,\nu'\beta}(\boldsymbol{Q}) u_{l\nu'\beta}$$

$$\bar{k}_{\nu\alpha,\nu'\beta}(\boldsymbol{Q}) = \sum_{l'} k_{l\nu\alpha,l'\nu'\beta} e^{i\boldsymbol{Q}\cdot(\boldsymbol{R}_{l'}-\boldsymbol{R}_l)}$$

- **Equation of Motion**

$$-\omega^2 M_\nu u_{\nu\alpha} = -\sum_{\nu'\beta} \bar{k}_{\nu\alpha,\nu'\beta}(\boldsymbol{Q}) u_{\nu'\beta}$$

mass

Phonon Calculation

- **Dynamical Matrix**

$$D_{\nu\alpha,\nu'\beta}(\boldsymbol{Q}) = (M_\nu M_{\nu'})^{-1/2} \bar{k}_{\nu\alpha,\nu'\beta}(\boldsymbol{Q})$$

- **Secular Equation**

$$\sum_{\nu'\beta} \left[D_{\nu\alpha,\nu'\beta}(\boldsymbol{Q}) - \omega^2 \delta_{\nu\nu'}\delta_{\alpha\beta} \right] u_{\nu'\beta} = 0$$

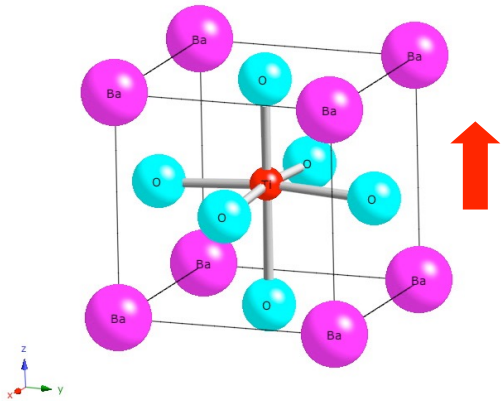
- **Eigenvalue**

$\omega^2(\boldsymbol{Q}) \geq 0$ **vibration mode**

$\omega^2(\boldsymbol{Q}) < 0$ **soft mode (instability)**

$BaTiO_3$

$P4mm$



P_s polarization

$c/a = 1.01$

ionic model: Ba^{2+} Ti^{4+} O^{2-}

$$P_S = \frac{e}{\Omega}\sum_n Z_n^* u_n = 0.16\mathrm{C/m}^2$$

experiment: $P_s = 0.27\mathrm{C/m}^2$

displacements

$u(\mathrm{Ti}) = 0.054$Å

$u(\mathrm{O1}) = -0.097$Å

$u(\mathrm{O2}) = -0.061$Å

Polarization enhancement

Electron response

Why?

Macroscopic Polarization

R. Martin, Phys Rev B 9,1998 (1974)

- Accurate electron density by first-principles calculations
- Sensitive response of electron density spatially distributed due to lattice distortion and ionic displacements
- Electron density: not sufficient to determine polarization

$$\boldsymbol{P} = \frac{1}{\Omega}\int_{\text{cell}} \boldsymbol{P}(\boldsymbol{r})d^3\boldsymbol{r} \qquad \nabla \cdot \boldsymbol{P}(\boldsymbol{r}) = -\rho(\boldsymbol{r})$$

$$\boldsymbol{P} = \frac{1}{\Omega}\int_{\text{cell}} \boldsymbol{r}\rho(\boldsymbol{r}) + \frac{1}{\Omega}\int_{\text{surface}} \boldsymbol{r}[\boldsymbol{P}(\boldsymbol{r}) \cdot d\boldsymbol{S}]$$

Theory of Macroscopic Polarization

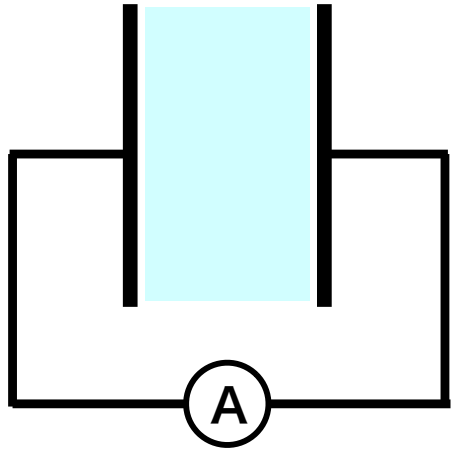
R. Resta, Ferroelectrics 136, 51 (1992).

- **Electric dipole is ill defined in a periodic charge distribution unless decomposed into neutral, localized charge segments.**

  ➡ **The absolute value of polarization *P* is not a bulk property and a variation in *P* is actually observable.**

Theory of Macroscopic Polarization

R. Resta, Ferroelectrics 136, 51 (1992).



- **Observation of polarization: current by adiabatic variation of state**

$$\lambda \to \lambda + d\lambda \qquad \boldsymbol{J}(\lambda) = \frac{\partial \boldsymbol{P}}{\partial \lambda}$$

- **First-order polarization variation**

$$\Delta \boldsymbol{P} = \int_0^1 \boldsymbol{J}(\lambda) d\lambda = \int_0^1 \left(\frac{\partial \boldsymbol{P}}{\partial \lambda} \right) d\lambda$$

$$\frac{\partial \boldsymbol{P}}{\partial \lambda} = \frac{i\hbar}{m} \frac{e}{\Omega} \sum_{\boldsymbol{k}, i \neq j} \frac{\langle \psi_i^{\boldsymbol{k}}(\lambda) | \boldsymbol{p} | \psi_j^{\boldsymbol{k}}(\lambda) \rangle \langle \psi_i^{\boldsymbol{k}}(\lambda) | \frac{\partial V}{\partial \lambda} | \psi_j^{\boldsymbol{k}}(\lambda) \rangle}{\left(E_i^{\boldsymbol{k}}(\lambda) - E_j^{\boldsymbol{k}}(\lambda) \right)^2}$$

$$\mathcal{H}(\lambda) \psi_i^{\boldsymbol{k}}(\lambda) = \left[\frac{\boldsymbol{p}^2}{2m} + V(\lambda) \right] \psi_i^{\boldsymbol{k}}(\lambda) = E_i^{\boldsymbol{k}}(\lambda) \psi_i^{\boldsymbol{k}}(\lambda)$$

Theory of Macroscopic Polarization

King-Smith & Vanderbilt, PRB 47, 1651 (1993).

$$\frac{\partial P_\alpha}{\partial \lambda} = -\frac{ie}{\Omega} \sum_{\boldsymbol{k},i}^{\text{occ.}} \left[\left\langle \frac{\partial u_i^{\boldsymbol{k}}(\lambda)}{\partial k_\alpha} \middle| \frac{\partial u_i^{\boldsymbol{k}}(\lambda)}{\partial \lambda} \right\rangle - \left\langle \frac{\partial u_i^{\boldsymbol{k}}(\lambda)}{\partial \lambda} \middle| \frac{\partial u_i^{\boldsymbol{k}}(\lambda)}{\partial k_\alpha} \right\rangle \right]$$

$$\psi_i^{\boldsymbol{k}}(\lambda) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_i^{\boldsymbol{k}}(\lambda)$$

$$\Delta \boldsymbol{P} = \int_0^1 \left(\frac{\partial \boldsymbol{P}}{\partial \lambda} \right) d\lambda = \boldsymbol{P}^{(1)} - \boldsymbol{P}^{(0)}$$

$$P_\alpha^{(\lambda)} = \frac{2ie}{\Omega} \sum_{\boldsymbol{k},i}^{\text{occ.}} \left\langle u_i^{\boldsymbol{k}}(\lambda) \right| \frac{\partial}{\partial k_\alpha} \left| u_i^{\boldsymbol{k}}(\lambda) \right\rangle$$

Berry phase $$\phi_{\mathbf{k}_\perp}^{(\lambda)} = i \sum_i^{\text{occ.}} \int dk_\alpha \left\langle u_i^{\mathbf{k}(\lambda)} \middle| \frac{\partial}{\partial k_\alpha} \middle| u_i^{\mathbf{k}(\lambda)} \right\rangle$$

Calculation of Macroscopic Polarization

- **Variation in polarization**

$$\Delta \boldsymbol{P} = \int_0^1 \left(\frac{\partial \boldsymbol{P}}{\partial \lambda} \right) d\lambda = \boldsymbol{P}^{(1)} - \boldsymbol{P}^{(0)}$$

$$\Delta \boldsymbol{P} = \Delta \boldsymbol{P}^{\mathrm{ion}} + \Delta \boldsymbol{P}^{\mathrm{el}}$$

ion=nucleus + core electrons

- **Localized charges**

$$\Delta \boldsymbol{P}^{\mathrm{ion}} = \frac{e}{\Omega} \sum_{\nu} Z_{\nu}^{*} \boldsymbol{u}_{\nu}$$

$Z_{\nu}^{*} = Z_{\nu} - N_{\mathrm{core}}$ **ionic charge**

$\boldsymbol{u}_{\nu}$ **atomic displacement**

Calculation of Macroscopic Polarization

- **Non-overlapping charges**

$$\Delta \boldsymbol{P}^{\mathrm{el}} = -\frac{e}{\Omega}\int \boldsymbol{r}\left[n_a^{(1)} - n_a^{(0)}\right] d\boldsymbol{r}$$

With boundary at zero density, integration can be made as a cell integral like localized density.

