ELECTRONICS DEVICES AND MATERIALS

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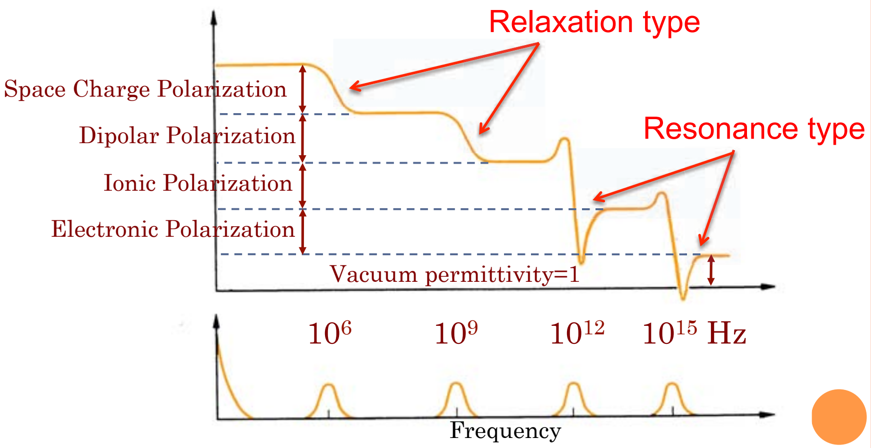
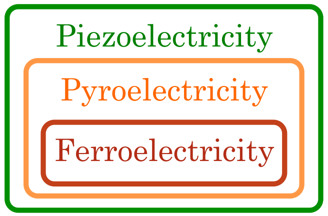
SYLLABUS

- Introduction to materials structure and dielectric physics (04/27)
- Ferroelectricity involved in structural phase transitions (05/25)
- Material design of dielectrics and introduction to metamaterials (06/01)
- Ferroelectric devices (06/08)

LAST TIME: DIELECTRIC DISPERSION ~ DIELECTRIC SPECTROSCOPY ~



LAST TIME: PIEZOELECTRICITY, PYROELECTRICITY AND FERROELECTRICITY



Piezoelectricity: the ability of some materials to generate an electric potential in response to applied mechanical stress
20 point groups lacking in a center of symmetry

Pyroelectricity: the ability of certain materials to generate an electrical potential when they are heated or cooled (having spontaneous polarization)
10 point groups including polar vectors

Ferroelectricity: Physical property of a material whereby it exhibits a spontaneous polarization, the direction of which can be switched between equivalent states by the application of an external electric field

FERROELECTRICITY INVOLVED IN STRUCTURAL PHASE TRANSITIONS

1. **Ferroelectricity**

2. **Phase Transition**

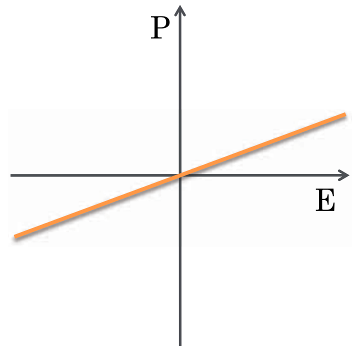
3. **First-order and Second-order Phase Transitions**
   - Ehrenfest Classification
   - Landau's Theorem

4. **Ferroelectricity Involved in Structural Phase Transitions**

5. **Classification of Ferroelectrics**
   - Displacive Type
   - Order-Disorder Type

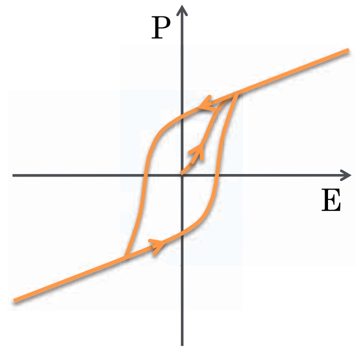
FERROELECTRICS: POLARIZATION REVERSAL (POLARIZATION SWITCHING)

