

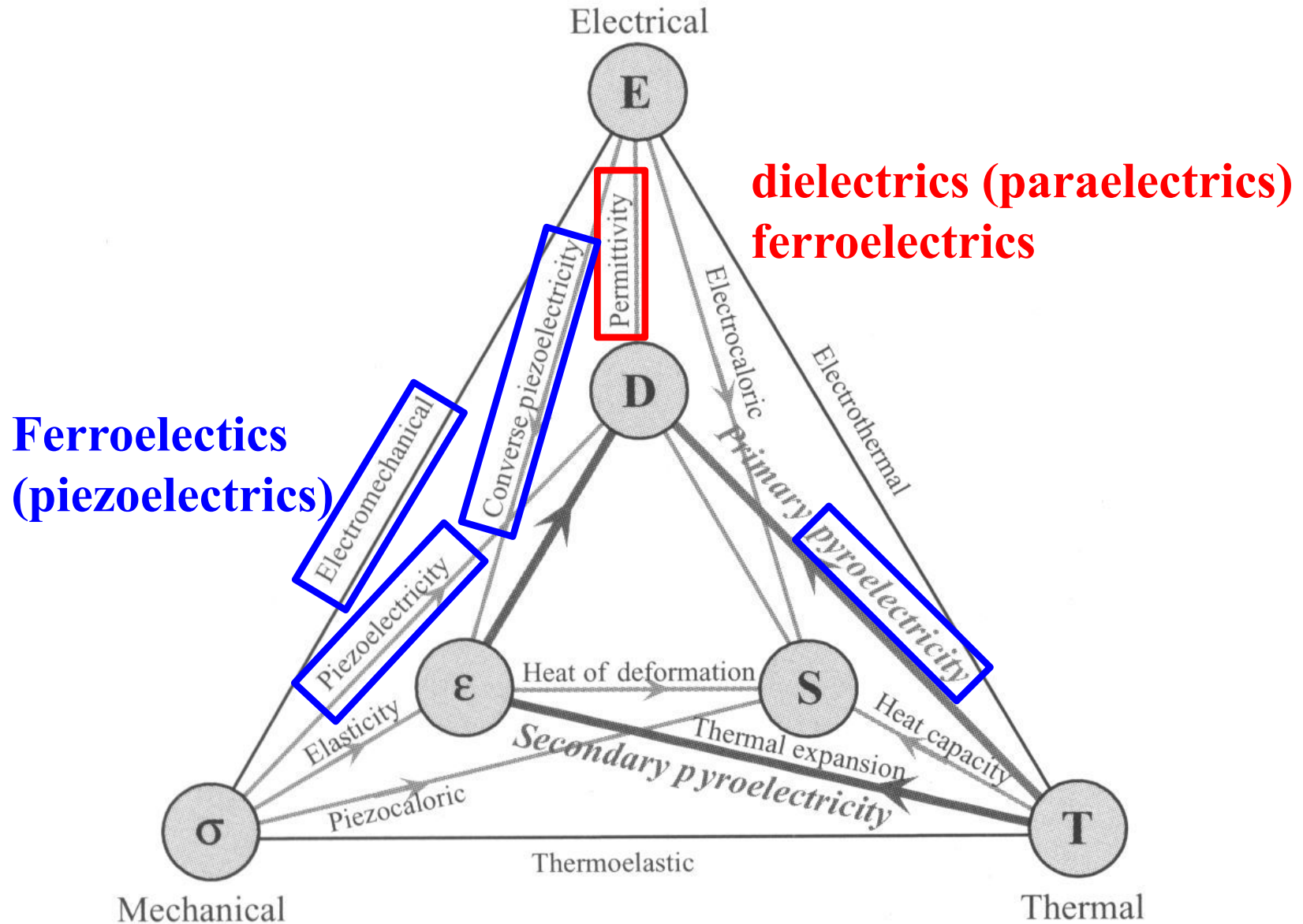
# Introduction to Solid State Science

**Toshio Kamiya**

Class 9 Jan. 11	Kamiya Toshio	Review of fundamental physics of dielectrics and ferroelectrics: Part 1	Understand fundamental physics of dielectrics and ferroelectrics
Class 10 Jan. 15	Kamiya Toshio	Review of fundamental physics of dielectrics and ferroelectrics: Part 2	Understand calculations of dielectric and ferroelectric properties

# What are material properties / functions?

Hadis Morkoc and Umit Ozgur, Zinc Oxide, Wiley-VCH



# Electromagnetism equations

## Maxwell equation

Gauss law

$$\operatorname{div} \mathbf{E}(\mathbf{r}, t) = \frac{1}{\varepsilon_0} \rho_e(\mathbf{r}, t)$$

Ampere-Maxwell law

$$\operatorname{rot} \mathbf{H}(\mathbf{r}, t) = \mathbf{i}_e(\mathbf{r}, t) + \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t}$$

Non-existence of magnetic monopole

$$\operatorname{div} \mathbf{B}(\mathbf{r}, t) = 0$$

Electromagnetic induction law

$$\operatorname{rot} \mathbf{E}(\mathbf{r}, t) + \frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t} = 0$$

## Derivatives

Electric field and electrostatic potential

$$\mathbf{E}(\mathbf{r}, t) = \frac{\partial \phi(\mathbf{r}, t)}{\partial \mathbf{r}}$$

Poisson equation

$$\nabla^2 \phi(\mathbf{r}, t) = -\frac{1}{\varepsilon_0} \rho_e(\mathbf{r}, t)$$

Charge conservation law

$$\operatorname{div} \mathbf{i}_e(\mathbf{r}, t) + \frac{\partial \rho_e(\mathbf{r}, t)}{\partial t} = 0$$

# Electromagnetism equations

## Constitutive equations (material equations)

**Ohm's law**  
**(Electrical conductivity)**

$$\mathbf{j}_e(\mathbf{r}, t) = \sigma \mathbf{E}(\mathbf{r}, t)$$

**Electric susceptibility**

$$\mathbf{P}_e(\mathbf{r}, t) = \chi_e \mathbf{E}(\mathbf{r}, t)$$

**Dielectric permittivity**  
**(Dielectric constant)**

$$\mathbf{D}_e(\mathbf{r}, t) = \varepsilon \mathbf{E}(\mathbf{r}, t)$$

**Relative dielectric permittivity (constant)**

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

**Magnetic susceptibility**

$$\mathbf{M}(\mathbf{r}, t) = \chi_M \mathbf{H}(\mathbf{r}, t)$$

**Magnetic permeability**

$$\mathbf{B}(\mathbf{r}, t) = \mu \mathbf{H}(\mathbf{r}, t)$$

# What is dielectrics?

## Electrical conductor (semiconductor, metal)

Characterized by electrical conductivity  $\sigma$       $\mathbf{j}_e(\mathbf{r}, t) = \sigma \mathbf{E}(\mathbf{r}, t)$   
(typically  $> 10^{-8}$  S/cm)

## Insulator

Characterized by very small electrical conductivity  $\sigma$   
(typically  $\ll 10^{-8}$  S/cm)

and by dielectric constant  $\epsilon$       $\mathbf{D}_e(\mathbf{r}, t) = \epsilon \mathbf{E}(\mathbf{r}, t)$

## Dielectrics

Good dielectrics (usually)

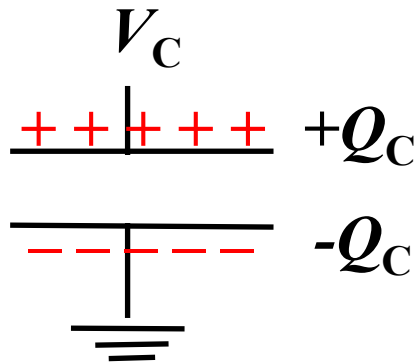
- are good electrical insulator (**very small  $\sigma$** )  
to minimize **dielectric loss** and **leakage current**
- have **high  $\epsilon$**   
to storage **large charges** at low applied voltage

Classified to

**paraelectrics (dielectrics), ferroelectrics, anti-ferroelectrics**

# Application of dielectrics: Capacitor

Capacitor: Storage charges by applied voltage  $V$



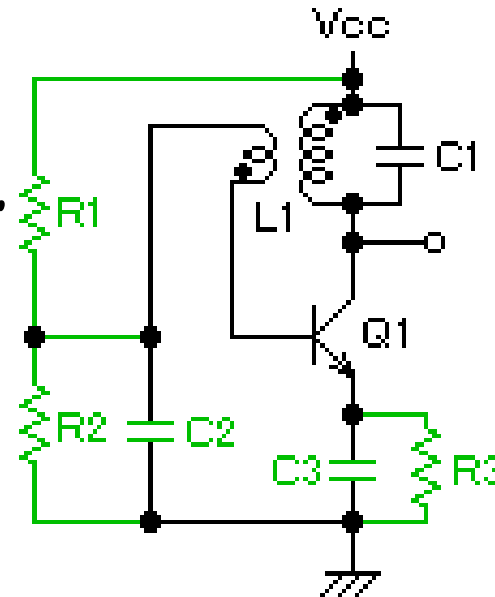
$$Q_C = |P| = CV_C = \epsilon_r \epsilon_0 \frac{S}{d} V_C$$

$\epsilon_r$  : Relative dielectric constant  
 $S$  : Electrode area of the capacitor  
 $d$  : Electrode distance

Circuits: Low (High) pass filter

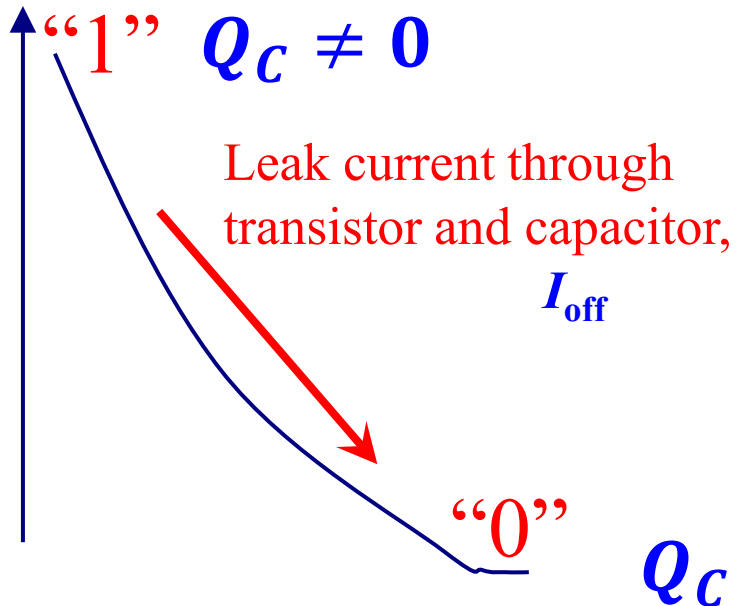
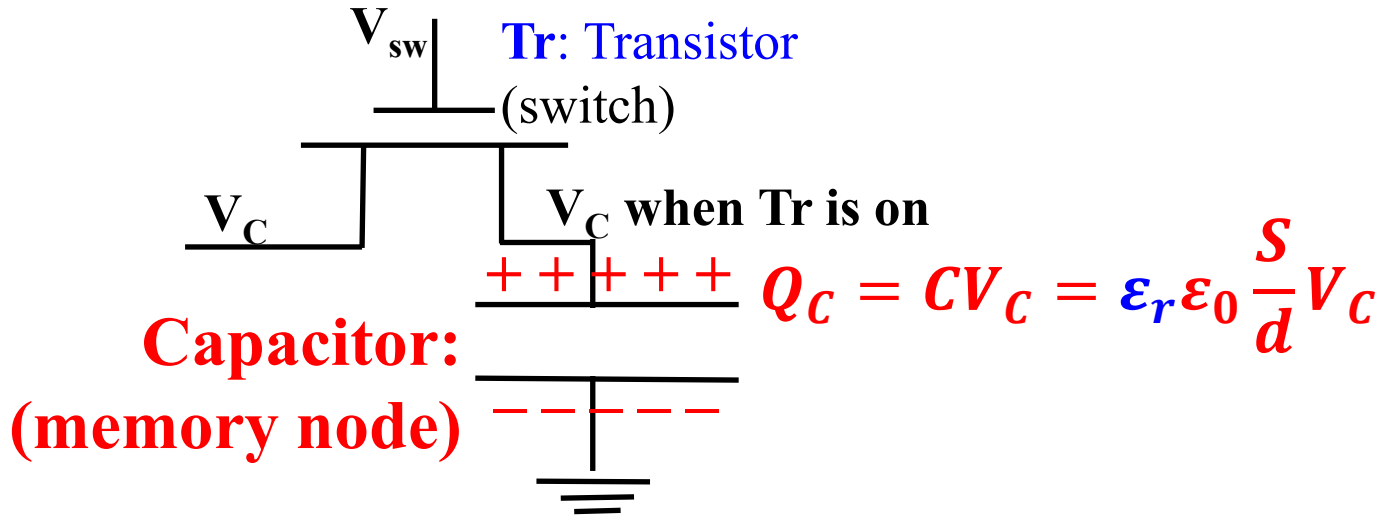
Oscillator

*Combined with resistor, inductor*



# Application of dielectrics: DRAM

**DRAM (dynamic random access memory)**



**Retention time**

$$t_r \sim Q_C / I_{off}$$

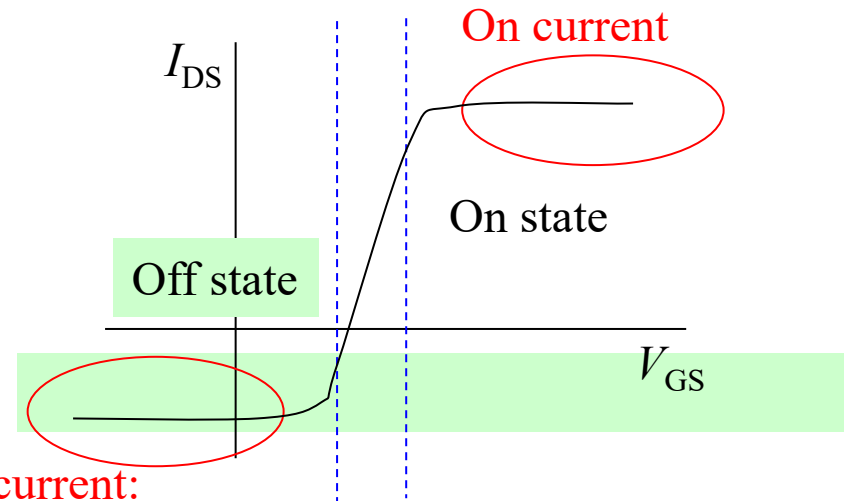
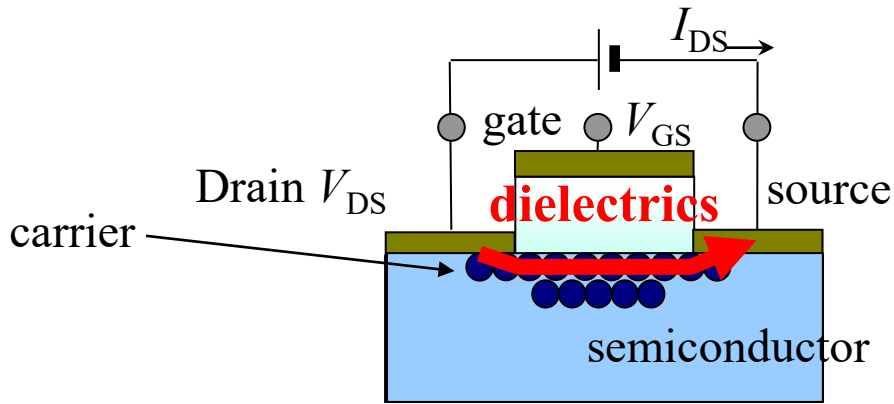
$$= \epsilon_r \epsilon_0 \frac{S}{d} \frac{1}{I_{off}} V_C$$