- **Charges with localized orbitals (Wannier ft.)**

$$n_a^{(\lambda)}(\boldsymbol{r}) = 2\sum_n \left|a_n^{(\lambda)}(\boldsymbol{r})\right|^2$$

$$\Delta \boldsymbol{P}^{\mathrm{el}} = -\frac{2e}{\Omega}\sum_n \left(\bar{\boldsymbol{r}}_n^{(1)} - \bar{\boldsymbol{r}}_n^{(0)}\right) \qquad \bar{\boldsymbol{r}}_n^{(\lambda)} = \int \boldsymbol{r}\left|a_n^{(\lambda)}\right|^2 d\boldsymbol{r}$$

center of gravity of Wannier ft.

Berry Phase

Berry, PRSL A 392, 45 (1984)

Phase associated with adiabatic process originating from geometric property of hamiltonian

Time-dependent Perturbation

$$|\Psi(t)\rangle = \sum_m |m(t)\rangle a_m(t)$$

$$\mathcal{H}(t)|m(t)\rangle = E_m(t)|m(t)\rangle$$

$$i\hbar|\dot{\Psi}(t)\rangle = \mathcal{H}(t)|\Psi(t)\rangle$$

$$i\hbar\dot{a}_n(t) = E_n(t)a_n(t) - i\hbar\sum_m \langle n(t)|\dot{m}(t)\rangle a_m(t)$$

Adiabatic Approximation (m=n only)

$$a_n(t) = a_n(0)\exp\left[-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right]\exp\left[i\gamma_n(t)\right]$$

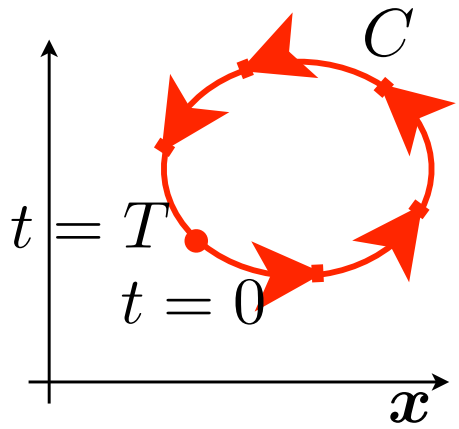
$$\gamma_n(t) = i\int_0^t \langle n(t')|\dot{n}(t')\rangle dt'$$

Berry Phase

- **Time dependence via a parameter** $x(t)$
- **A one-turn process in the parameter space with time from** 0 **to** T

$$\gamma_n(T) = i \int_0^T \langle n(\boldsymbol{x}(t'))|\dot{n}(\boldsymbol{x}(t'))\rangle dt'$$

$$= i \oint_C \langle n(\boldsymbol{x})|\nabla_{\boldsymbol{x}} n(\boldsymbol{x})\rangle \cdot d\boldsymbol{x}$$



Berry Phase of Bloch Function

Zak, PRL 62, 2747(1989)

1D Bloch function in a vector potential

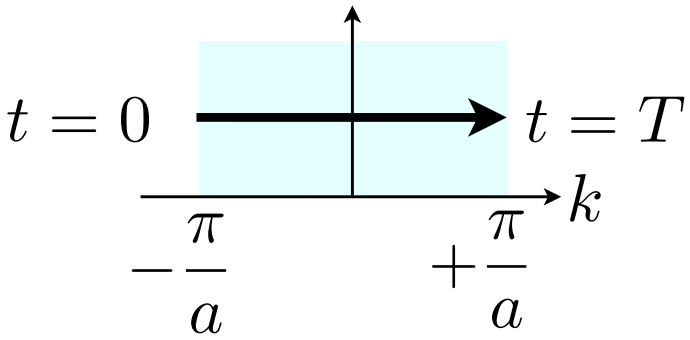
$$i\hbar\dot{\psi}(x,t) = \left[\frac{1}{2m}\left(p - \frac{e}{c}A(t)\right)^2 + V(x)\right]\psi(x,t) \qquad V(x+a) = V(x)$$

$$\left[\frac{1}{2m}\left(p - \frac{e}{c}A(t)\right)^2 + V(x)\right]\phi_n(x,t) = \varepsilon_n(t)\phi_n(x,t)$$

Generalized Bloch function

$$\phi_n(x,t) = e^{ikx}u_n(x,k(t)) \qquad k(t) = k - \frac{e}{\hbar c}A(t)$$

$$\gamma_n = i\int_0^T \langle\phi_n(k(t'))|\dot{\phi}_n(k(t'))\rangle dt'$$



$$= i\int_{-\frac{\pi}{a}}^{+\frac{\pi}{a}} \langle\phi_n(k)|\frac{\partial}{\partial k}\phi_n(k)\rangle dk$$

Berry Phase and Wannier Function

1D Wannier Function

$$a_i(x - X_l) = \frac{1}{\sqrt{N}} \sum_k e^{ik(x-X_l)} u_i(x,k)$$

$$u_i(x,k) = \frac{1}{\sqrt{N}} \sum_l e^{-ik(x-X_l)} a_i(x - X_l)$$

$$\frac{\partial}{\partial k} u_i(x,k) = \frac{1}{\sqrt{N}} \sum_l -i(x - X_l) e^{-ik(x-X_l)} a_i(x - X_l)$$

Berry Phase

$$\gamma_i = i \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \left\langle u_i(k) \middle| \frac{\partial}{\partial k} u_i(k) \right\rangle dk$$

$$= \left(\frac{2\pi}{a} \right) \int x |a_i(x)|^2 dx$$

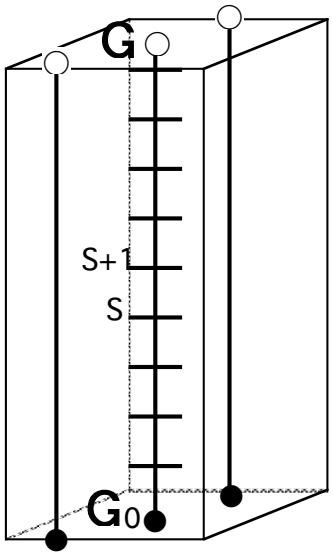
center of gravity

Calculation of Polarization with Berry Phase

Electric Polarization of 3D System

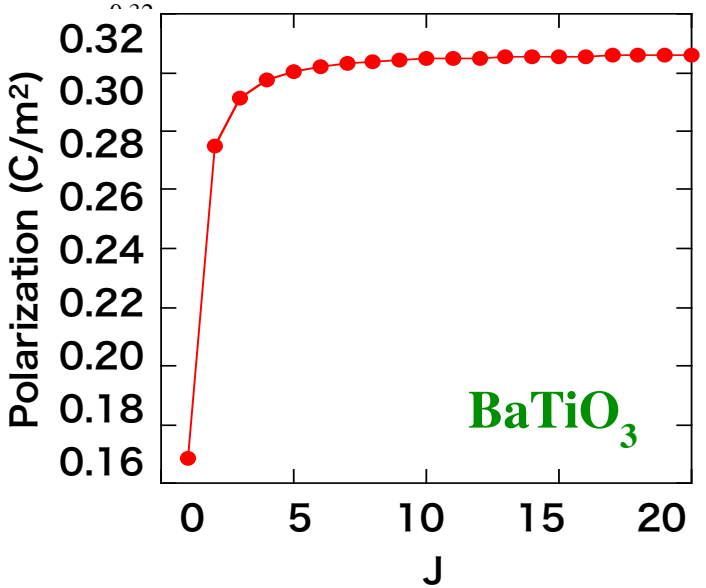
$$\boldsymbol{P}_{el}^{(\lambda)} = \frac{-2ie}{(2\pi)^3}\sum_n \int d^3\boldsymbol{k}\langle u_n^{(\lambda)}(\boldsymbol{k})|\nabla_{\boldsymbol{k}} u_n^{(\lambda)}(\boldsymbol{k})\rangle$$

$$= \frac{2e}{(2\pi)^3}\int d^2\boldsymbol{k}_\perp \gamma^{(\lambda)}(\boldsymbol{k}_\perp)$$



$$\gamma^{(\lambda)}(\boldsymbol{k}_\perp) = \mathrm{Im}\left\{\lim_{J\to\infty}\prod_{s=0}^{J-1}\det S_{ij}^{(\lambda)}(k_s, k_{s+1})\right\}$$