Dielectric



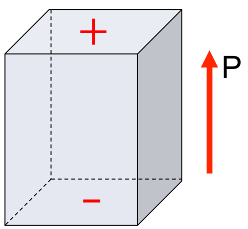
Linear response

Ferroelectric



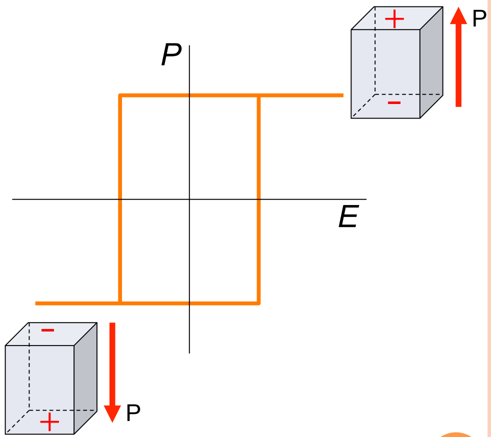
Strongly nonlinear field dependence
⇒ **polarization hysteresis loop**

POLARIZATION REVERSAL (POLARIZATION SWITCHING)



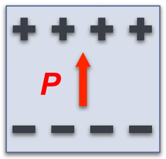
Vertical planes
- no 2-fold rotation (C^2)
- no mirror (m)

Polar Crystal Structure

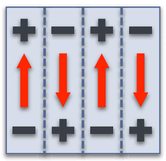


Polarization Reversal
(Single domain crystal)

FERROELECTRIC DOMAINS



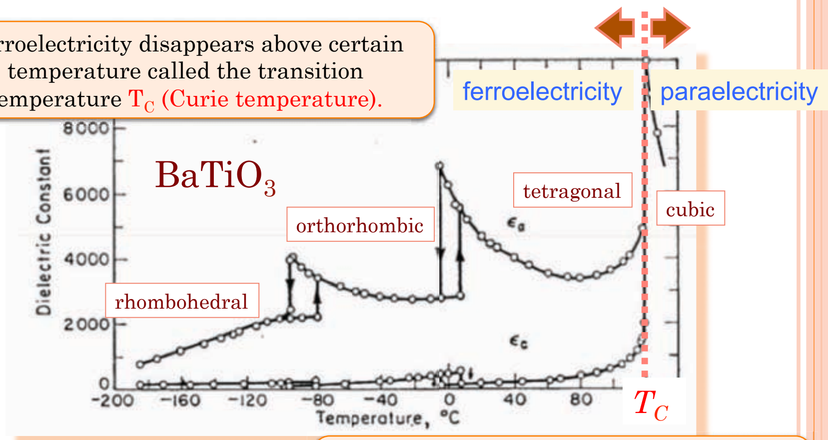
Single domain crystal:
energetically non-favorable
ⓘFabrication -heating above T_c
-cooling in an external E-field



Multi-domain crystal:
energetically favorable
ⓘControlled fabrication via E-field poling

FERROELECTRICS: CURIE TEMPERATURE

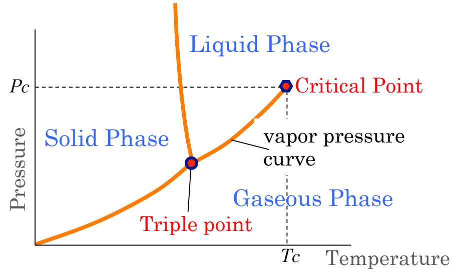
Ferroelectricity disappears above certain temperature called the transition temperature T_C (Curie temperature).



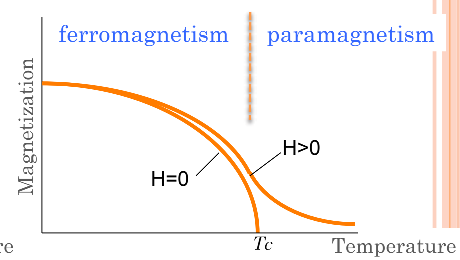
Above T_C the crystal is in a paraelectric phase where e > 1 and e(T) decreases rapidly with increasing T, P(E=0)=0.

