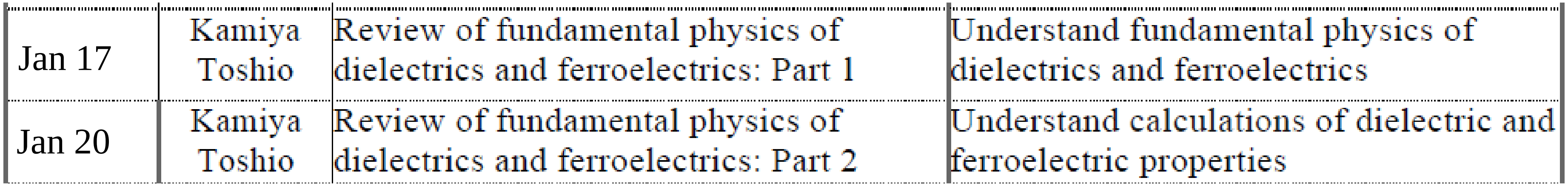
Introduction to Solid State Science

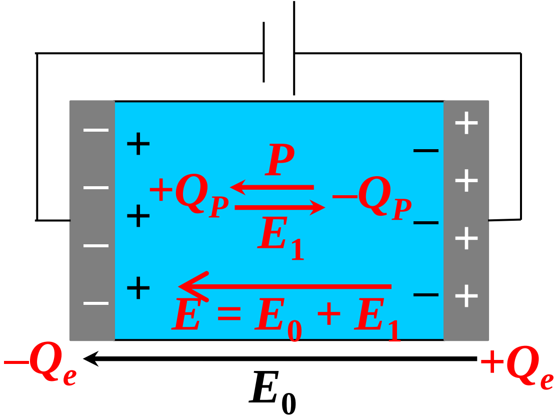
Toshio Kamiya



Jan 17	Kamiya Toshio	Review of fundamental physics of dielectrics and ferroelectrics: Part 1	Understand fundamental physics of dielectrics and ferroelectrics
Jan 20	Kamiya Toshio	Review of fundamental physics of dielectrics and ferroelectrics: Part 2	Understand calculations of dielectric and ferroelectric properties

Internal macroscopic field is different from external field: Depolarization field

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 457



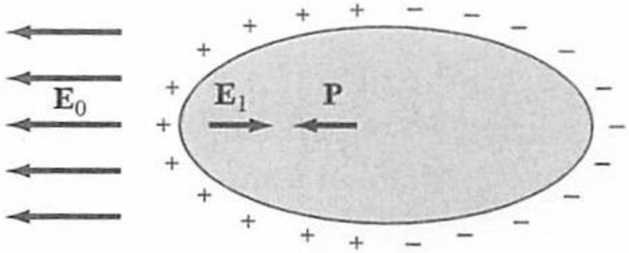


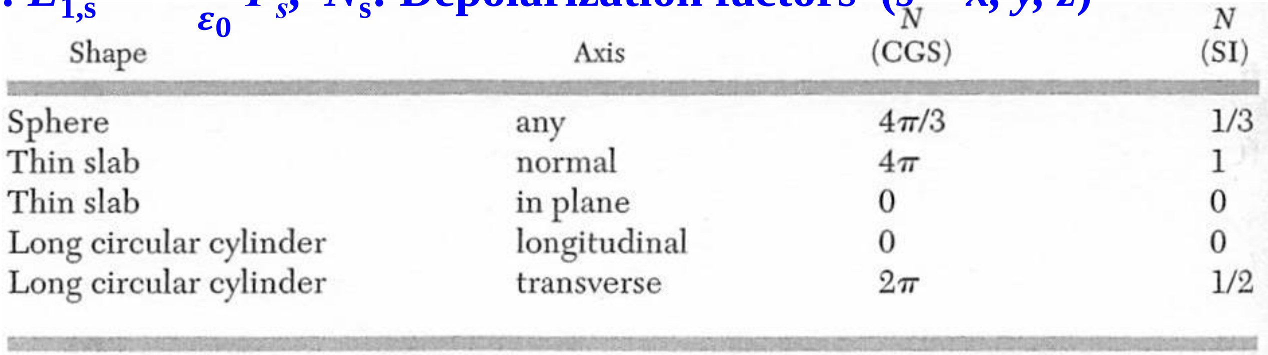
Figure 4 The depolarization field E_1 is opposite to **P**. The fictitious surface charges are indicated: the field of these charges is E_1 within the ellipsoid.

External field E_0: formed by the charges on the electrodes Q_e

Surface charges: induced from internal polarization $\pm Q_P = n_{surface} \cdot P = \pm|P| = \pm\chi|E_0|$, which forms extra electric field: $E_1 = -\frac{|P|}{\varepsilon_0}$

Internal macroscopic field E in the dielectrics: $E = E_0 + E_1 = E_0 - \frac{P}{\varepsilon_0}$

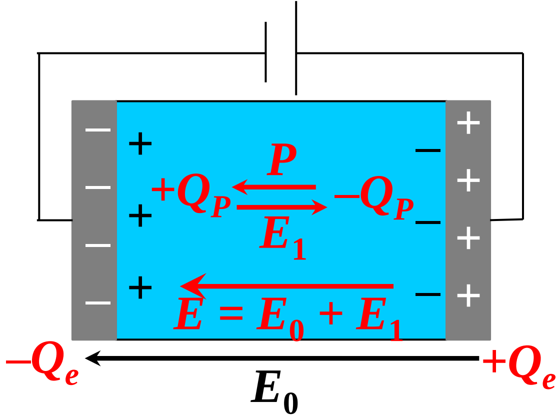
General shapes of dielectrics: $E_{1,s} = -\frac{N_s}{\varepsilon_0} P_s$, N_s: Depolarization factors ($s = x, y, z$)



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

Internal macroscopic field is different from external field: Depolarization field

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 457



χ is defined by internal electric field E

$$E = E_0 + E_1 = E_0 - \frac{N}{\varepsilon_0} P :$$

$$P = \varepsilon_0 \chi E = \varepsilon_0 \chi \left(E_0 - \frac{N}{\varepsilon_0} P \right)$$

$$\Rightarrow \ P = \frac{\varepsilon_0 \chi}{1 + N\chi} E_0$$

Macroscopic theory => Microscopic theory

Understand properties of dielectric from those of atoms/ions

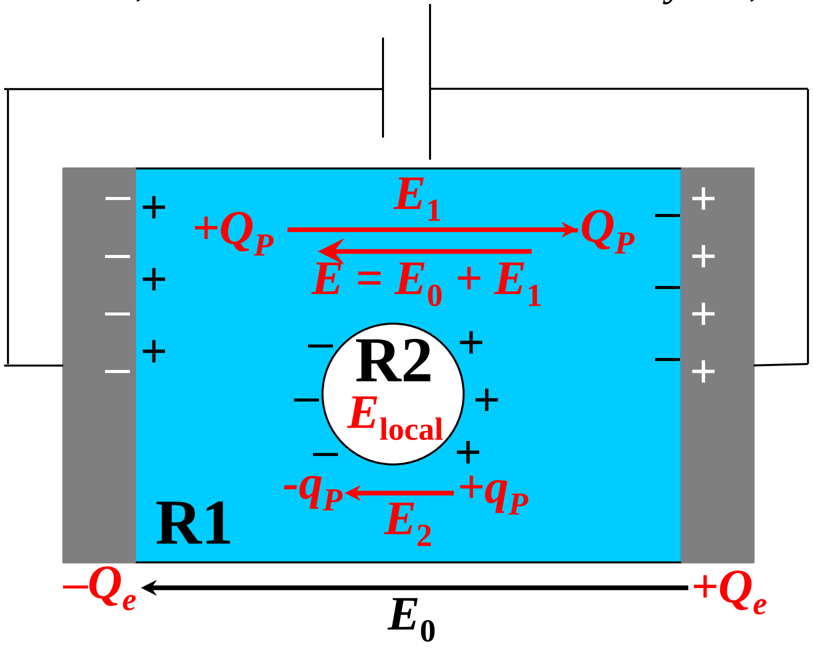
Polarizability of the atom i (α_i) is defined by atomic polarization p_i and local electric field E_{local}

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

How is E_{local} different from the macroscopic internal field E ?

Internal electric field at an atomic site: Lorentz field

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 460



At an atom site r_0, polarizations from surrounding atoms form an extra field: Lorentz field

R2: Contribution to E_{local} at r_0, the center of the sphere, is calculated by summing up the ion charges in R2.

=> the net charges appear on the surface of the sphere

$$E_2 = \frac{1}{3\varepsilon_0} P \text{ : Lorentz field}$$

For cubic symmetry

$$E_{\text{local}} = E + \frac{1}{3\varepsilon_0} P$$

Atom polarizability to dielectric permitivity

Polarizability of the atom *i* (α_i) is defined by atomic polarization p_i and E_{local}

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

$$E_{\text{local}} = E + \frac{1}{3\varepsilon_0} P$$

Assume the atomic polarization is independent from each other.

$$P = \sum_i N_i \alpha_i E_{\text{local}}(r_i) = \sum_i N_i \alpha_i \left(E + \frac{1}{3\varepsilon_0} P \right)$$

$$\varepsilon_0 \chi = \frac{P}{E} = \frac{\sum_i N_i \alpha_i}{1 - \frac{1}{3\varepsilon_0} \sum_i N_i \alpha_i}$$

Using $\varepsilon_r = 1 + \chi$

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{1}{3\varepsilon_0} \sum_i N_i \alpha_i$$

