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Ferroelectrics: Theoretical Concepts and Applications

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Ferroelectrics: Theoretical Concepts and Applications

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Plan du cours

- Dielectric Materials
- Local Field
- Dielectric Relaxation
- Ferroelectric Materials
- Landau Theory
- Applications

Dielectric Materials

- Definition of permittivity

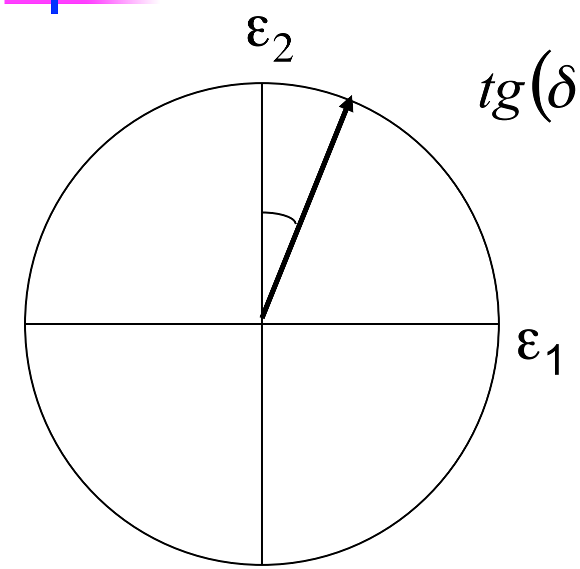
$$\vec{P} = \varepsilon_0 \chi \vec{E}_{ext}$$

$$\vec{D} = \varepsilon_0 \vec{E}_{ext} + \vec{P}$$

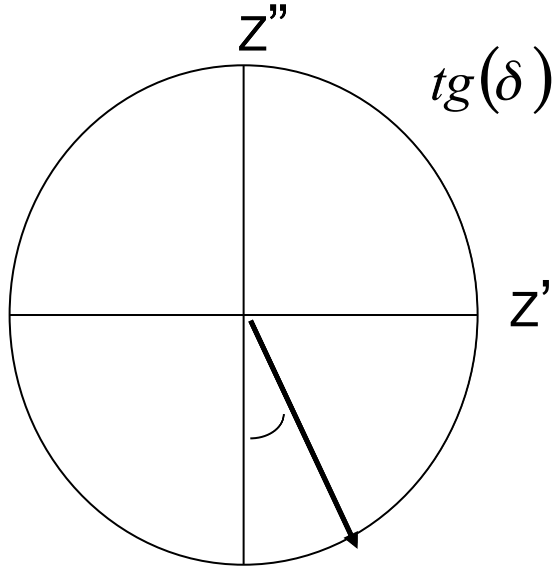
$$\varepsilon_r = \varepsilon_0 (1 + \chi)$$

- Complex representation $\varepsilon_r^*(\omega) = \varepsilon_{1r}(\omega) + j\varepsilon_{2r}(\omega)$

Dielectric Materials



$$tg(\delta) = \frac{\varepsilon_2}{\varepsilon_1}$$



$$tg(\delta) = \frac{Z''}{Z'}$$

$$\frac{1}{Z} = jC^{*}\omega \quad \text{avec} \quad C^{*}(\omega) = \varepsilon^{*}(\omega)C_0$$

$$\frac{1}{Z} = jC\omega + \frac{1}{R} = j\omega\varepsilon_1(\omega)C_0 + \omega\varepsilon_2(\omega)C_0$$

Dielectric Materials

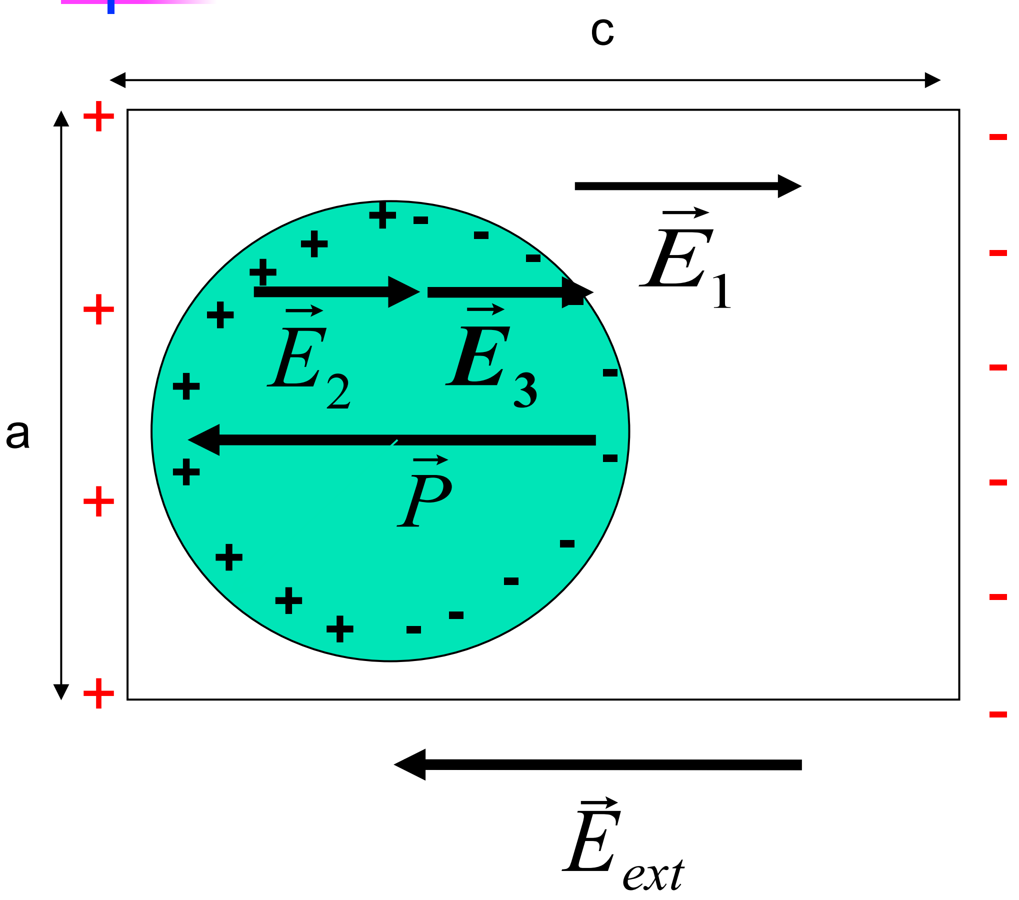
$$\vec{P} = \frac{d\vec{p}}{d\tau}$$

$P = P_e + P_a + P_d + P_c$

- Electronic Polarization : P_e
- Atomic or ionic polarization: P_a
- Dipolar polarization: P_d
- Space charge polarization : P_C

Dielectric Materials

Local Field



$\vec{E}_{Loc} = \vec{E}_{ext} + \vec{E}_1 + \vec{E}_2 + \vec{E}_3$

$\vec{E}_{ext}$ = External field

$\vec{E}_1$ = Depolarizing field due to charge density

$\vec{E}_2$ = Lorentz field

$\vec{E}_3$ = field of atoms inside the cavity

Local Field

Determination of E1

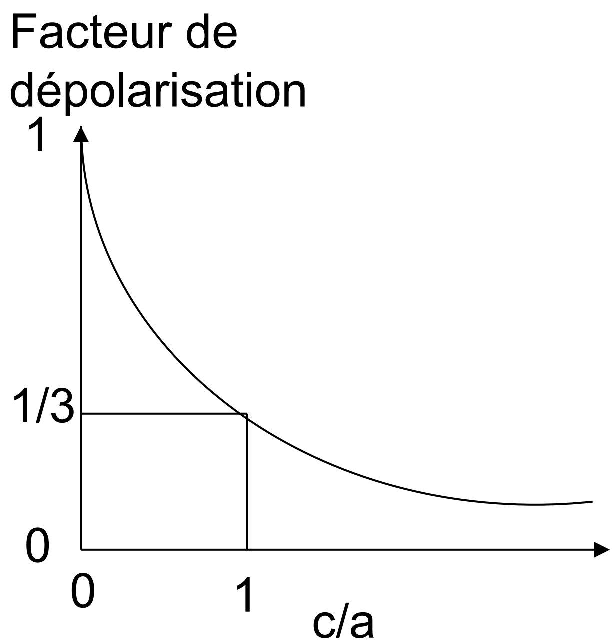
Materials that have an ellipsoidal shape have an important property:

-When the field is uniform, the polarization is uniform.