PHASE TRANSITION

Phase Transision: the transformation of a thermodynamic system from one phase to another with a change in a variable such as the temperature, pressure, external magnetic field.



Schematic Phase Diagram of water



Phase Transition of ferromagnetism

THERMODYNAMICS OF PHASE TRANSITION ~EHRENFEST CLASSIFICATION ~

Ehrenfest's definition of phase transition: In an n-th order phase transition, the n-th and higher thermodynamic derivatives of Gibbs free energy G with respect to T and P show discontinuities.

Ehrenfest Classification

- first order phase transtion (1次相転移)
- second order phase transtion (2次相転移)
- n-th order phase transtion (n次相転移)

REVIEW OF THERMODYNAMICS

Gibbs free energy $G=H-TS=U+pV-TS$

Total differentiation⇒ $dG=dU+pdV+Vdp-TdS-SdT$

(First law of thermodynamics: $dU=TdS-pdV$)

$$dG=Vdp-SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_p=-S \qquad \left(\frac{\partial G}{\partial p}\right)_T=V$$

S, V = the first derivatives of Gibbs energy

THERMODYNAMICS OF PHASE TRANSITION ~EHRENFEST CLASSIFICATION ~

When entropy changes discontinuously,

↳ The 1st derivative of G with respect to T

The transition occurs at T_{trns} under constant pressure

The value of entropy jump : $\Delta_{trns}S$

$\Delta_{trns}H = T_{trns}\Delta_{trns}S$

$dH = TdS + Vdp$

The enthalpy change : Latent heat of 1st order phase transtion

notable characteristic of 1st order phase transition !

THERMODYNAMICS OF PHASE TRANSITION ~EHRENFEST CLASSIFICATION ~

definition of constant-pressure specific heat capacity :

$$Cp = \left(\frac{\partial H}{\partial T}\right)_p$$

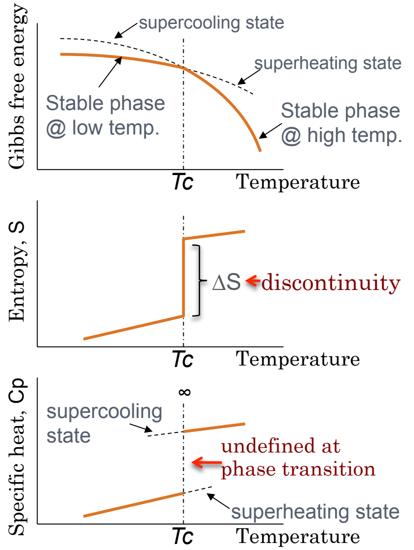
$$Cp = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

