NOTES 2: Electrostatic Behavior of Solids#2

Microscopic Models of Polarizability:

Like many other physical models developed for the solid state, the Clausius-Mosotti formula is to be used with caution because of its simplifying assumptions. But it demonstrates certain behavior that are important qualitatively and justify our inspecting the microscopic electrostatic behavior in more detail via the polarizability α. By including only one dipole type of density n, we find

$$\alpha = \frac{3\varepsilon_0}{n} \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \tag{1}$$

This is this can be normalized vs $3\varepsilon_0/n$ to yield the plot in Fig. 1. Clearly α goes to zero as ε_r goes to unity, as expected physically. But also note the saturation behavior at large ε_r - above a certain value of α, which is roughly 0.6 ($3\varepsilon_0/n$) in Fig. 1, ε_r rises very quickly with any further increase in α. In other words, *ε_r becomes very sensitive to α.*   In analogy with our feedback model developed for χ_e previously, and since $\varepsilon_r = 1 + \chi_e$, we can say that the closed loop (macroscopic) "gain" of the system is becoming is very sensitive to the open loop (microscopic) "gain". In electronics, this is a sign that the system is close to instability.

As mentioned earlier, there are two fundamentally different mechanisms for α at the microscopic level: (1) induced dipoles of the individual atoms, and (2) re-orientation of
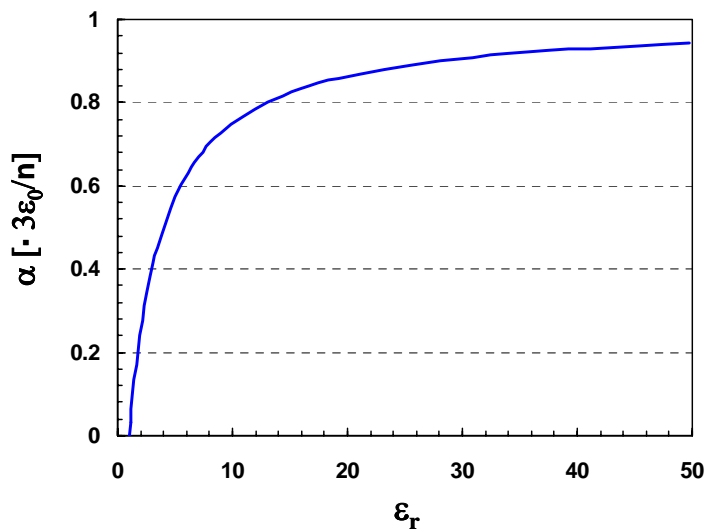

Fig. 1.

existing dipoles. The first is most important in covalently bonded solids. The second is most important in ionic solids. So not surprisingly, the microscopic electrostatic behavior is strongly correlated to the type of molecular bonding going on in the solid.

Atomic Polarizability

A fundamental part of atomic structure is the vastly different spatial distributions for the positive and negative charge, as shown in the sketch of Fig. 2. The nucleus harbors all the positive-charge (protons) in a radius of between ~1 and 5 x10^{-15} m, depending on the atomic weight. The electron orbitals harbor all the negative-charge in a radius of ~5x10^{11} m (Bohr radius). This big difference in radii allows us to treat the nucleus like a point charge, +Ze, where Z is the atomic number. Furthermore, if there are enough electrons to fill several different shells, in a first approximation we can treat them all as a "cloud" of radius R and uniform charge density, -Ze/[(4/3)πR^3). The resulting atomic model is as shown in Fig. 1(a).

Now if an electric field is applied as in Fig. 1(b), the nucleus will be repelled slightly and the electron cloud attracted in such a way that the nucleus will no longer be located at the geometric center of the cloud. If we further assume that the uniformity and sphericity of the electron cloud are not perturbed significantly, then we can show the effect of the field simply as an offset of the nucleus by a distance r from the center of the spherical cloud. Next we invoke yet another powerful result from electrostatic theory whereby the electric field at a test charge Q_1 located on the surface of a sphere containing a uniform charge distribution can be described by only the total charge contained within the sphere, Q_2. Furthermore, the same electric field is obtained by replacing Q_2 with a point charge at the center. Associating Q_1 with the nucleus and calculating the electronic charge Q' inside the inner sphere of radius r in Fig. 1(b), we get a local electric field of $\vec{E}_{local}$ = Q'/[4$\pi\varepsilon_0$r^2] $\hat{r}$ where $\hat{r}$ is the unit vector connecting the Q' charge to Q_1. Since the cloud density remains uniform and spherical, this can be re-written

$$\vec{E}_{local} = Ze[(4/3)\pi r^3/(4/3)\pi R^3]/[4\pi\varepsilon_0 r^2]\,\hat{x} = -\,Zer\,\hat{x}\,/[4\pi\varepsilon_0\,R^3]. \tag{2}$$