-Polarization is related to the field by the depolarization factor N:

$$E_{1x} = -\frac{N_x P_x}{\varepsilon_0}; E_{1y} = -\frac{N_y P_y}{\varepsilon_0}; E_{1z} = -\frac{N_z P_z}{\varepsilon_0}$$

- $N_x + N_y + N_z = 1$



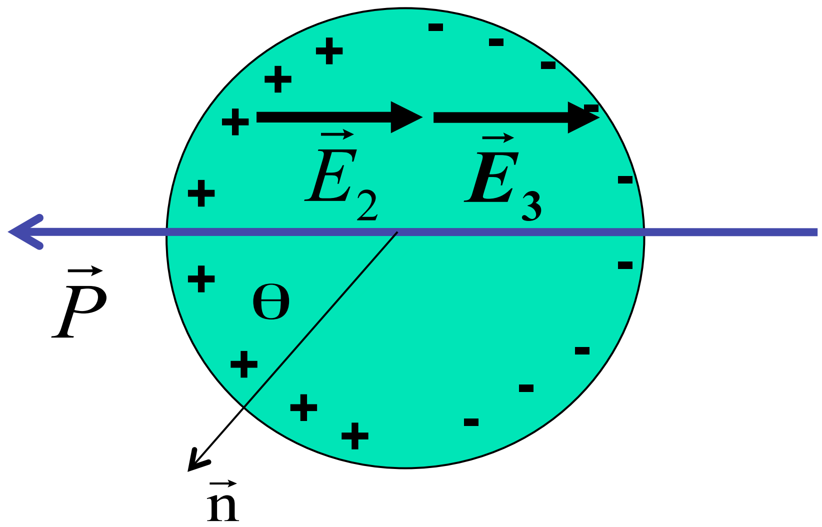
Rq: Nx, Ny et Nz are the depolariztion factors, their values depend on the relationship between the principal axes of the ellipsoid.

For a sphere Nx=Ny=Nz = 1/3

$$E_1 = -\frac{P}{3\varepsilon_0}$$

Local Field

Determination of E2



$$\sigma_p = \vec{P}.\vec{n} = P\cos\theta$$

$$E_2 = \frac{1}{4\pi\varepsilon_0}\iint\frac{\sigma ds}{r^2}\cos\theta$$

$$E_2 = \frac{1}{4\pi\varepsilon_0}\int_0^{\pi}\frac{P\cos\theta}{a^2}a^2.2\pi.\sin\theta.\cos\theta.d\theta$$

$$E_2 = \frac{P}{2\varepsilon_0}\int_0^{\pi}\cos\theta^2.\sin\theta.d\theta = \frac{P}{3\varepsilon_0}$$

Local Field

Determination of E3

Field E3, due to the dipoles inside the cavity is the only term that depond of the crystal structure. It has been shown that for a reference site with a cubic environment into a sphere, that:

E3 = 0

$$E_{Loc} = \underbrace{E_0 + E_1}_{E_{Mac}} + E_2 + E_3 = E_{Mac} + \frac{\mathbf{P}}{3\varepsilon_0}$$

Local Field

Clausius Mossotti law

The polarization is expressed in terms of local field by :

$P = N\alpha E_{loc}$: which is the microscopic representation

α: is the polarizability of material

- In the case of a material with several kind of atom j, the polarization is written:

$$P = \sum_j N_j \alpha_j E_{loc}(j) = \sum_j N_j \alpha_j \left(E_{Mac} + \frac{P}{3\varepsilon_0}\right) \Rightarrow$$

$$\chi = \varepsilon_r - 1 = \frac{P}{\varepsilon_0 E_{Mac}} = \frac{\sum_j N_j \alpha_j}{\varepsilon_0 - \frac{1}{3}\sum_j N_j \alpha_j}$$

$$\text{On a } \chi = \varepsilon_r - 1 \Rightarrow \frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{1}{3\varepsilon_0}\sum_j N_j \alpha_j \quad : \text{Clausius Mossotti relation}$$

