**Chapter 13.**

**Dielectrics and Ferroelectrics**

applied electric field와 internal electric field 사이의 관계

Maxwell eq

$$\mathrm{div}E = 4\pi\rho$$

$$\nabla\times\vec{E} = -\frac{1}{c}\frac{\partial\vec{B}}{\partial t}$$

$$\mathrm{div}B = 0$$

$$\nabla\times\vec{H} = \frac{4\pi}{c}\vec{J} + \frac{1}{c}\frac{\partial\vec{D}}{\partial t}$$

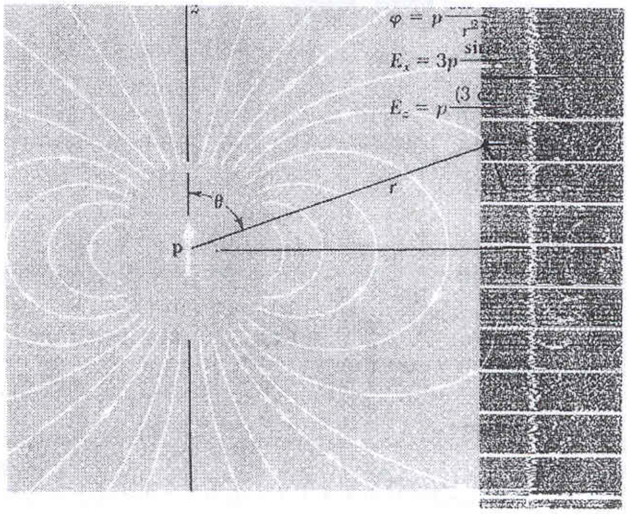
Polarization

P : total dipole moment per unit volume

$$p = \sum_n q_n r_n$$

dipole moment P일때 r 만큼 떨어진 곳에서 E field

$$\vec{E}(\vec{r}) = \frac{3(\vec{p}\cdot\vec{r})\vec{r} - r^2\vec{p}}{r^5}$$




Microscopic Electric field

$E_0$ : 외부에서 걸어준 E field

Arrange field 의 정의 : 그 점을 포함한 물체내의 모든 field의 평균

$$\vec{E}(r_0) = \frac{1}{V_c}\int dV\vec{e}(\vec{r})$$

r에서의 microscopic field

E, P, J 사이의 관계를 알아야 한다.

Polarization에 의한 field

평면에 charge가 있다고 가정하고 푼다.

$\sigma = \hat{n} \cdot \vec{p}$ $\qquad\qquad$ $E_1 = -4\pi\sigma = -4\pi p$

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↑p

+++++

$$\vec{E} = \vec{E_0} + \vec{E_1} = E_0 - 4\pi\rho\hat{z}$$

$E_1$ : field of the surface charge density $\hat{n} \cdot \vec{p}$ on the boundary

Depolarization field, E1

만약 $P_x, P_y, P_z$가 polarization $\vec{P}$의 component 이면

depolarization field 는

$E_{1x} = -N_x P_x$, $E_{1y} = -N_y P_y$, $E_{1z} = -N_z P_z$

$N_x + N_y + N_z = 4\pi$

Dielectric susceptibility $\chi$

$$\vec{P} = \chi\vec{E}$$

만약 $E_0$가 ellipsoid의 principal axis와 같은 방향이면

$$\vec{E} = \vec{E_0} + \vec{E_1}$$

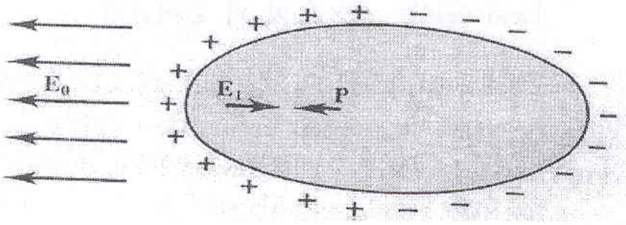
$$= E_0 - NP$$

$$\vec{P} = \chi\vec{E} = \chi(\vec{E_0} - N\vec{P})$$

$$\therefore \vec{P} \cdot (1 + \chi N) = \chi\vec{E_0}$$

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

local electric field at a atom




$$\vec{E}(\vec{r}) = \frac{3(\vec{p} \cdot \vec{r})\vec{r} - r^2\vec{p}}{r^5}$$

$$E_z = \frac{3(pz)z - r^2 p_z}{r^5}$$

한점에서의 field와 macroscopic field는 물론 다르다.