Clausius-Mossotti relation

Simple model of electronic polarizability

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 464

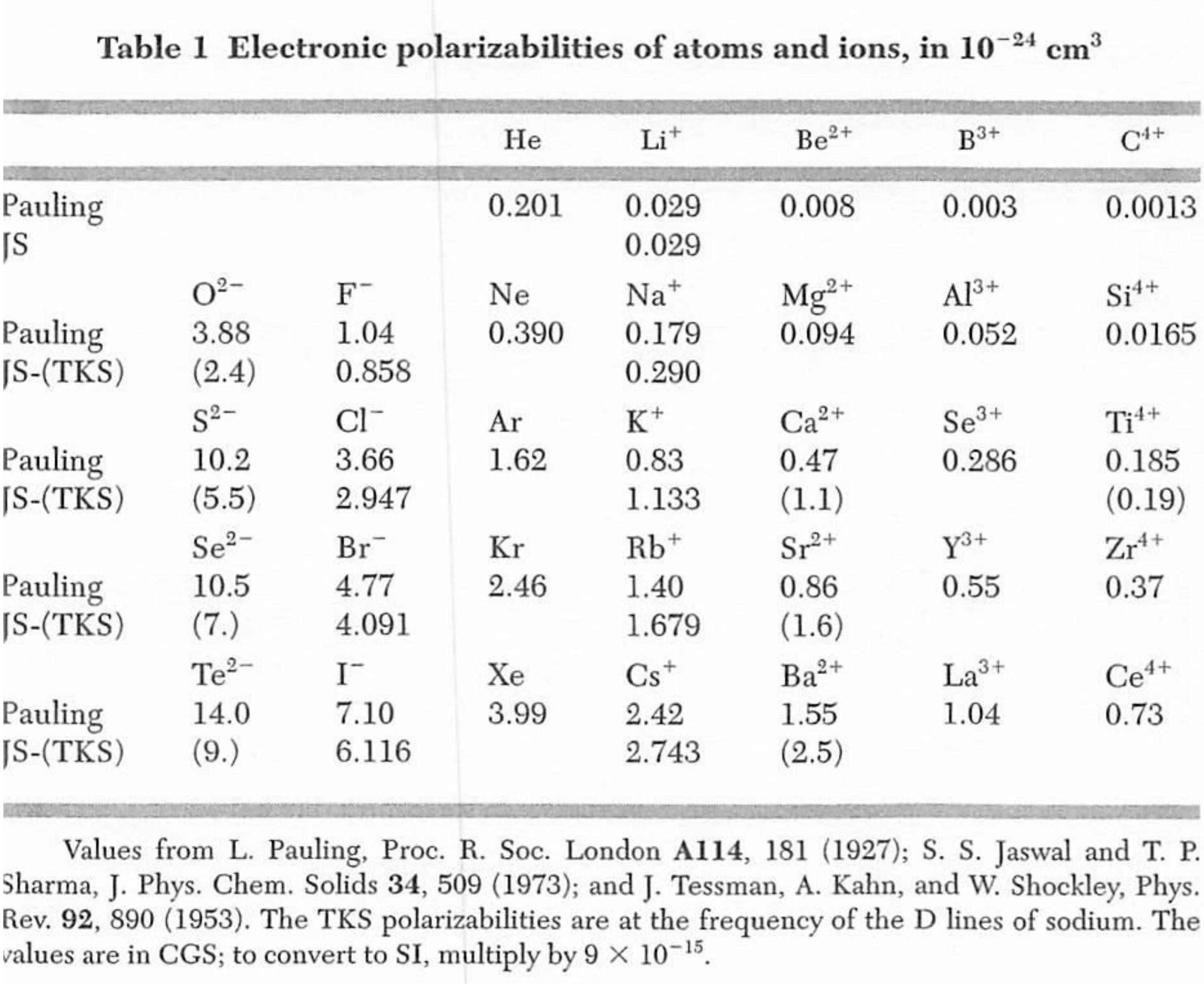


Table 1 Electronic polarizabilities of atoms and ions, in 10^{-24} cm^3

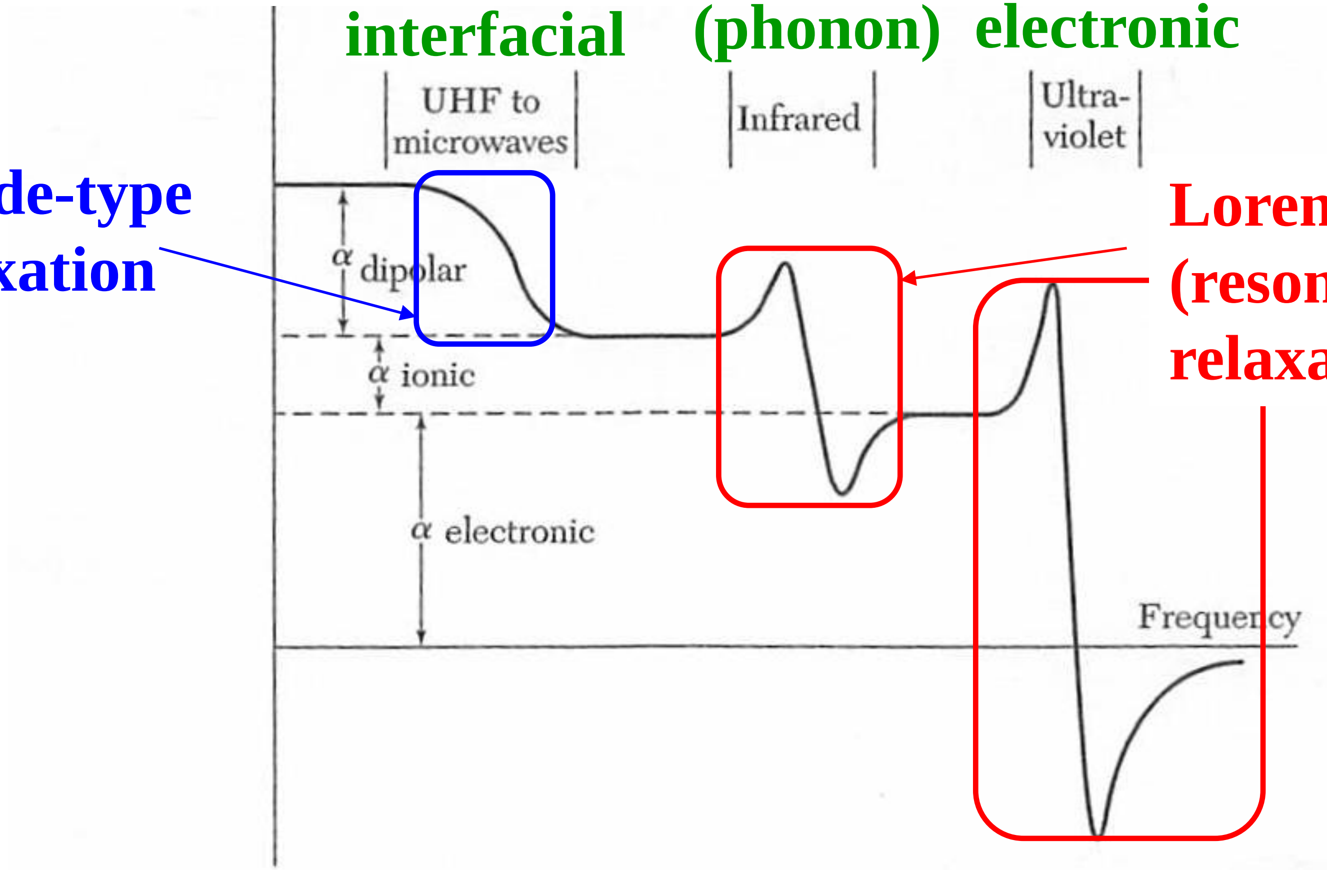
			He	Li^+	Be^{2+}	B^{3+}	C^{4+}
Pauling			0.201	0.029	0.008	0.003	0.0013
JS				0.029			
	O^{2-}	F^-	Ne	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}
Pauling	3.88	1.04	0.390	0.179	0.094	0.052	0.0165
JS-(TKS)	(2.4)	0.858		0.290			
	S^{2-}	Cl^-	Ar	K^+	Ca^{2+}	Se^{3+}	Ti^{4+}
Pauling	10.2	3.66	1.62	0.83	0.47	0.286	0.185
JS-(TKS)	(5.5)	2.947		1.133	(1.1)		(0.19)
	Se^{2-}	Br^-	Kr	Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}
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^{2-}	I^-	Xe	Cs^+	Ba^{2+}	La^{3+}	Ce^{4+}
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 × 10^{-15}.

Electronic polarizability

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 464

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



dipolar interfacial

Ionic (phonon)

electronic

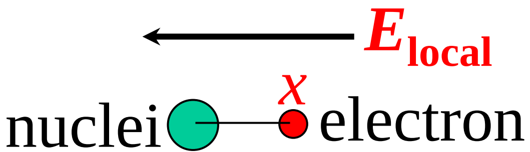
Drude-type relaxation

Lorentz-type (resonant-type) relaxation

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

Frequency dependence: Lorentz model

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 466



$$k = m\omega_0^{\ 2}$$

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

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

Similar expression is obtained by quantum theory

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

ω_{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 $-eE_{\mathrm{local}} = kx = m\omega_0{}^2 x$:

The recovery force kx results in the resonant-type relaxation with the relaxation frequency ω_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 term, but charge distribution also forms recovery force => Non-resonant-type relaxation: Drude model

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

$$\omega_p = \sqrt{\frac{e^2 N_{free}}{\varepsilon_\infty \varepsilon_0 m_e^*}}$$ Plasma frequency

Applied to free carrier polarization,

dipolar interfacial polarization

Lyddane–Sachs–Teller relation

Kittel, Introduction to Solid State Physics, 8th 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

$$\frac{\varepsilon}{\varepsilon_\infty} = \frac{{\omega_{LO}}^2}{{\omega_{TO}}^2}$$

Lyddane–Sachs–Teller–Kurosawa (LSTK) relation

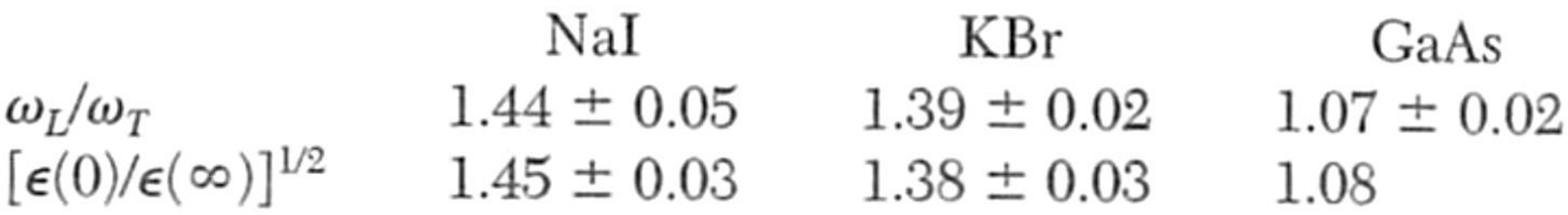
$$\frac{\varepsilon(\omega)}{\varepsilon_\infty(\omega)} = \prod \frac{{\omega_{LO,i}}^2 - \omega^2}{{\omega_{TO,i}}^2 - \omega^2}$$

ω_{TO}: Resonance frequency of transversal phonon
Polarization formed by phonon is macroscopically zero.