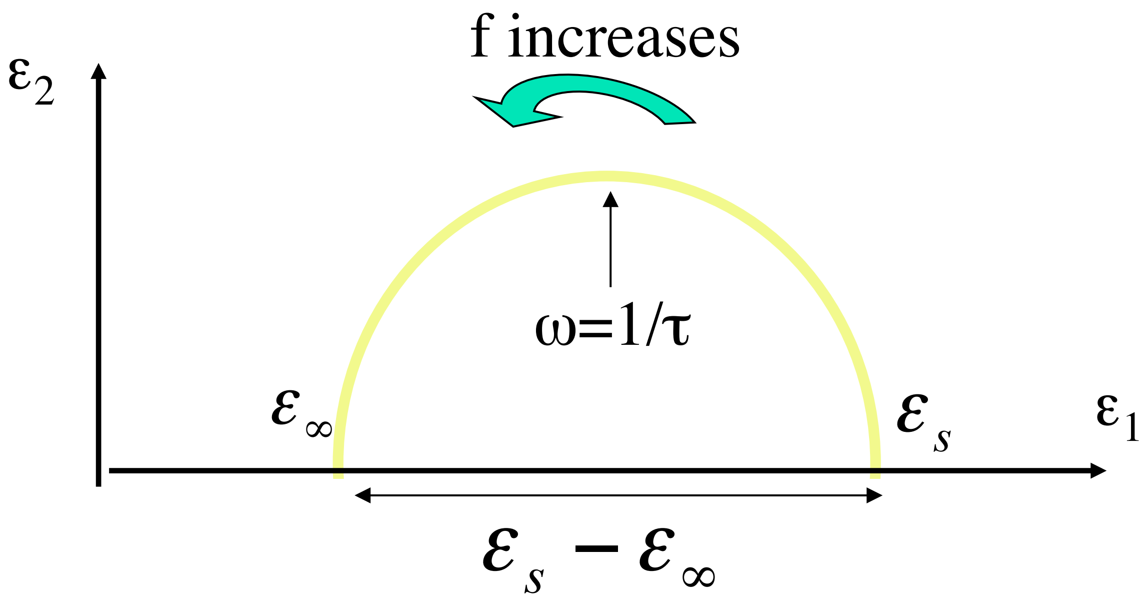
Catastrophe de Mossotti

Dielectric Relaxation

Dielectric Relaxation

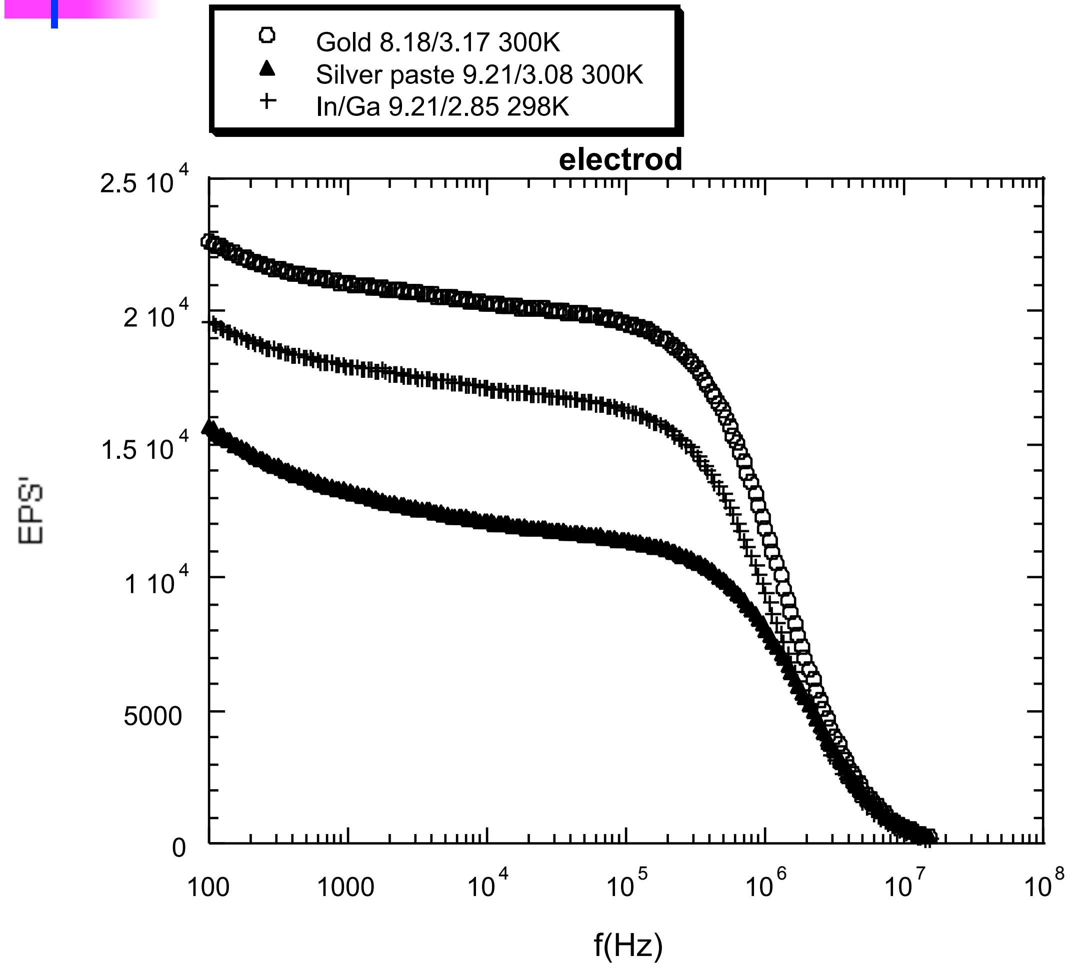
Cole-Cole Diagram

$$\varepsilon^*(\omega) = \varepsilon_1(\omega) - j\varepsilon_2(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau}$$