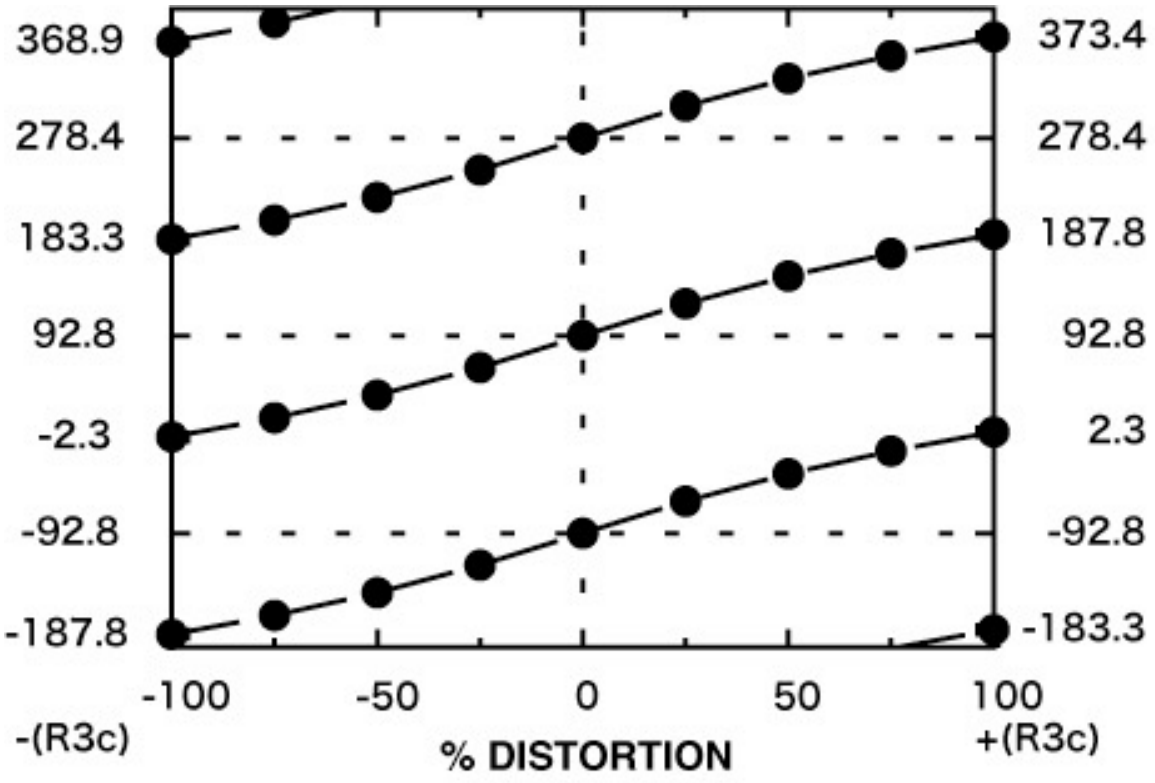
$$S_{ij}^{(\lambda)}(k_s, k_{s+1}) = \langle u_i^{(\lambda)}(\boldsymbol{k}_\perp, k_s)|u_j^{(\lambda)}(\boldsymbol{k}_\perp, k_{s+1})$$



Convergency with respect to number of k-points

Phase Problem of Polarization

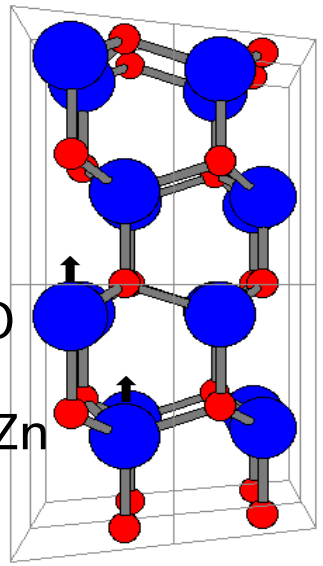
$$\frac{eR}{\Omega} \sim \frac{1.6 \times 10^{-19}\mathrm{C} \cdot 4 \times 10^{-8}\mathrm{cm}}{(4 \times 10^{-8})\mathrm{cm}^3} = 100\mu\mathrm{C/cm}^2$$

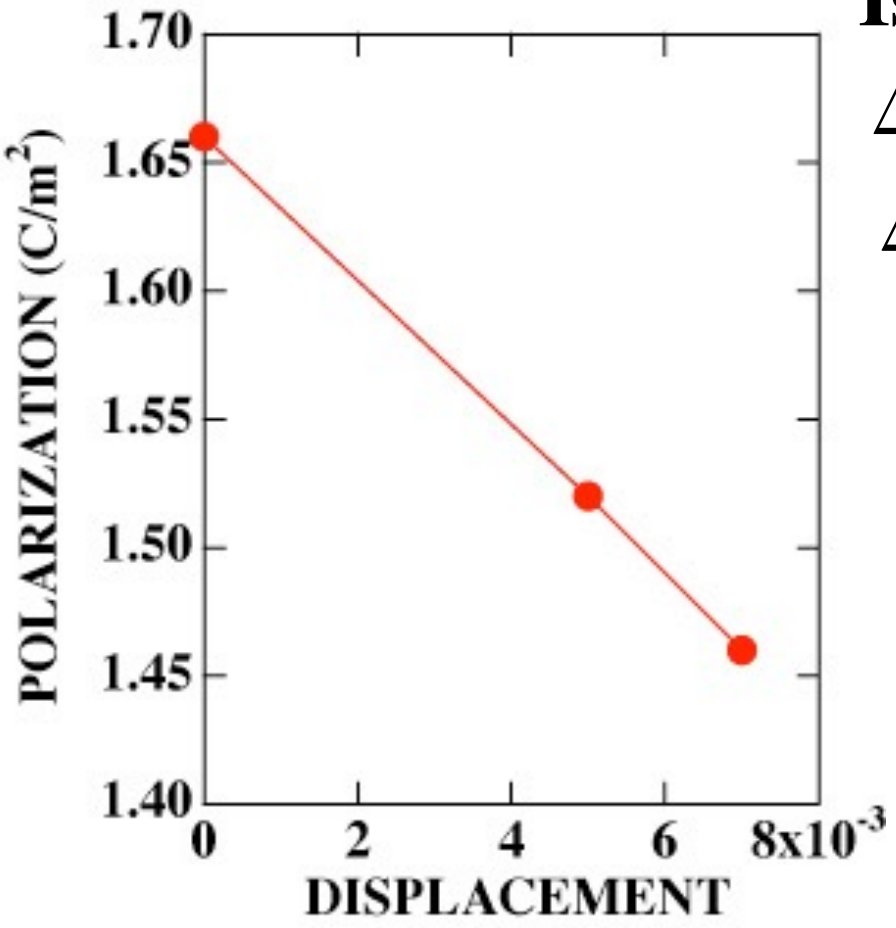


$BiFeO_3$

PRB 71, 014113 (2005)

ZnO





Ishii, TO (unpublished)

$$\Delta P_{\rm ion} = +14.7\mu{\rm C/cm}^2$$

$$\Delta P_{\rm el} = -19.6\mu{\rm C/cm}^2$$

$$\Delta P_{\rm ion} + \Delta P_{\rm el} = -4.9\mu{\rm C/cm}^2$$

Posternak $-5\mu{\rm C/cm}^2$

Vanderbilt $-5.7\mu{\rm C/cm}^2$

experiment $-7 \pm 2\mu{\rm C/cm}^2$

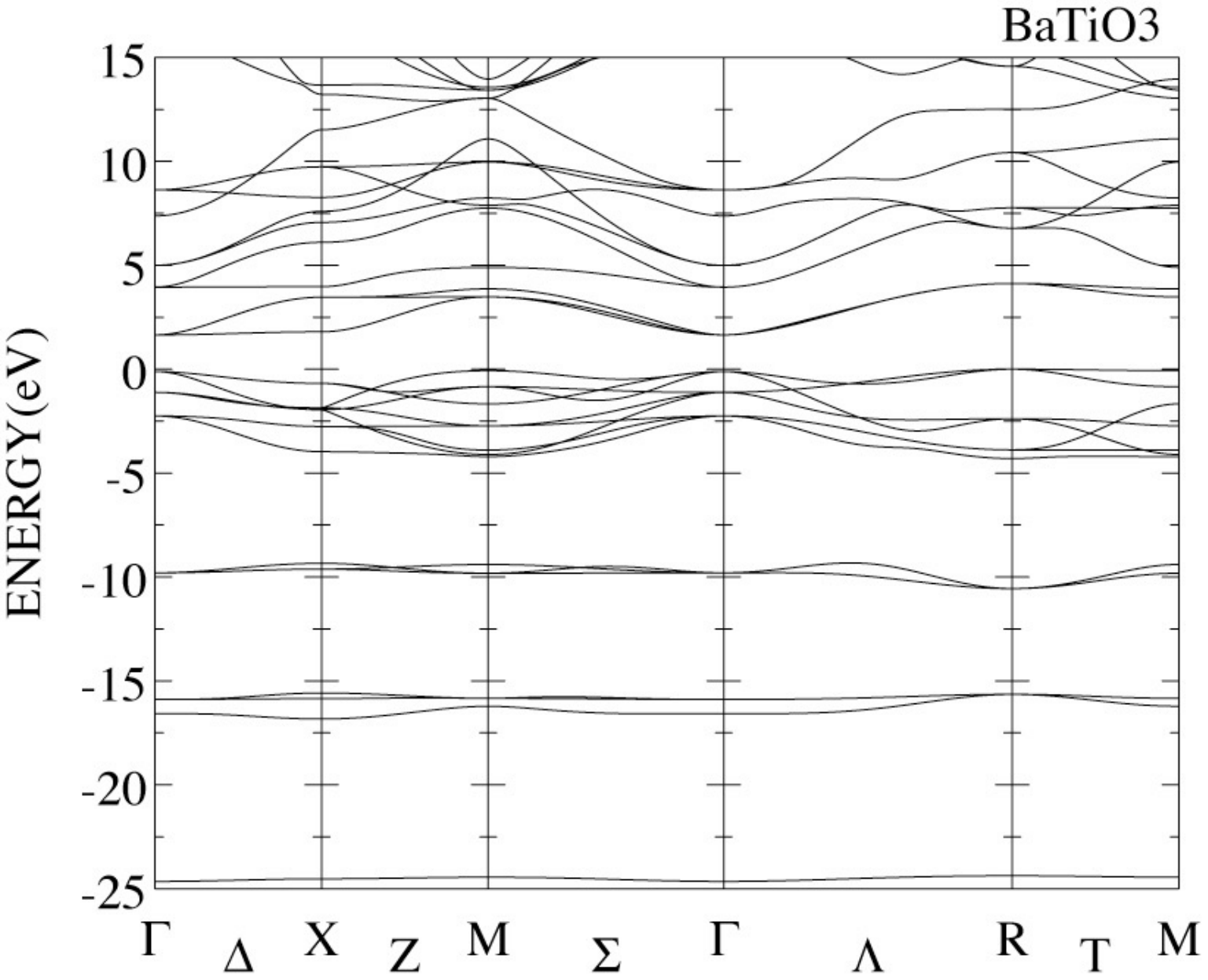
$$\Delta \mathbf{P} = \frac{e}{\Omega} Z^* \mathbf{u} \;\Rightarrow\; Z^* = -1.99$$