Now the dipole moment associated with Q_1 and Q' is just $\vec{p} = Q_1\vec{r} = -Zer\hat{x} \equiv \alpha\vec{E}_{local}$.
Substitution for - Zer$\hat{x}$ from (2) leads to the interesting result:
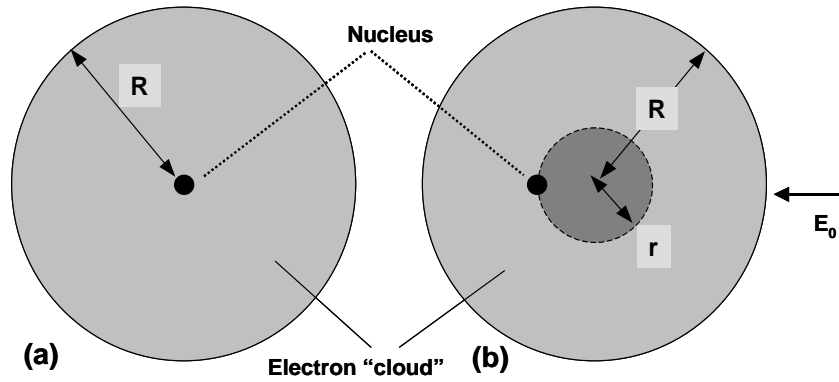
$$\alpha = 4\pi\varepsilon_0\,R^3 \tag{3}$$

Fig. 2

The interesting part is that the atomic polarizability is so strongly dependent on the *size* of the electronic cloud. According to (3), it scales with the atomic volume.

We should then expect that solids with "large" atoms might have high polarizability and, therefore, high ε_r. A good type of solid to test this thinking is one in which the atoms "spread" their electronic charge in space for some reason. As discussed previously in the section on bonding, this happens naturally in strongly-covalent solids since each covalent bond will draw at least one electron away from the atom of reference roughly half-way to the neighboring atom; i.e., half of the nearest-neighbor separation. In most solids, this means that the bonding electron will end up much further away from the reference atom than it would be for the same (neutral) atom in vacuum. This is what we mean by "spread."

In the special case of column-IV elemental semiconductors, viz. diamond, silicon, and germanium, we have four such covalent bonds between each atom and its nearest neighbors, neighbor lying at the vertex of a tetrahedron. This four-fold "spreading" of atomic electrons should create a very large effective radius R of the atomic clouds, a large atomic polarizability, and a large dielectric constant. Table I lists the results for the elemental semiconductors. Indeed, Si and Ge have surprisingly high dielectric constants – a fact that has plagued semiconductor devices and integrated circuit technology forever since high ε_r usually means high specific capacitance, be it in a transistor or in a transmission line.

Table I.		
Material	ε_r	α [Cb-m^2/V] {according to (1)]}[1]
Diamond	5.5	9.0×10^{-41}
Si	11.8	4.1×10^{-40}
Ge	15.7	5.0×10^{-40}

[1] Note the interesting MKSA units for α, which can also be expressed as F-m^2.

<u>Ionic Polarizability</u>

A fundamental aspect of compound materials[2] – the vast majority of solids – is some degree of ionicity between nearest neighbor atoms. This was discussed earlier in the text and arises naturally from the differences in atomic electron affinity. Built-in ions are pervasive in solids but, interestingly, do not create a built-in nonzero macroscopic polarization $\vec{P}_e$ unless other conditions are satisfied (more on this in the section on ferroelectricity). The usual condition is a net cancellation of all the atomic dipoles such that $\vec{P}_e = 0$. This is true even in highly ionic solids such as the alkali halides (NaCl, KCl, etc).