# Application of dielectrics: FET

## FET (Field-effect transistor)

Two representative functions of transistor

1. Amplification Use linear region ( $I_{DS} \propto V_{GS}$ )
2. **Switching** Use large on/off current ratio



Leak current:  
power consumption

At  $V_{GS} = 0V$

On state: Normally-on  
Depletion-type

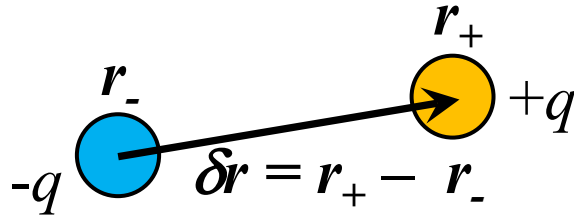
Off state: Normally-off  
Enhancement-type



# Electric polarization

## Definition of electric polarization $p$

Two point charges  $+q$  and  $-q$  are located at  $r_+$  and  $r_-$ , respectively.



$$p = +qr_+ + (-q)r_- = q\delta r$$

$$\begin{aligned} \Delta U_{p-E} &= -qr_+ \cdot E - (-q)r_- \cdot E \\ &= -p \cdot E \end{aligned}$$

## General definition of electric polarization density, $P$

$N$  point charges with  $q_i$  are located at  $r_i$ , respectively, in the volume  $V$ .

$$P = \frac{1}{V} \sum_{i=1}^N q_i r_i$$

*Note: Uniquely defined*

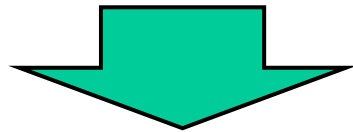
*only when the charge neutrality is satisfied.*

# Dielectric constant

## Definition of electric flux density $D$

$$\mathbf{D}_e(\mathbf{r}, t) = \varepsilon_0 \mathbf{E}(\mathbf{r}, t) + \mathbf{P}(\mathbf{r}, t)$$

**Electric susceptibility**      $\mathbf{P}_e(\mathbf{r}, t) = \chi_e \mathbf{E}(\mathbf{r}, t)$



$$\mathbf{D}_e(\mathbf{r}, t) = (\varepsilon_0 + \chi_e) \mathbf{E}(\mathbf{r}, t) = \varepsilon \mathbf{E}(\mathbf{r}, t)$$

$\varepsilon$  : Dielectric constant (permittivity)

$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$  : Relative dielectric constant

### $\varepsilon_r$ of representative crystals

CaO	11.8	MgO	9.8
SrO	13.3	KBr	4.78
KCl	4.68	KF	6.05
KI	4.94	LiI	11.03
LiCl	11.05	NaCl	5.62

TiO<sub>2</sub> (rutile) //c: 173, in a-b: 89

SnO<sub>2</sub> (rutile) //c: 9.9, in a-b: 14

Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> (25°C) up to 1600

# Representative dielectric crystals

## $\epsilon_r$ of representative crystals

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SrO 13.3

KCl 4.68

KI 4.94

LiCl 11.05

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Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> (25°C)

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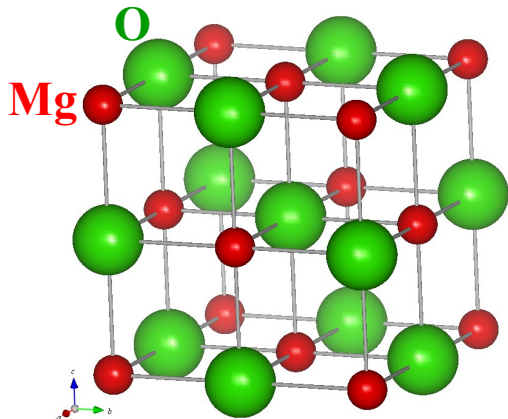
//c: 9.9, in a-b: 14

up to 1600

## General trend (there should be many exceptions)

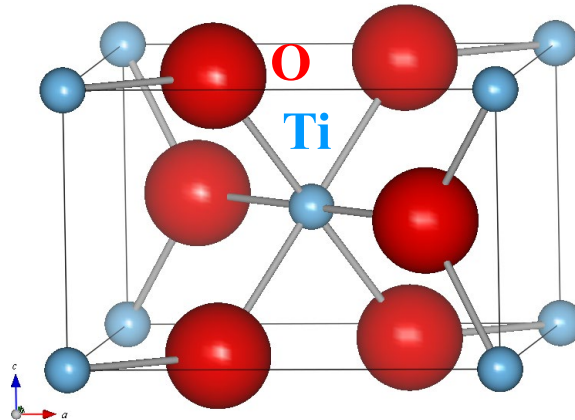
### Rock-salt structure

(usually  $\epsilon_r < 10$ )



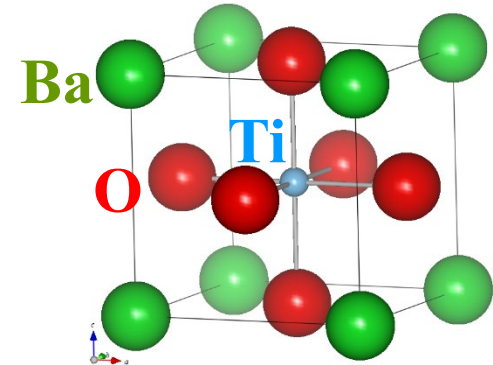
### Rutile structure

TiO<sub>2</sub> have large  $\epsilon_r // c \sim 180$



### Perovskite structure

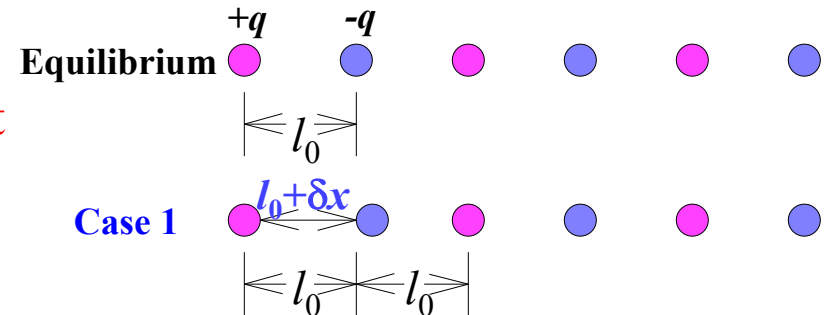
Many extraordinary high  $\epsilon_r > 10^3$   
(anti-)ferroelectrics, piezoelectrics



# Simple model: 1D ionic crystal at 0 K

## Ion polarization

Polarization formed by ion displacement induced by external electric field  $E$ .



## Calculation of ion replacement

Internal energy **without**  $E$ :

$$U_0 = \sum U_{ij}(r_{ij}) = \sum \frac{1}{2} k (x_i - x_{i-1} - l_0)^2$$

$x_i$ : Coordinate of  $i$ -th ion  
 $k$ : Force constant (spring constant)

If ions are displaced by  $E$ , internal energy will be:

$$U = \sum \frac{1}{2} k \{(x_i - x_{i-1} - l_0)\}^2 - \sum q_i x_i E$$

## Mechanical equilibrium condition at 0K

$$\frac{\partial U}{\partial x_j} = 0 = k(x_j - x_{j-1} - l_0) - k(x_{j+1} - x_j - l_0) - q_j E = 2k\delta x_j - q_j E$$

$$\Rightarrow \delta x_j = \frac{q_j}{2k} E$$

# Simple model: 1D ionic crystal at 0 K

Ion displacement  $\delta x_j = \frac{q_j}{2k} E \Rightarrow$  Polarization density  $P$

$$P = \frac{\sum q_j \delta x_j}{2l_0} = \frac{q^2}{4l_0 k} E$$

**Dielectric constant**

$$D = \epsilon E = \epsilon_0 E + P$$

$$\epsilon = \epsilon_0 + \frac{q^2}{4l_0 k} \left( \epsilon_r = 1 + \frac{q^2}{4l_0 k \epsilon_0} \right)$$

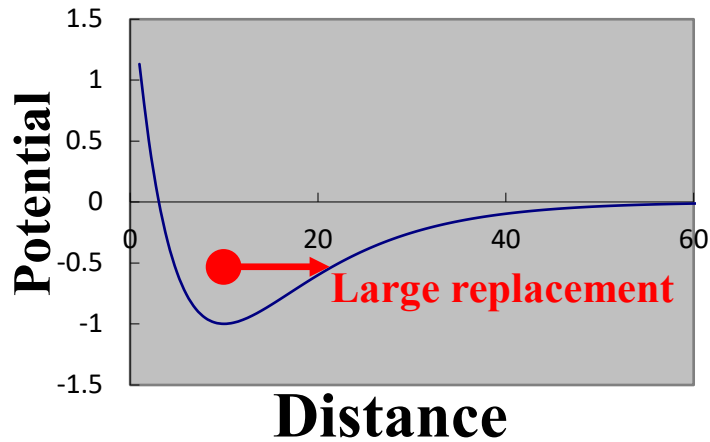
Dielectric constant is determined by  $k$

$k$ : Force constant, or

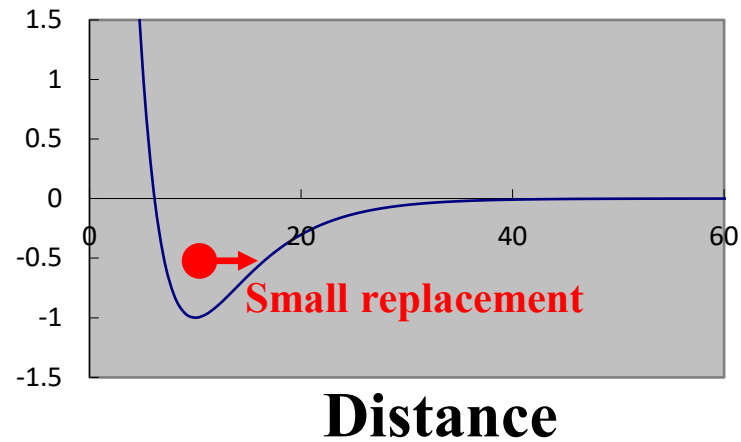
$$\text{Curvature of ion potential } k = \frac{1}{2} \frac{\partial^2 U}{\partial x_i^2}$$

# Dielectric constant vs potential curvature

## Gentle potential



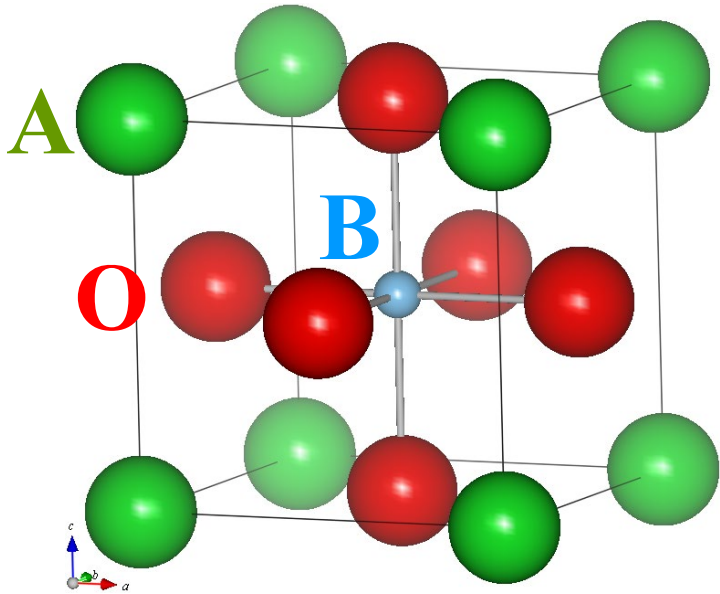
## Sharp potential



$$\epsilon = \epsilon_0 + \frac{q^2}{4l_0k}$$

	Gentle potential	Sharp potential
Potential <b>curvature</b> $k$	<b>Small</b>	Large
Ion displacement	Large	Small
<b>Dielectric constant</b>	<b>Large</b>	Small

# Why perovskite-type crystals exhibit high $\epsilon$ ?



## Structural instability by the sub-lattice structure

Case 1:

Unit cell is stabilized by B-O

A ion is loosely embedded

Case 2:

Unit cell is stabilized by A-O

B ion is loosely embedded

For ideal cubic perovskite structure:

Each ion makes just contact with neighbor ions  
if their ion radii satisfy

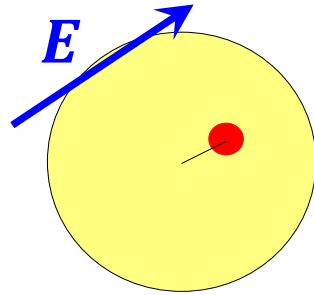
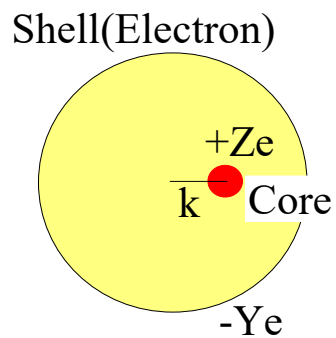
$$a = \sqrt{2}(r_A + r_O) = 2(r_B + r_O)$$

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} = 1.0 \quad \text{**Tolerance factor**}$$

For  $t$  apart from 1.0, the cubic structure  
would be distorted:

$t$	Lattice	Explanation	Example
$>1$	Hexagonal	Large $r_A$ Small $r_B$	BaNiO <sub>3</sub>
0.9-1	Cubic	Ideal contact	SrTiO <sub>3</sub> , BaTiO <sub>3</sub>
0.71 - 0.9	Orthorhombic Rhombohedral	Small $r_A$ in B ion interstitial	GdFeO <sub>3</sub> (Orth.) CaTiO <sub>3</sub> (Orth.)
$<0.71$	Different structures	Small $r_A, r_B$	FeTiO <sub>3</sub> (Tri.)

# How to incorporate electronic polarization: Shell model



+Ze: **Effective core charge** of ion  
-Ye : **Charge of valence electron**  
contribute to polarization  
(electron cloud)  
(Z-Y)e: **Ion charge**

1. Ion is separated to ‘effective core’ and ‘electron cloud’, which are bound by spring with the force constant  $k$ .
2. The core and the electron cloud have their own charges, +Ze and -Ye, respectively.