Dielectric Relaxation

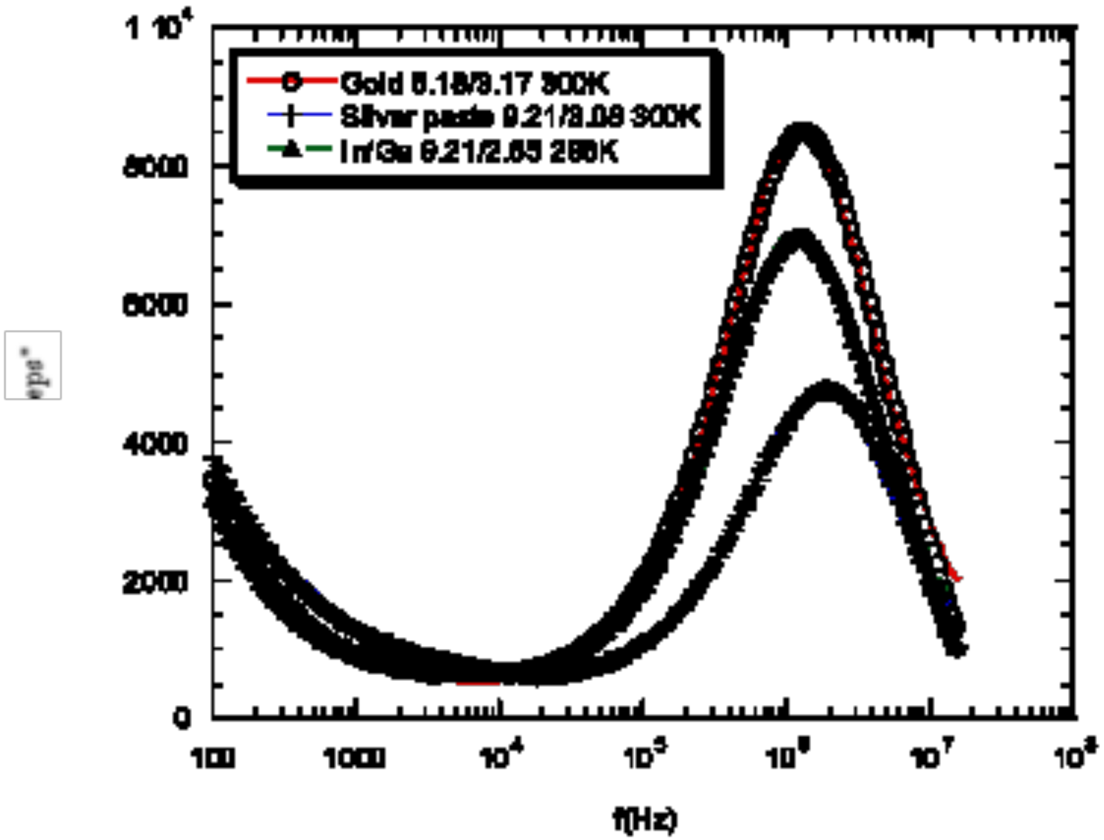
Real part of permittivity



$$\varepsilon_1 = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2}$$

Dielectric Relaxation

Imaginary part

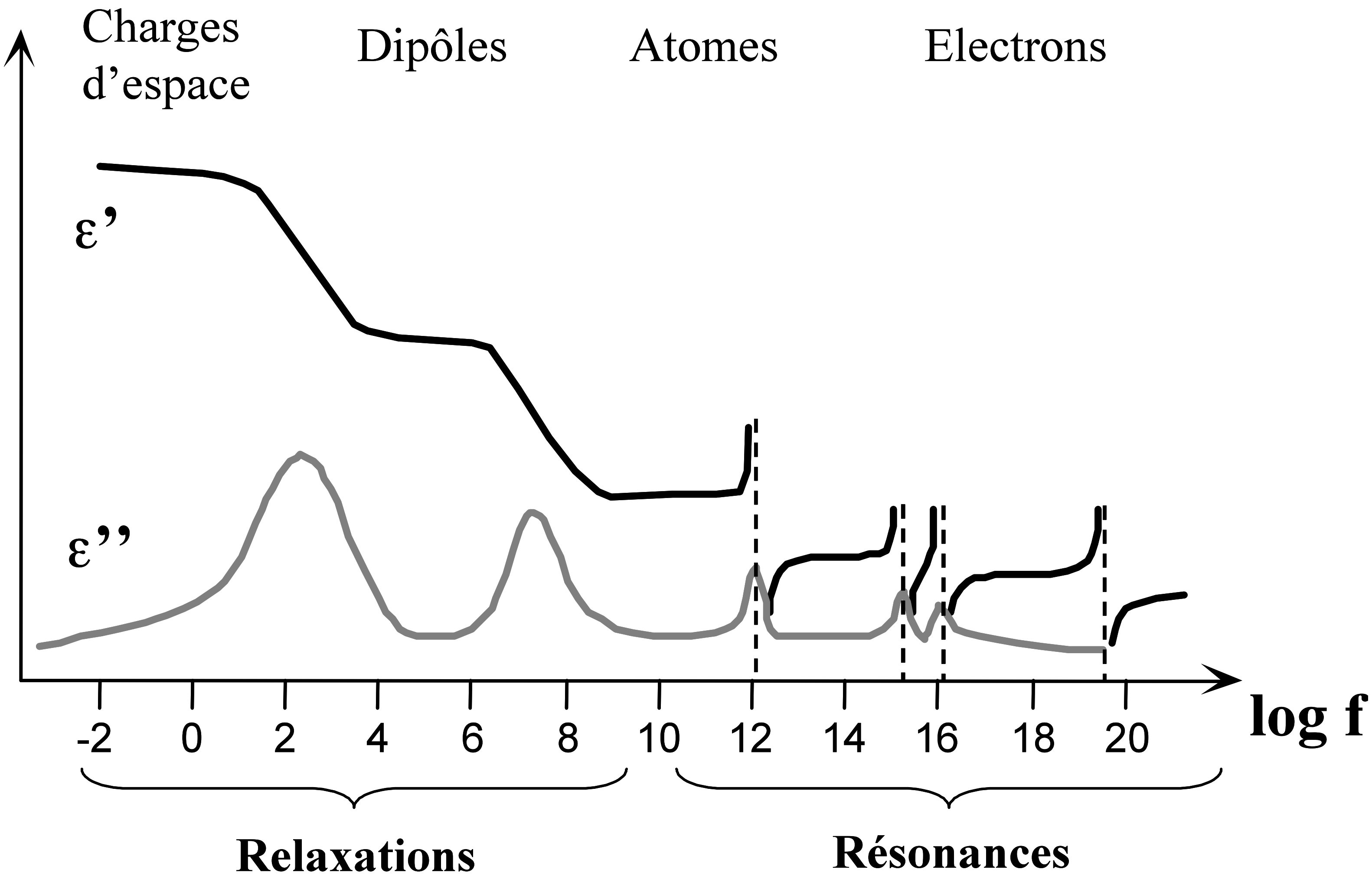


$$\varepsilon_1 = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1+\omega^2\tau^2}$$

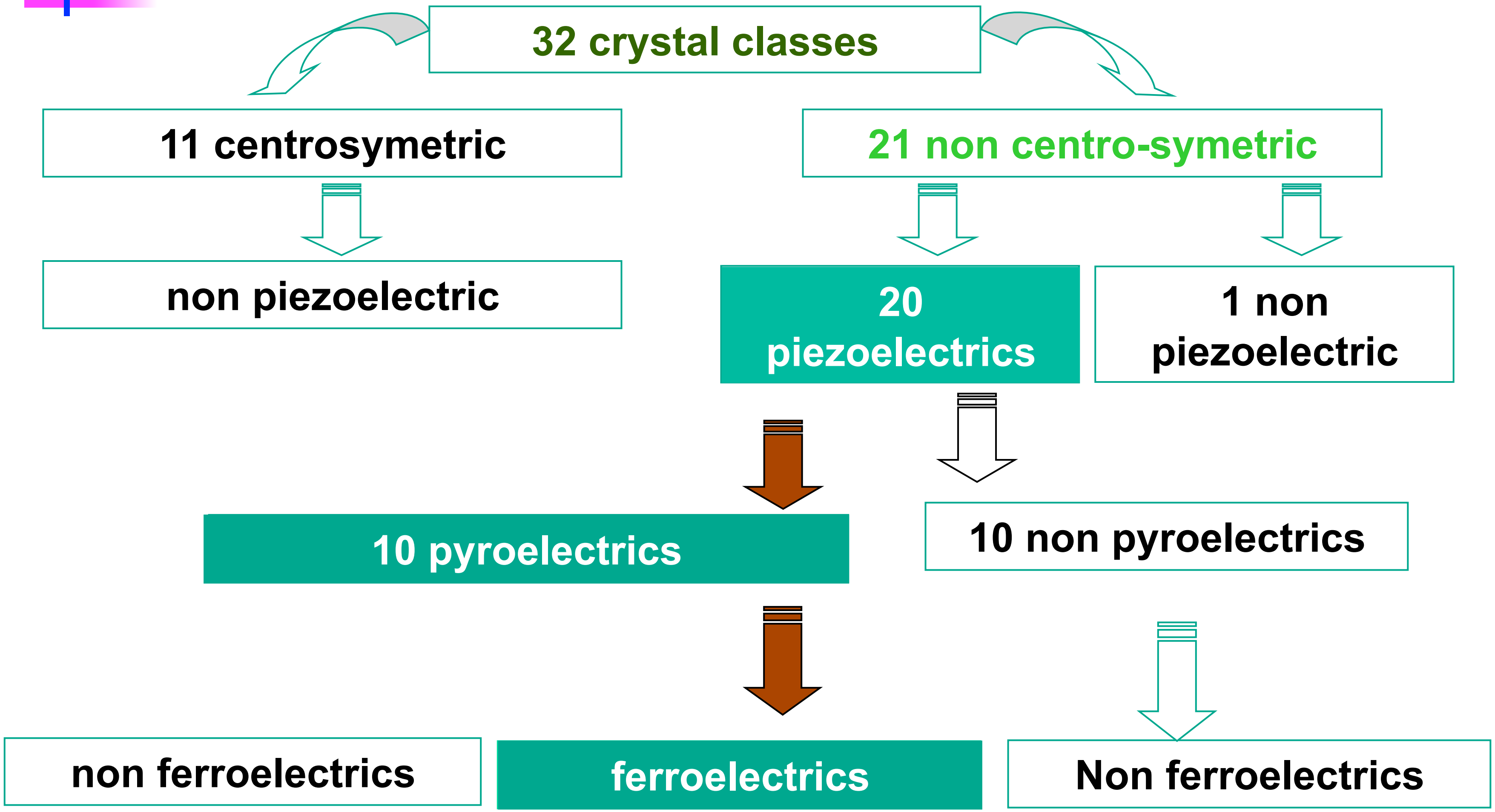
Effet de la température et de la conductivité