$dH = TdS + Vdp$

Cp = 2nd derivative of G with respect to T

⇒ Cp also shows discontinues in 1st order phase transition

THE FIRST-ORDER PHASE TRANSITION



Characteristic of 1st order phase transition

- coexsisting of high and low temp. phase

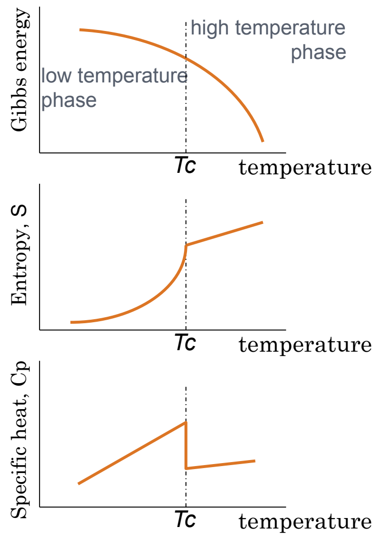
ex) ice melting

Tc=0 ˚C: coexisting of water and ice

- temperature hysteresis of phase transition

ex) supercooling phenomenon

THE SECOND-ORDER PHASE TRANSITION



@ phase transition temperature

Gibbs free energy (G): continuous & smooth change

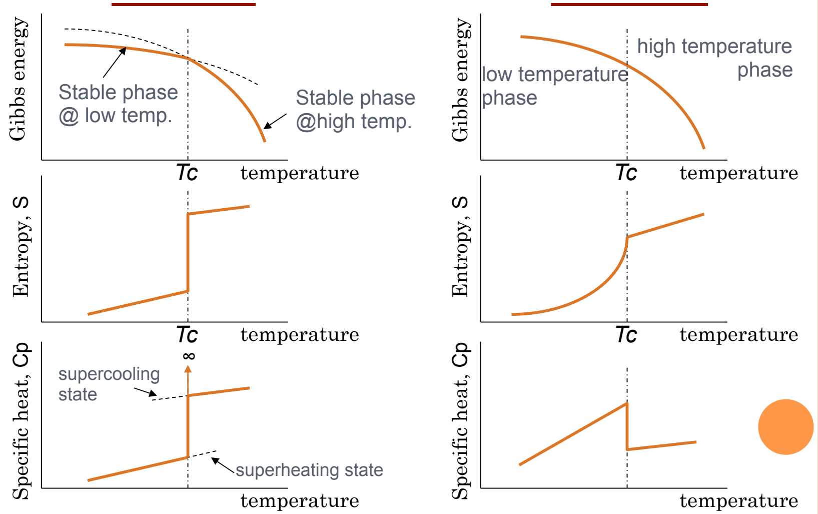
Entropy: 1st derivative of G continuous change

Specific heat: 2nd derivative of G *dis*continuous change

no associated latent heat !!

EHRENFEST CLASSIFICATION

1st order **2nd order**



MODERN CLASSIFICATION OF PHASE TRANSITIONS

Weakness of Ehrenfest scheme

Ehrenfest scheme does not take into account the case where a derivative of free energy diverges (which is only possible in the thermodynamic limit).

ex) the specific heat in ferromagnetic transition diverges to infinity.

Modern classification of Phase Transitions

The second-order phase transition (continuous phase transition)

- No latent heat

SYMMETRY-BREAKING TRANSITION ~ INTRODUCTION TO LANDAU'S THEORY~

In general thermodynamics, **phase transition** indicates the transformation from one phase to another.

In a narrow sense, phase transition take place between phases with different symmetry and without long-range atomic diffusion.

The terminology "phase transtiion " is used as this narrow sense in ferroelectric physics.

Symmetry-breaking process: the transition from the more symmetrical phase to the less symmetrical one

LANDAU PHENOMENOLOGICAL THEORY OF PHASE TRANSITIONS

- Thermodynamic potential density of free energy
- Quantity exists which could be used as a measure of order which appears in the ordered phase → order parameter
- Landau-Devonshire theory → order parameter spatially constant (spatial fluctuations are neglected, ferroelectrics P≠ F(m))

Free energy of Landau Theory

$$F(m)=F_0+\frac{1}{2}am^2+\frac{1}{4}bm^4+\frac{1}{6}cm^6+\cdots-HM$$

ORDER PARAMETER

Partial list of transitions and order parameters

Transition	Order parameter
Liquid-gas	density
Ferromagnetic	magnetization
Ferroelectric	polarization
Superconductors	complex gap parameter
Siperfluid	condensate wave function
Phase Separation	concentration

L. P. Kadanoff *et al.*, Rev. Mod. Phys., **39** (1967), 395.

FREE ENERGY OF FERROELECTRICITY IN LANDAU TREATMENT

Order parameter of ferroelectricity: polarization, P

$$F(m)=F_0+\frac{1}{2}aP^2+\frac{1}{4}bP^4+\frac{1}{6}cP^6+\cdots - EP$$

Simplifications: we neglect dependence of parameters on p and for simplicity only $a = f(T) = a_0(T-T_0)$