=> **The electron cloud can be treated as if it is a rigid ion.**  
**The previous 1D model@0K is applied.**

**Electronic polarization of an ion:**  $\alpha_{ion} = \frac{Y^2}{k}$



# Extension to 3D model @ 0 K, non-harmonic interionic potential

Internal energy **without  $E$** :

$$U_0 = \frac{1}{2} \sum_{i,j} U_{ij}(\mathbf{r}_{i0}, \mathbf{r}_{j0}, \dots)$$

$\mathbf{r}_{i0}$ : Equilibrium coordinate of  $i$ -th ion  
 $U_{ij}(\mathbf{r}_k)$ : Interionic potential between  $i$ -th and  $j$ -th ions

If ions are displaced by  $E$ , internal energy will be:

$$\begin{aligned}
 U_{pE} &= U_0(\mathbf{r}_{i0} + \delta\mathbf{r}_i, \dots) - \sum_i q_i \delta\mathbf{r}_i \cdot \mathbf{E} \\
 &= U_0 + \frac{1}{2} \sum_{i,s,j,s'} \frac{\partial^2 U_0}{\partial x_{i,s} \partial x_{j,s'}} \delta x_{i,s} \delta x_{j,s'} - \sum_i q_i \delta\mathbf{r}_i \cdot \mathbf{E} \\
 &= U_0 + \frac{1}{2} \sum_{i,s,j,s'} W_{i,s,j,s'} \delta x_{i,s} \delta x_{j,s'} - \sum_i q_i \delta\mathbf{r}_i \cdot \mathbf{E}
 \end{aligned}$$

$\delta\mathbf{r}_i$ : Ion displacement by  $E$

$\delta x_{i,s}$ :  $s$  direction component ( $s = x, y, z$ ) of  
 $i$ -th ion replacement

$W_{i,s,j,s'} = \frac{\partial^2 U_0}{\partial x_{i,s} \partial x_{j,s'}}$ : Hessian matrix (potential curvature)

# Extension to 3D model @ 0 K, non-harmonic interionic potential

$$U_{pE} = U_0 + \frac{1}{2} \sum_{i,s,j,s'} W_{i,s,j,s'} \delta x_{i,s} \delta x_{j,s'} - \sum_i q_i \delta \mathbf{r}_i \cdot \mathbf{E}$$

**Mechanical equilibrium condition at 0K**

$$\frac{\partial U_{pE}}{\partial x_{i,s}} = 0 = \sum_{j,s'} W_{i,s,j,s'} \delta x_{j,s'} - q_j E_s = 0$$

**Ion displacements are calculated easily by the matrix calculation:**

$$\left( \delta x_{j,s'} \right) = \left( W^{-1}_{i,s,j,s'} \right) \left( q_j E_s \right) \quad (\text{cf. 1D case: } \delta x_j = \frac{q_j}{2k} E)$$

**Dielectric constant tensor  $\epsilon_{ss'}$ ,**

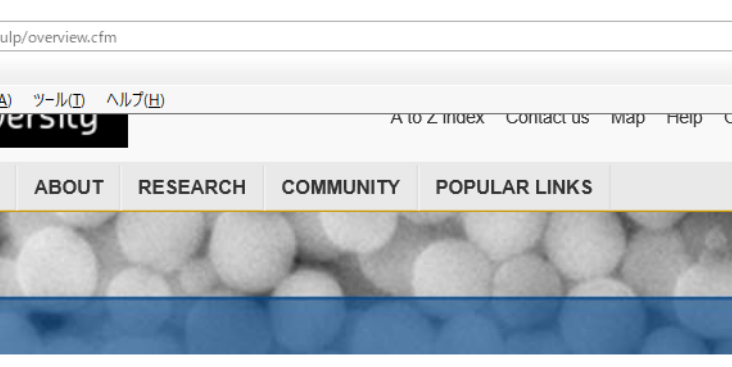
$$\begin{aligned} \mathbf{D} &= \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 \mathbf{E} + \frac{1}{V} \sum_j q_j \delta \mathbf{r}_j \\ &= \epsilon_0 \mathbf{E} + \frac{1}{V} \sum_j q_j \sum_{i,s'} \left( W^{-1}_{i,s',j,s} \right) \left( q_i E_{s'} \right) \end{aligned}$$

$$\epsilon_{ss'} = \epsilon_0 \delta_{ss'} + \frac{1}{V} \sum_{i,j,s'} q_j q_i W^{-1}_{i,s',j,s}$$

$$D_s = \sum_{s'} \epsilon_{ss'} E_{s'} = \sum_{s'} \left( \epsilon_0 \delta_{ss'} + \frac{1}{V} \sum_{i,j,s'} q_j q_i W^{-1}_{i,s',j,s} \right) E_{s'}$$

# Lattice dynamics simulation: GULP - General Utility Lattice Program

<http://gulp.curtin.edu.au/gulp/>

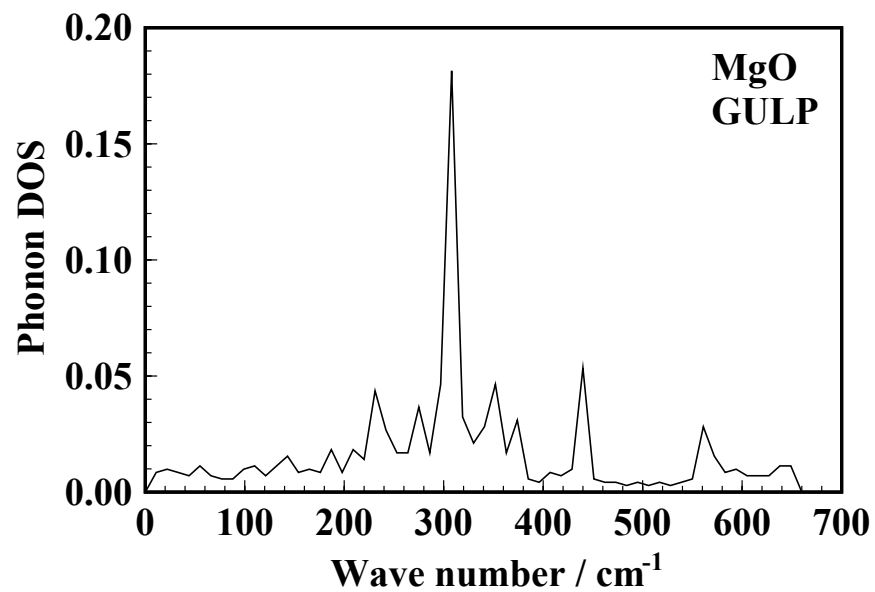
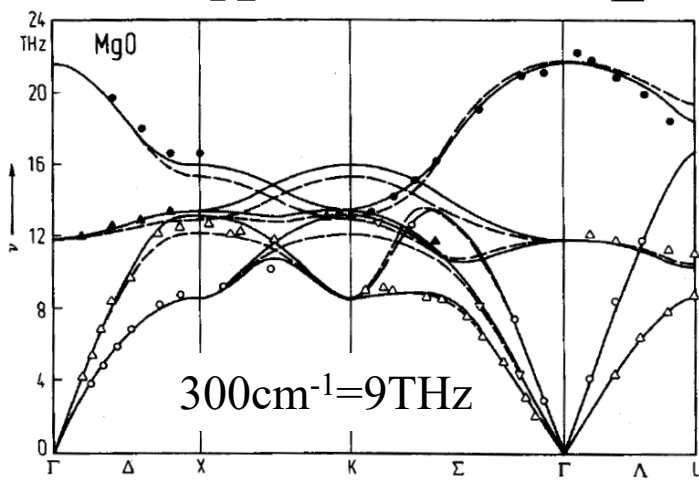
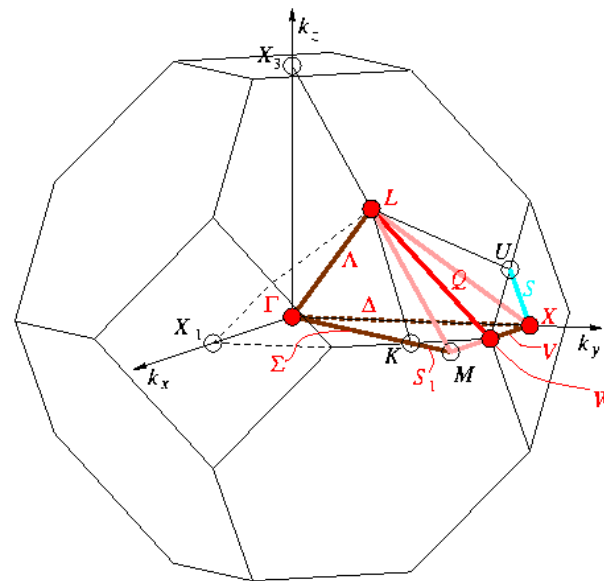
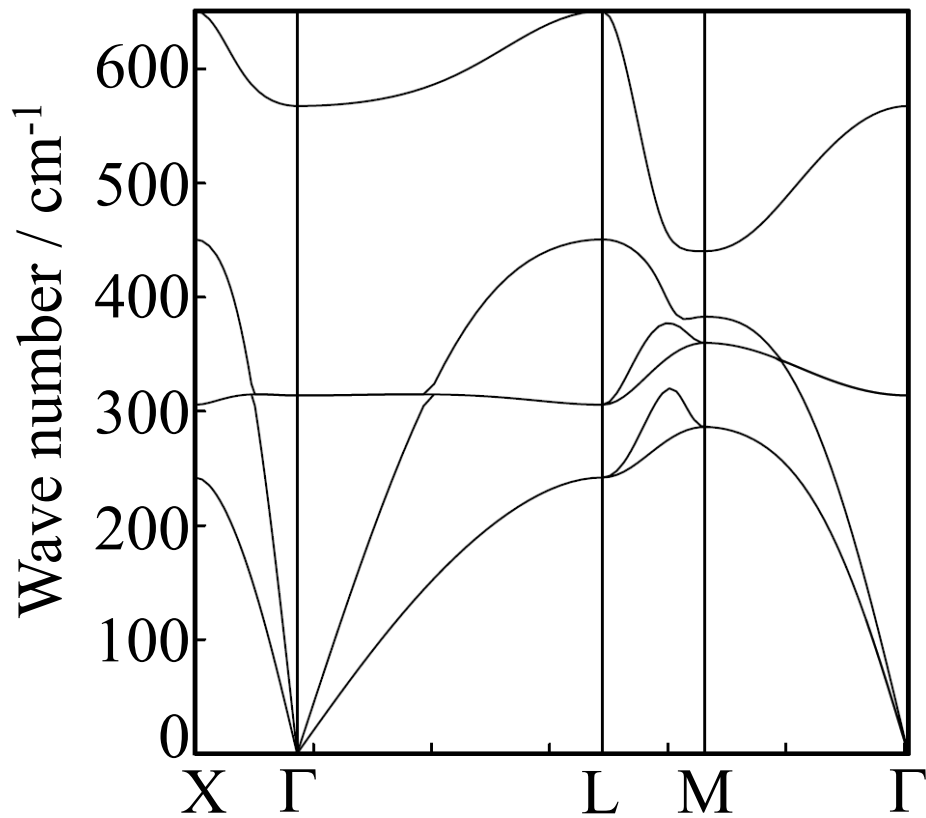


Curtin Home > Science and Engineering > GULP > GULP > Overview of GULP

## Overview of GULP capabilities

- System types
  - clusters (0-D)
  - defects (0-D)
  - polymers (1-D)
  - line defects (1-D)
  - surfaces (2-D)
  - slabs (2-D)
  - grain boundaries (2-D)
  - bulk materials (3-D)
- Energy minimisation
  - constant pressure / volume
  - shell only relaxations (optical)
  - breathing only relaxations
- Crystal properties
  - elastic constants
  - bulk moduli
  - Young's modulus
  - Poisson's ratios
  - shear moduli
  - static dielectric constants
  - high frequency dielectric constants
  - refractive indices
  - piezoelectric constants
  - phonon frequencies
  - non-analytic correction for gamma point modes
  - phonon densities of states
  - projected phonon densities of states
  - phonon dispersion curves
  - Patterson symmetry used in k space
  - zero point vibrational energies
  - entropy (constant volume)
  - heat capacity (constant volume)
  - Helmholtz free energy
  - electrostatic potential
  - electric field
  - electric field gradients
  - Born effective charges
  - frequency dependent dielectric constant tensor
  - reflectivity
  - mean kinetic energy of phonons

# GULP (Phonon)



# Polarization of polar molecules at finite $T$

Polar molecule like HF: H and F are charged with  $+q|e|$  and  $-q|e|$ , respectively, and form **electrical dipole**  $\mathbf{p}_0 = q\mathbf{d}$  ( $d$  is the chemical bond vector).

When  $\mathbf{E}$  is applied along the  $z$  direction and  $\mathbf{p}_0$  is declined from the  $z$  axis by  $\theta$  degree as shown in Fig. 1:

$$U_p = -\mathbf{p}_0 \cdot \mathbf{E} = -p_0 E \cos\theta \quad (5.28)$$

Fig. 1 Dipole in electric field  $\mathbf{E}$

Polarization density  $\mathbf{P}$ :

$$\mathbf{P} = \frac{N}{V} \frac{\int p_0 \cos\theta \cdot \exp(\beta p_0 E \cos\theta) \sin\theta d\theta d\varphi}{\int \exp(\beta p_0 E \cos\theta) \sin\theta d\theta d\varphi}$$

Replace by  $\beta p_0 E = \alpha$  and  $\cos\theta = x$ , and integrate w.r.t.  $\varphi$ :

$$\mathbf{P} = \frac{N}{V} p_0 \frac{\int x \exp(\alpha x) dx}{\int \exp(\alpha x) dx}$$

Partial integration gives  $\int x \exp(\alpha x) dx = \frac{\exp(\alpha x)}{\alpha^2} (\alpha x - 1)$ :

$$\mathbf{P} = \frac{N}{V} p_0 L(\alpha) \quad (5.49)$$

$$L(\alpha) = \coth(\alpha) - \frac{1}{\alpha} \quad \text{Langevin function}$$

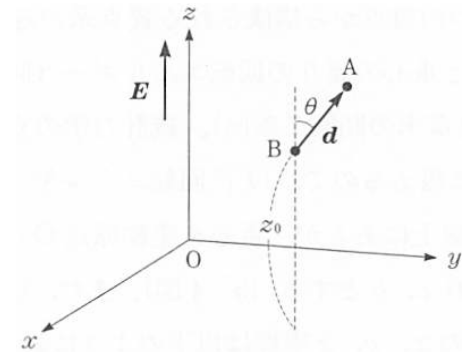
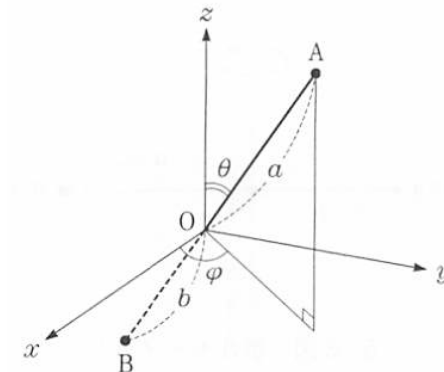


Fig. 2 Polar coordinates



# Polarization of polar molecules at finite $T$

Electrical susceptibility  $\chi$ :  $P = \chi E = \frac{N}{V} p_0 L(\beta p_0 E)$