Although $\vec{P}_e = 0$ in the absence of applied field, the built-in ions can create $\vec{P}_e \neq 0$ when $E_0 \neq 0$ through the process of dipole re-orientation. We need to define "re-orientation" broadly since by definition $\vec{p} = q \cdot d \cdot \hat{r}$ and $\vec{P} = n \cdot \vec{p}$ where d is the physical separation between the minus and plus charges of the dipole, and $\hat{r}$ is the unit vector connecting them. Hence, we can get a change in $\vec{p}$, and thus a non-zero polarizability α, from an applied E_o in two ways: (1) a change of $\hat{r}$ through angular re-orientation of the dipole, and (2) a change in d through compression or expansion of molecular bond. Many books on dielectrics discuss only the first effect, largely because of its predominance in liquids. But in solids, both effects are important and, indeed, the second one becomes the predominant one and the simplest to understand in many crystals such as the alkali halides.

To derive an expression for the ionic microscopic polarizability, we imagine a simple two-dim (square) lattice as shown in Fig. 3 in which without external forces all ions are separated by the same distance d. This can be considered as a cut through one lattice plane of a NaCl crystal (one of the cubic facets), for example. In the absence of external electric field, the built-in dipoles along any *line* of atoms parallel to the applied field cancel by pairs, as shown through the opposing $\vec{p}_1$ and $\vec{p}_2$ atomic dipoles. Similarly, any chosen dipole in a *line* of atoms along the applied field will be cancelled by a dipole in the closest parallel line. The combination of these two reasons is why ionic crystals have no built-in polarization $\vec{P}$ no matter how the surfaces are terminated. In other words, the unit cell (primitive and

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[2] Here, "compound" means that the solid contains at two or more atomic species.

conventional) of an ionic crystal is electrically neutral both in a unipolar (i.e., $Q_{total} = 0$) and dipolar ($\vec{P} = 0$) sense.

In the presence of the external field E_0, all the positive ions are displaced by u in the direction of the field, and all the negative ions are displaced oppositely by the same amount. In other words, if we choose any atomic ion and consider only its nearest-neighbor interactions along the direction of the applied field, each contributes to two equal and opposite dipoles. The induced dipole moment from the parallel dipole pair is

$$\vec{p}' = \vec{p}'_1 + \vec{p}'_2 = q[(d + 2u)]\hat{x} - q[(d - 2u)]\hat{x} = 4qu \cdot \hat{x} \tag{4}$$

where d is the interatomic separation with zero field. If the electric field is small enough, we can assume $u \ll d$ and then u can be approximated in the linear elastic limit. By choosing any ion in the lattice in Fig. 3, inspection of the elastic response yields a restoring force

$$F_m = C \cdot (d + 2u) - C(d - 2u) = 4Cu \tag{5}$$

where C is the interplanar atomic spring constant. Note that the factor of 4 arises because the electrostatic displacement creates "cooperative" elastic response from the two planes nearest to the plane containing the chosen atom (i.e., if the spring connecting to one nearest-neighbor plane is in compression, then the spring to the opposite plane is in tension; and vice versa). In equilibrium this elastic force must balance the electrostatic force, qE_{local}, ion by ion, so that we can write $u = qE_{local}/4C$. Substitution back into (4) yields.

$$\vec{p}' = 4qd \cdot \hat{x} = \frac{q^2}{C}\vec{E}_{local} \equiv \alpha\vec{E}_{local} \tag{6}$$
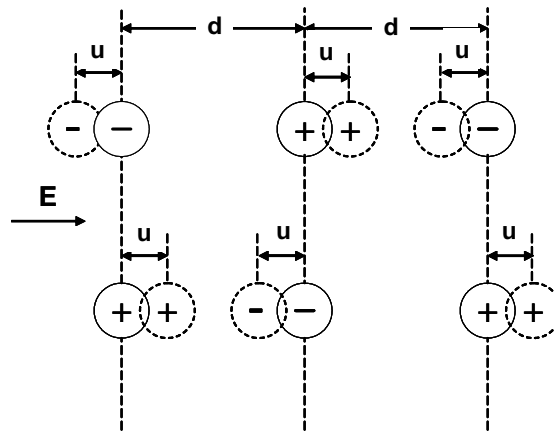

Fig. 3. Sketch of the electrostatic response of two neighboring rows of atoms in an ionic crystal to an electric field. The vertical dashed lines denote parallel planes which, collectively, account for all atoms of the crystal (see ECE215A Notes # XX).