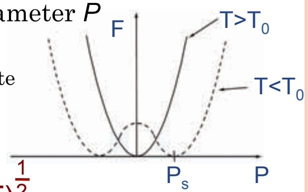
SECOND ORDER TRANSITION OF LANDAU THEORY

$$F(m)=F_0+\frac{1}{2}aP^2+\frac{1}{4}bP^4+\frac{1}{6}cP^6+\cdots - EP$$

$b \geq 0$ ➔ second order transition

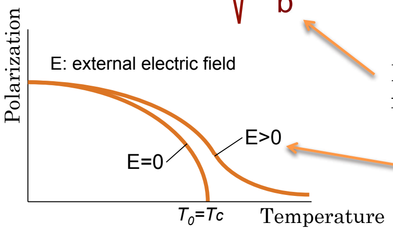
minimization of F ➔ equilibrium order parameter *P*

$$\frac{\partial F}{\partial P} = aP + bP^3 + \ldots - E = 0$$ equation of state



If E=0:

$$a+bP^2=0 \rightarrow P=\sqrt{-\frac{a}{b}} \rightarrow P=\sqrt{\frac{a_0}{b}}(T_0-T)^{\frac{1}{2}}$$

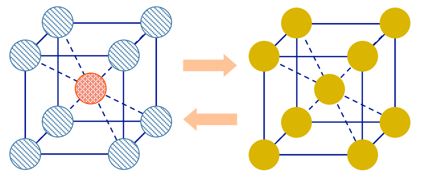


Nontrivial solution; only if T<T0, for T>T0 ➔P≅0

If E≠0:
cubic equation to solve ➔P≠0 above T_c

ORDER PARAMETER AND THE SECOND-ORDER PHASE TRANSITION

β-brass(CuZn)



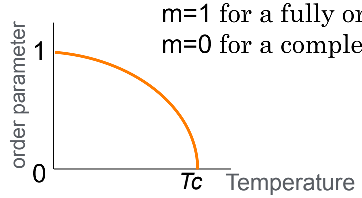
order structure (B2) | disorder structure (A2)

Cu
Zn
random occupation

Occupation fraction
Cu on body-center: ω(Cu)
Zn on body-center: ω(Zn)
When the occupation is random,
ω(Cu)= ω(Zn)=0.5
Order parameter: m

$$m=\left\langle \frac{\omega(Cu) - \omega(Zn)}{\omega(Cu) + \omega(Zn)} \right\rangle$$

m=1 for a fully ordered state
m=0 for a completely random state



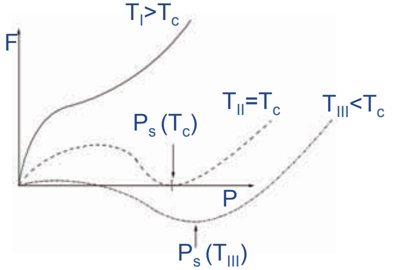
FIRST ORDER TRANSITION OF LANDAU THEORY

$b < 0$ ➔ first order transition

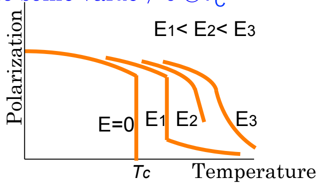
We need term $+\frac{1}{6}cP^6$ in order to keep F positive.

If E=0: $\frac{\partial F}{\partial P} = 0$ ➔ $aP - |b|P^3 + cP^5 = 0$ ➔ trivial solution P=0

nontrivial solution ↔ $a - |b|P^2 + cP^4 = 0$



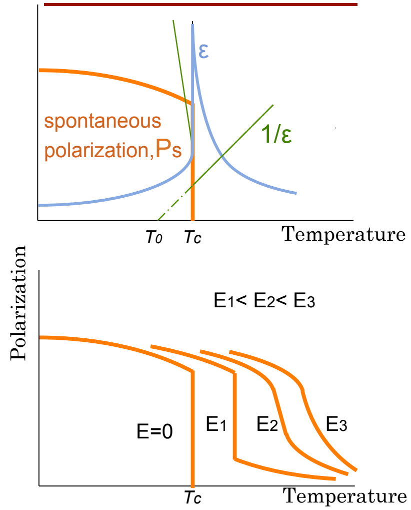
@T_C minimum of F appears at P≠0
➔ discontinuous jump of P from 0 to some value ≠ 0 @T_C