Born effective charges

Polarization of Ferroelectric $BaTiO_3$

- **Tetragonal** (ionic model: 0.16 C/m^2)
  - 0.31 C/m^2 Ishii, TO
  - 0.28 C/m^2 Zhong, Vanderbilt
  - 0.27 C/m^2 experiment
- **Rhombohedral**
  - 0.37 C/m^2 Ishii, TO
  - 0.43 C/m^2 Zhong, Vanderbilt
  - 0.33 C/m^2 experiment

Band Structure of Cubic $BaTiO_3$



ionic crystal

conduction bands
Ti 3*d*

gaps

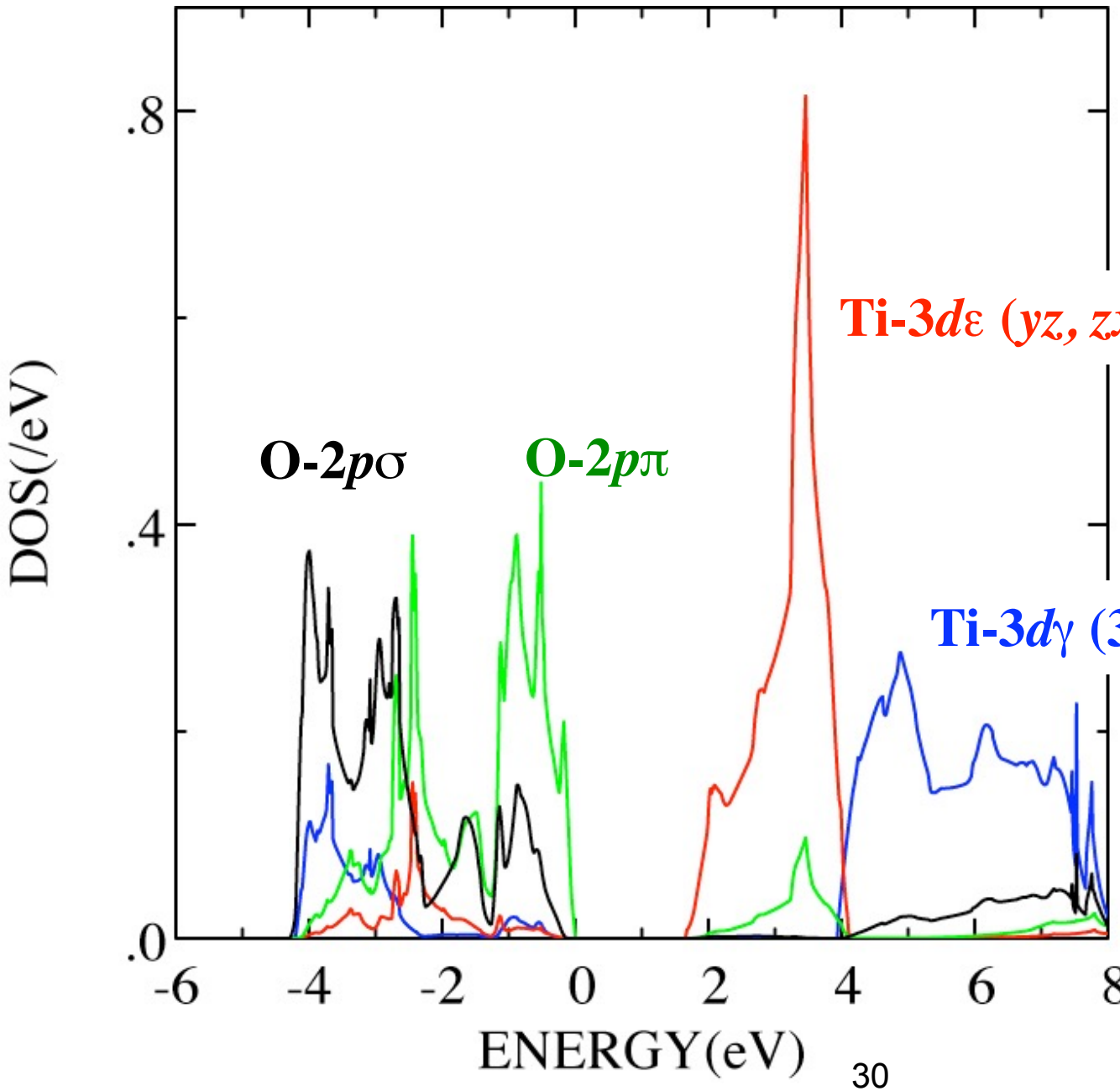
valence bands
O 2*p*

Ba 5p

O 2s

Ba 5s

Density of States of Cubic $BaTiO_3$

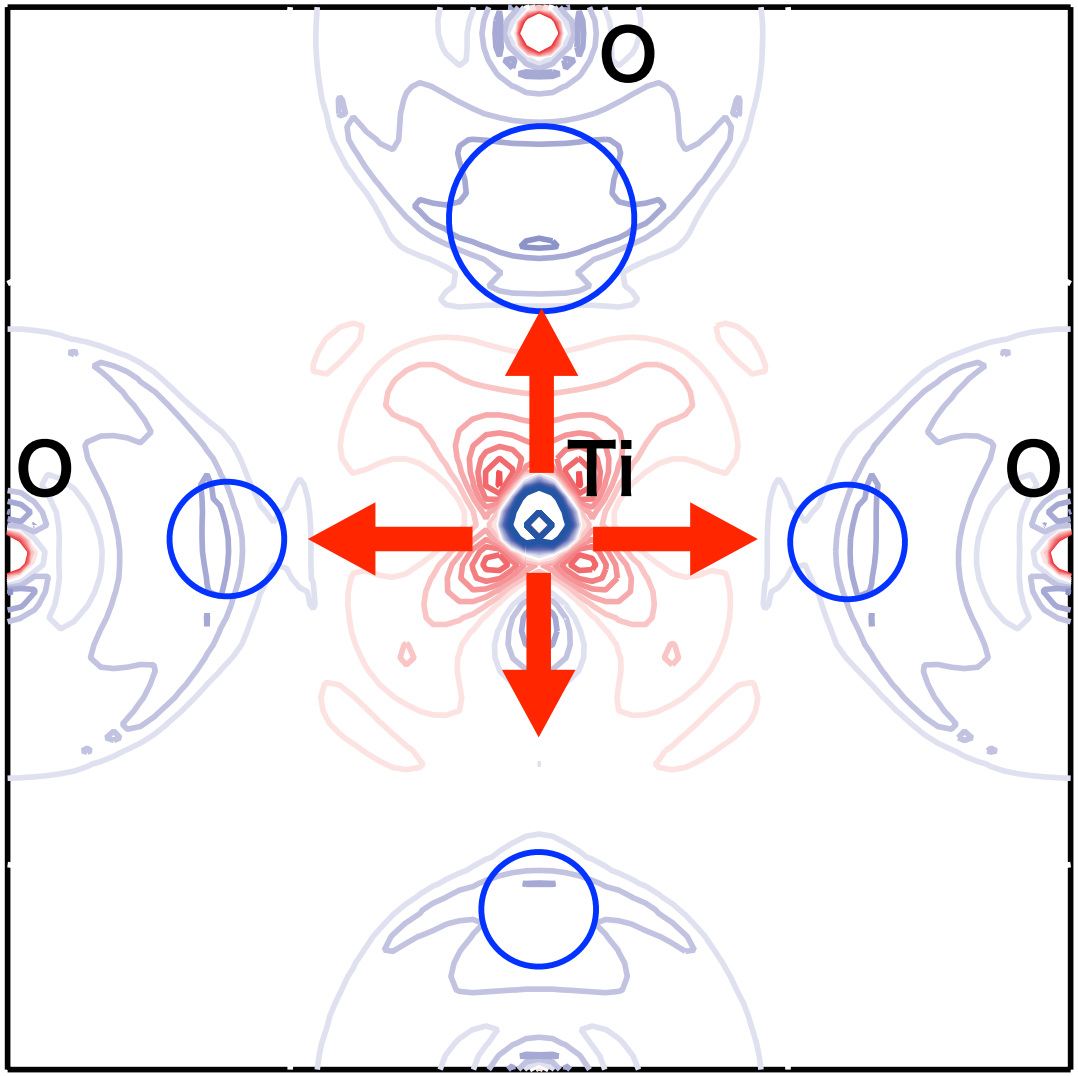


ionic crystal
+
strong hybridization

no Ba orbital around gaps: Ba^{2+}

Electron Density of Tetragonal $BaTiO_3$

$$\Delta n(\boldsymbol{r}) = n(\boldsymbol{r}) - \sum_{\nu} n_{\nu}^{atom}(\boldsymbol{r} - \boldsymbol{R}_{\nu})$$