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

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

Possible to estimate ε from infrared / Raman spectrum



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

Dielectric constant and Born effective charge

上江洲由晃 緒、強誘電体 (内田老鶴圃)

Polarization change ΔP is related to ion displacement Δu_i.

- One may use formal ion charges or calculated ion charges to calculate the dielectric constant.
- This may work satisfactory for low ε materials.
- **For high ε materials, the ε 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 ε materials**
- **Extraordinary large for high ε materials**

  <= Redistribution of electron and its polarization are not negligible for some materials

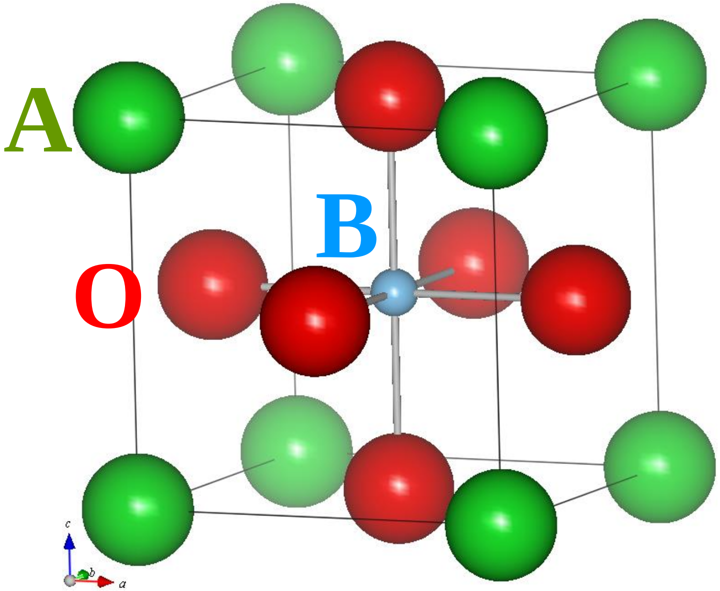
Dielectric constant and Born effective charge

上江洲由晃 緒、強誘電体 (内田老鶴圃)

ABO_3	**Z^*_A**	**Z^*_B**	**$Z^*_{O(1)}$**	**$Z^*_{O(2)}$**
Formal charge	+2	+4	-2	-2
$CaTiO_3$	2.58	7.08	-5.65	-2
$SrTiO_3$	2.56 2.54 2.55	7.26 7.12 7.56	-5.73 -5.66 -5.92	-2.15 -2.00 -2.12
$BaTiO_3$	2.77 2.75 2.61	7.25 7.16 5.88	-5.71 -5.69 -4.43	-2.15 -2.11 -2.03
$BaZrO_3$	2.73	6.03	-4.74	-2.01
$PbTiO_3$	3.90	7.06	-5.83	-2.56
$PbZrO_3$	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 ε?



For ideal cubic perovskite structure:

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

$$a=\sqrt{2}\left(r_A+r_\mathrm{O}\right)=2\left(r_B+r_\mathrm{O}\right)$$

$$t=\frac{r_A+r_\mathrm{O}}{\sqrt{2}\left(r_B+r_\mathrm{O}\right)}=1.0$$

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	$BaNiO_3$
0.9-1	Cubic	Ideal contact	$SrTiO_3$, $BaTiO_3$
0.71 - 0.9	Orthorhombic Rhombohedral	Small r_A in B ion interstitial	$GdFeO_3$ (Orth.) $CaTiO_3$ (Orth.)
<0.71	Different structures	Samll r_A, r_B	$FeTiO_3$ (Tri.)

Structural instability by the sub-lattice structure

Case 1:

Unit cell is stabilized by B-O

A ion is loosely embedded

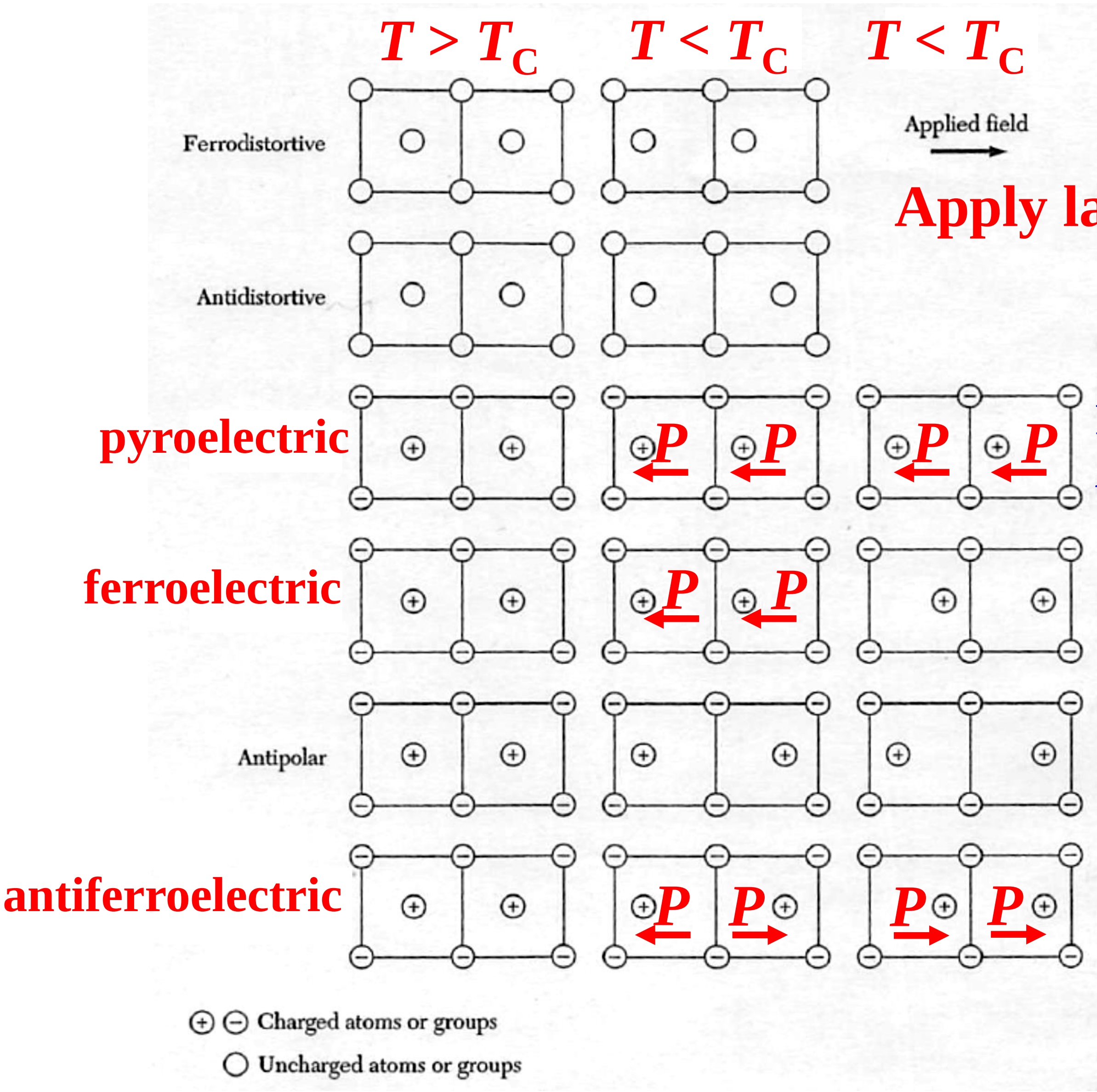
Case 2:

Unit cell is stabilized by A-O

B ion is loosely embedded

Ferroelectricity and Anti-ferroelectricity

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 478



Apply large reverse field

Finite P_s
P_s not necessary reversed by E

Finite P_s
P_s must be reversed by E

Finite local P_s,
macroscopic P_s is cancelled
Local P_s can be reversed
by large E
and may exhibit ferroelectric
behavior

Classification of ferroelectrics related phases

Dielectrics:

Symmetry: any

Spontaneous polarization: not necessary

Piezoelectircs: Part of dielectirics,

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

Pyroelectircs: Part of piezoelectrics,

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

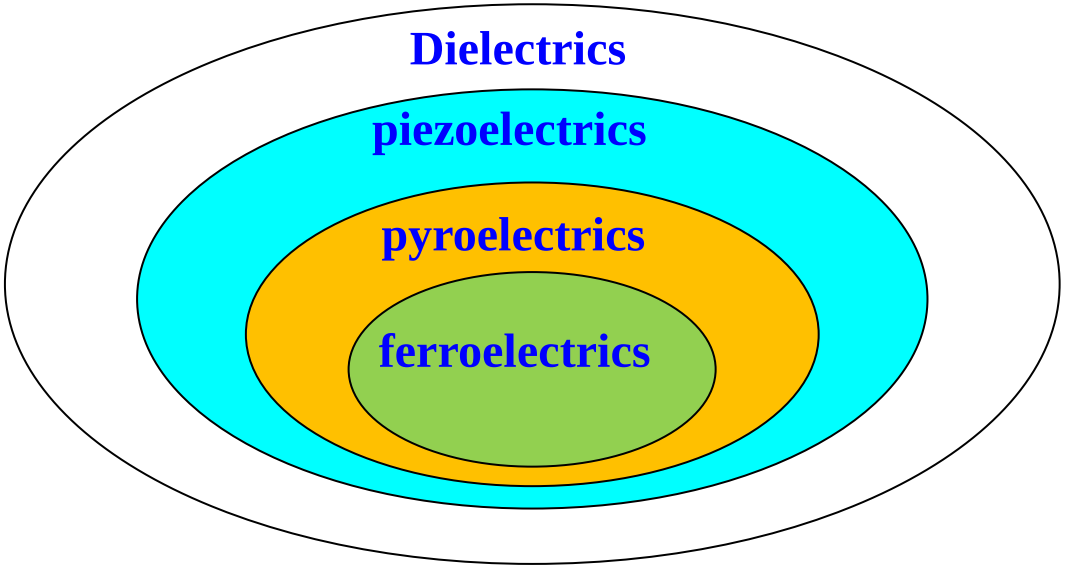
Ferroelectrics: Part of pyroelectrics,

polarization is flipped by external electric field

Symmetry: non-centrosymmetric & polar

Spontaneous polarization: necessary

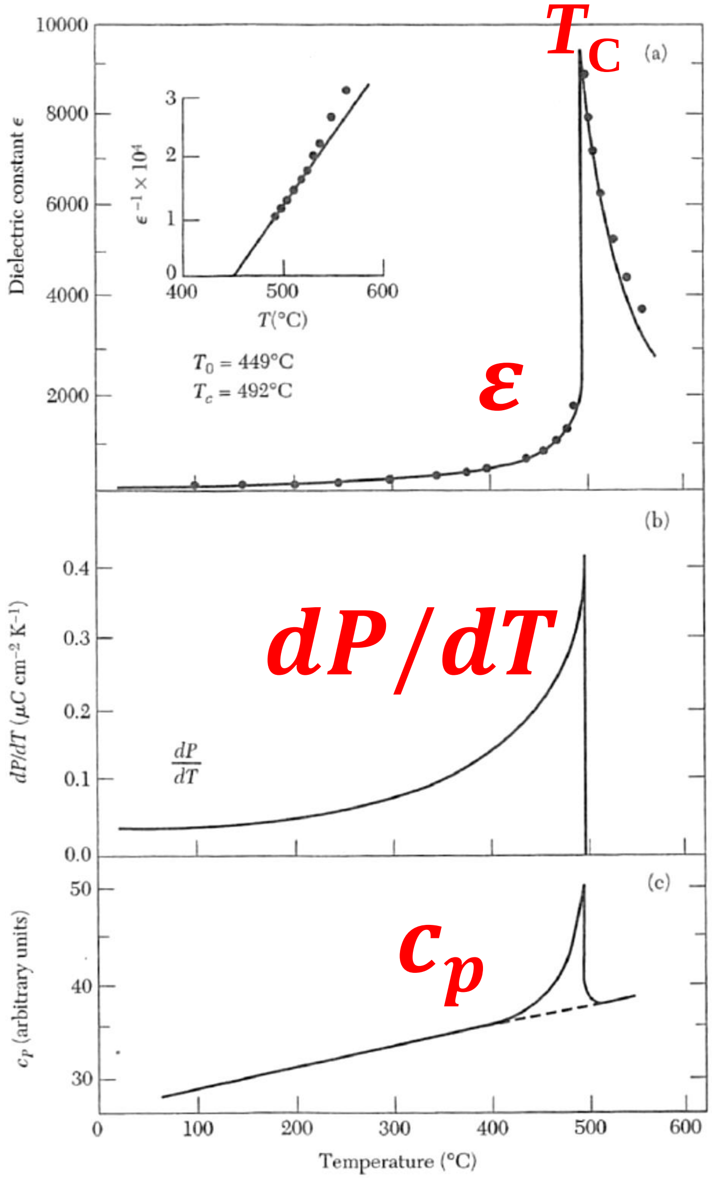
10 Space groups: 1, 2, m, mm2, 4, 4mm,
3, 3m, 6, 6mm



Ferroelectrics

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

Temperature dependences for $PbTiO_3$



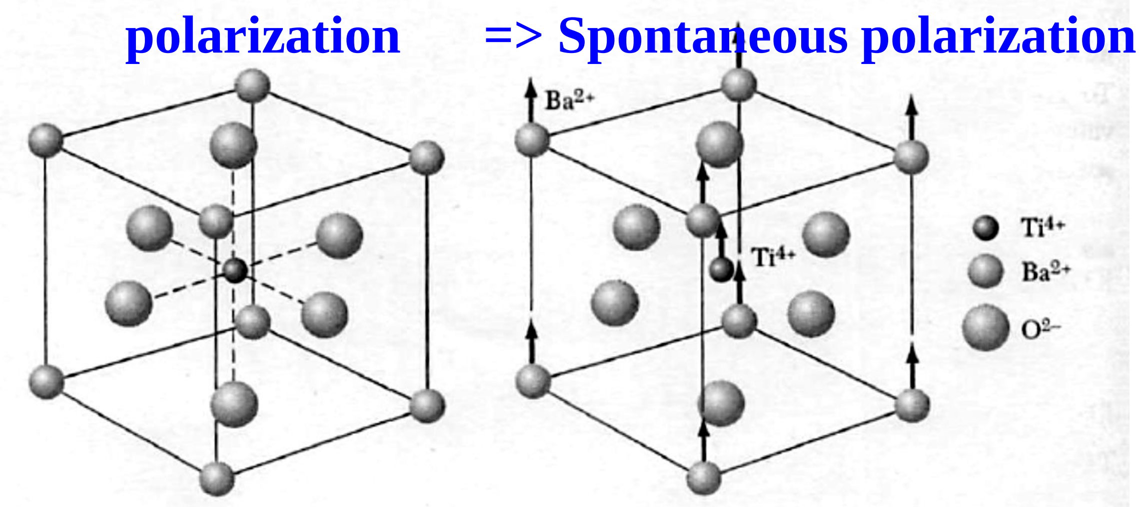
ε diverges and discontinuously changes at the transition temperature (Curie temperature) T_C, like λ:

λ transition

Feature of first order phase transition

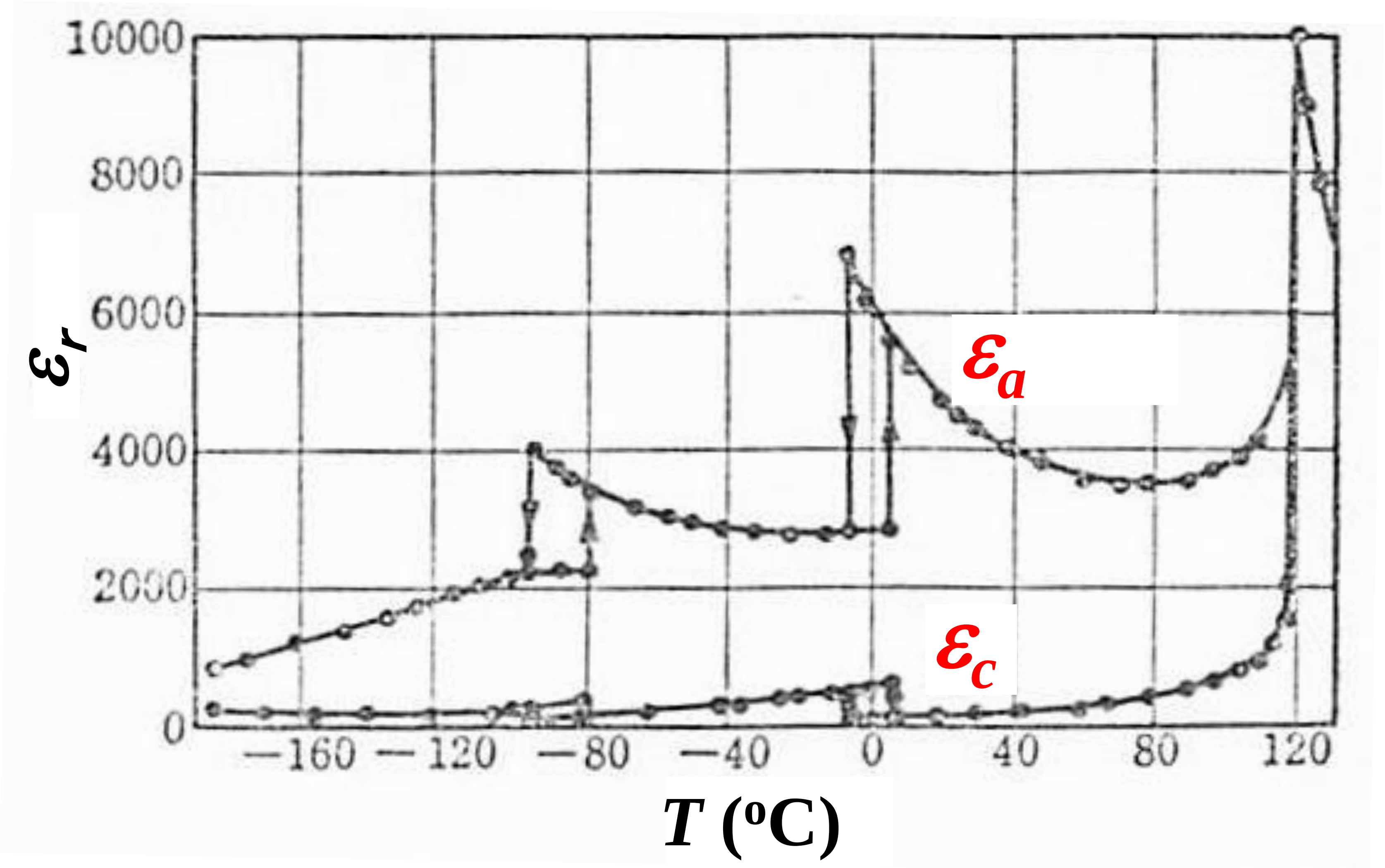
$T > T_C$
Cubic structure
No spontaneous polarization

$T < T_C$ stabilizes
ions displaced and
lattice distorted
=> Spontaneous polarization



Ferroelectrics: $BaTiO_3$

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 471
三井利夫 編著、強誘電体 (槇書店, 1969)



Sequential phase transition of $BaTiO_3$

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 471
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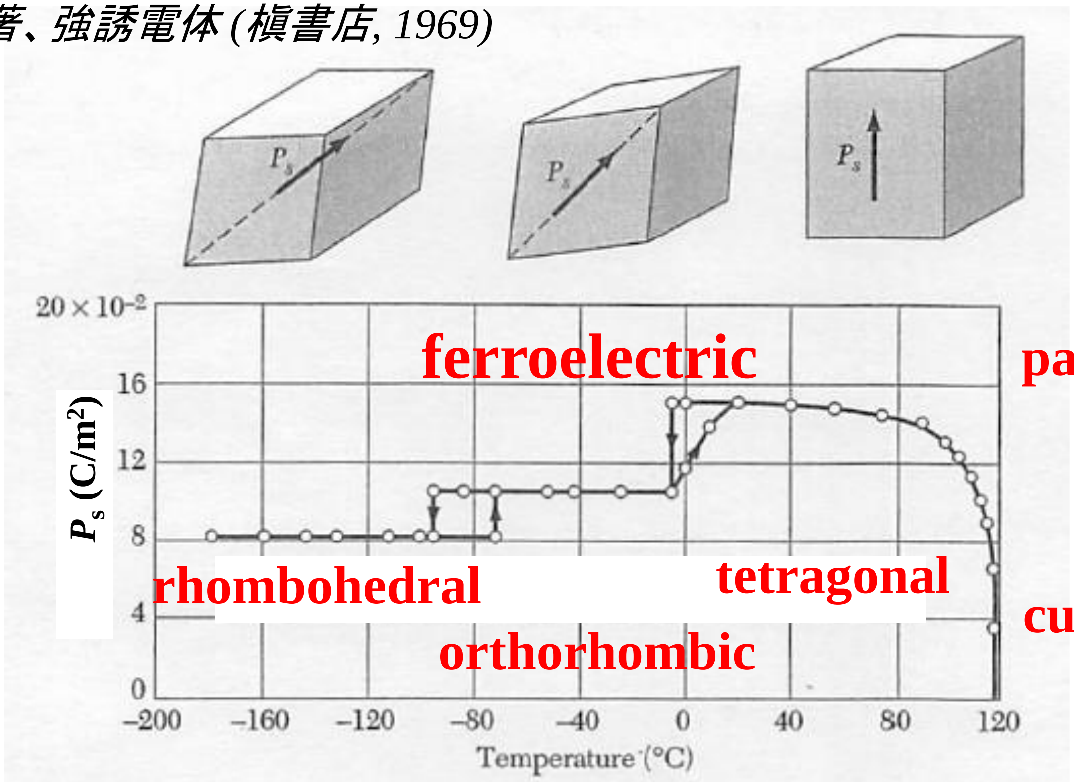