이점에 작용하는 dipole field는 $E_{dipole} = P\sum_i \frac{3Z_i^2 - r_i^2}{r_i^5} = P\sum \frac{2Z_i^2 - x_i^2 - y_i^2}{r_i^5}$

$$\sum\frac{z_i^2}{r_i^5} = \sum\frac{x_i^2}{r_i^5} = \sum\frac{y_i^2}{r_i^5}$$

∴local field는 macroscopic average field $\vec{E}$와 다르다.

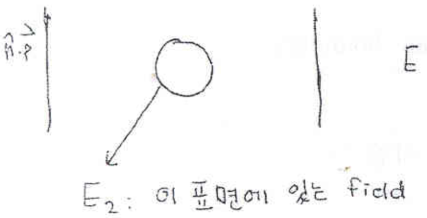
$$\vec{E}_{local} = \vec{E}_0 + \vec{E}_1 + \vec{E}_2 + \vec{E}_3$$

$E_0$ = field produced by fixed charges external to the body

$E_1$ = depolarization field (surface charge density $\hat{n}\cdot\vec{p}$ ) (outer surface)

$E_3$ : field of atomic inside cavity

$E_2$ : 이 표면에 있는 field




$E_2$ 정도는 약 50Å 반경의 radius로 잡자

$$E_1 + E_2 + E_3 = \sum_i \frac{3(\vec{p}_i\cdot\vec{r}_i)\vec{r}_i - r_i^2\vec{p}_i}{r_i^5}$$

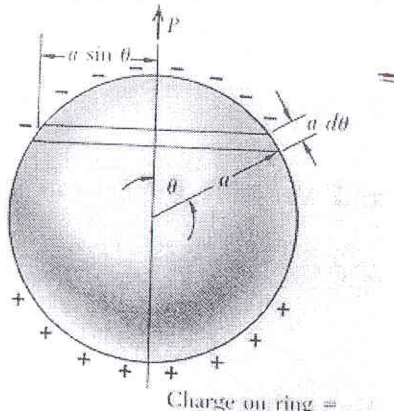
거리가 짧으면 잘 맞지 않는다.

따라서 $E_1$, $E_2$는 적분으로, $E_3$는 직접 한다.

p·cosθ : charge density

$$E_2 = \int_0^{\pi}\frac{2\pi a\sin\theta a d\theta p\cos\theta\cos\theta}{a^2} = 2\pi p\int_0^{\pi}\sin\theta\cos^2\theta d\theta$$

$$= -2\pi p\int_1^{-1}t^2dt = 2\pi p\frac{2}{3} = \frac{4\pi}{3}p$$



Charge on ring = $2\pi\, a\sin\theta\cdot a\, d\theta\cdot P\cos\theta$

$$\Rightarrow \frac{2\pi a\sin\theta d\theta}{a^2}(p\cos\theta)\cos\theta$$

$\sigma$-방향 [$\cos\theta$=t $\sim\sin\theta\, d\theta$=dt]

$$\vec{E}_{loc} = \vec{E}_0 + \vec{E}_1 + \frac{4\pi}{3}\vec{P} = \vec{E} + \frac{4\pi}{3}\vec{P}$$

Inside 에서의 dipole moment의 합은 zero 였다.

$$\vec{E}_{loc} = \vec{E} + \frac{4\pi}{3}\vec{P}$$

local field는 $\frac{4\pi}{3}\vec{P}$ 가 더 들어간다.