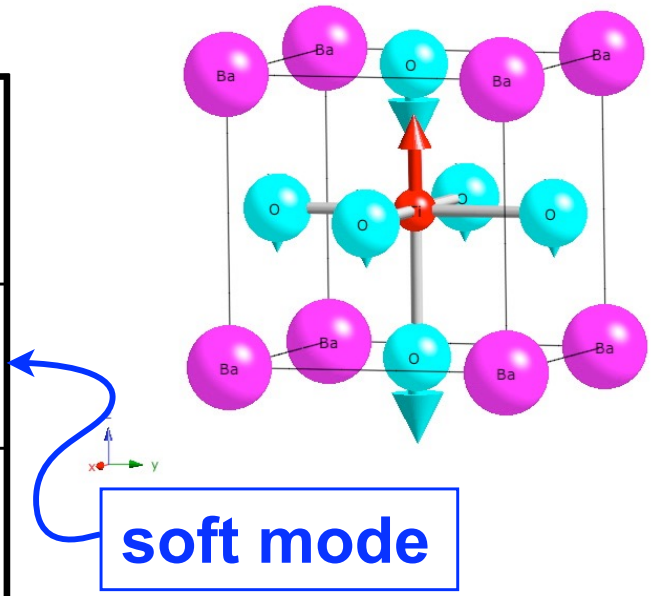
reduction
increase

charge transfer from Ti to O
→ ionic bonding

bond charge between Ti and O
→ covalent bonding

Phonon Mode of Cubic $BaTiO_3$

ω (cm^{-1})	Ba	Ti	O1	O2	O2'
186i	-0.01	-0.62	1	0.51	0.51
0	1	1	1	1	1
165 180*	-0.66	1	0.78	0.97	0.97
277	0	0	0	1	-1
458 482*	-0.01	0.16	1	-0.69	-0.69

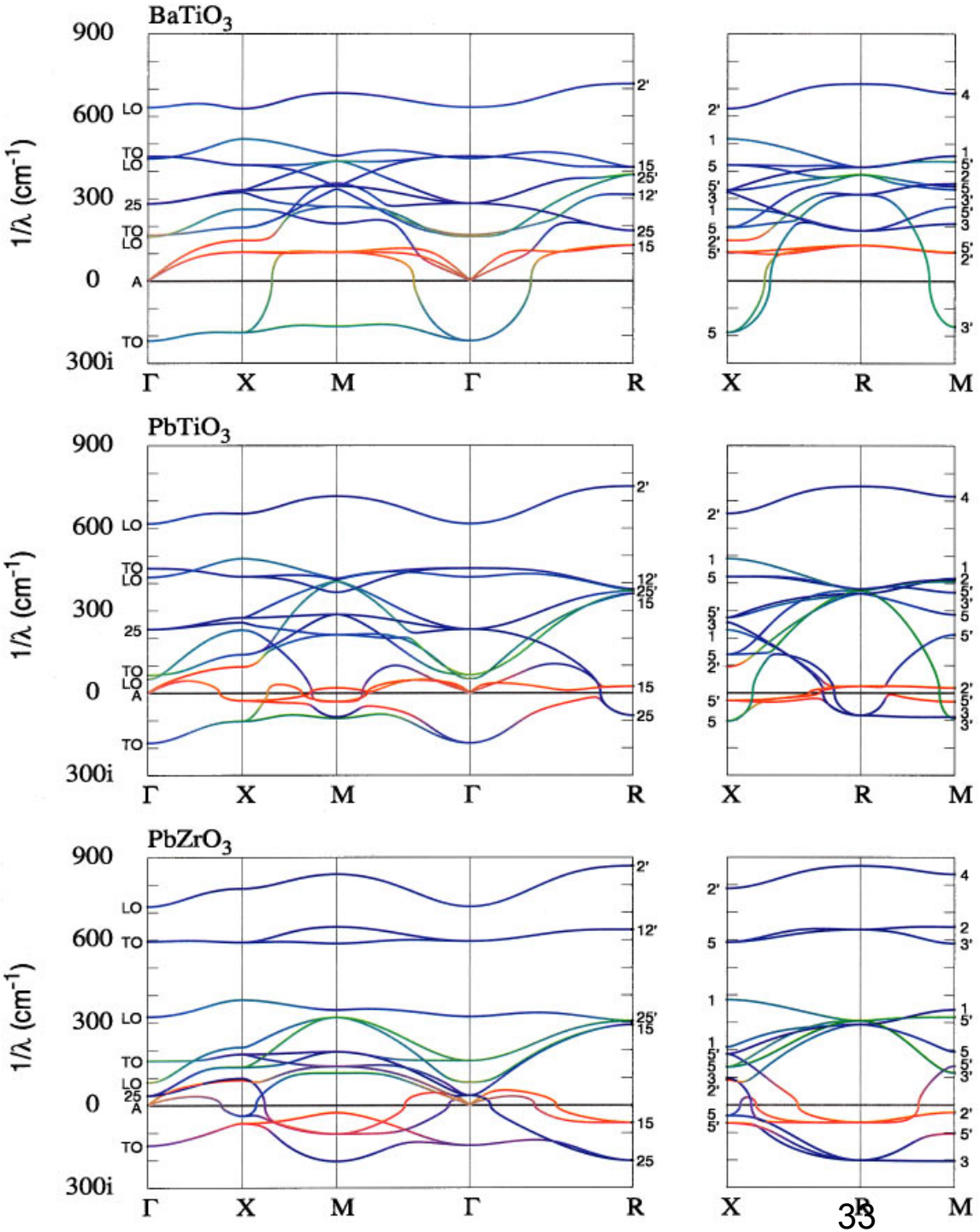


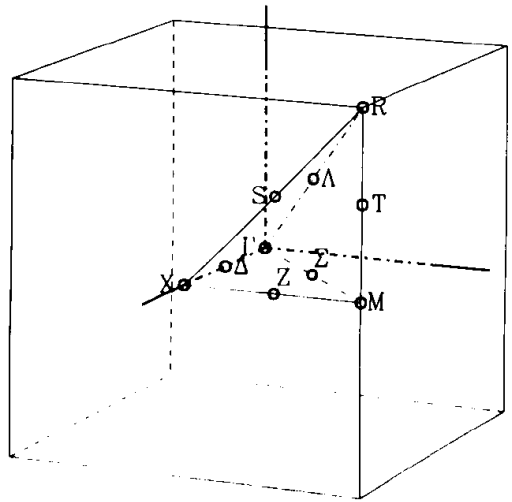
Ba^{2+} not joining soft mode

*IR @395K

a = 4.00Å

Phonon Band of Perovskite Oxides: ABO_3





Eigenvector:

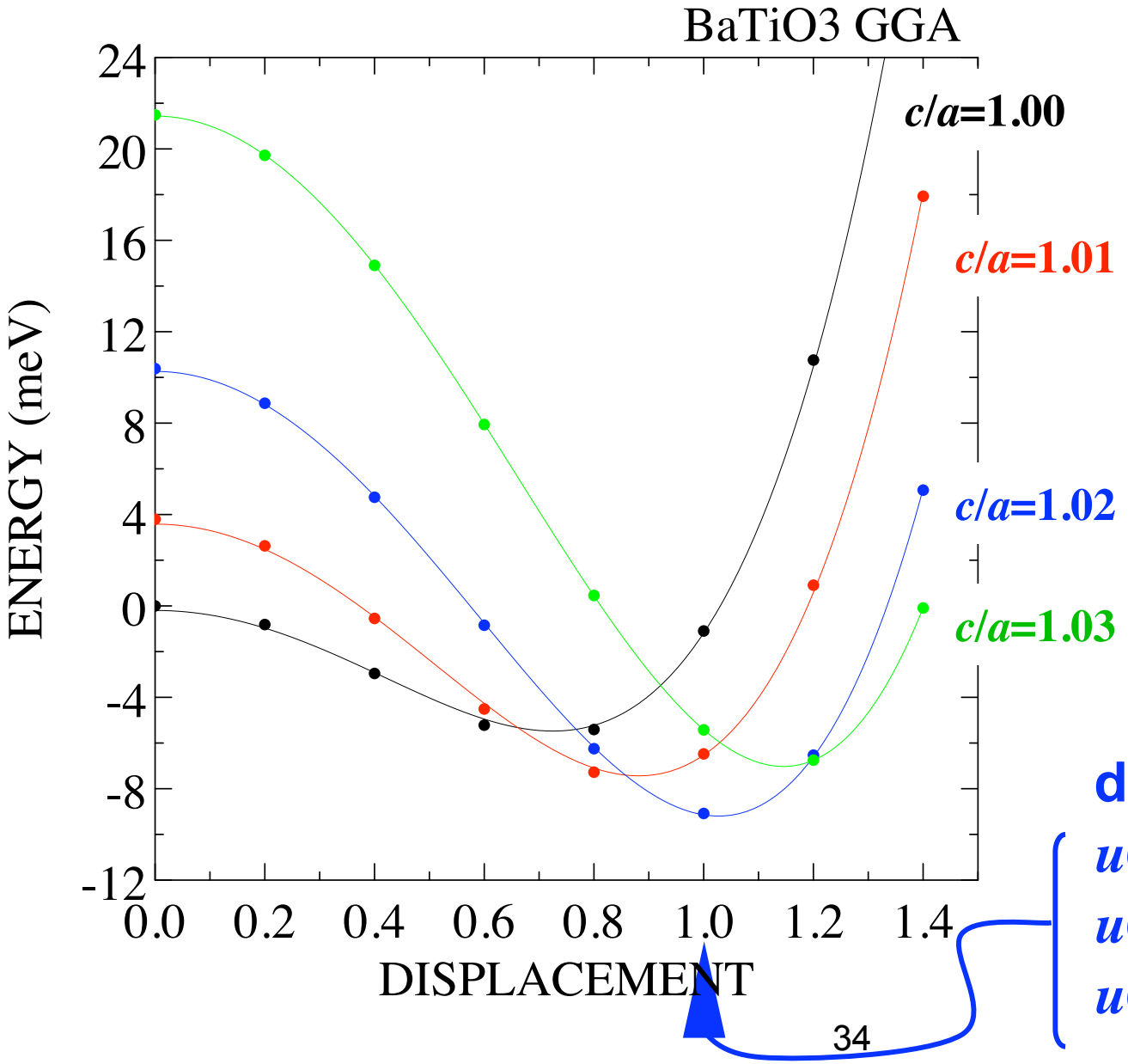
red: A

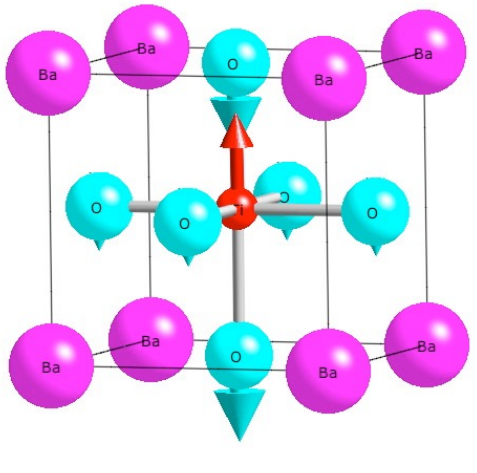
green: B

blue: O

Phys. Rev. B 60, 836 (1999)