$L(\alpha) = \coth(\alpha) - \frac{1}{\alpha}$  Langevin function

$$\coth(\alpha) = \frac{e^{\alpha} + e^{-\alpha}}{e^{\alpha} - e^{-\alpha}}$$

$$L(\alpha) \sim \frac{\alpha}{3} - \frac{\alpha^3}{45} + \dots \quad (\alpha = \beta p_0 E \ll 1)$$

$$L(\alpha) \sim 1 \quad (\alpha = \beta p_0 E \gg 1)$$

$\Rightarrow$

Low  $T$  / High  $E$ : asymptotic to  $P \sim \frac{N}{V} p_0$

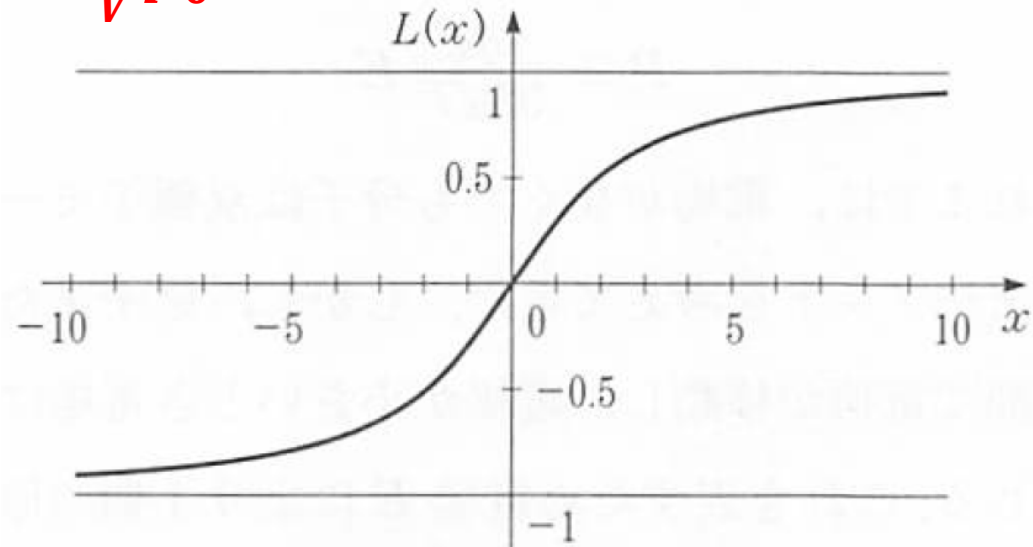
High  $T$  / Low  $E$ :  $\chi \sim \frac{N/V}{3k_B T} p_0^2$

Dielectric constant  $\epsilon$ :

$$\epsilon E = \epsilon_0 E + P$$

$$\epsilon = \epsilon_0 + \frac{N/V}{3k_B T} p_0^2$$

Fig. 3 Langevin function



# Internal macroscopic field is different from external field: Depolarization field

Kittel, *Introduction to Solid State Physics*, 8<sup>th</sup> ed (2005) p. 457

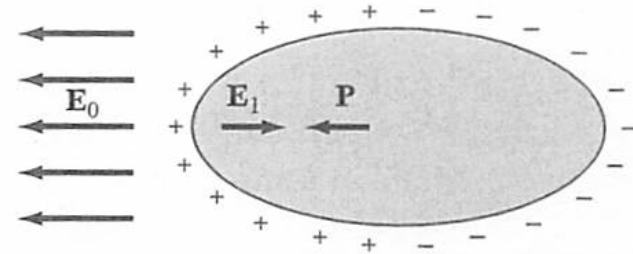
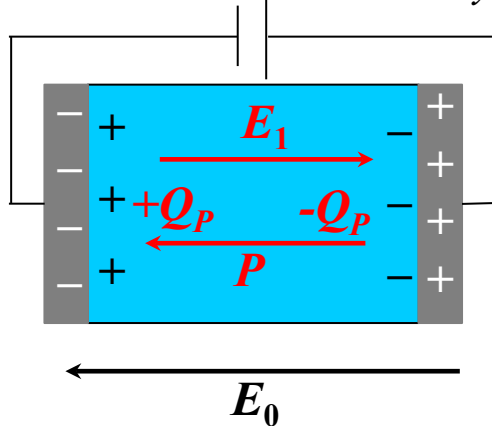


Figure 4 The depolarization field  $E_1$  is opposite to  $\mathbf{P}$ . The fictitious surface charges are indicated: the field of these charges is  $E_1$  within the ellipsoid.

**External field  $E_0$**

**Surface charges are induced from internal polarization  $\sigma = n_{surface} \cdot P = \pm|P| = \chi E_0$**

**forms extra electric field:  $E_1 = -\frac{P}{\epsilon_0}$**

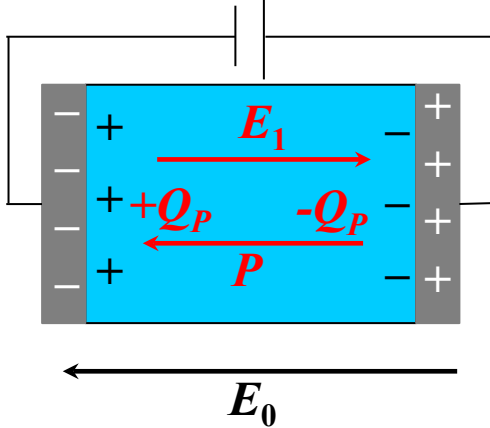
**Internal macroscopic field in the dielectrics:  $E = E_0 + E_1 = E_0 - \frac{P}{\epsilon_0}$**

**General shapes of dielectrics:  $E_{1,s} = -N_s P_s$ ,  $N_s$ : Depolarization factors ( $s = x, y, z$ )**

Shape	Axis	$N$ (CGS)	$N$ (SI)
Sphere	any	$4\pi/3$	$1/3$
Thin slab	normal	$4\pi$	$1$
Thin slab	in plane	$0$	$0$
Long circular cylinder	longitudinal	$0$	$0$
Long circular cylinder	transverse	$2\pi$	$1/2$

# Internal macroscopic field is different from external field: Depolarization field

Kittel, *Introduction to Solid State Physics*, 8<sup>th</sup> ed (2005) p. 459



$\chi$  is defined by internal electric field

$$E = E_0 + E_1 = E_0 - \frac{N}{\epsilon_0} P :$$

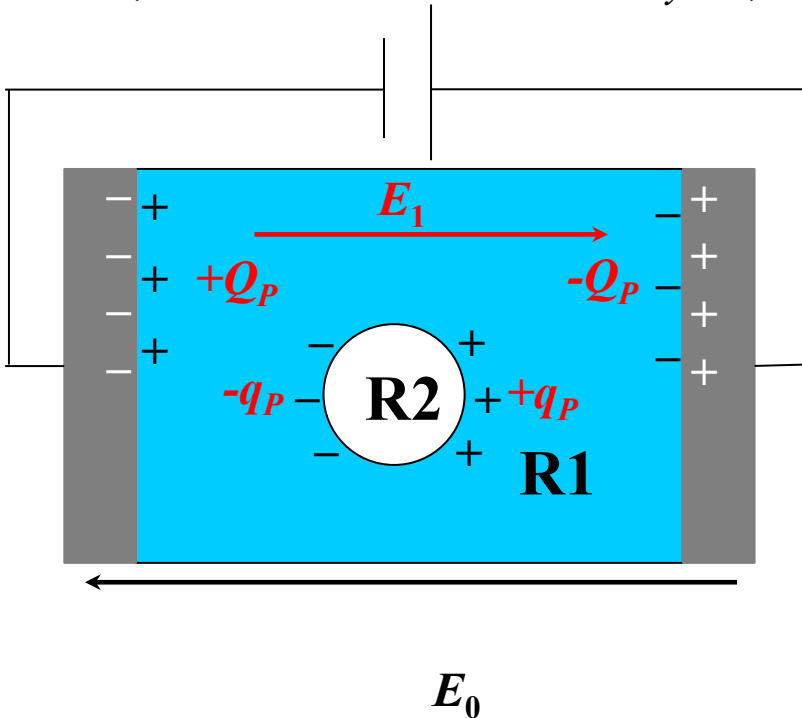
$$P = \epsilon_0 \chi E = \epsilon_0 \chi \left( E_0 - \frac{N}{\epsilon_0} P \right)$$

$$\Rightarrow P = \frac{\epsilon_0 \chi}{1 + N \chi} E_0$$



# Internal electric field at an atomic site: Lorentz field

*Kittel, Introduction to Solid State Physics, 8<sup>th</sup> ed (2005) p. 460*



**R1:** Assume continuous media with  $\epsilon$   
(no charge distribution in R1).

Contribution to  $E_{\text{local}}$  is calculated from  $q_P$ .  
The deformation field in a sphere is

$$E_2 = \frac{1}{3\epsilon_0} P : \text{Lorentz field}$$

**R2:** Contribution to  $E_{\text{local}}$  at the center of  
the sphere is calculated  
by summing up the ion charges in R2.

**For cubic symmetry**

$$E_{\text{local}} = E + \frac{1}{3\epsilon_0} P$$

# Polarizability of an atom $\alpha$

*Kittel, Introduction to Solid State Physics, 8<sup>th</sup> ed (2005) p. 463*

**Polarizability of the atom  $i$  ( $\alpha_i$ ) is defined by the atomic polarization  $p_i$  and the local electric field**

$$E_{\text{local}} = E + \frac{1}{3\epsilon_0} P$$

$$p_i = \alpha_i E_{\text{local}}(r_i)$$

**Assume the atomic polarization is independent from each other.**

$$\begin{aligned} P &= \sum_i N_i \alpha_i E_{\text{local}}(r_i) \\ &= \sum_i N_i \alpha_i \left( E + \frac{1}{3\epsilon_0} P \right) \end{aligned}$$

$$\epsilon_0 \chi = \frac{P}{E} = \frac{\sum_i N_i \alpha_i}{1 - \frac{1}{3\epsilon_0} \sum_i N_i \alpha_i}$$

**Using  $\epsilon_r = 1 + \chi$**

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} \sum_i N_i \alpha_i \quad \text{Clausius-Mossotti relation}$$

# Simple model of electronic polarizability

*Kittel, Introduction to Solid State Physics, 8<sup>th</sup> ed (2005) p. 464*

**Table 1 Electronic polarizabilities of atoms and ions, in  $10^{-24} \text{ cm}^3$**

			He	Li <sup>+</sup>	Be <sup>2+</sup>	B <sup>3+</sup>	C <sup>4+</sup>
Pauling			0.201	0.029	0.008	0.003	0.0013
JS				0.029			
	O <sup>2-</sup>	F <sup>-</sup>	Ne	Na <sup>+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	Si <sup>4+</sup>
Pauling	3.88	1.04	0.390	0.179	0.094	0.052	0.0165
JS-(TKS)	(2.4)	0.858		0.290			
	S <sup>2-</sup>	Cl <sup>-</sup>	Ar	K <sup>+</sup>	Ca <sup>2+</sup>	Se <sup>3+</sup>	Ti <sup>4+</sup>
Pauling	10.2	3.66	1.62	0.83	0.47	0.286	0.185
JS-(TKS)	(5.5)	2.947		1.133	(1.1)		(0.19)
	Se <sup>2-</sup>	Br <sup>-</sup>	Kr	Rb <sup>+</sup>	Sr <sup>2+</sup>	Y <sup>3+</sup>	Zr <sup>4+</sup>
Pauling	10.5	4.77	2.46	1.40	0.86	0.55	0.37
JS-(TKS)	(7.)	4.091		1.679	(1.6)		
	Te <sup>2-</sup>	I <sup>-</sup>	Xe	Cs <sup>+</sup>	Ba <sup>2+</sup>	La <sup>3+</sup>	Ce <sup>4+</sup>
Pauling	14.0	7.10	3.99	2.42	1.55	1.04	0.73
JS-(TKS)	(9.)	6.116		2.743	(2.5)		

Values from L. Pauling, Proc. R. Soc. London **A114**, 181 (1927); S. S. Jaswal and T. P. Sharma, J. Phys. Chem. Solids **34**, 509 (1973); and J. Tessman, A. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953). The TKS polarizabilities are at the frequency of the D lines of sodium. The values are in CGS; to convert to SI, multiply by  $9 \times 10^{-15}$ .

# Electronic polarizability

*Kittel, Introduction to Solid State Physics, 8<sup>th</sup> ed (2005) p. 464*

Total polarizability may be separated into (i) **electronic**, (ii) **ionic**, and (iii) **dipolar / interfacial** parts.

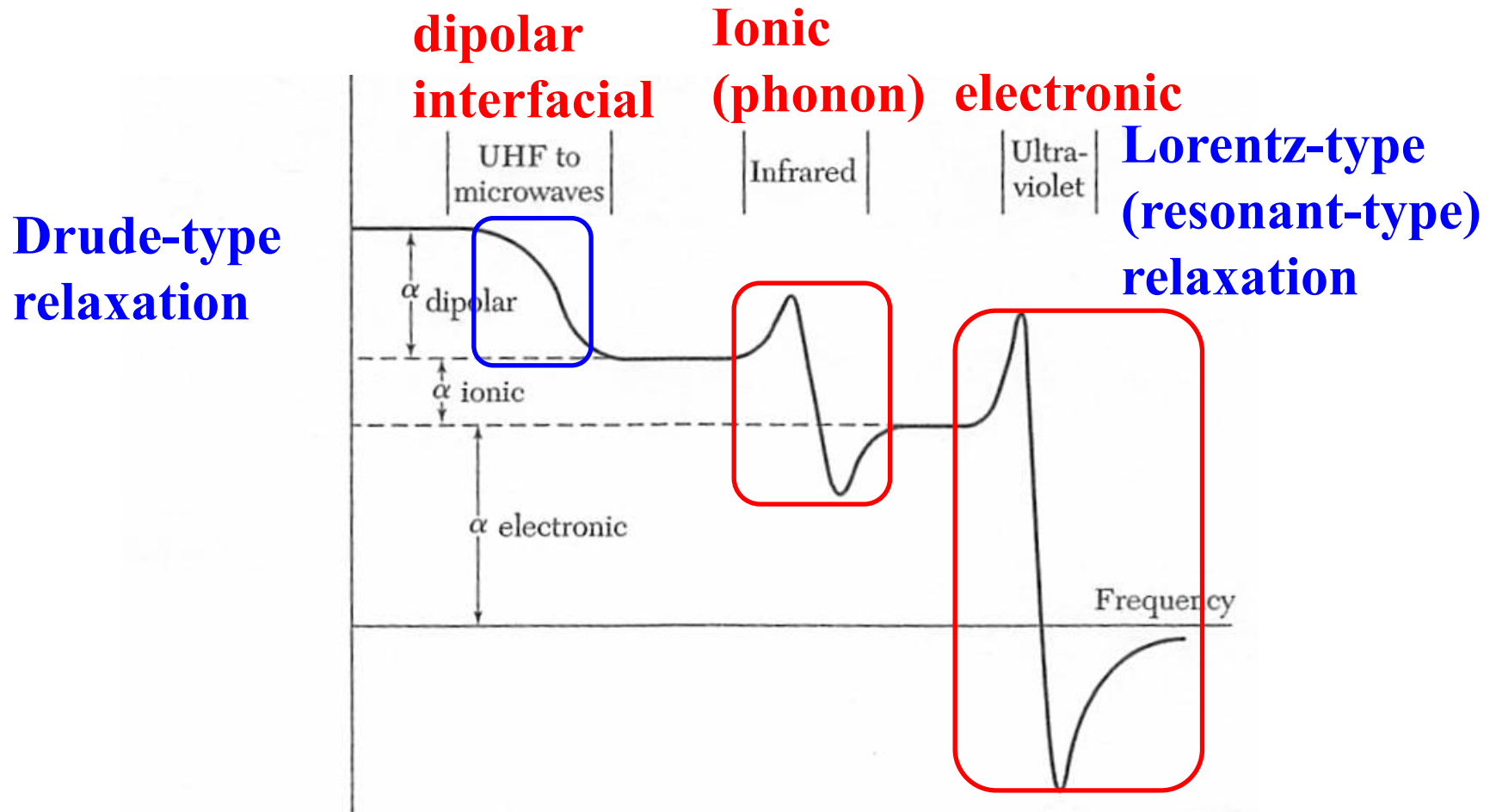
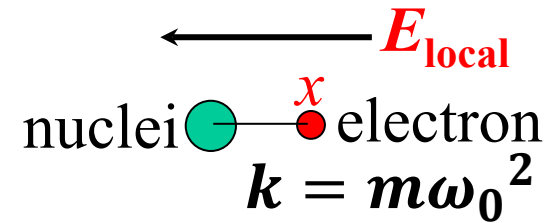


Figure 8 Frequency dependence of the several contributions to the polarizability.