Dielectric Constant and Polirizaability

$$\varepsilon \equiv \frac{E+4\pi p}{E} = 1 + 4\pi\chi$$

만약 Non cubic crystal 이었다면

$$P_{\mu} = \chi_{\mu\nu}E_{\nu} \quad ; \quad \varepsilon_{\mu\nu} = 1 + 4\pi\chi_{\mu\nu}$$

The polarizability $\alpha$ of an atom

$$P = \alpha E_{local}$$

$$P = \sum N_j P_j = \sum N_j \alpha_j E_{loc}(j)$$

dielcctric constant 와 polarizabilities

local field

$$P = (\sum N_j \alpha_j)(E + \frac{4\pi}{3} P)$$

$$\chi = \frac{P}{E} = \frac{\sum N_j \chi_{aj}}{1 - \frac{4\pi}{3} \sum N_j \chi_j}$$

$$\varepsilon = 1 + 4\pi\chi$$

$$= 1 + \frac{4\pi \sum N_j \chi_j}{1 - \frac{4\pi}{3} \sum N_j \chi_j} = \frac{1 + \frac{8\pi}{3} \sum N_j \chi_j}{1 - \frac{4\pi}{3} \sum N_j \chi_j}$$

$$\therefore 12\pi a = (\varepsilon - 1)(1 - a) = \varepsilon - 1 - (\varepsilon - 1)a$$

$$\therefore 12\pi a + (\varepsilon - 1)a = \varepsilon - 1$$

$$a[12\pi + (\varepsilon - 1)] = \varepsilon - 1$$

Let $\sum N_j \chi_j = a$

$$\chi = \frac{a}{1 - \frac{4\pi}{3} a} = \frac{\varepsilon - 1}{4\pi}$$

$$\therefore \quad 4\pi a = (\varepsilon - 1)(1 - \frac{4\pi}{3} a)$$

$$= \varepsilon - 1 - \frac{4\pi}{3}(\varepsilon - 1)a$$

$$\therefore \quad 4\pi a + \frac{4\pi}{3}(\varepsilon - 1)a = \varepsilon - 1$$

$$\frac{4\pi}{3}[3 + \varepsilon - 1]a = \varepsilon - 1$$

$$\therefore \quad \frac{4}{3}\pi a = \frac{\varepsilon - 1}{\varepsilon + 2}$$

$$\therefore \quad \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \sum N_j \alpha_j$$ Clausius Mossotti relation

Electronic Polarizability

total polarizability : electronic : 핵에 대해 얼마나 움직이나?

: ionic : ion에 대해 얼마나 움직이나?

: dipolar : permanent dipole에 대해

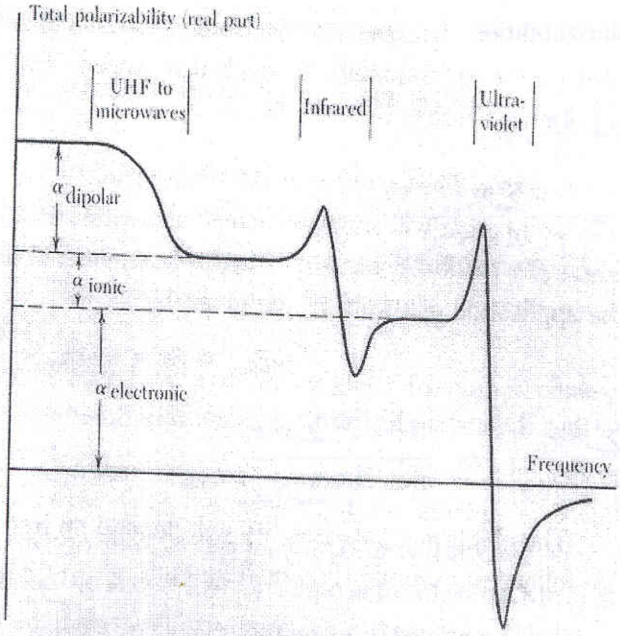



Figure 8 Frequency dependence of the several contributions to the polarizability.

momentum inertia 가 제일 작은 것은 electron이다.

$$\frac{n^2-1}{n^2+3} = \frac{4\pi}{3}\sum N_j\alpha_j \quad \text{(electronic)}$$

$$n^2 = \varepsilon$$

Classical theory of electronic polarizability

electron이 harmonically bound 되어 있다.

$$-e\,E_{loc} = \beta\,\chi = m\,\omega_0^2\,\chi$$

$$\alpha\,(\text{electronic}) = P/E_{loc} = -e\,\chi/E_{loc} = e^2/m\,\omega_0^2$$

$$-e\,E_{loc} = M\ddot{\chi} + m\,\omega_0^2\,\chi$$

$$= -M\,\omega^2\,\chi + M\,\omega_0^2\,\chi$$

$$\therefore \quad \chi = \frac{-eE_{loc}}{M(\omega_0^2-\omega^2)}$$

$$\alpha\,(\text{electronic}) = \frac{P}{E_{loc}} = \frac{-e\chi}{E_{loc}} = \frac{e^2}{M(\omega_0^2-\omega^2)}$$

Quantum theory

$$\alpha\,(\text{electronic}) = \frac{e^2}{m}\sum\frac{f_{ij}}{\omega_{ij}^2-\omega^2}$$

$f_{ij}$ : oscillator 의 strength라 불리 운다.