Dielectric Relaxation

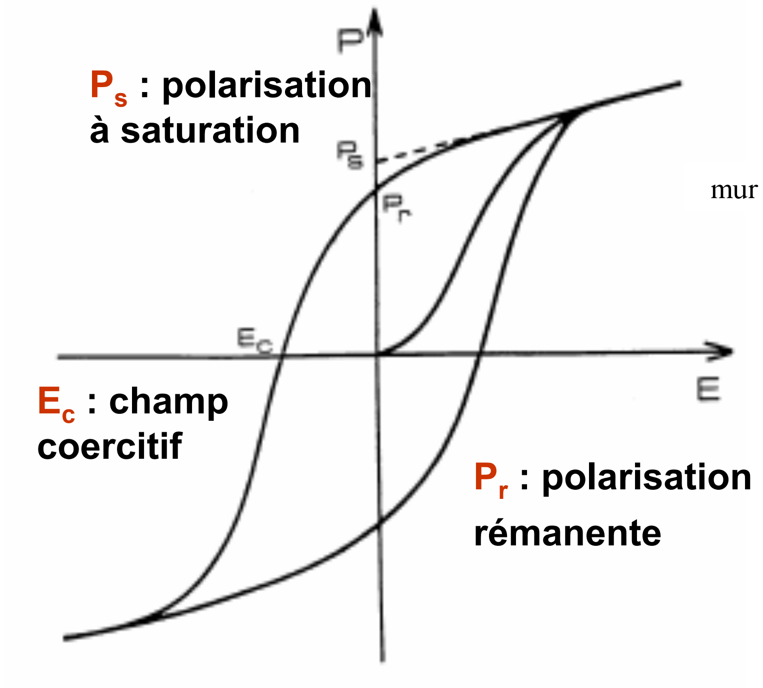
Relaxation and resonance

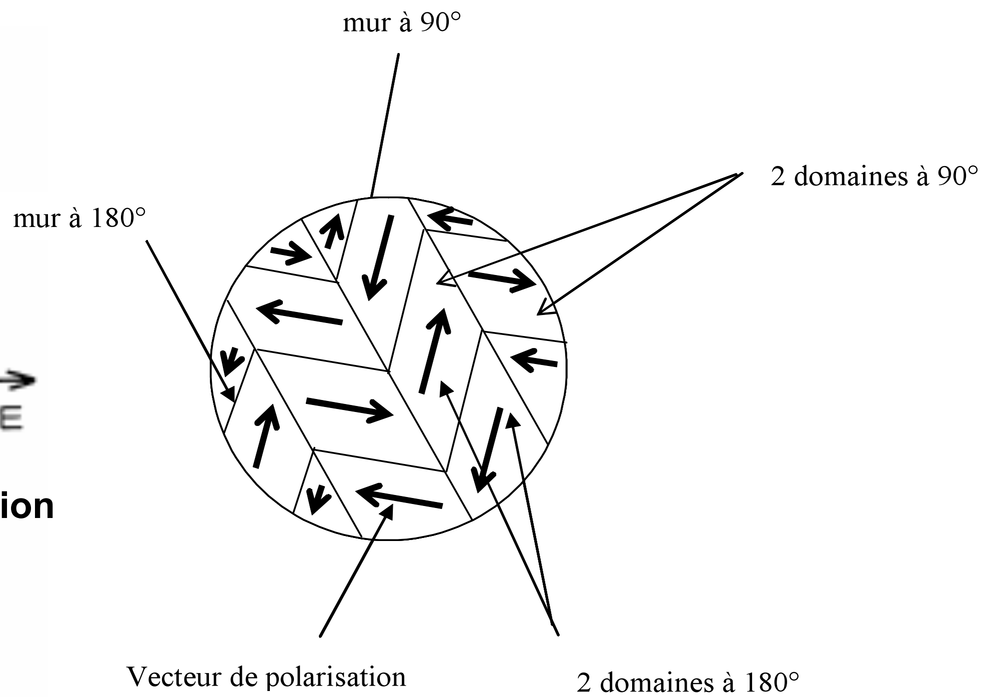


Ferroelectric Materials



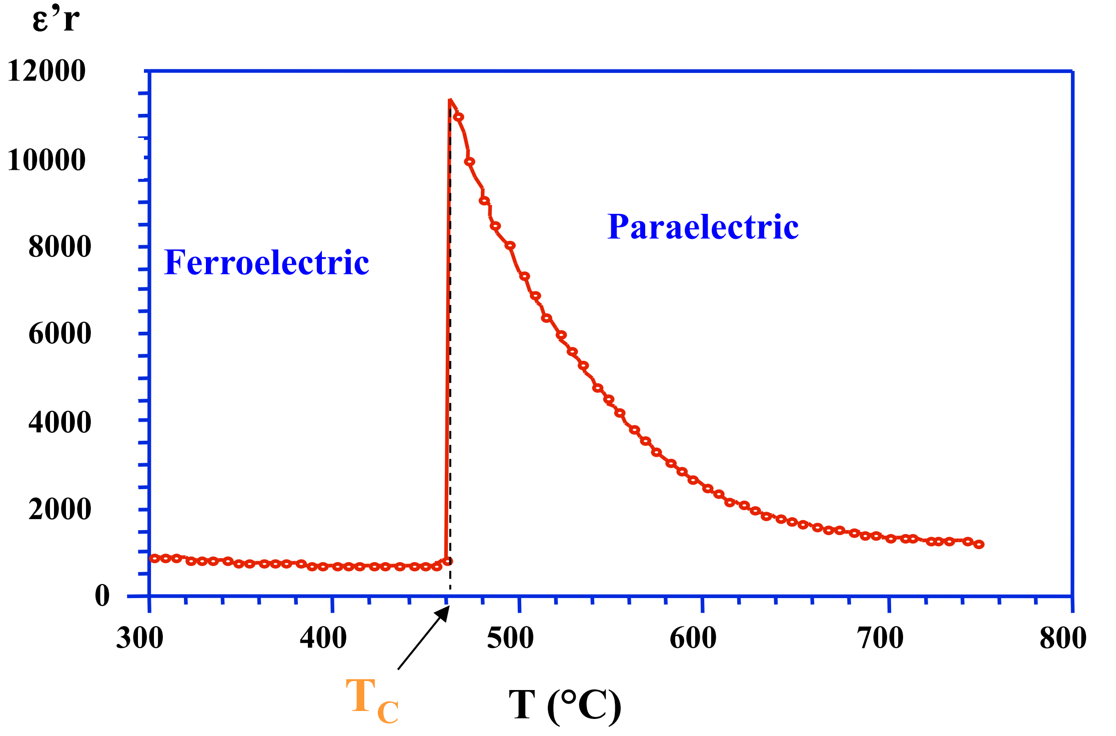
Ferroelectric Materials



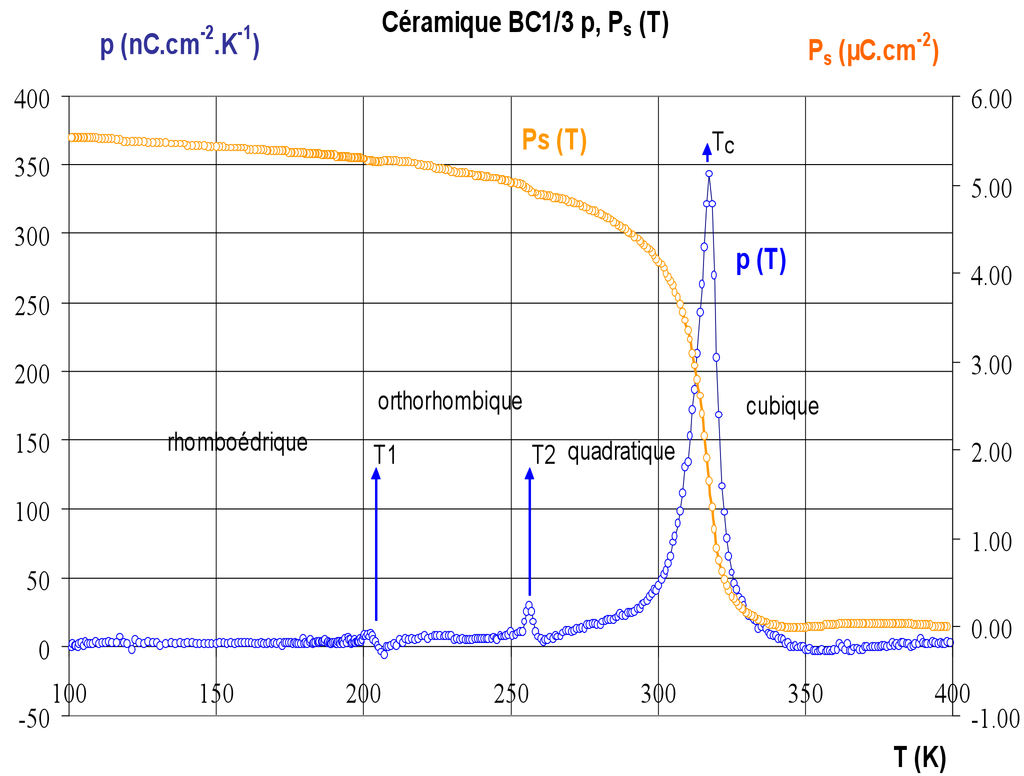


Hysteresis Loop

Ferroelectric Materials



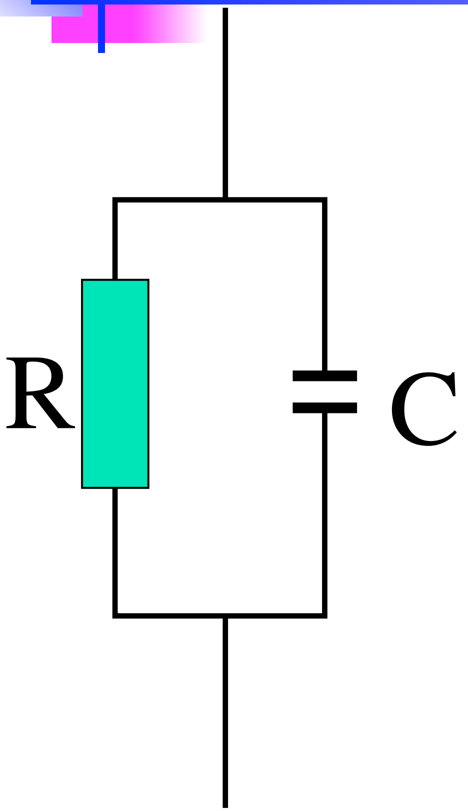
Pyroelectric parameter



Le courant de polarisation est proportionnel à la vitesse de changement de température et au signe de variation

$$i = \frac{\partial P}{\partial t} = \frac{\partial P}{\partial T}\frac{\partial T}{\partial t} = \frac{\partial P}{\partial T}k$$