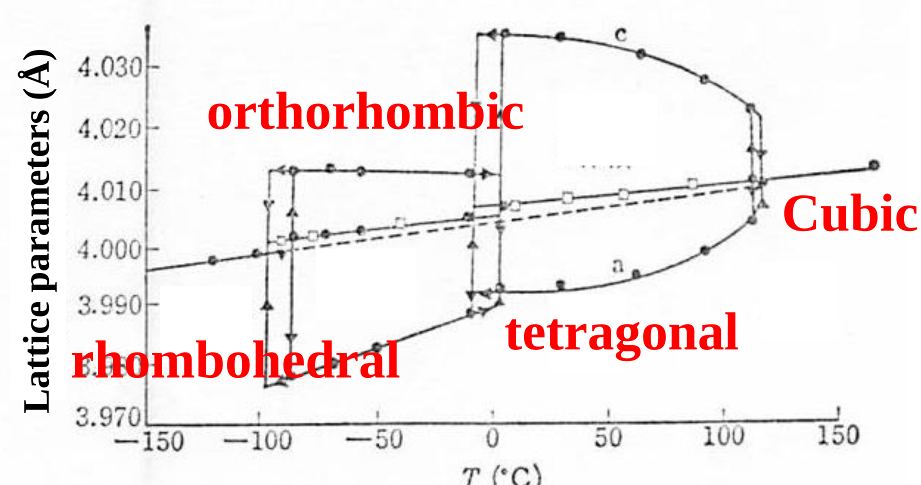

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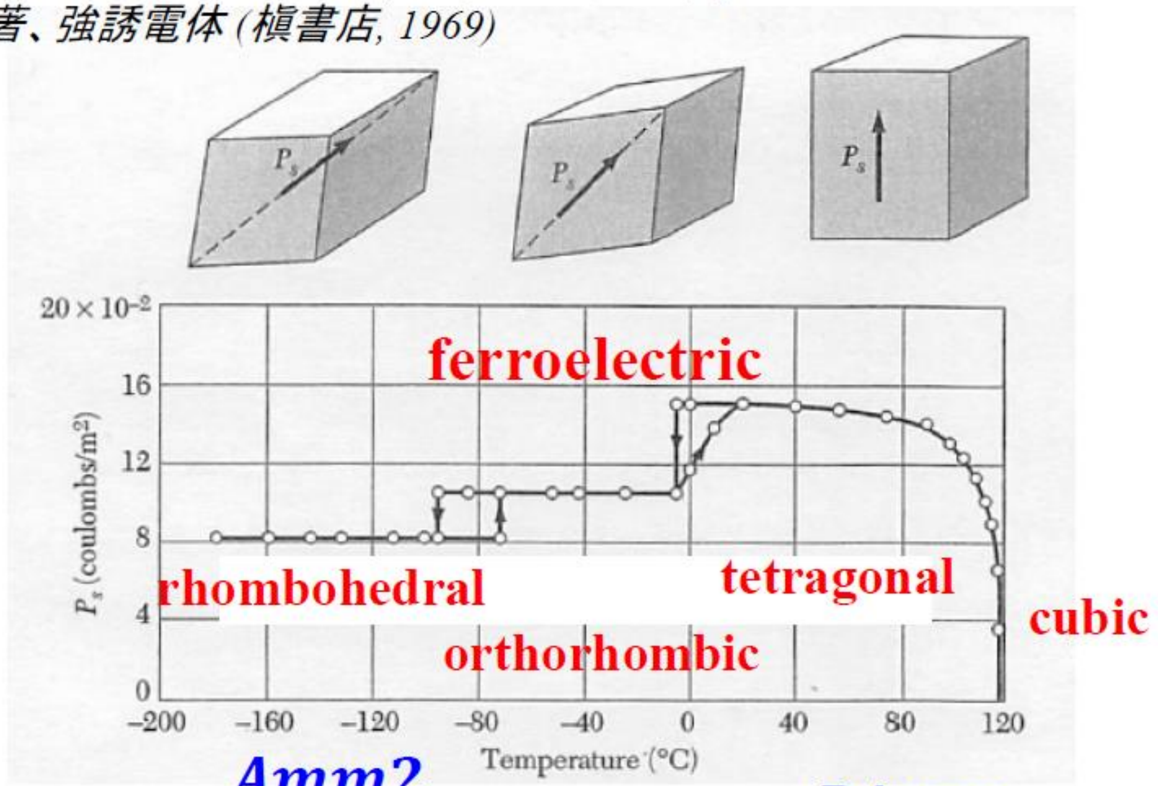
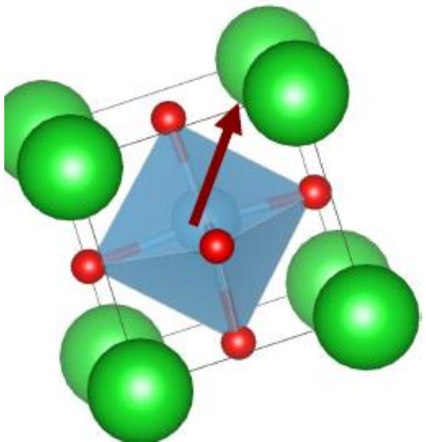
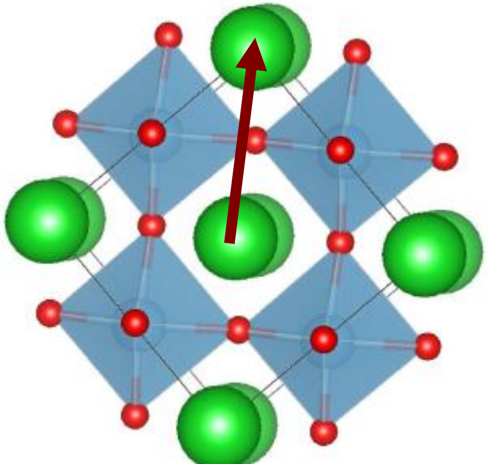