Structural phase transition

온도와 압력을 변화시킨다.

lowest accessble internal energy

온도 T=0

A ———————————— B

phonon spectrum을 보면 soft 하다.

lowest freq에서 phonon이 증가

entropy가 A보다 높다.

F = U - TS 로 결정한다.

$F_A(T_c) = F_B(T_c)$

· Applied stress

· macroscopic electrical properties

Spontaneous dielectric polarization

Ferroelectrics 재미난 temp-dependent

dielectric constant

piezoelectric effect

pyroelectric effect

electrioptical effect [optical frequency doubling]

Ferroelectric crystal

· positive charge와 negative charge의 중심이 맞지 않는다.

E field 증가 ⇄ 감소

significient hysteresis

갑자기 polarizability가 변한다. 이런 결정을 pyroelectric이라 부른다.

$LiN_1O_3$ : Tc = 1480K에서 spontaneous polarization

Ferroelectricity —— $T_c$ —— T > Tc paraelectricity

Classification of Ferroelectric Crystal

Order - disorder : paraelectric 이 반발 random하게 있다가 ordered phase로 바뀐다.

displacive : 한쪽으로 가서 생김

displaceive : perovskite , ilmente

초전도연구단
단장 이 성 익

perovskite

$T^{4+}Ba^{2+}O_3^{2-}$

[below curi
temp.]
-약간 변형.

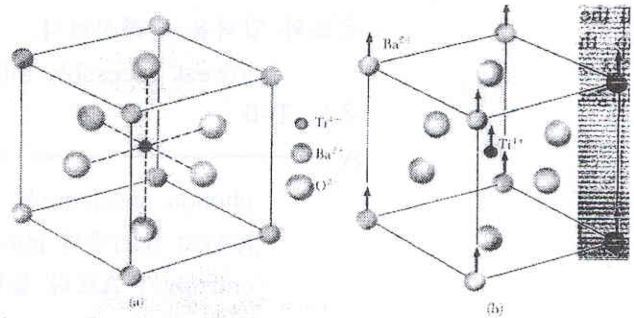



**Figure 10** (a) The crystal structure of barium titanate. The prototype crystal is calcium titanate (perovskite). The structure is cubic, with $Ba^{2+}$ ions at the cube corners, $O^{2-}$ ions at the face centers, and a $Ti^{4+}$ ion at the body center. (b) Below the Curie temperature the structure is slightly deformed, with $Ba^{++}$ and $Ti^{4+}$ ions displaced relative to the $O^{2-}$ ions, thereby developing a dipole moment. The upper and lower oxygen ions may move downward slightly.

ferroelectric effect in barium titanate

$$P_S = 8\times 10^4 esu \cdot cm^{-2}$$

cell's volume $(4\times 10^{-8})^3 = 64\times 10^{-24}\ cm^3$

dipole moment per unit cell

$$P = (8\times 10^4\ esu \cdot cm^{-2})(64\times 10^{-24} cm^3)$$

$$= 5\times 10^{-18} esu \cdot cm$$

Displaceive trasition

어떤 순간에 Foarier component of polarization이 매우 커진다.

같은 말로 Transverse phonon이 condense한다.

To phonon vanish

local electric field가 electric restoring force를 넘어서 돌아가지 않는다.