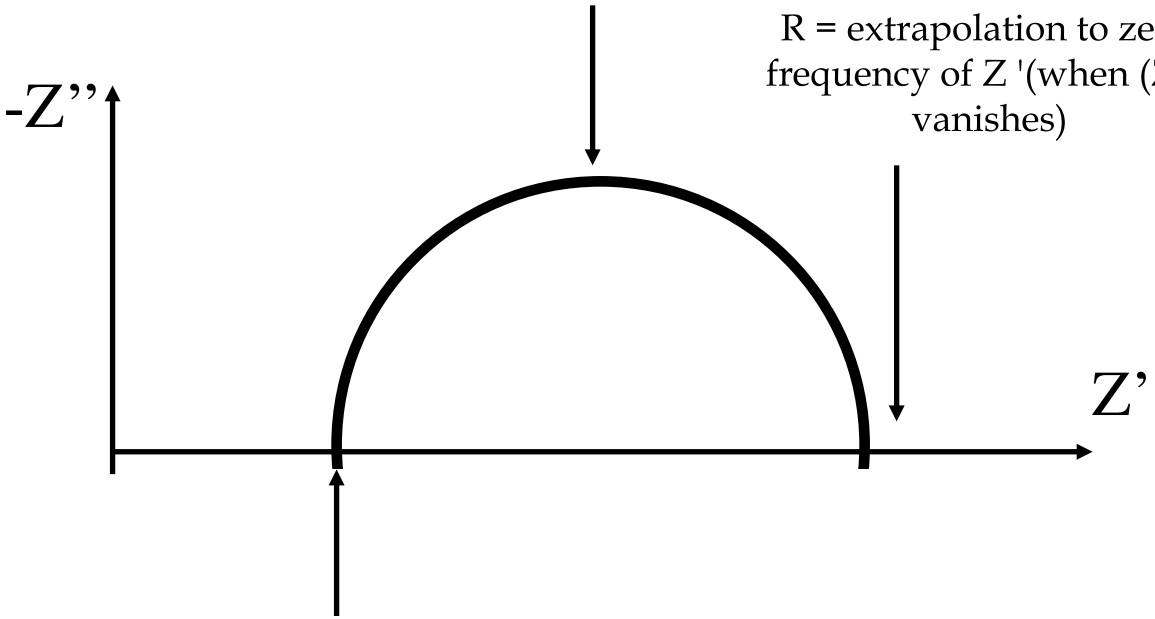
Impedance of a circuit R, C parallel



if R and C are independent of frequency,
we write Z = Z'-jz''

at the top of the semicircle we have: RC= $1/\omega$

R = extrapolation to zero frequency of Z '(when (Z'') vanishes)



When the frequency tends towards infinity (Z'') vanishes

Landau Theory

Landau Model for ferroelectric-paraelectric phase transition

$$F = F_0 + \alpha P^2 + \beta P^4 + \gamma P^6 - \vec{P}.\vec{E}$$

$\alpha = k(T - T_C)$; k is a constant

at thermodynamic equilibrium: $\frac{\partial F}{\partial P} = 0$

$$\Rightarrow 2k(T - T_C)P + 4\beta P^3 - E = 0$$

When $E = 0$ and according the temperature T, the crystal is in a state of stable equilibrium if :

- For $T > T_C$, the polarization is zero ($P = 0$), its the paraelectric state $\Rightarrow \frac{\partial F}{\partial P} = 0 \Rightarrow P = 0$

- For $T < T_C$, the polarization is nonzero ($P \neq 0$), its the ferroelectric state $\Rightarrow \frac{\partial F}{\partial P} = 0$

$$\Rightarrow 2k(T - T_C)P + 4\beta P^2 = 0 \qquad (E = 0)$$

$P = \pm\sqrt{-\frac{k}{2\beta}(T - T_C)}$: This assumption corresponds to a second order transition

Landau Theory

Curie Weiss law

$$\frac{\partial F}{\partial P} = 0 \Rightarrow 2k(T - T_C)P + 4\beta P^3 - E = 0$$

$$E = 2k(T - T_C)P + 4\beta P^3$$

or on a : $P = (\varepsilon - \varepsilon_0)E \Rightarrow dP = \varepsilon\, dE$

$$\frac{1}{\varepsilon} = \frac{\partial E}{\partial P} = 2k(T - T_C) + 12\beta P^2$$ (paraelectric phase), the stable state is obtained for $P = 0$

$$\Rightarrow \frac{1}{\varepsilon} = 2k(T - T_C) = C(T - T_C) \text{ with } k_C = 2k$$

$$\varepsilon = \frac{C}{T\text{-}T_C} \text{ avec } C = \frac{1}{k_C} \text{ : Curie Weiss law}$$

Landau Theory

Curie Weiss law

- in the ferroelectric state, the equilibrium state is obtained for:

$$P = \pm\sqrt{-\frac{k}{2\beta}(T - T_C)}$$

$$\Rightarrow \frac{\partial F}{\partial P} = 0 \Rightarrow \frac{1}{\varepsilon} = \frac{\partial E}{\partial P})_T = 2k(T - T_C) + 12\beta P^2$$

$$\frac{1}{\varepsilon} = 2k(T - T_C) + 12\beta\frac{k}{2\beta}(T_C - T)$$

$$= 2k(T - T_C) + 6k(T_C - T)$$

$$= 4k(T_C - T) = 2k_C(T_C - T) = C'(T_C - T)$$

with $C' = \frac{1}{2k_C} = \frac{1}{2}C$

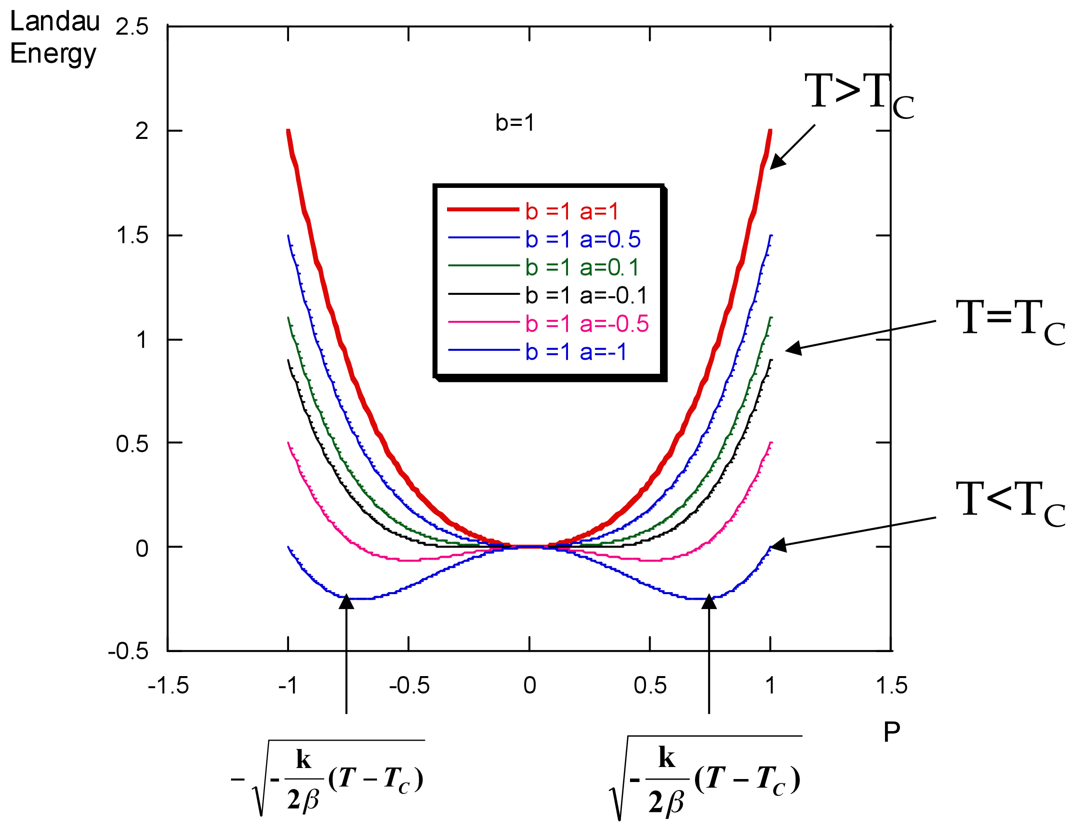
so $\varepsilon = \frac{\frac{1}{2}C}{T_C - T}$ et $\varepsilon = \frac{C'}{T_C - T}$