# Frequency dependence: Lorentz model

Kittel, *Introduction to Solid State Physics*, 8<sup>th</sup> ed (2005) p. 466

**Shell model:** Electron bound by spring constant  $k$



**Classical mechanics approximation**

$$-eE_{\text{local}} = kx = m\omega_0^2 x$$

**Electronic polarizability**

$$\alpha = \frac{p}{E_{\text{local}}} = -ex/E_{\text{local}} = e^2/m\omega_0^2$$

**Frequency dependence:**  $E_{\text{local}} = E_0 e^{i\omega t}$

$$\alpha = \frac{e^2/m}{\omega_0^2 - \omega^2}$$

**The same expression is obtained by quantum theory**

$$\alpha = \frac{e^2}{m} \sum_{i,j} \frac{f_{ij}}{\omega_{ij}^2 - \omega^2}$$

$\omega_{ij}$ : Transition energy from  $I$  to  $j$  states  
 $f_{ij}$ : Oscillator strength

**Generalized to ion displacement polarization**

# Lorentz model and Drude model

**Lorentz model** is derived from  $-eE_{\text{local}} = kx = m\omega_0^2 x$ :

**The recovery force  $kx$  results in the resonant-type relaxation with the relaxation frequency  $\omega_0$ .**

$\alpha = \frac{e^2/m}{\omega_0^2 - \omega^2}$ : Applied to **electronic polarization** in atom,  
**ionic polarization (phonon)**

**For the case of no recovery form, but charge distribution also forms recovery force => Non-resonant-type relaxation: Drude model**

$$\epsilon_{1,Drude}(\omega) = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \quad \epsilon_{2,Drude}(\omega) = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)}$$

$$\omega_p = \sqrt{\frac{e^2 N_{\text{free}}}{\epsilon_\infty \epsilon_0 m_e^*}} \quad \text{Plasma frequency}$$

Applied to **free carrier polarization**,  
**dipolar interfacial polarization**

# Lyddane–Sachs–Teller relation

Kittel, *Introduction to Solid State Physics*, 8<sup>th</sup> ed (2005) p. 414

中村輝太郎 編著、強誘電体構造相転移 (裳華房, 1988)

## Lyddane–Sachs–Teller (LST) relation

$$\frac{\epsilon}{\epsilon_{\infty}} = \frac{\omega_{LO}^2}{\omega_{TO}^2}$$

## Lyddane–Sachs–Teller–Kurosawa (LSTK) relation

$$\frac{\epsilon(\omega)}{\epsilon_{\infty}(\omega)} = \prod \frac{\omega_{LO,i}^2 - \omega^2}{\omega_{TO,i}^2 - \omega^2}$$

$\omega_{TO}$ : Resonance frequency of transversal phonon  
Polarization formed by phonon is  
**macroscopically zero.**

$\omega_{LO}$ : Resonance frequency of longitudinal phonon  
Polarization formed by phonon gives  
recovery force to phonon: Higher than  $\omega_{TO}$

At  $\omega_{LO,i}$ :  $\epsilon(\omega) = 0$

At  $\omega_{TO,i}$ :  $\epsilon_{\infty}(\omega) = 0$

## Possible to estimate $\epsilon$ from **infrared / Raman spectrum**

	NaI	KBr	GaAs
$\omega_L/\omega_T$	$1.44 \pm 0.05$	$1.39 \pm 0.02$	$1.07 \pm 0.02$
$[\epsilon(0)/\epsilon(\infty)]^{1/2}$	$1.45 \pm 0.03$	$1.38 \pm 0.03$	1.08

# Dielectric constant and Born effective charge

上江洲由晃 緒、強誘電体 (内田老鶴園)

**Polarization change  $\Delta P$  is related to ion displacement  $\Delta u_i$ .**

- One may use formal ion charges or calculated ion charges to calculate the dielectric constant.
- This may work satisfactory for low  $\epsilon$  materials.
- **For high  $\epsilon$  materials, the  $\epsilon$  value calculated from those ion charges would very often underestimated**

**Ion charges inversely calculated from dielectric tensor and ion displacements**

$$\Delta P = \frac{e}{V} \sum Z^*_i \Delta u_i$$

**$Z^*_i$ : Born effective charge** (tensor in general case  $Z^*_{i,ss'} = \frac{V}{e} \frac{\partial P}{\partial \Delta u_{i,s'}}$ )

- **Agree well with usual ion charge for low  $\epsilon$  materials**
- **Extraordinary large for high  $\epsilon$  materials**
  - <= Redistribution of electron and its polarization are not negligible for some materials



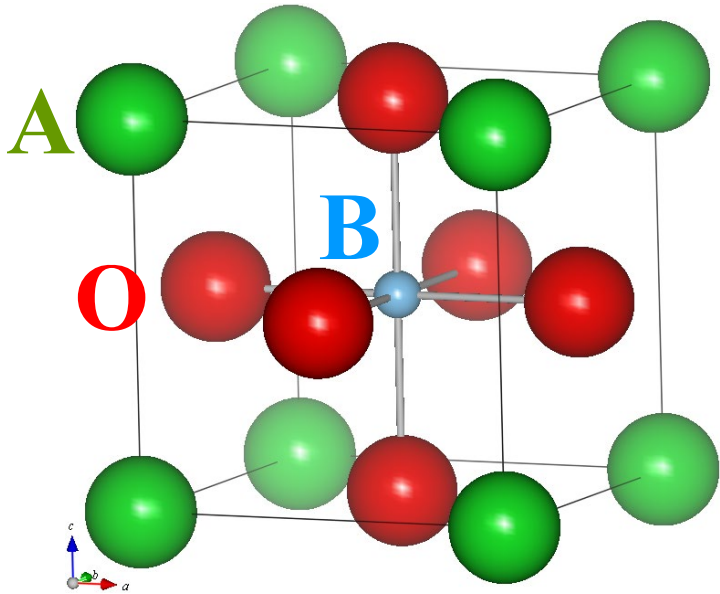
# Dielectric constant and Born effective charge

上江洲由晃 緒、強誘電体 (内田老鶴園)

$ABO_3$	$Z_A^*$	$Z_B^*$	$Z_{O(1)}^*$	$Z_{O(2)}^*$
Formal charge	+2	+4	-2	-2
CaTiO <sub>3</sub>	2.58	7.08	-5.65	-2
SrTiO <sub>3</sub>	2.56	7.26	-5.73	-2.15
	2.54	7.12	-5.66	-2.00
	2.55	7.56	-5.92	-2.12
BaTiO <sub>3</sub>	2.77	7.25	-5.71	-2.15
	2.75	7.16	-5.69	-2.11
	2.61	5.88	-4.43	-2.03
BaZrO <sub>3</sub>	2.73	6.03	-4.74	-2.01
PbTiO <sub>3</sub>	3.90	7.06	-5.83	-2.56
PbZrO <sub>3</sub>	3.92	5.85	-4.81	-2.48

For perovskite crystals, the B and O(1) have large Born effective charges: **Effect of electron transfer between B and O(1)**

# Why perovskite-type crystals exhibit high $\epsilon$ ?



## Structural instability by the sub-lattice structure

Case 1:

Unit cell is stabilized by B-O

A ion is loosely embedded

Case 2:

Unit cell is stabilized by A-O

B ion is loosely embedded

For ideal cubic perovskite structure:

Each ion makes just contact with neighbor ions  
if their ion radii satisfy

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

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} = 1.0 \quad \text{Tolerance factor}$$

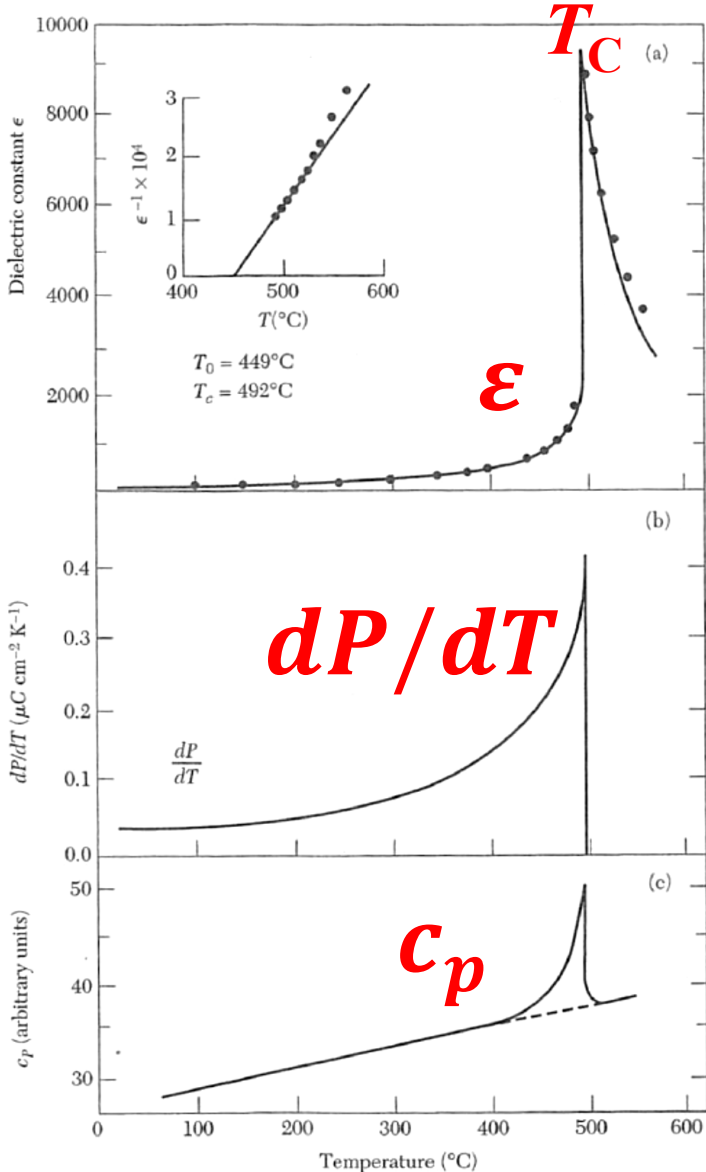
For  $t$  apart from 1.0, the cubic structure  
would be distorted:

$t$	Lattice	Explanation	Example
$>1$	Hexagonal	Large $r_A$ Small $r_B$	BaNiO <sub>3</sub>
0.9-1	Cubic	Ideal contact	SrTiO <sub>3</sub> , BaTiO <sub>3</sub>
0.71 - 0.9	Orthorhombic Rhomboidal	Small $r_A$ in B ion interstitial	GdFeO <sub>3</sub> (Orth.) CaTiO <sub>3</sub> (Orth.)
$<0.71$	Different structures	Small $r_A, r_B$	FeTiO <sub>3</sub> (Tri.)

# Ferroelectrics

Kittel, Introduction to Solid State Physics, 8<sup>th</sup> ed (2005) p. 467

## Temperature dependences for PbTiO<sub>3</sub>



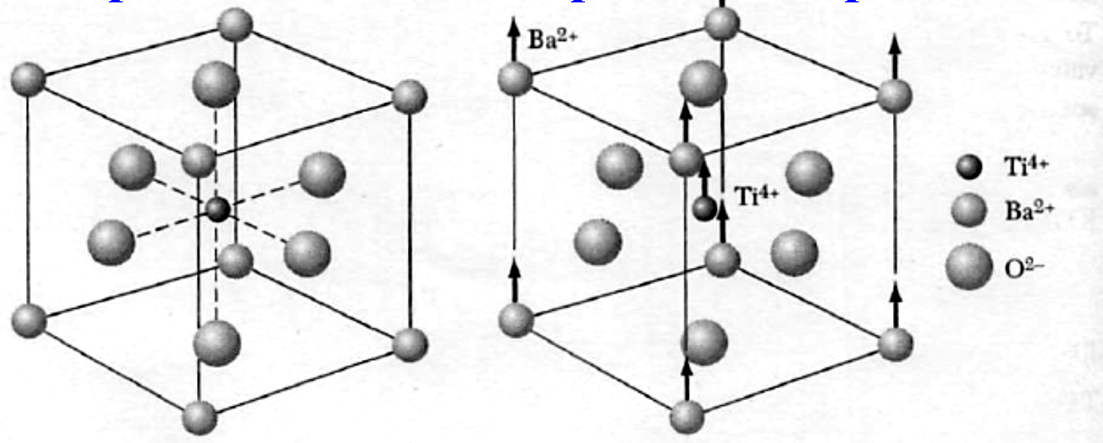
$\epsilon$  diverges and discontinuously changes at the transition temperature (Curie temperature)  $T_C$ , like  $\lambda$ :

**$\lambda$  transition**

**Feature of first order phase transition**

$T > T_C$   
Cubic structure  
No spontaneous polarization

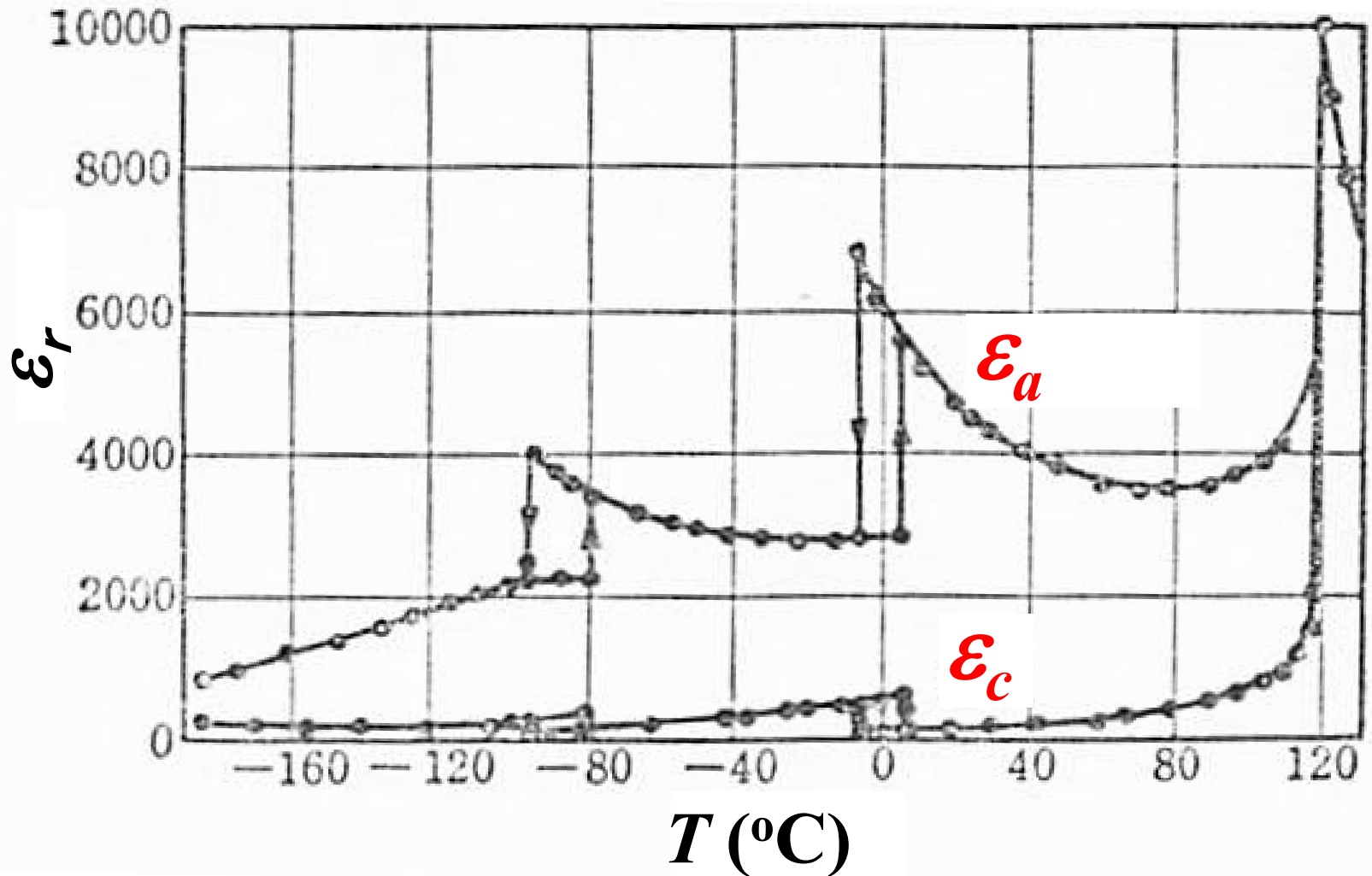
$T < T_C$  stabilizes ions displaced and lattice distorted  
 $\Rightarrow$  Spontaneous polarization