DIELECTRIC CONSTANT

$$\varepsilon = \frac{1+\frac{8\pi}{3}\sum N_i\alpha_i}{1-\frac{4\pi}{3}\sum N_i\alpha_i}$$

dielectric constant become infinite

$$\frac{4\pi}{3}\sum N_i\alpha_i = 1-3S$$

$|S| \ll 1$이면 dielectric constantbecome infinite

$$\varepsilon \cong \frac{1}{S}$$

Critical temp 근처에서는

$S \cong \frac{T-T_c}{\xi}$ 라 하면, dielectric const는 $\varepsilon \simeq \frac{\xi}{T-T_c}$

Soft-optional phonon

$$\frac{\omega_T^2}{\omega_L^2} = \frac{\varepsilon(\infty)}{\varepsilon(0)} \quad ; \text{LST relation}$$

$\varepsilon(0) \rightarrow \infty \qquad \omega_T \rightarrow 0$

no effective restoring force

실험 $\frac{1}{\varepsilon(0)} \propto T - T_0, \qquad \omega_T^2 \propto T - T_0$ 가 된다.

실험으로 증명이되다 [참고그림:ch13-fig13]

Landau theory of the phase transition

polarization

ferroelectric ———————— paraelectric

discontinuous

charge

$$\hat{F}(P : T : E) = -EP + g_0 + \frac{1}{2} g_2 P^2 + \frac{1}{4} g_4 P^4 + \frac{1}{6} g_6 P^6$$

P가 center of inversion symmetry를 갖고 있기에

이 series가 odd power를 갖고 있지 못하다.

extream condition

$$\frac{\partial \hat{F}}{\partial P} = 0 = -E + g_2 P + g_4 P^3 + g_6 P^5$$

$g_2$가 온도 항을 갖고 있다면

$g_2 = \gamma (T - T_0)$

2nd-order transition

Zero applied field

$$\gamma (T - T_0) P_s + g_4 p_s^3 = 0$$

$P_s = 0$ or $P_s^2 = \frac{\gamma}{g_4}(T_0 - T)$

만약 $T \geq T_0$, $\gamma$, $g_4$ 가 positive Nothing happen

$T \leq T_0$, $\gamma$, $g_4$ 가 positive

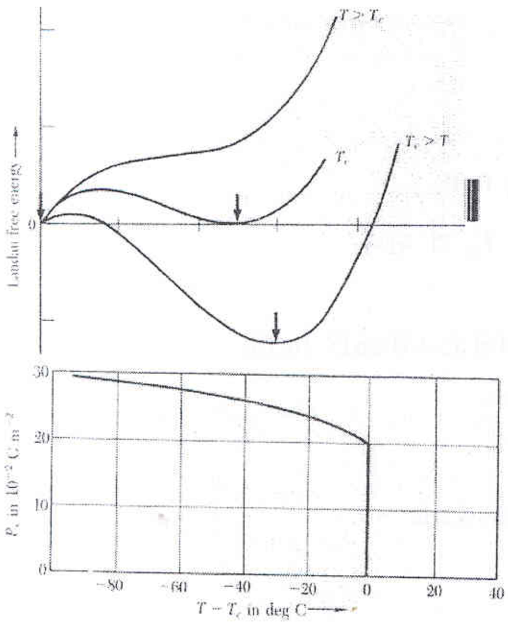
$$|P_s| = \sqrt{\frac{\gamma}{g_4}(T_0 - T)}^{\frac{1}{2}}$$

polarization이 continuously charge

→ 2nd order phase transition

First order transition

$g_4$ 가 negative 일 때, $g_6$ 까지 가자 $\gamma(T - T_0) p_s - |g_4| P_s^3 + g_6 P_s^5 = 0$