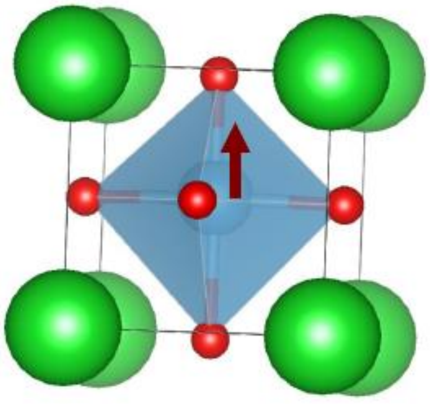
$R3m$



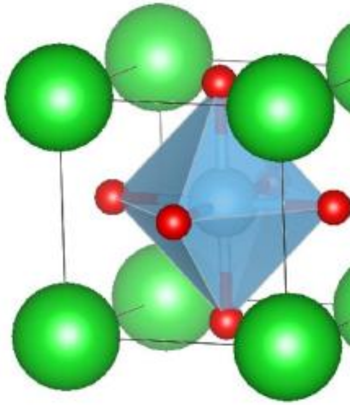
$Amm2$



$P4mm$



$Pm\bar{3}m$



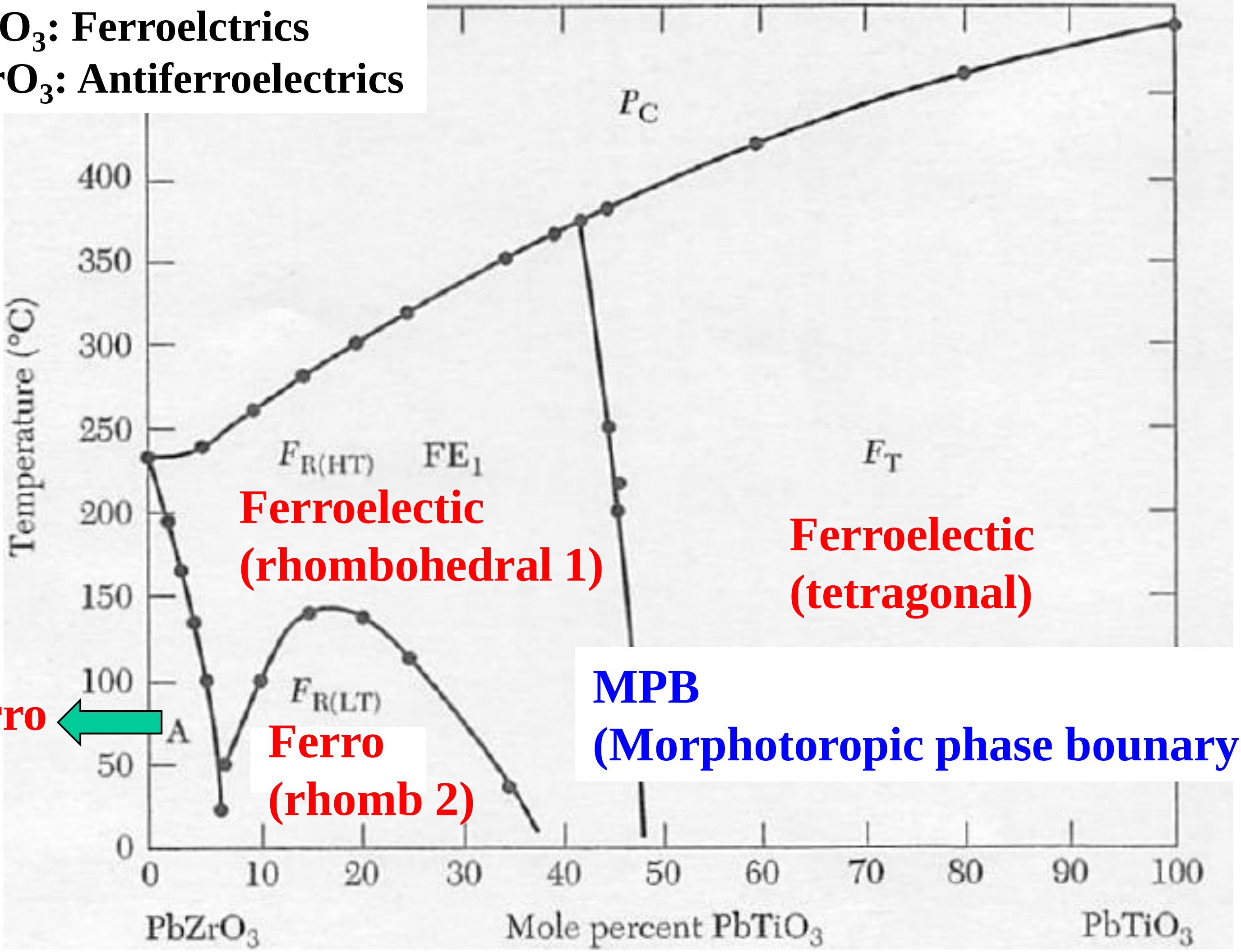
Anti-ferroelectricity

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 479

PZT: $PbTiO_3$ – $PbZrO_3$

$PbTiO_3$: Ferroelctrics

$PbZrO_3$: Antiferroelectrics



Ferroelectic (rhombohedral 1)

Ferroelectic (tetragonal)

Ferro (rhomb 2)

Anti-ferro

MPB (Morphotoropic phase bounary)

Two types of ferroelectricity

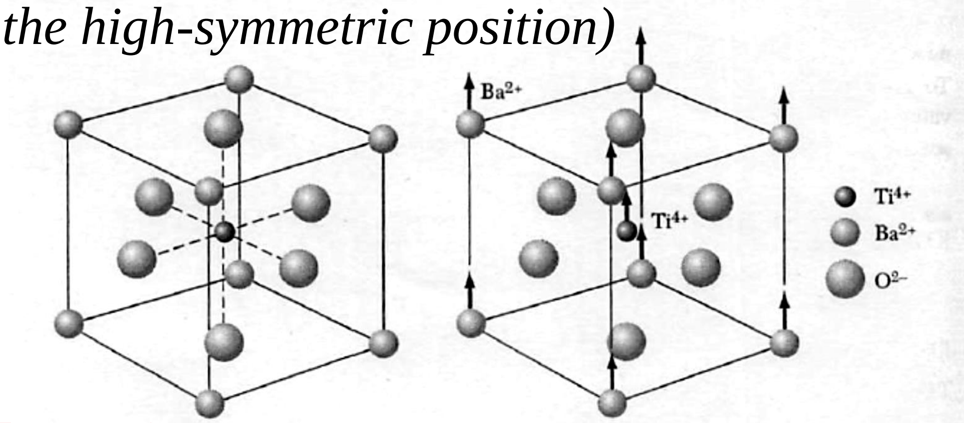
強誘電体物理入門

Displacement type ferroelectric

Small displacement of ions form P_s

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

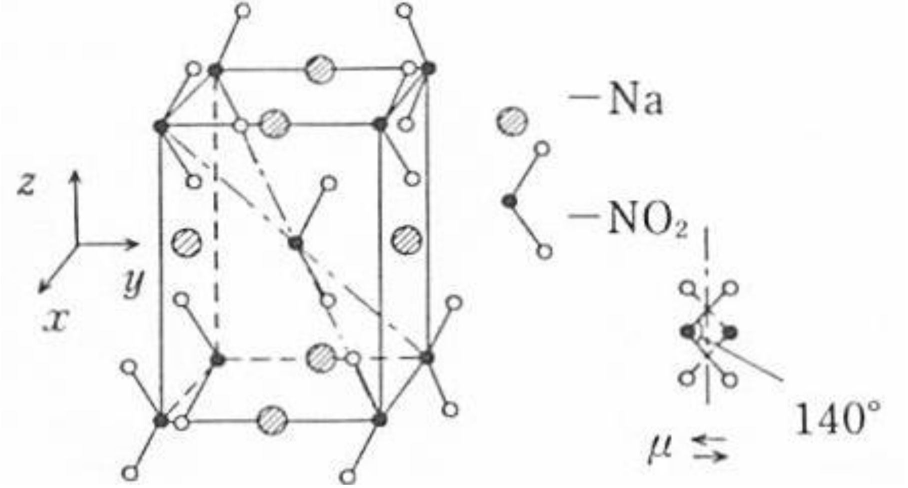
Perovskite type crystals
$BaTiO_3$, $Pb(Zr,Ti)O_3$



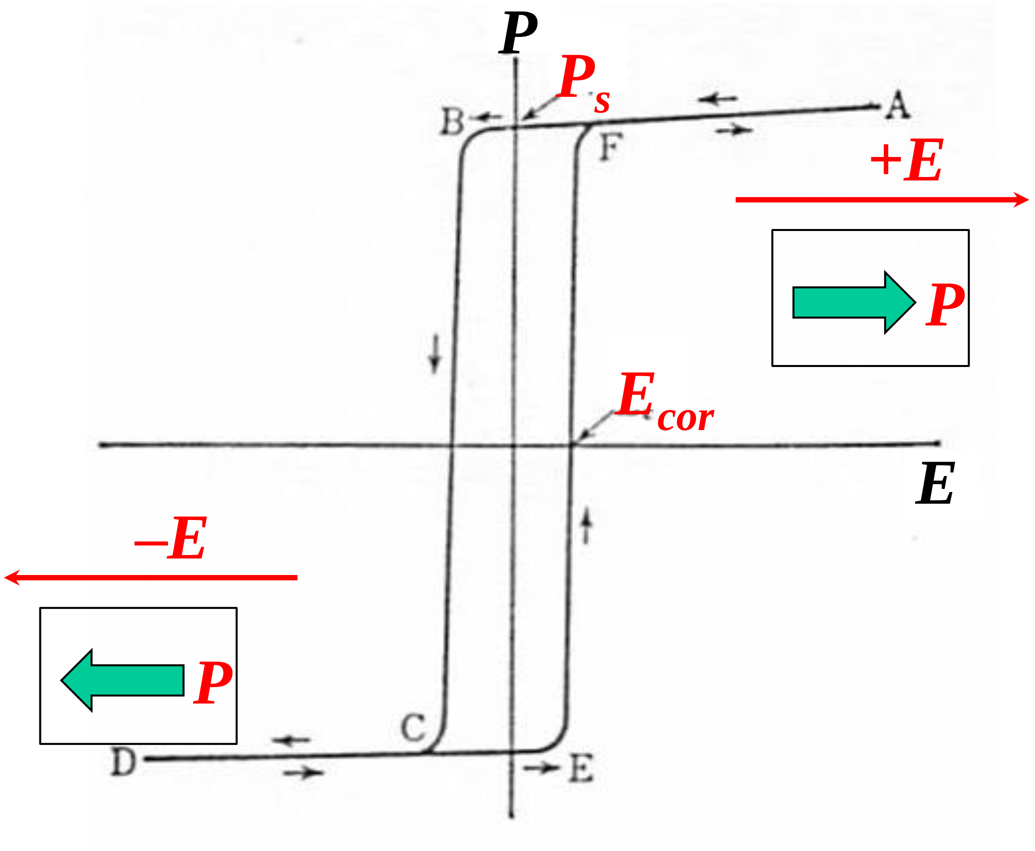
Order-disorder type ferroelectric

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

$NaNO_2$: NO_2 group
KDP (KH_2PO_4): H^+



Feature of ferroelectrics:
$D – E$ / $P – E$ hysteresis loop



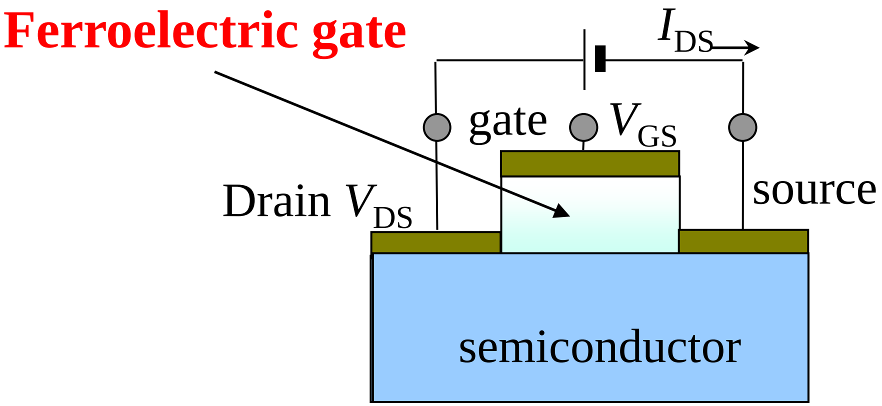
P_s : Spontaneous polarization
E_{cor}: Coercive electric field

Application of ferroelectrics

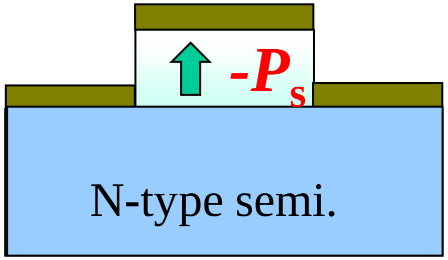
FeRAM (Ferroelectric RAM)

- Gate dielectric in conventional FET is replaced with ferroelectrics
- Spontaneous polarization Ps retains if gate voltage VGS is off

=> **Non-volatile memory**



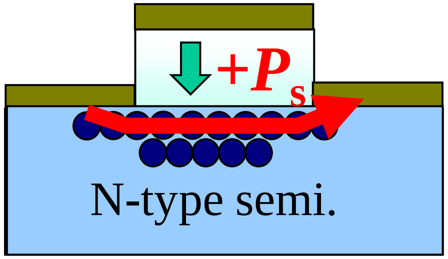
Memory state “0”