Energy Variation of $BaTiO_3$ due to Displacement





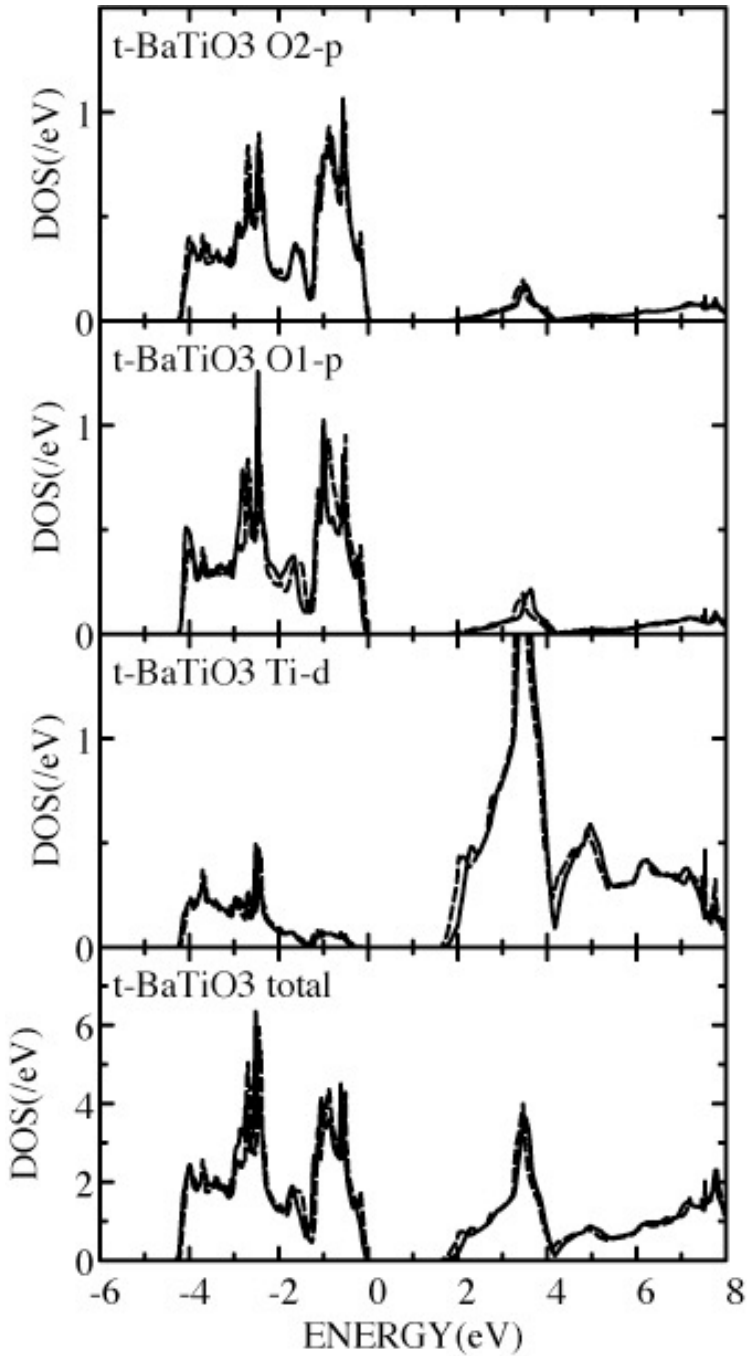
displacements

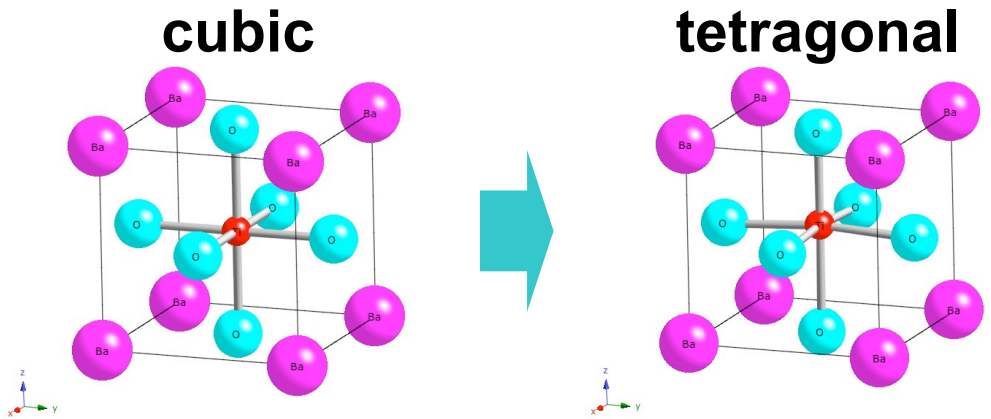
***u*(Ti) = 0.054Å**

***u*(O1) = –0.097Å**

***u*(O2) = –0.061Å**

Electronic Structure Variation of $BaTiO_3$ due to displacement

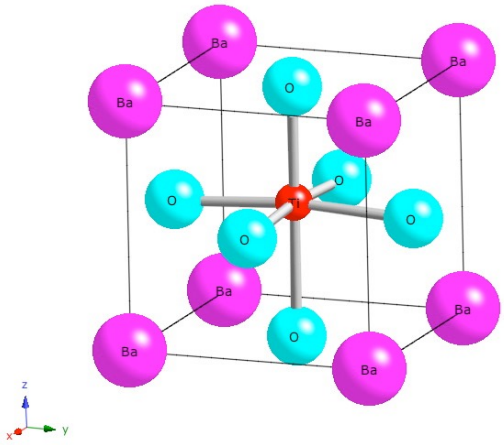




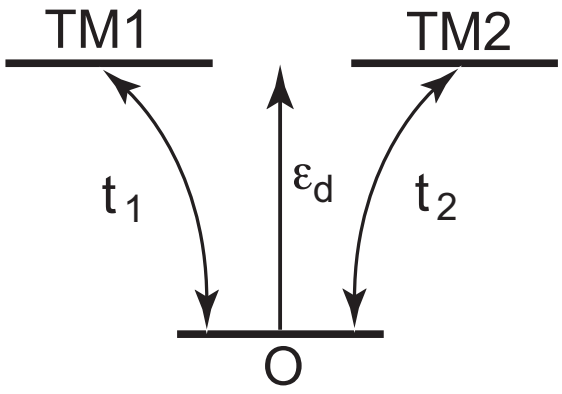
displacement
→ Enhancement in hybridization
→ band shift
→ energy gain

broken lines: cubic
solid lines: tetragonal

Instability to Ferroelectric Phase



perovskite structure



three-site model

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_t + \mathcal{H}_{ela}$$

$$\mathcal{H}_0 = \sum_\sigma \varepsilon_d (d^\dagger_{1\sigma} d_{1\sigma} + d^\dagger_{2\sigma} d_{2\sigma})$$

$$\mathcal{H}_t = t_1 \sum_\sigma \left(d^\dagger_{1\sigma} p_\sigma + h.c. \right)$$

$$+ t_2 \sum_\sigma \left(d^\dagger_{2\sigma} p_\sigma + h.c. \right)$$

$$\mathcal{H}_{ela} = \frac{\lambda}{2} x^2$$

Instability to Ferroelectric Phase

Variation of hopping integral by O-ion displacement

$$t_1 = -t(1+\delta \cdot x) \qquad t_2 = +t(1-\delta \cdot x)$$

electron-lattice coupling

Energy variation up to 4th order of hopping t

$$\Delta E = \left[-\frac{8t^2\delta^2}{\varepsilon_d} + \frac{32t^4\delta^2}{\varepsilon_d^3} + \lambda \right] \frac{x^2}{2} + \frac{32t^4\delta^4}{\varepsilon_d^3} \frac{x^4}{4}$$

Negative coefficient of 2nd order term → instability

$$\left| \frac{t}{\varepsilon_d} \right| \ll 1 \qquad \frac{8t^2\delta^2}{\varepsilon_d} > \lambda$$

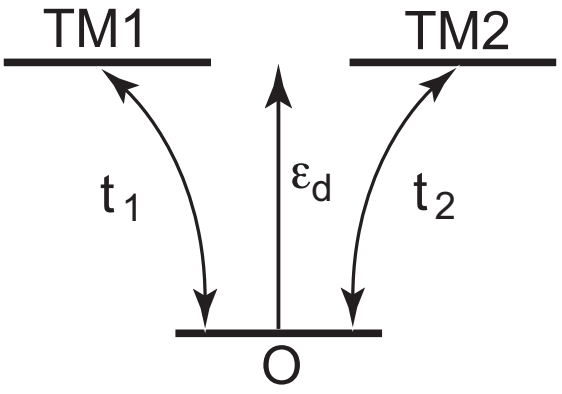
- **large δ**
- **small λ**

Instability to Ferroelectric Phase

Equilibrium displacement

$$x^2 = \frac{\varepsilon_d^3}{32t^4\delta^4}\left[\frac{8t^2\delta^2}{\varepsilon_d} - \lambda\right]$$