# Ferroelectrics: BaTiO<sub>3</sub>

Kittel, *Introduction to Solid State Physics*, 8<sup>th</sup> ed (2005) p. 471

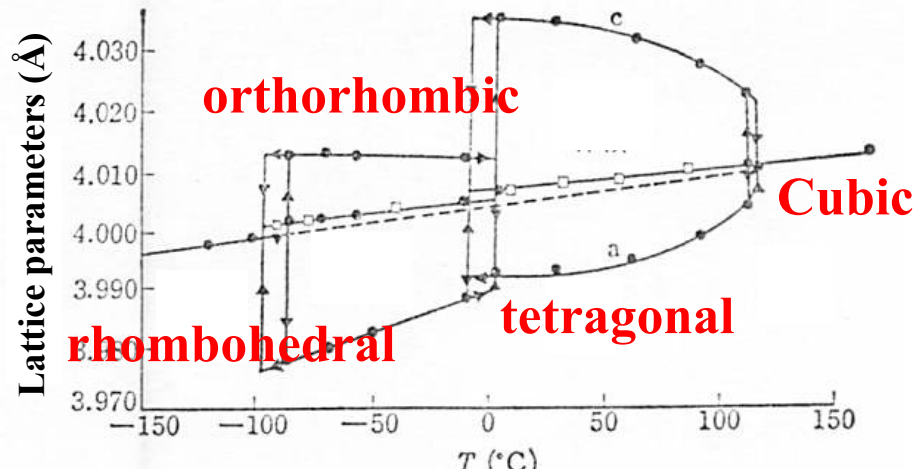
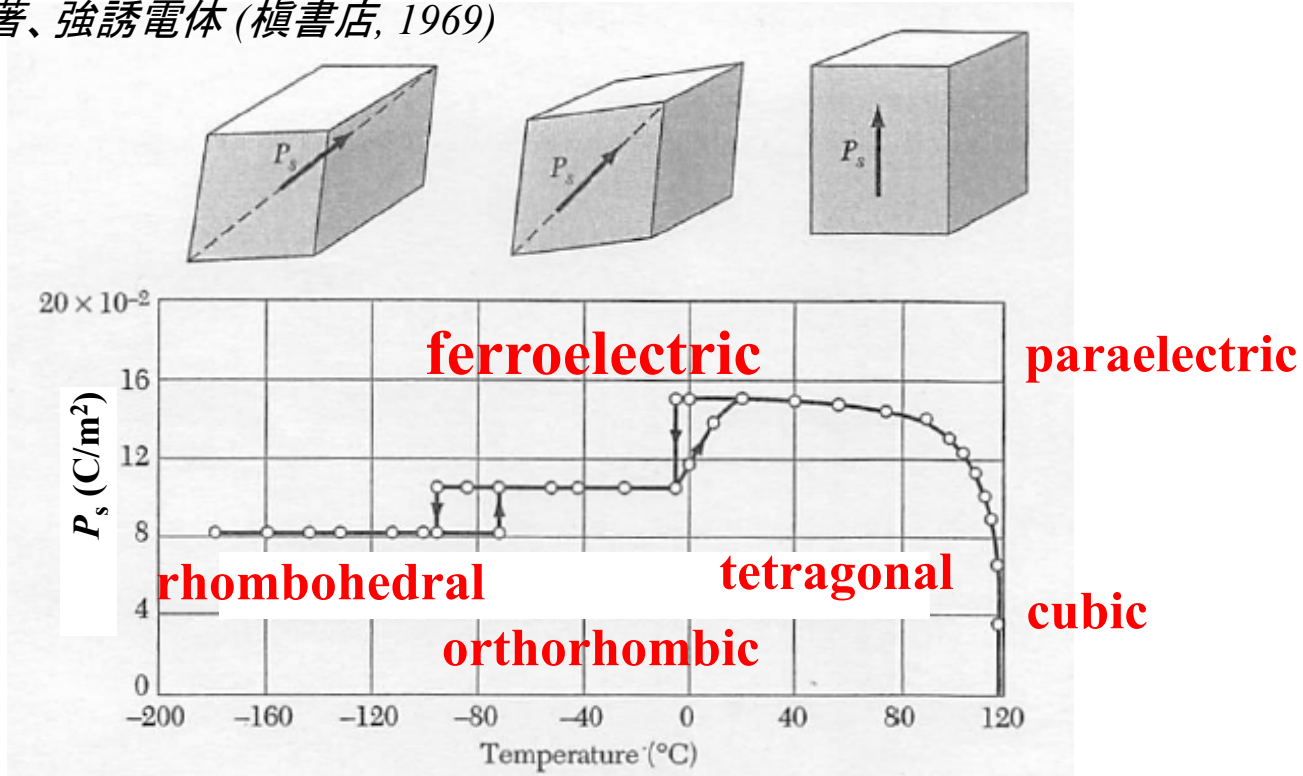
三井利夫 編著、強誘電体 (槓書店, 1969)



# Sequential phase transition of BaTiO<sub>3</sub>

Kittel, *Introduction to Solid State Physics*, 8<sup>th</sup> ed (2005) p. 471

三井利夫 編著、強誘電体 (槇書店, 1969)



# Two types of ferroelectricity

強誘電体物理入門

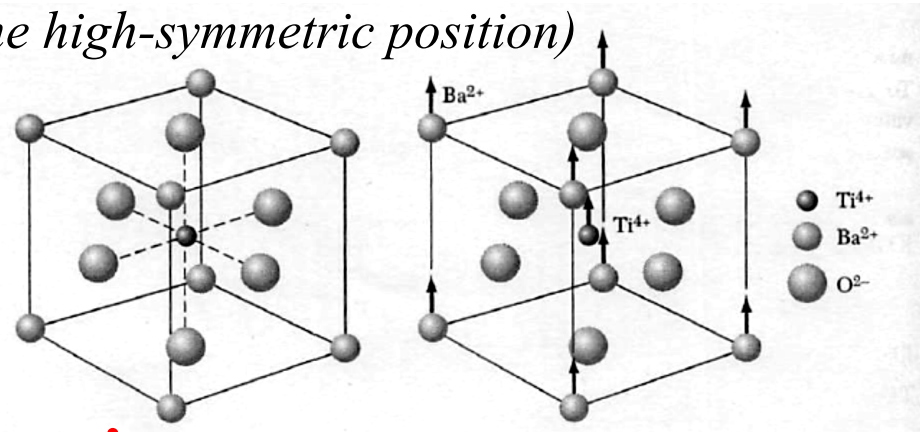
## Displacement type ferroelectric

Small displacement of ions from  $P_s$

(Ions are bound by recovery force to the high-symmetry position)

Perovskite type crystals

$\text{BaTiO}_3$ ,  $\text{Pb}(\text{Zr,Ti})\text{O}_3$

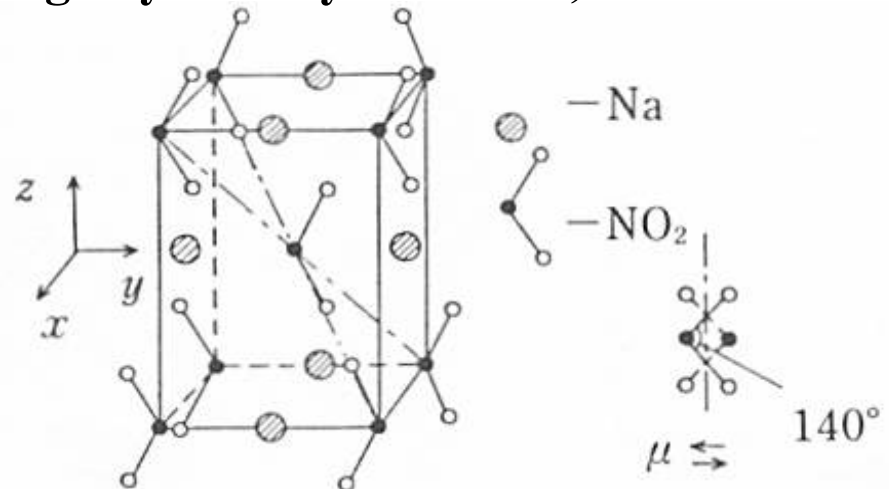


## Order-disorder type ferroelectric

Ions find different stable positions in high-symmetry structure, hop to another site in a long distance

$\text{NaNO}_2$  :  $\text{NO}_2$  group

$\text{KDP} (\text{KH}_2\text{PO}_4)$ :  $\text{H}^+$



# Classification of ferroelectrics related phases

## Dielectrics:

**Symmetry:** any

**Spontaneous polarization:** not necessary

## Piezoelectrics:

**Stress induces surface charges (voltage) / Voltage induces strain**

**Symmetry:** non-centrosymmetric

**Spontaneous polarization:** not necessary (e.g., Wurtzite-type GaAs)

**21 Space groups:** 1, 2, m, 222, mm2, 4, -4, 422, 4mm, -42m, 3, 32, 3m, 6, -6, 622, 6mm, -62m, 23, -43m, 432

## Pyroelectrics:

**Temperature change induces spontaneous polarization change and surface charge change**

**Symmetry:** non-centrosymmetric & polar

**Spontaneous polarization:** necessary

**10 Space groups:** 1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6mm

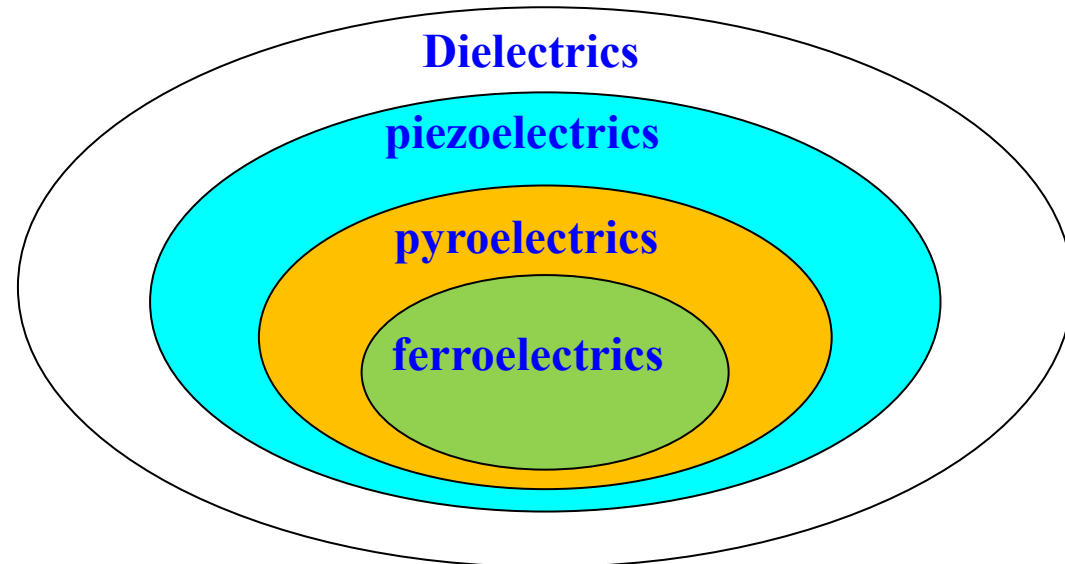
## Ferroelectrics:

**polarization is flipped by external electric field**

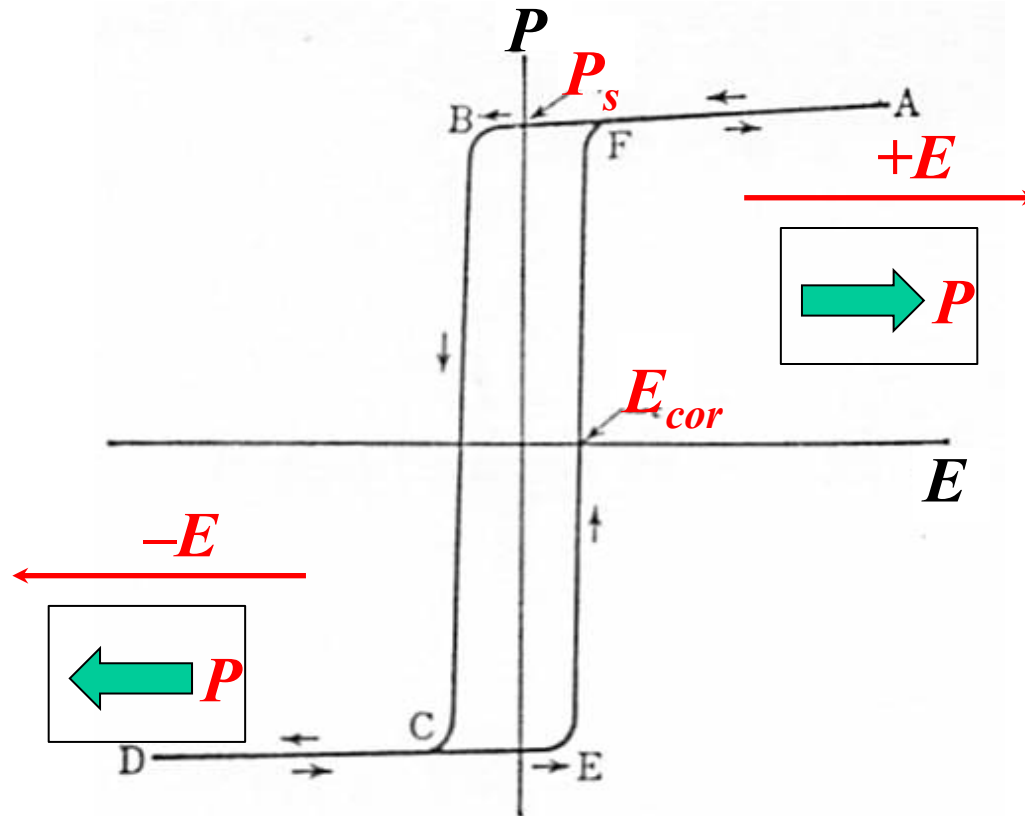
**Symmetry:** non-centrosymmetric & polar