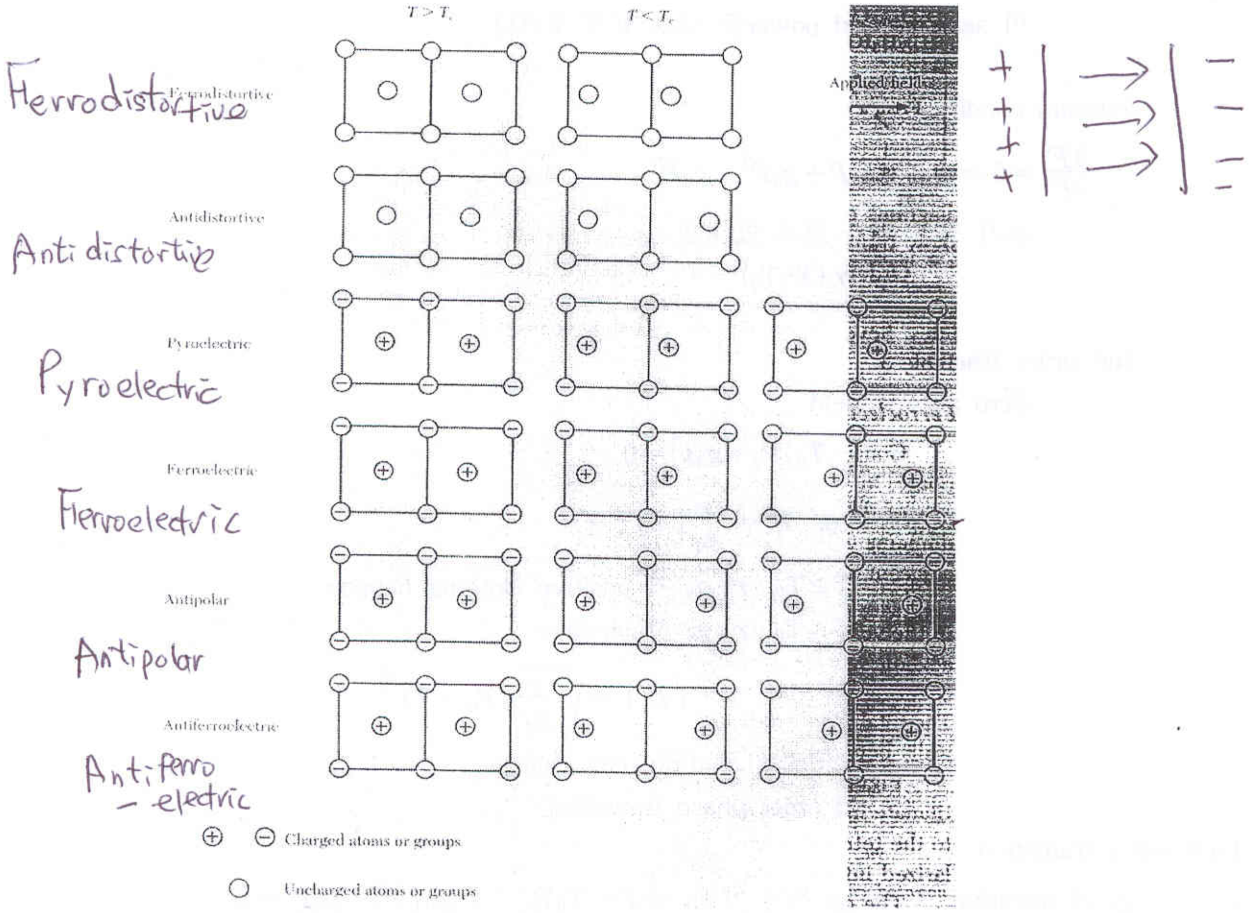

Ps = 0 or $\gamma(T-T_0)p_s - |\,g_4\,|\,P_s^3 + g_6 P_s^5 = 0$

$$P_s^2 = \frac{|\,g_4\,| \pm \sqrt{g_4^2 - 4\gamma(T-T_0)g_6}}{2g_6}$$

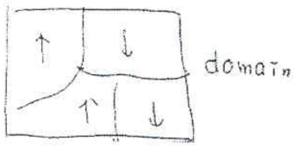
갑자기 변한다. ∴ firsr order transition 이다.

Anti ferroelectricity

One type of deformation으로 antiferroelectric



Ferroelectric Domain




domain

total dipole moment of the crystal은
domain의 움직임으로 결정이 된다.

Thermal fluctuation과 경쟁

piezoelectricity

모든 ferroelectric state는 piezoelectric이다.

stree Z가 electric polarization을 바꾼다.

$P = Zd + E\chi, \quad e = Zs + Ed$

P : polarization   d : piezoelectric strain constant

Z : stress

$\chi$ : dielectric susceptibility

e : electric strain

s : electric compilance constant

ferroelectric이 아니더라도 piezoelectric이 될 수 있다.

Piezoelectric strain constant

$$d_{ik} = \left( \frac{\partial e_k}{\partial E_i} \right)_Z$$

i=x, y, z   k=xx, yy, yz, zx, xy

PZT : lead zirconate - lead titanate

$PVF_2$ : 매우 강하다.

medical applications to monitor blood pressure and respiration