To satisfy the instability condition, appropriately large size of hopping integral *t* compare to ε_d



- **large δ**
- **small λ**
- **appropriate *t***

ionic + covalent bonding

Instability to Ferroelectric Phase

Coupling constant δ

$$t(R) \propto R^{-(l+l'+1)} \approx t(R_0)\left(1 - \frac{l+l'+1}{R_0}x\right)$$

- **kind of orbital**
- **local structure**

Elastic constant λ

$$\mathcal{H}_t = \frac{\lambda}{2}x^2$$

- **local structure: tolerance**

- **Tolerance factor of perovskite structure**

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

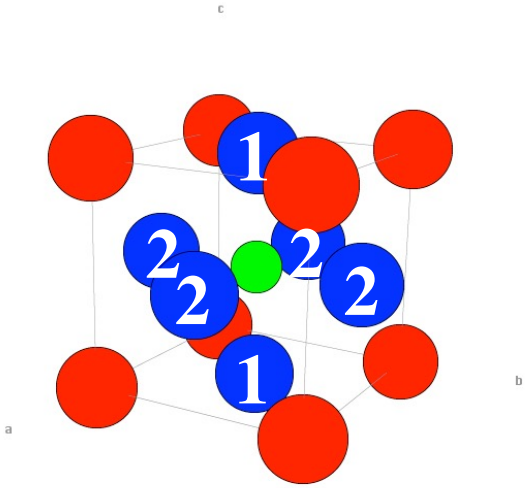
$t > 1$ **Ferroelectric instability of B ion**

$t < 1$ **Antiferroelectric instability of A ion**

Born Effective Charge

$$\Delta \mathbf{P} = \frac{e}{\Omega} Z^* \mathbf{u}$$

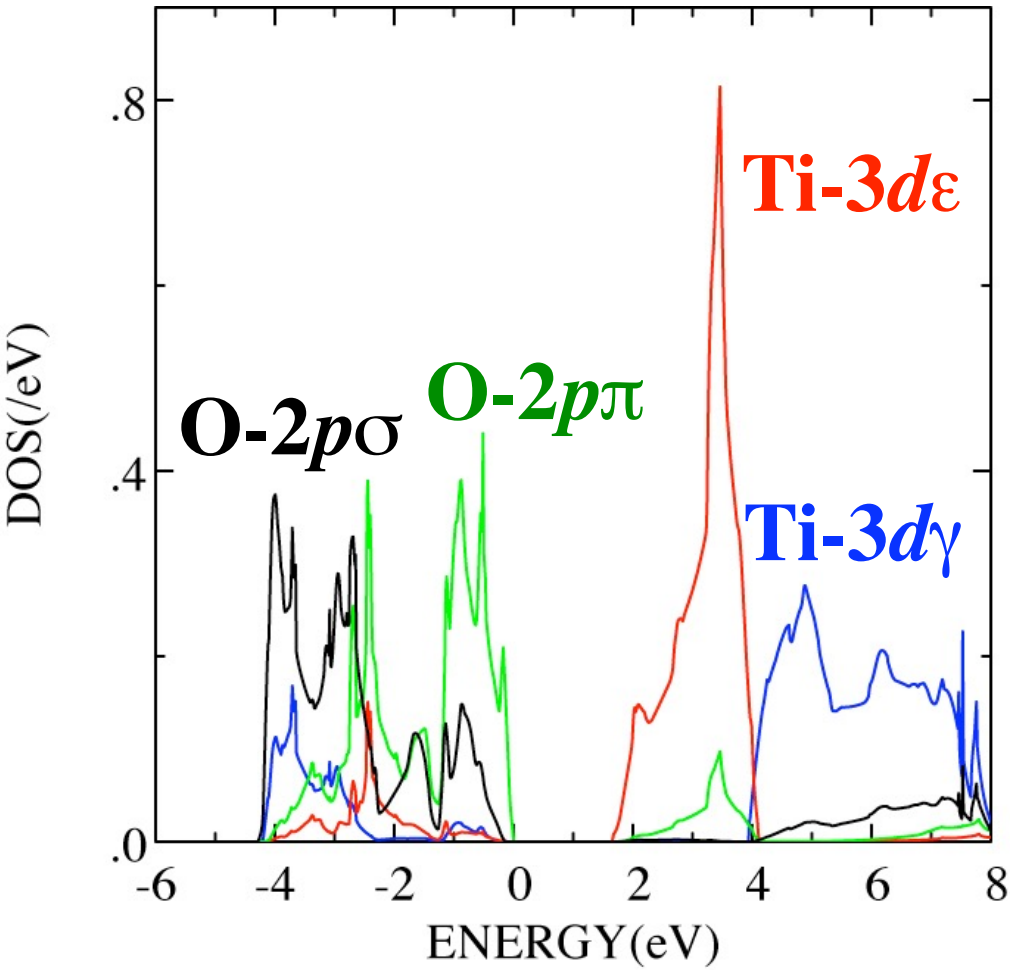
u // <001>

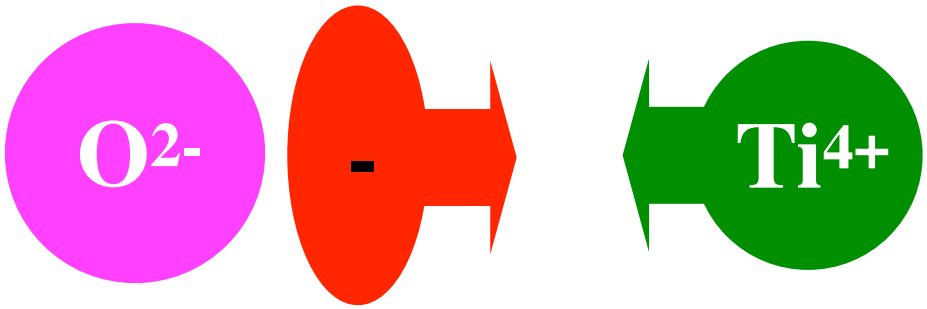


	A	*B*	O1	O2
$BaTiO_3$	2.75	7.16	-5.69	-2.11
$SrTiO_3$	2.54	7.12	-5.66	-2.00
$CaTiO_3$	2.58	7.08	-5.65	-2.00
$KNbO_3$	1.14	9.23	-7.01	-1.68
$NaNbO_3$	1.13	9.11	-7.01	-1.61
$PbTiO_3$	3.90	7.06	-5.83	-2.56
$PbZrO_3$	3.92	5.85	-4.81	-2.48
$BaZrO_3$	2.73	6.03	-4.74	-2.01

Zhong, Vanderbilt, PRL 72, 3618 (1994).

Mechanism of Effective Charge Enhancement





Movement of bond charge due to variation in hybridization between Ti-3*d* and O-2*p* orbitals