$-P_s$ 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 negative charge at the insulator-semiconductor interface, then n-type semi induces mobile carriers

=> **FET is “On” state**

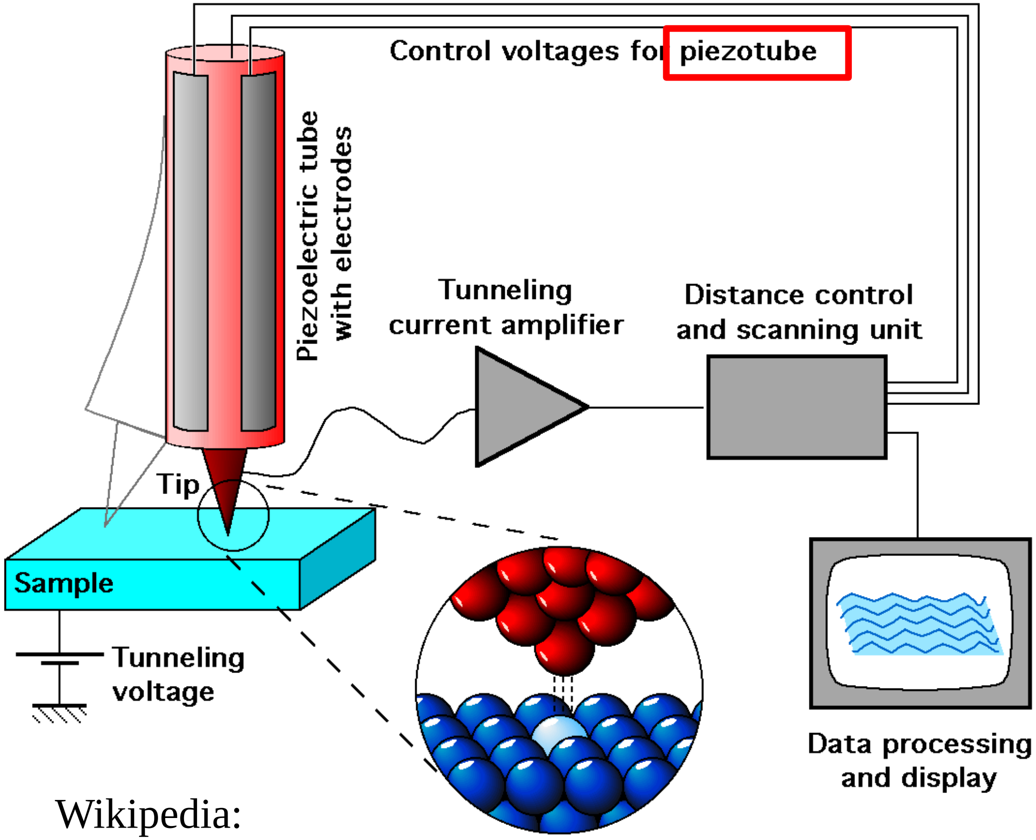
Applications of piezoelectrics

Scanning Probe Microscope (SPM)

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

piezoelectrics is used as **piezoactuator**

Fast response, atomic-order precision



PZT: d_{33} = 400x10^{-12} m/V

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

For $V = 100$ V, $l = 1$ cm,

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

Δl = 400 Å

For $V = 0.1$ V

Δl = 0.4 Å

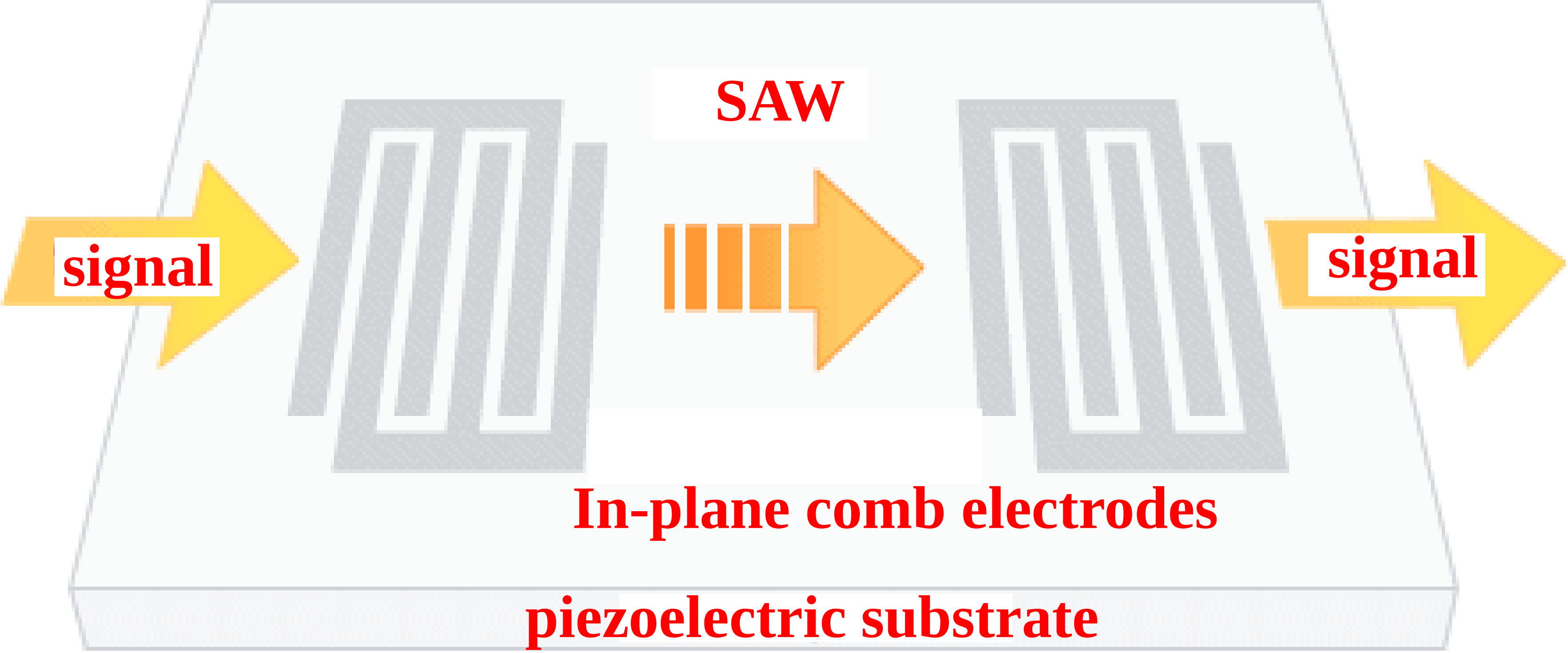
Wikipedia: https://ja.wikipedia.org/wiki/%E8%B5%B0%E6%9F%BB%E5%9E%8B%E3%83%88%E3%83%B3%E3%83%8D%E3%83%AB%E9%A1%95%E5%BE%AE%E9%8F%A1

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

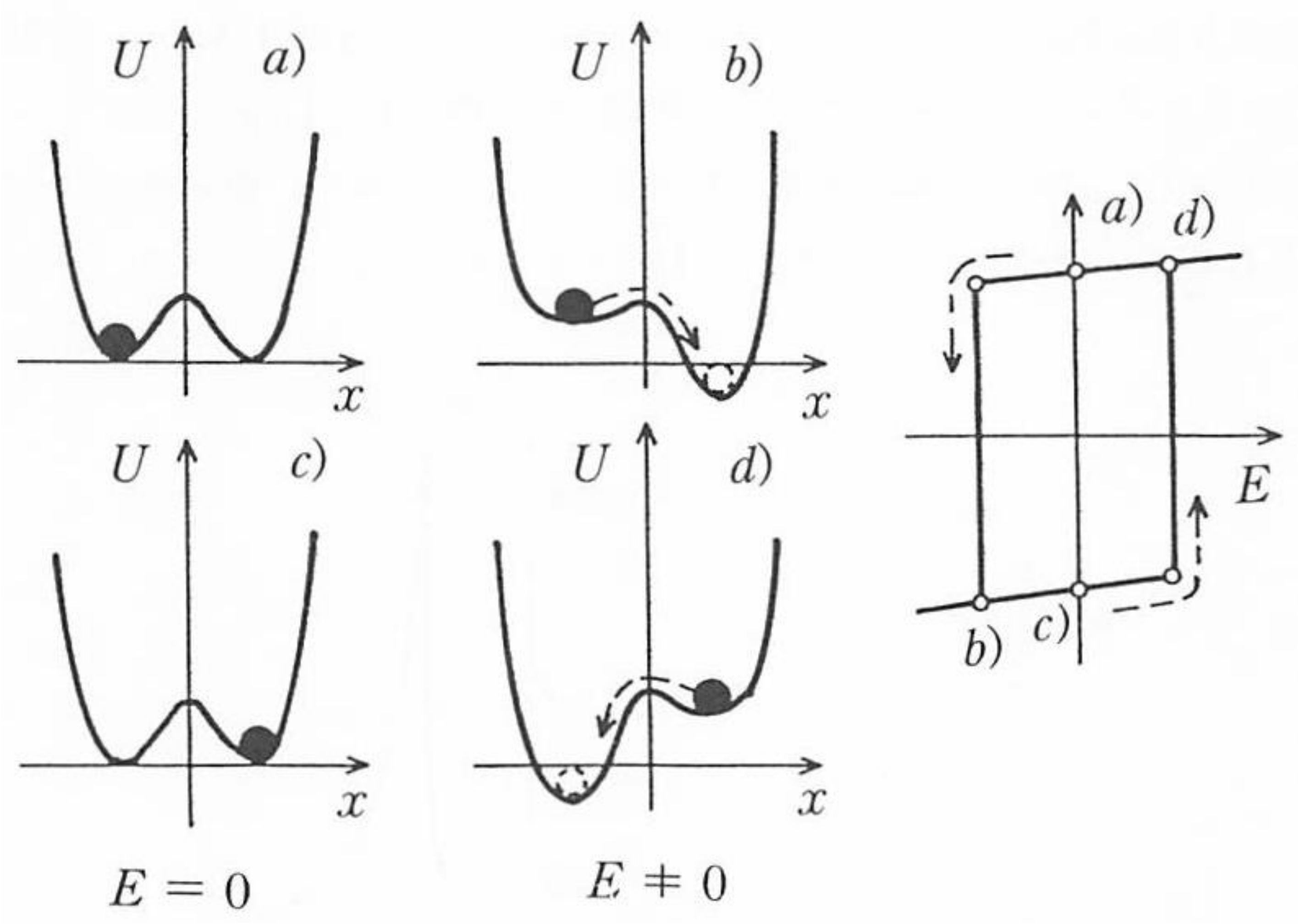
  => **Transmit signals with $f \sim f_r$: Band pass filter**
- **f_r: up to several GHz, used e.g. in mobile phones**



https://www.murata.com/ja-jp/group/kanazawamurata/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, 8th 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)

$$\varepsilon_0\chi = \frac{\sum_i N_i\alpha_i}{1 - \frac{1}{3\varepsilon_0}\sum_i N_i\alpha_i}$$