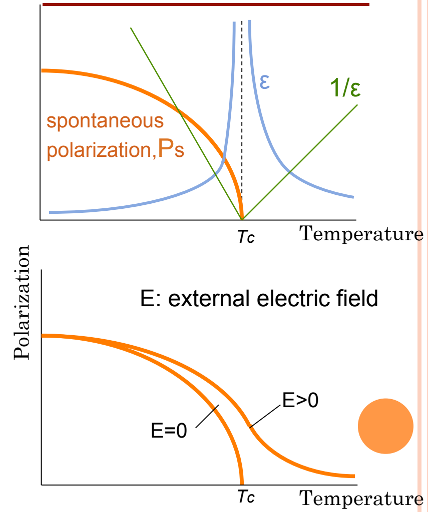
If E≠0: at some critical E_C discontinuous transition becomes continuous critical point defined by (T_C,E_C)

PHASE TRANSITION OF FERROELECTRISITY

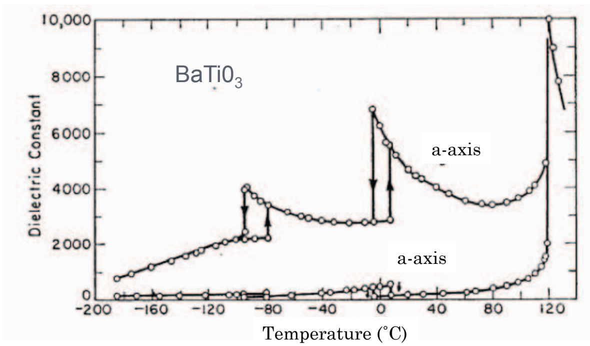
1st order transition

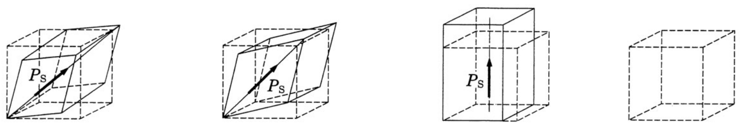


2nd order transition



WHICH DOES BARIUM TITANATE BEHAVE 1ST OR 2ND ORDER PHASE TRANSITION?





rhombohedral (C_{3v}) orthorhombic(D_{2v}) tetragonal(C_{4v}) cubic(O_h)

CLASSIFICATION OF FERROELECTRICS

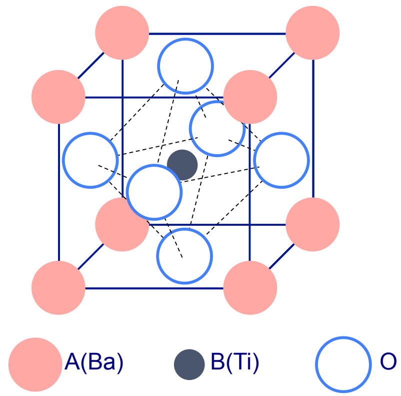
~ACCORDING TO THE NATURE OF THE FERROELECTRIC PHASE TRANSITION ~

- Displacive Type
- Order-Disorder Type

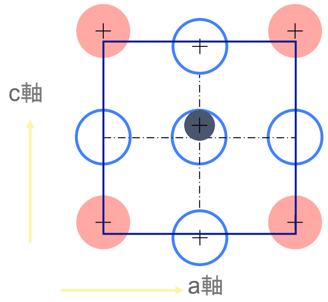
DISPLACIVE TYPE

Perovskite-type Oxide, ABO_3 ex) $BaTiO_3$, $PbTiO_3$

Cubic Perovskite Structure (Oh)