**Spontaneous polarization:** necessary

**10 Space groups:** 1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6mm



# Feature of ferroelectrics: $D - E / P - E$ hysteresis loop



$P_s$  : Spontaneous polarization  
 $E_{cor}$  : Coercive electric field



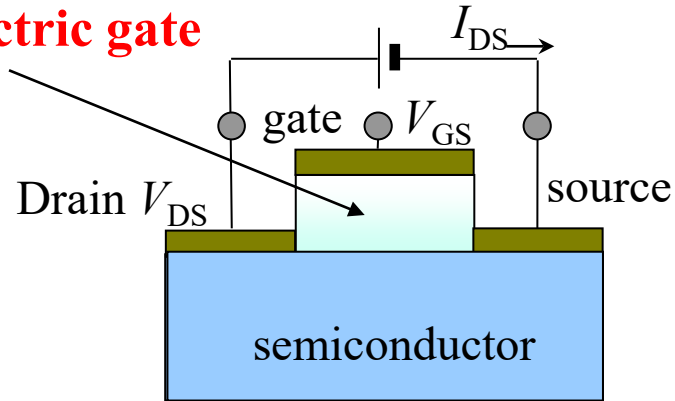
# Application of ferroelectrics

## FeRAM (Ferroelectric RAM)

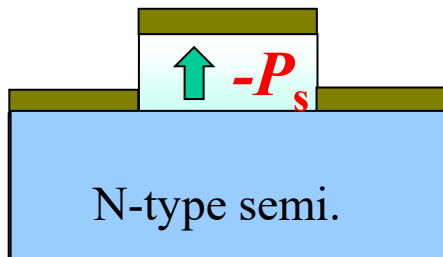
- Gate dielectric in conventional FET is replaced with ferroelectrics
- Spontaneous polarization  $P_s$  retains if gate voltage  $V_{GS}$  is off

=> **Non-volatile memory**

**Ferroelectric gate**



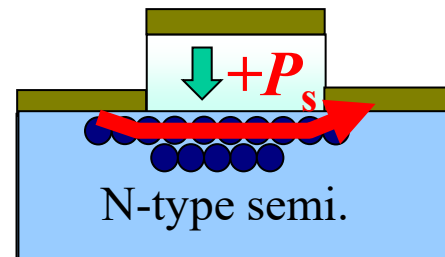
**Memory state “0”**



$-P_s$  induces positive charge at the insulator-semiconductor interface, but n-type semi does not induce mobile carriers

=> **FET is “Off” state**

**Memory state “1”**



$-P_s$  induces positive charge at the insulator-semiconductor interface, but n-type semi does not induce mobile carriers

=> **FET is “On” state**

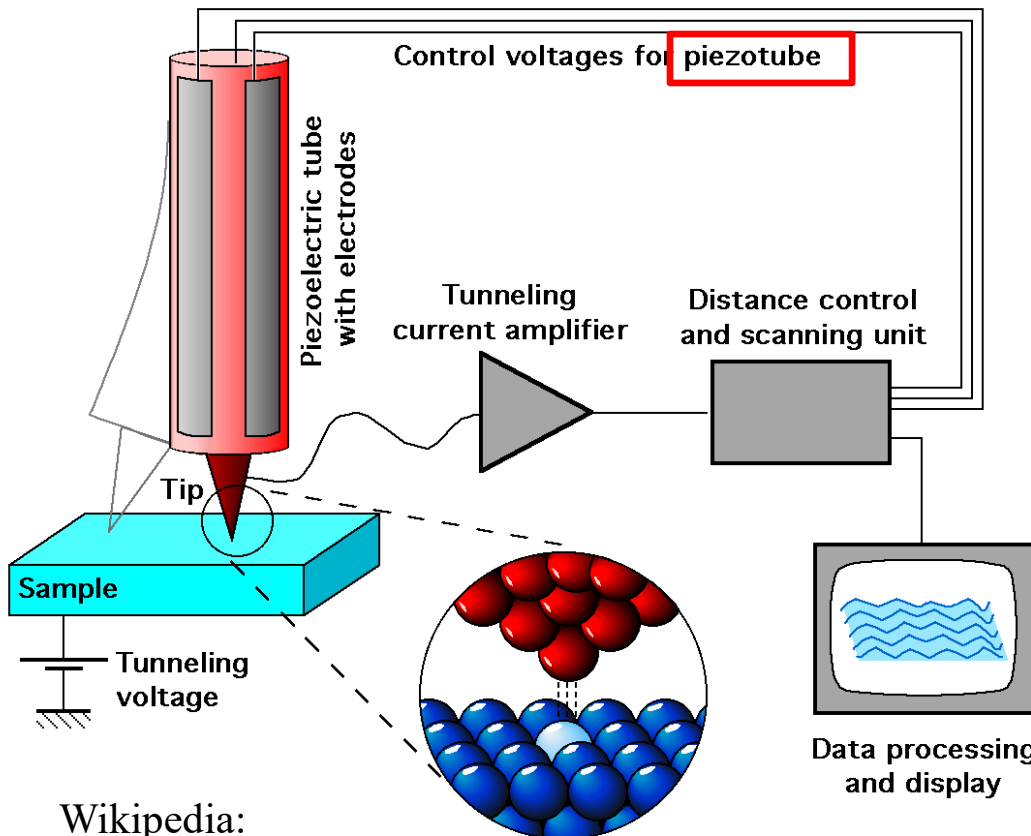
# Applications of piezoelectrics

## Scanning Probe Microscope (SPM)

- Atomic Force Microscope (AFM)
- Scanning Tunneling Microscope (STM)

piezoelectrics is used as **piezoactuator**

Fast response, atomic-order precision



$$\text{PZT: } d_{33} = 400 \times 10^{-12} \text{ m/V}$$

$$\sigma_{33} = \Delta l / l = d_{33} E$$

$$\text{For } V = 100 \text{ V, } l = 1 \text{ cm,}$$

$$\sigma_{33} = d_{33} E = 400 \times 10^{-8}$$

$$\Delta l = 400 \text{ \AA}$$

$$\text{For } V = 0.1 \text{ V}$$

$$\Delta l = 0.4 \text{ \AA}$$

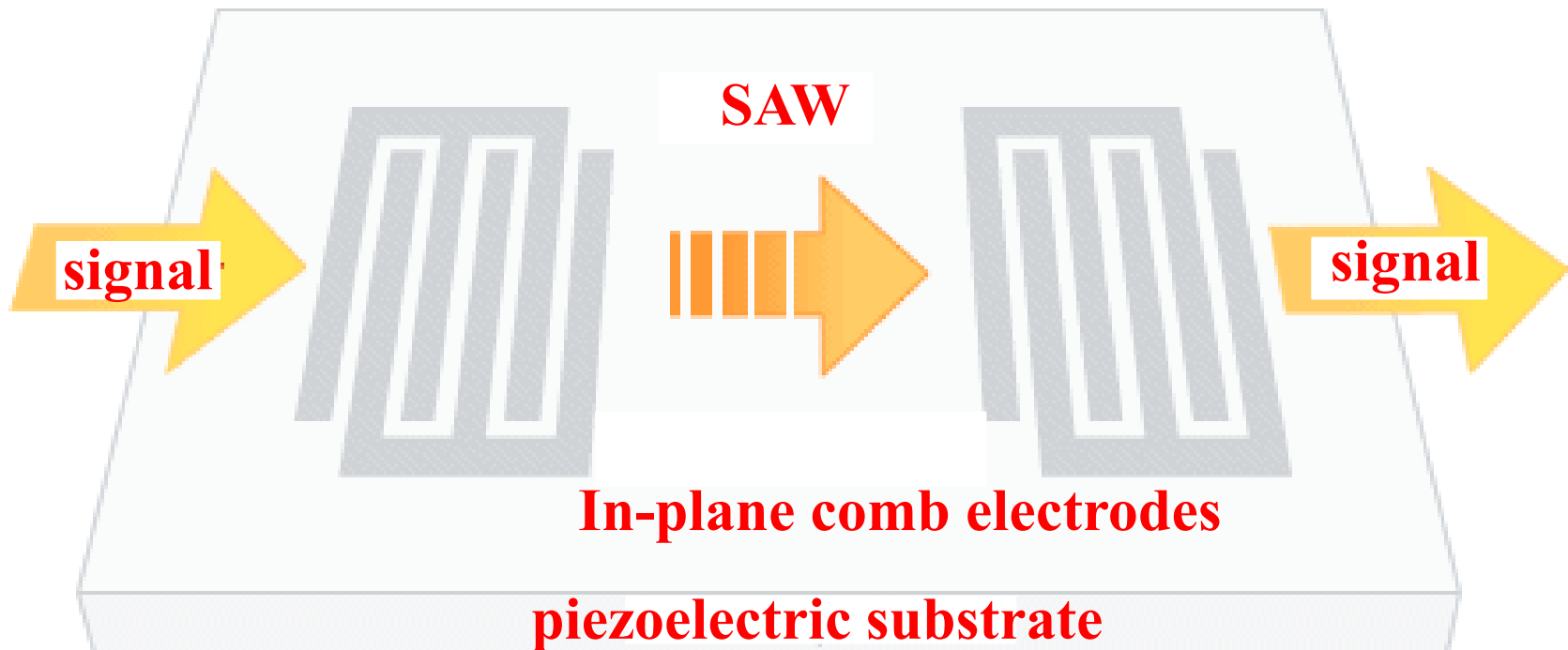
Wikipedia:

<https://ja.wikipedia.org/wiki/%E8%B5%B0%E6%9F%BB%E5%9E%8B%E3%83%88%E3%83%B3%E3%83%8D%E3%83%AB%E9%A1%95%E5%BE%AE%E9%8F%A1>

# Applications of piezoelectrics

## Surface Acoustic Wave (SAW) filter

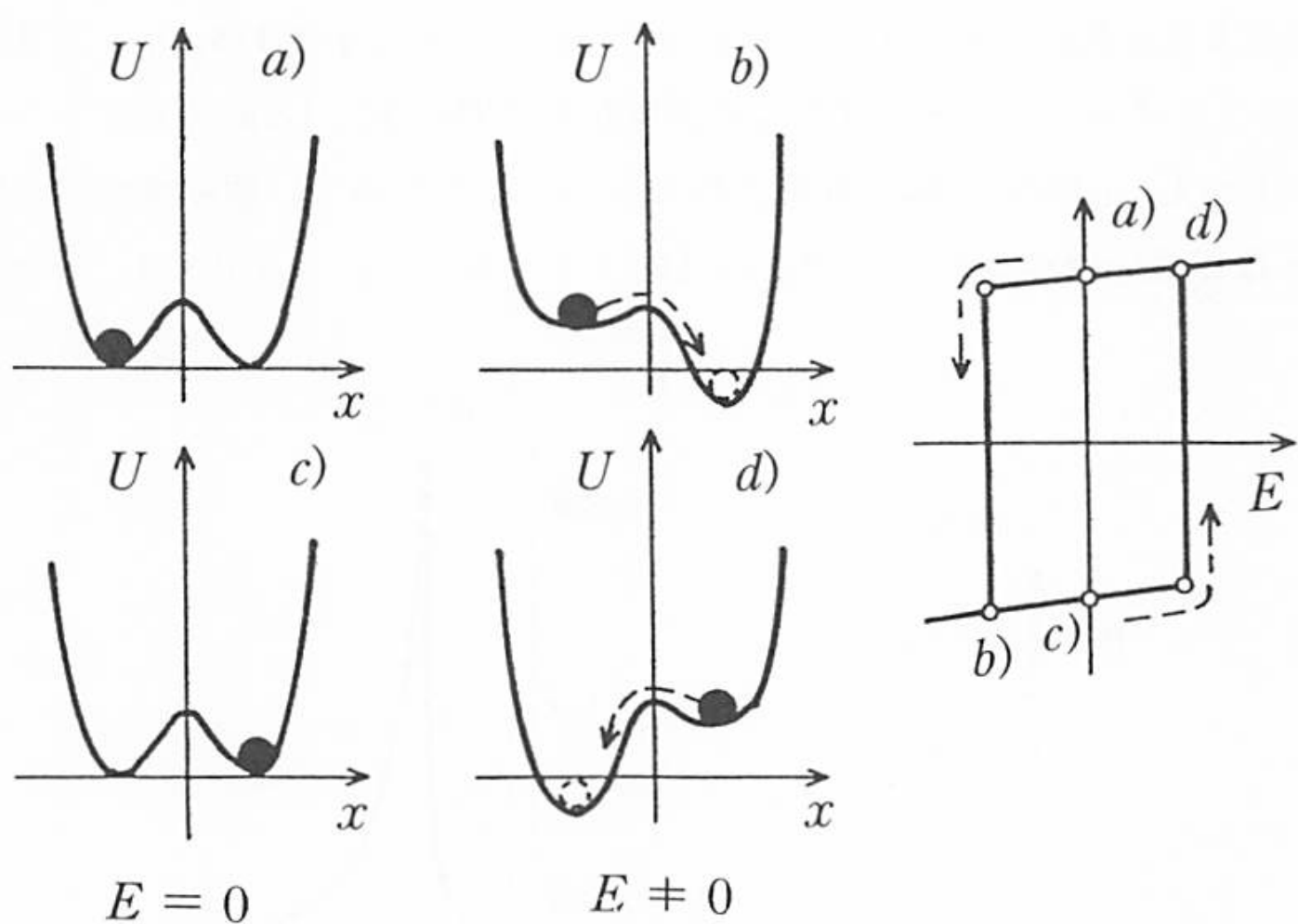
- Surface acoustic wave is induced by piezoelectrics
- SAW is resonant with the piezoelectric body at the frequency  $f_r$   
=> **Transmit signals with  $f < f_r$**
- $f_r$ : up to several GHz, used e.g. in mobile phones



<https://www.murata.com/ja-jp/group/kanazawamura/products/device/saw>

# Spontaneous polarization and double-well potential

疋田朋幸 訳 (B.A. Strykob, A.P. Rebaniok)、強誘電体物理入門 (吉岡書店, 1993)



# 4π/3 catastrophe:

## Slater theory of ferroelectricity

Kittel, *Introduction to Solid State Physics*, 8<sup>th</sup> ed (2005) p. 471

中村輝太郎 編著、強誘電体と構造相転移 (裳華房、1988)

$$\epsilon_0 \chi = \frac{\sum_i N_i \alpha_i}{1 - \frac{1}{3\epsilon_0} \sum_i N_i \alpha_i}$$

For single-type atom system

$$\epsilon_0 \chi = \frac{N\alpha}{1 - \frac{1}{3\epsilon_0} N\alpha}$$

If  $N\alpha$  has a temperature dependence  $\frac{1}{N\alpha} = \frac{T}{C}$

$$\epsilon_0 \chi = \frac{C}{T - C \frac{1}{3\epsilon_0}} \quad \text{Curie-Weiss law}$$

The local field  $E_{\text{local}}$  formed by  $N\alpha E_{\text{local}}$  increases  $N\alpha E_{\text{local}}$ , forms positive feedback

$$\Rightarrow P = \epsilon_0 \chi \text{ is diverged if } T = C \frac{1}{3\epsilon_0}, \text{ i.e., } \frac{1}{N\alpha} = \frac{1}{3\epsilon_0}$$

$\Rightarrow$  Spontaneous polarization  $P_s$  appears: Ferroelectric transition  
'4π/3 catastrophe' (the coefficient  $1/3\epsilon_0$  is  $4\pi/3$  in CGI unit)