Role of Pb

- **Lone pair**

  Repulsion of $[6s]^2$ or $[6sp]^2$

widely accepted since 70s especially in Chemistry

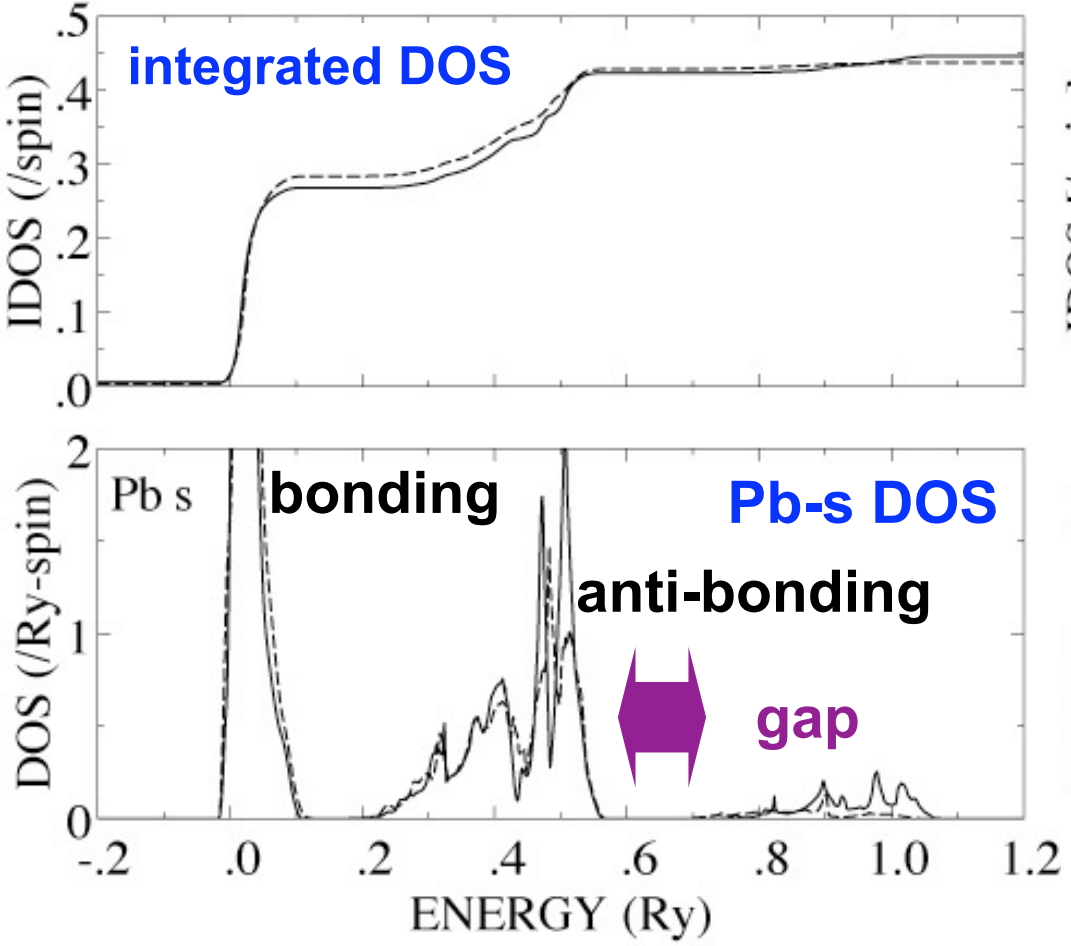
- **Covalent bond with O-2*p***

  6*s*=O-2*p* **Cohen（1992-)**

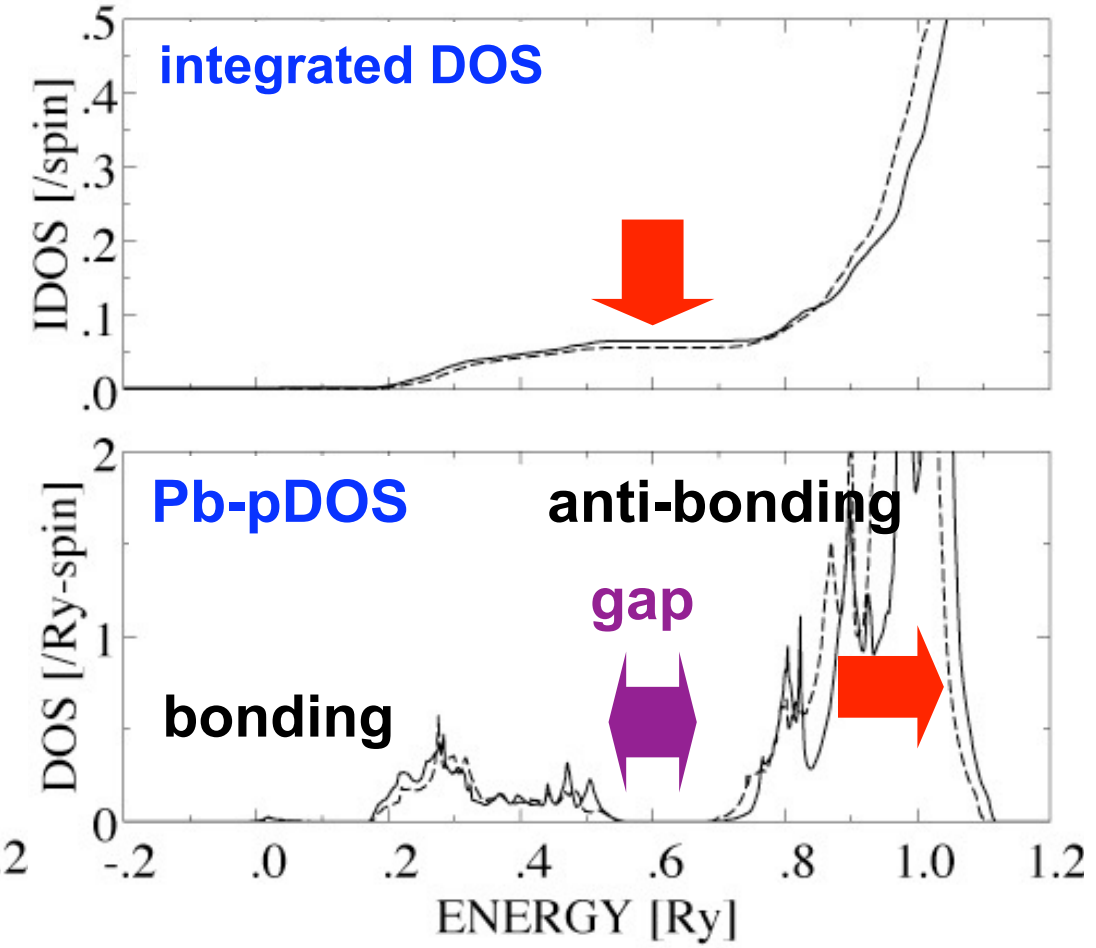
  6*p*=O-2*p* **Miyazawa (2000-)**

Role of Pb: $PbTiO_3$

Pb-6*s*



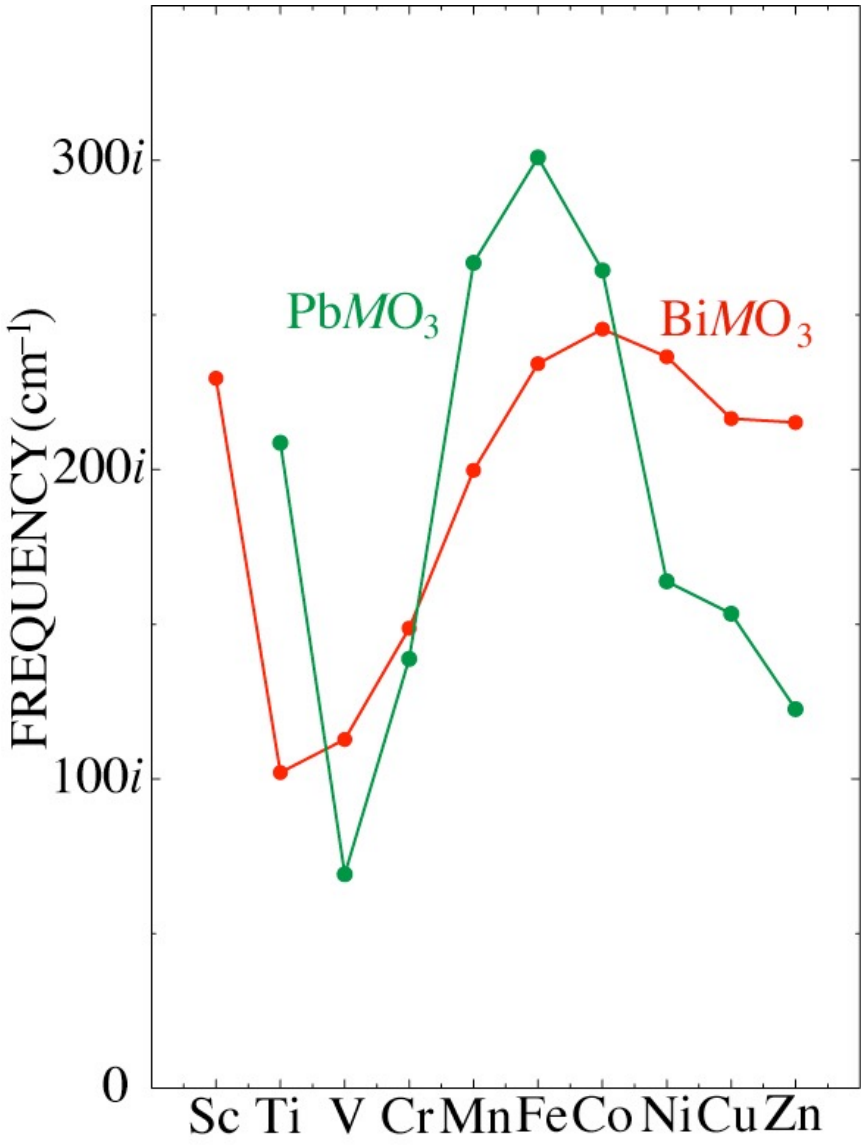
Pb-6*p*

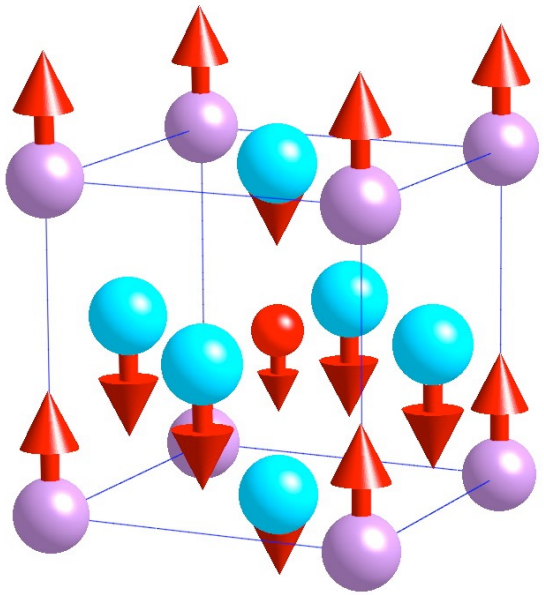


fully occupied Pb-6*s* bonding and anti-bonding

occupied Pb-6*p* bonding states only →covalent

Soft Mode in Cubic $PbMO_3$ and $BiMO_3$





Summary

- Electron Theory of Ferroelectrics
  - BO Potential
  - QM Representation of Polarization
- Typical Ferroelectric $BaTiO_3$
  - Ionic and Covalent Bonding
  - Ferroelectric Instability
  - Born Effective Charge

References

- **Reviews**
  - 寺倉清之：固体物理 35, 620 (2000).
  - R. Resta: Modelling Simul. Mater. Sci. Eng. 11, R69 (2003).
  - M. Dawber, K.M. Rabe, and J.F. Scott: Rev. Mod. Phys. 77, 1083 (2005).