For single-type atom system

$$\varepsilon_0\chi = \frac{N\alpha}{1 - \frac{1}{3\varepsilon_0}N\alpha}$$

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

$$\varepsilon_0\chi = \frac{C}{T - C\frac{1}{3\varepsilon_0}}$$ **Curie-Weiss law**

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

=> $P = \varepsilon_0\chi$ is diverged if $T = C\frac{1}{3\varepsilon_0}$, *i.e.*, $\frac{1}{N\alpha} = \frac{1}{3\varepsilon_0}$

=> Spontaneous polarization P_s appears: Ferroelectric transition

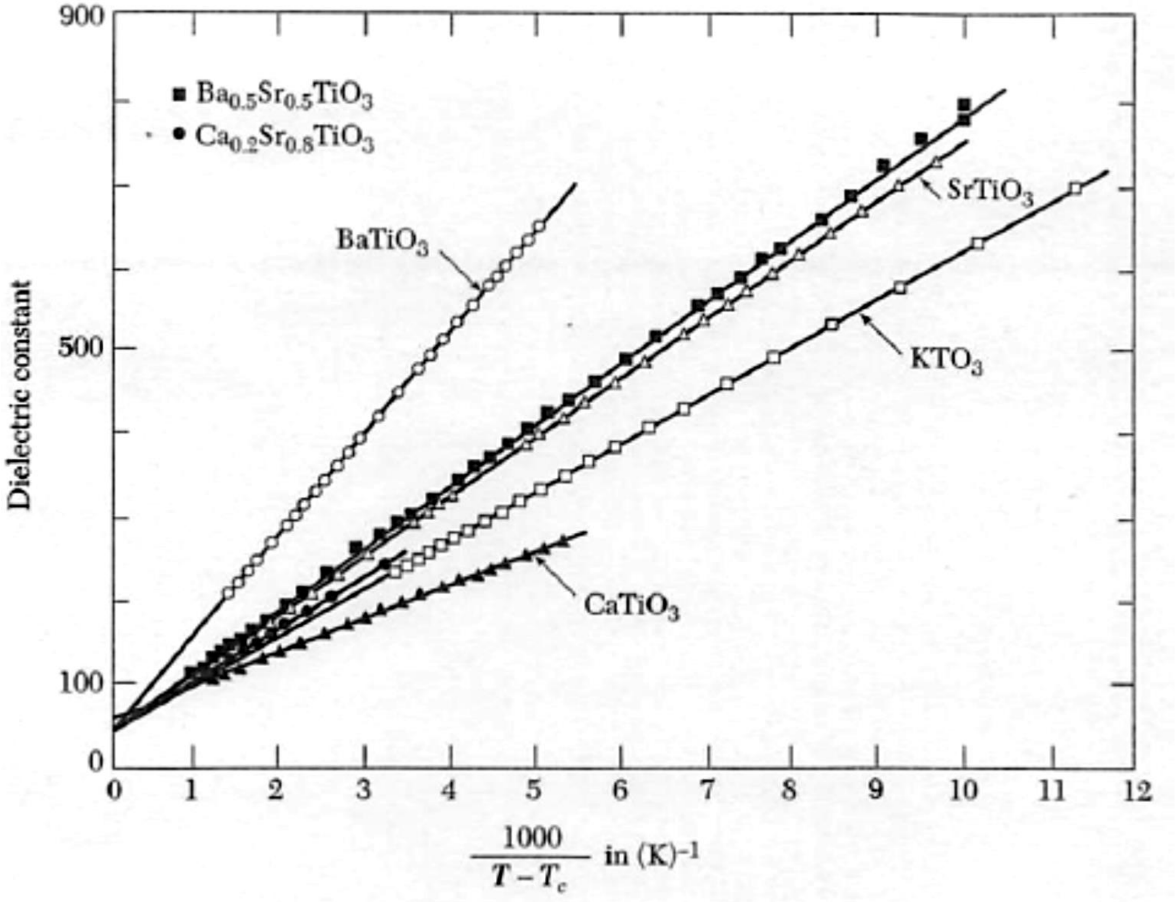
'4π/3 catastrophe' *(the coefficient $1/3\varepsilon_0$ is 4π/3 in CGI unit)*

4π/3 catastrophe: Slater theory of ferroelectricity

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 471

$$\varepsilon_0\chi = \frac{C}{T - C\frac{1}{3\varepsilon_0}}$$

Curie-Weiss law (applied for the paraelectric region)



Landau Theory of Phase Transition

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 474

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

=> Free energy is expanded by

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

Equilibrium polarization is obtained by

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

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

Landau Theory of Phase Transition

Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 476

Consider $E = 0$ for spontaneous polarization

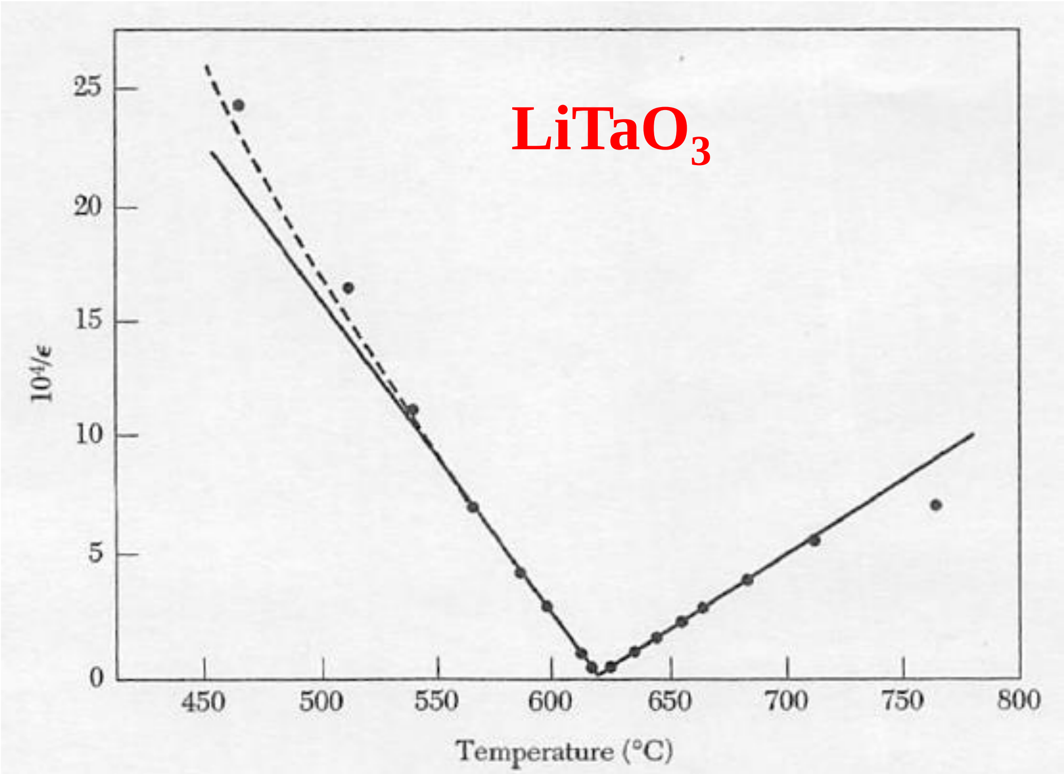
Second-order transition

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

$$\gamma(T - T_0)P_s + g_4 P_s^3 = 0 \ , \qquad (40)$$

$$\textbf{For } T \geq T_0\text{: } P_s = 0$$

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



Landau Theory of Phase Transition

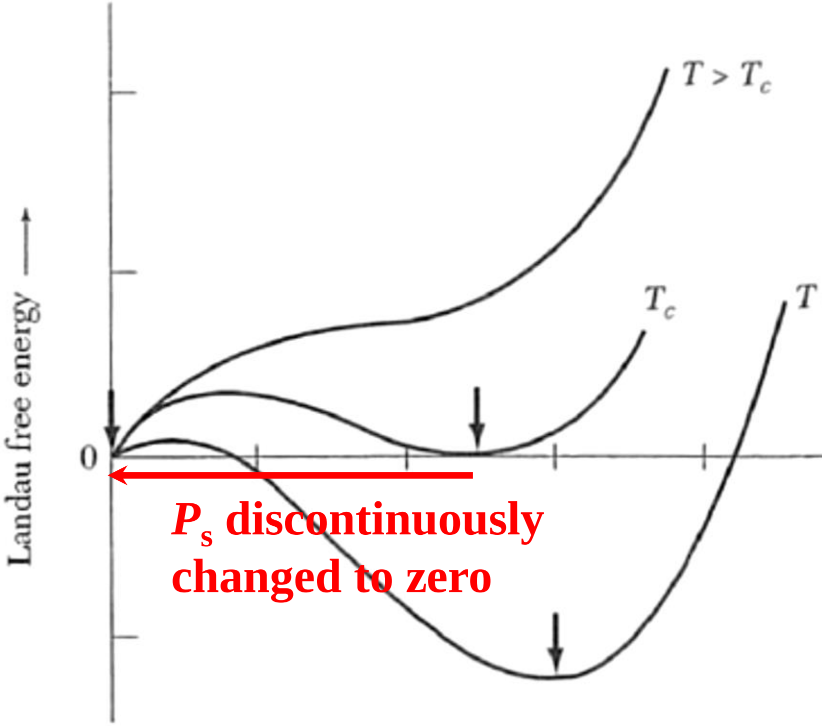
Kittel, Introduction to Solid State Physics, 8th ed (2005) p. 477

First-order transition

If g$_4$ is negative, the g$_6$ term must be retained.

$$\gamma(T-T_0)P_s - |g_4|P_s^3 + g_6 P_s^5 = 0 \ , \tag{42}$$

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



P_s discontinuously changed to zero