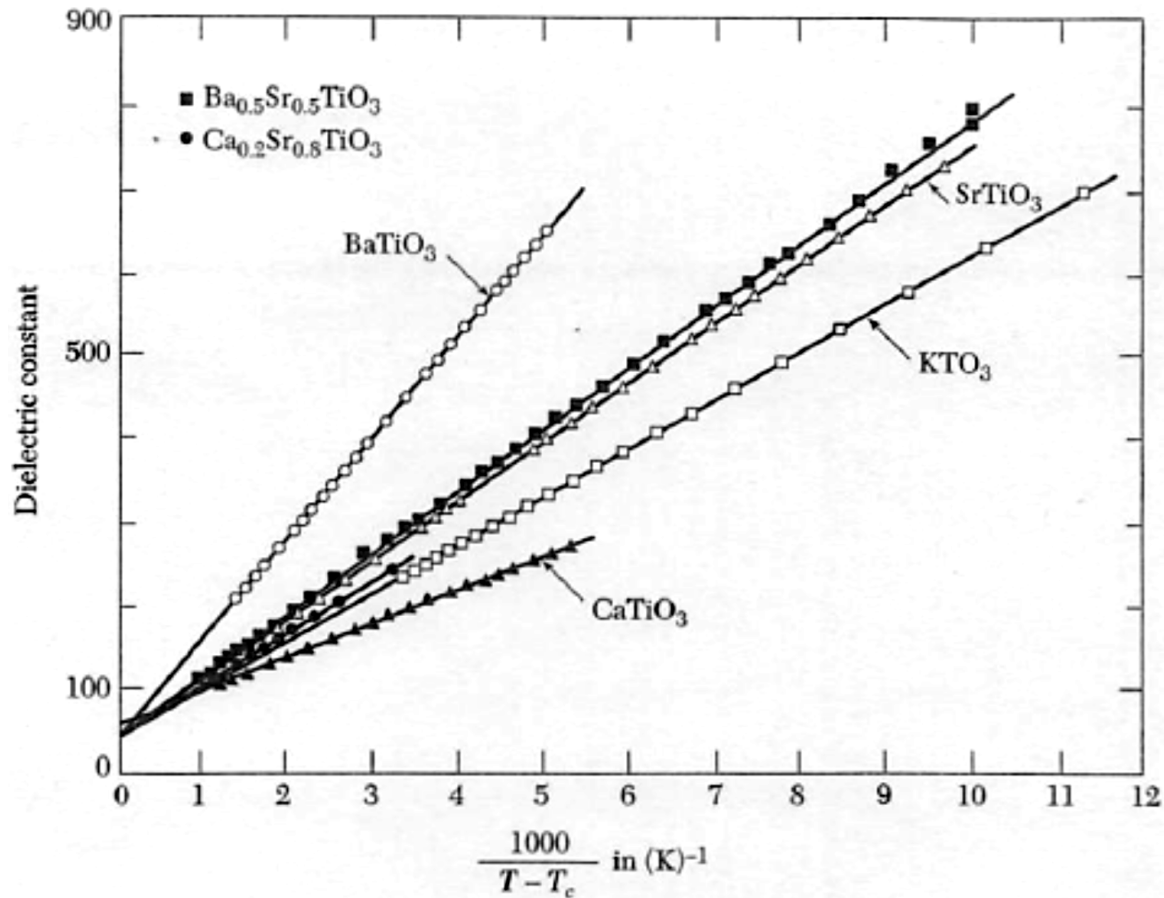
# $4\pi/3$ catastrophe:

## Slater theory of ferroelectricity

Kittel, *Introduction to Solid State Physics*, 8<sup>th</sup> ed (2005) p. 471

$$\epsilon_0 \chi = \frac{C}{T - C \frac{1}{3\epsilon_0}}$$

Curie-Weiss law (applied for the paraelectric region)



# Landau Theory of Phase Transition

*Kittel, Introduction to Solid State Physics, 8<sup>th</sup> ed (2005) p. 474*

**Perovskite-type ferroelectrics takes cubic crystal structure in the paraelectric phase (high temperature)**

**=> Free energy is expanded by**

$$\hat{F}(P;T,E) = -EP + g_0 + \frac{1}{2}g_2P^2 + \frac{1}{4}g_4P^4 + \frac{1}{6}g_6P^6 + \dots, \quad (37)$$

**Equilibrium polarization is obtained by**

$$\frac{\partial \hat{F}}{\partial P} = 0 = -E + g_2P + g_4P^3 + g_6P^5 + \dots. \quad (38)$$

**To explain ferroelectric transition (Curie-Weiss law),  $g_2 = \gamma(T - T_0)$**

# Landau Theory of Phase Transition

*Kittel, Introduction to Solid State Physics, 8<sup>th</sup> ed (2005) p. 476*

Consider  $E = 0$  for spontaneous polarization

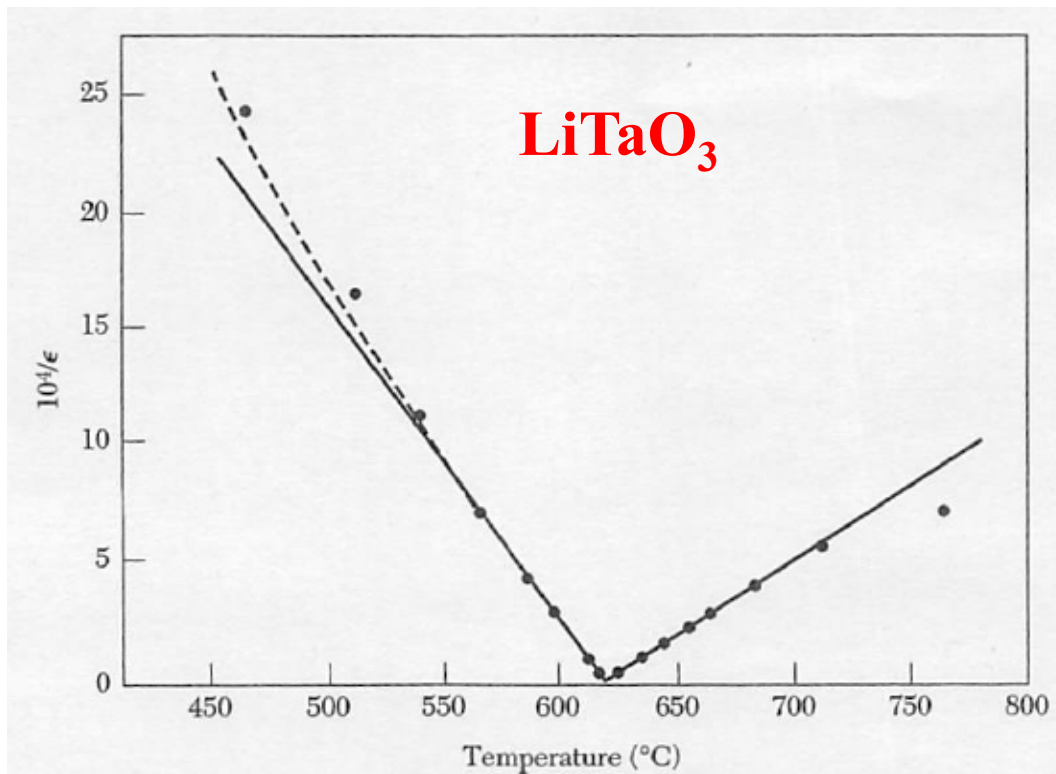
**Second-order transition**

If  $g_4$  is positive, the  $g_6$  term has no effect and can be neglected.

$$\gamma(T - T_0)P_s + g_4P_s^3 = 0 \quad , \quad (40)$$

For  $T \geq T_0$ :  $P_s = 0$

For  $T \leq T_0$ :  $P_s^2 = (\gamma/g_4)(T - T_0)$





# Landau Theory of Phase Transition

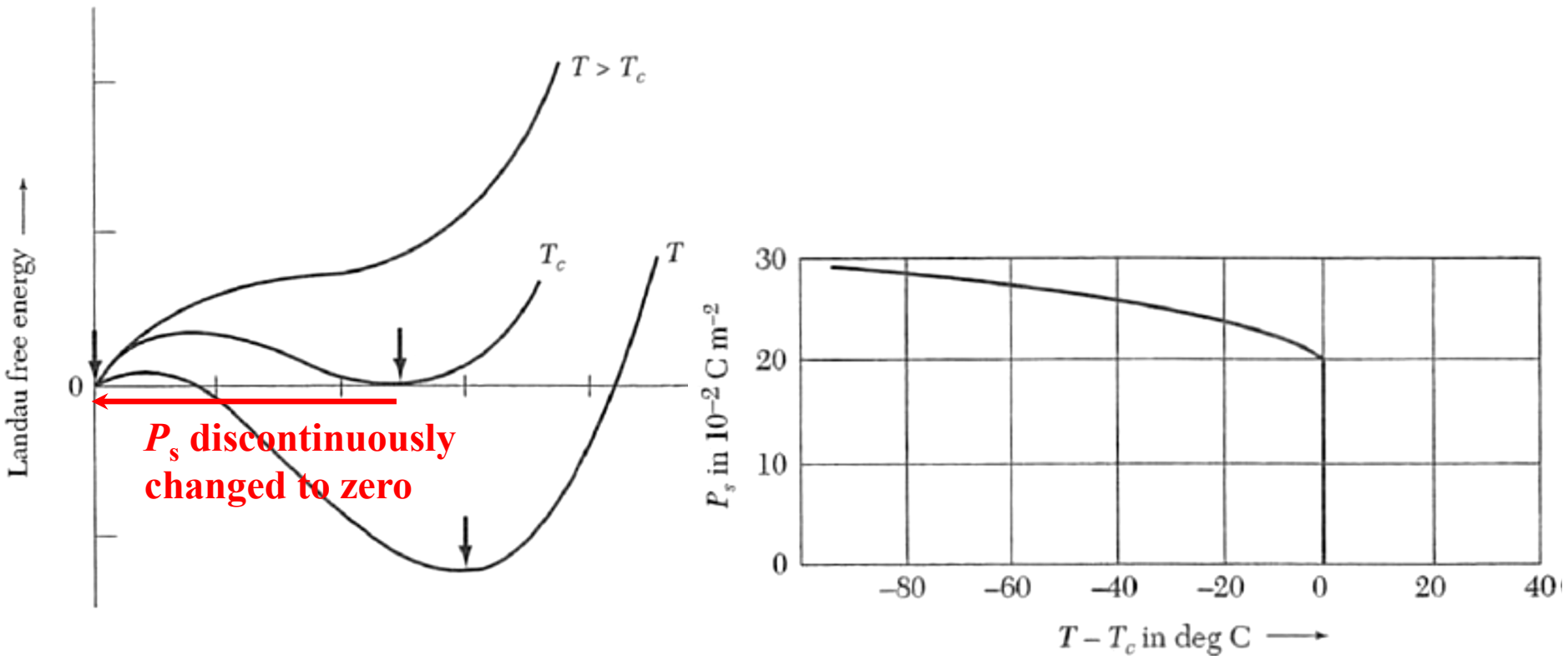
*Kittel, Introduction to Solid State Physics, 8<sup>th</sup> ed (2005) p. 477*

## First-order transition

If  $g_4$  is negative, the  $g_6$  term must be retained.

$$\gamma(T - T_0)P_s - |g_4|P_s^3 + g_6 P_s^5 = 0 \quad (42)$$

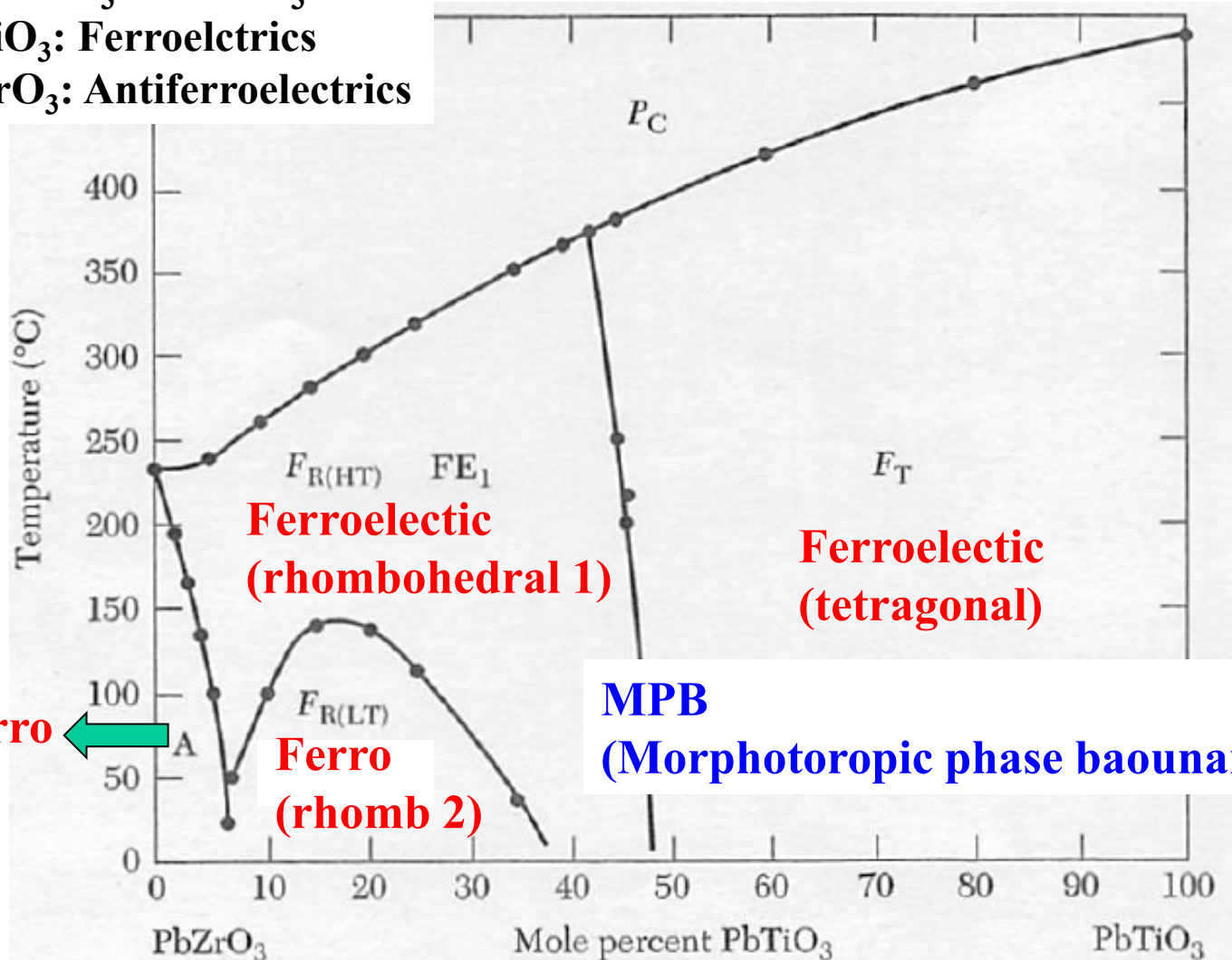
$$P_s = 0 \text{ or } \gamma(T - T_0) - |g_4|P_s^2 + g_6 P_s^4 = 0 \quad (43)$$



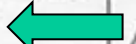
# Anti-ferroelectricity

Kittel, *Introduction to Solid State Physics*, 8<sup>th</sup> ed (2005) p. 479

**PZT: PbTiO<sub>3</sub> – PbZrO<sub>3</sub>**  
**PbTiO<sub>3</sub>: Ferroelctrics**  
**PbZrO<sub>3</sub>: Antiferroelectrics**



Anti-ferro



**MPB**  
(Morphotropic phase boundary)

# Anti-ferroelectricity

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