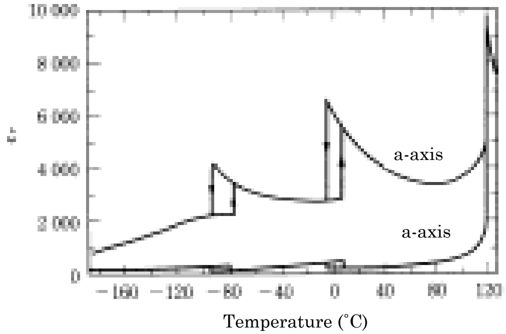


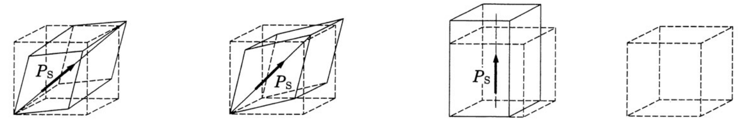
Projection of the ABO_3 structure on to the (010) plane



Dsiplacement of atoms

SUCCESSIVE PHASE TRANSITION OF BARIUM TITANATE



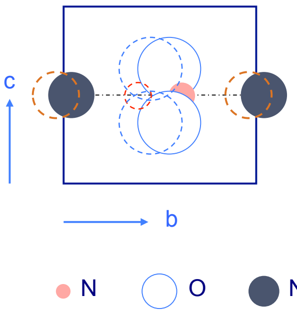


rhombohedral (C_{3v}) 3m
orthorhombic(D_{2v}) mm2
tetragonal(C_{4v}) 4mm
cubic(O_h) m3m

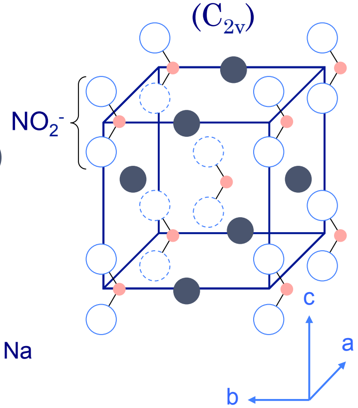
ORDER-DISORDER TYPE

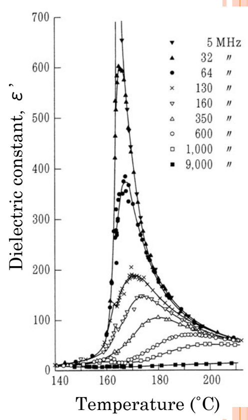
Sodium Nitrite, NaNO2

Paraelectric phase (D_{2h})



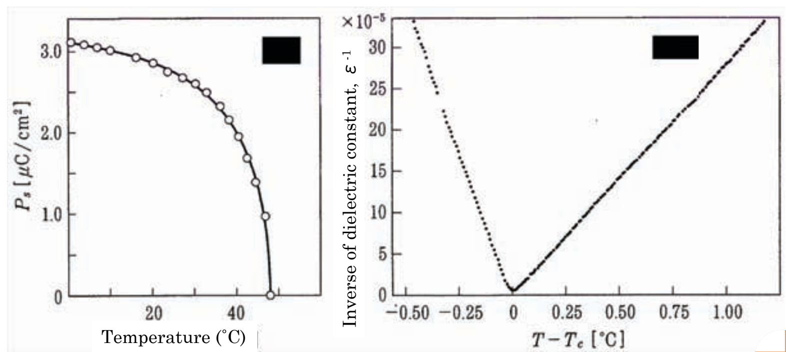
Ferroelectric phase (C_{2v})





ORDER-DISORDER TYPE

TGS; tri-glycine sulfate, $(NH_2CH_2COOH)_3H_2SO_4$



Spontaneous Polarization   Inverse of dielectric constant