$\Rightarrow$ the variation of $\frac{1}{\varepsilon}$ is linear in the ferroelectric phase but

the slope is less than that of the paraelectric phase $(C' = \frac{1}{2}C)$

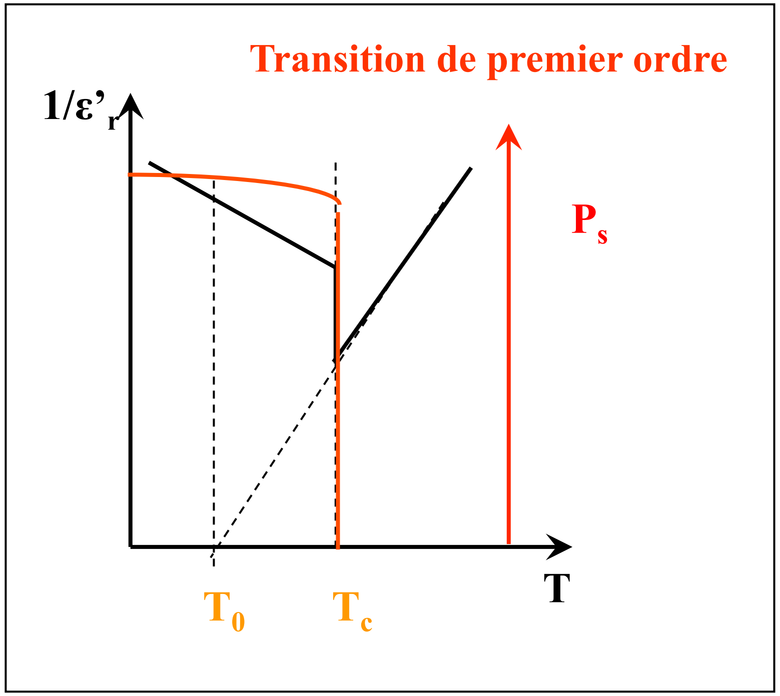
Landau Theory

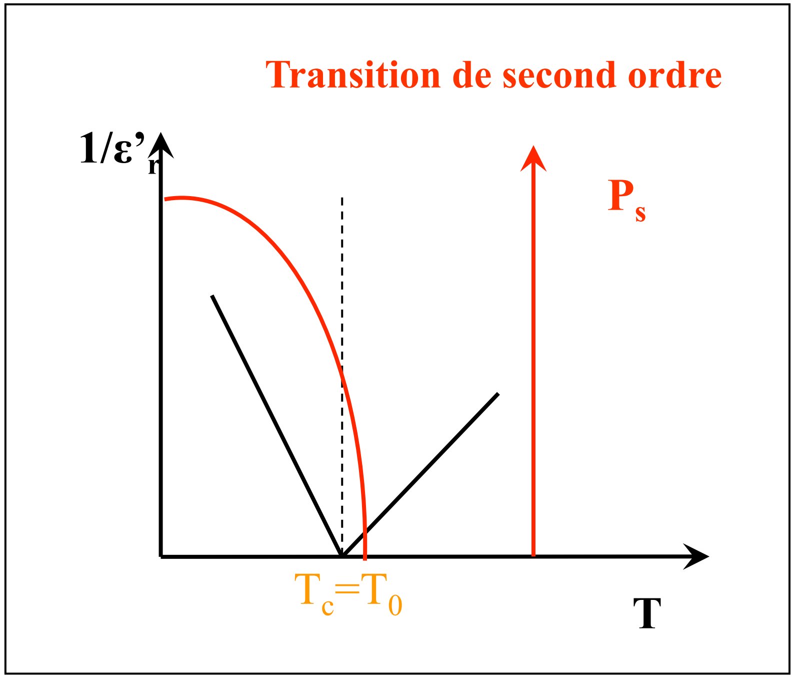
Free energy : Second order transition



Landau Theory

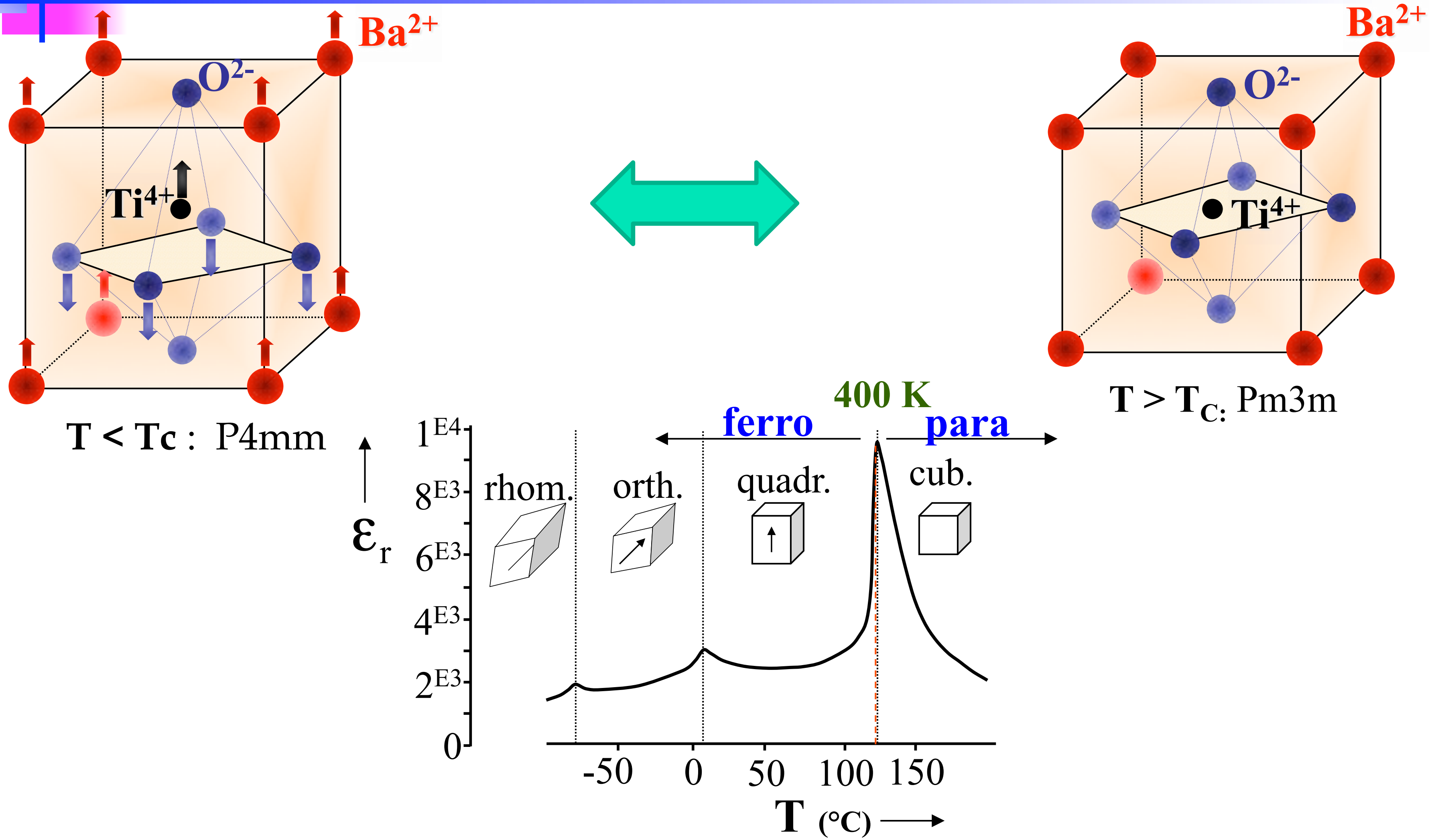
Variation of permittivity and polarization





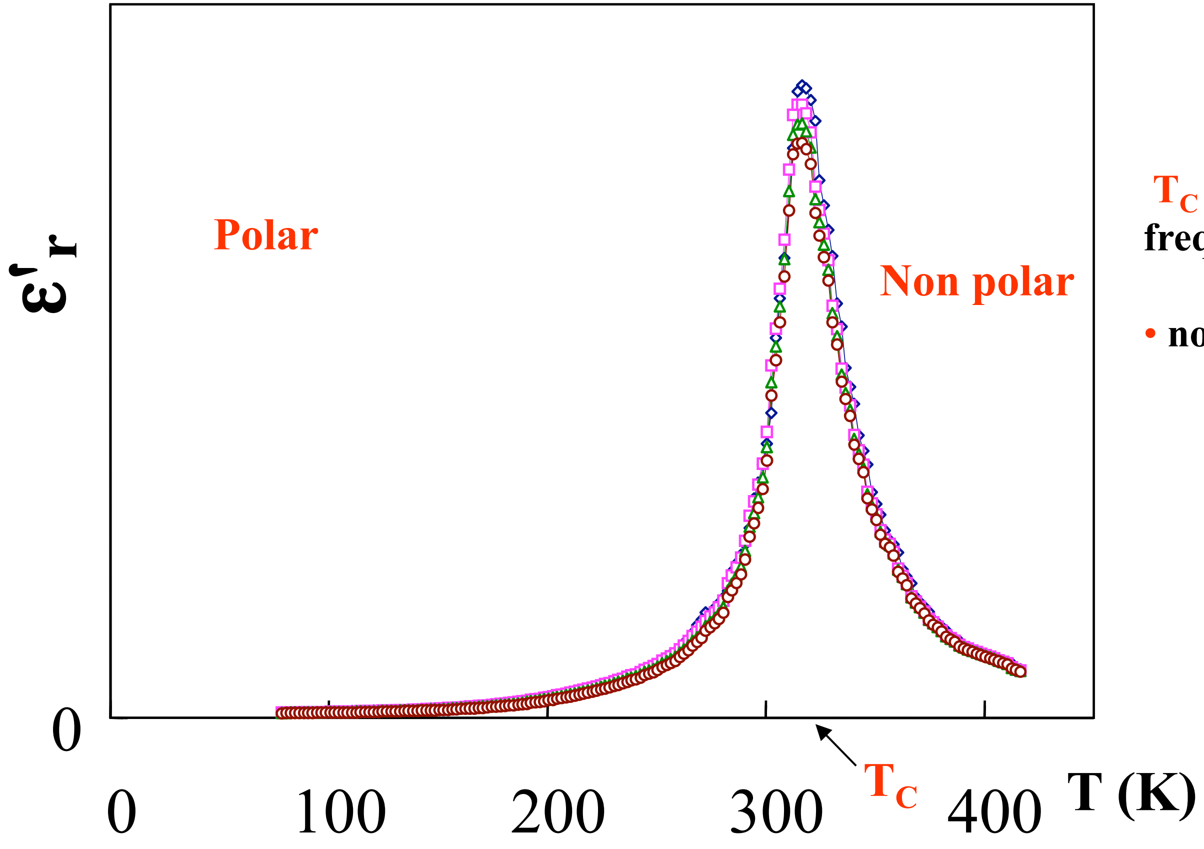
Applications

Perovskite structure (ABO3): BaTiO3



Applications

Classic Ferroelectric

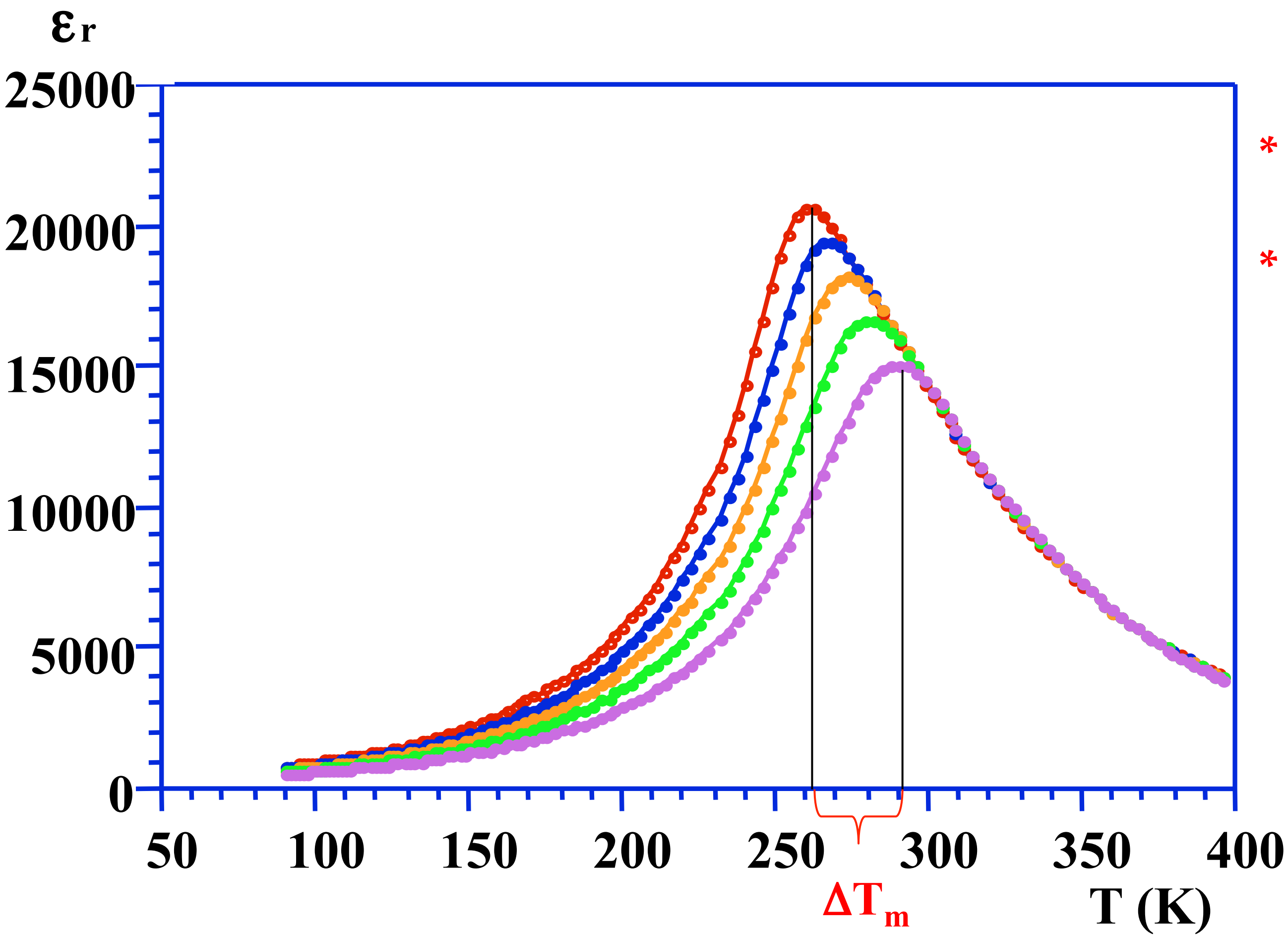


T_C and ε'_r does not vary with frequency

- no dispersion

Applications

Relaxor



* Dispesion in ferroelectric state
* Variation of Tm with frequency

Applications

Relaxor

Local fluctuation of composition in the A site caused by the substitution

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Nanometric areas