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So we end up with the remarkably simple result $\alpha = q^2/C$, which is intuitively correct in that an increase in C is tantamount to an increase in "stiffness" and thus a reduced displacement to any applied force. Intuitively, the ionic charge should occur quadratically, once for the dipolar magnitude and once for the unipolar reaction to the applied field.

To test this result against experiment we harken back to the analysis of lattice waves for a crystal having a basis of two atoms. In this case the interplanar spring constant was essential to the dispersion curves (ω vs k) for acoustic and optical lattice waves, the acoustical waves being described in the small k limit as

$$\omega^2 \approx \frac{C}{2(m_1 + m_2)}(ka)^2$$

where a = 2d is the crystal period. This leads to $C \approx 2(m_1 + m_2)(\omega/ka)^2 = (1/2)(m_1+m_2) \cdot (v_s/d)^2$ where $v_s = \omega/k$ is the speed of sound in the small-k limit. This leads to the interesting result

$$\alpha \approx \frac{2q^2 d^2}{(m_1 + m_2)v_s^2}$$

showing, once again, that the atomic size scale matters ! As an example, we take NaCl along the [100] direction for which q = e; d = a/2 = 5.63 Ang/2 = 2.815 Ang; $v_s = (C_{11}/\rho)^{1/2} = 4820$ m/s , where the stiffness coefficient $C_{11} = 4.87 \times 10^{10}$ N/m^2 and the density $\rho = 2096$ KG/m^3 ;[3] $m_1 = 22 \cdot m_p$ (atomic weight of Na), and $m_2 = 34 \cdot m_p$ (atomic weight of Cl) with $m_p = 1.67 \times 10^{-27}$ KG, the proton mass. The result (show for HW problem) is $\alpha = 1.87 \times 10^{-39}$ Cb-m^2/V. .

We focus only on nearest-neighbor built-in dipoles. The clue to understanding the result harkens back to our analysis of lattice waves and phonons. If we assume the crystal is perfect, the displacement shown in Fig. 3 will be uniform over the entire solid sample. Since different atoms in a crystal form all or part of the "basis" of a non-Bravais lattice, the displacement shown in the figure must be occurring within a primitive cell of the lattice. Therefore, because the field is static, this displacement is analogous to a *longitudinal optical* (LO) lattice wave of infinite wavelength, i.e., k = 0.

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[3] See Kittel, "Introduction to Solid State Physics," 7th Ed., Chap 3, Eqn (6).

Classification of Dielectric Types

- The connection of microscopic to macroscopic also allows us to classify macroscopic effects based on microscopic quantities.

- In addition to classical dielectric response of induced dipoles already described, we also have paraelectric and ferroelectric. To separate out shape (depolarization) effects, the classification is based on the relationship of $\vec{P}_e$ to $\vec{E}_{in}$ (i.e., on χ_e).

material	relation of $\vec{P}_e$ to $\vec{E}_{in}$	χ_e
Normal dielectric (induced dipoles in electrical insulator)	Parallel $(E_{in} < E_0)$	> 0
Paraelectric (permanent dipoles)	Parallel $(E_{in} < E_0)$	> 0
Ferroelectric	Independent ($\vec{P}_e \rightarrow$ spontaneous)	singular
Metallic (good electrical conductor)	Parallel	Undefined[4] since $\chi_e \equiv P_e/(\varepsilon_0 E_{in})$ and $E_{in} \rightarrow 0$

- To quantify these relationships better, we assume the Lorentz relation again:

$$\vec{p} = \alpha \vec{E}_{local} \approx \alpha \left(\vec{E}_{in} + \vec{P}_e / 3\varepsilon_0 \right) \Rightarrow \vec{P}_e = \sum_j n_j \vec{p}_j \approx \sum_j n_j \alpha_j \left(\vec{E}_{in} + \frac{\vec{P}_e}{3\varepsilon_0} \right)$$

and solving for $\vec{P}_e$ we get $\vec{P}_e \approx \dfrac{\sum_j n_j \alpha_j \vec{E}_{in}}{1 - \sum_j n_j \alpha_j / 3\varepsilon_0}$

Now the definitions becomes more obvious:

| Material	$\sum_j n_j \alpha_j / 3\varepsilon_0$
Dielectric, Paraelectric	< 1
Ferroelectric	≈ 1
Metallic	Effectively $>> 1$ (owing to the macroscopic displacement of free carriers in any E field)

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[4] A metallic sample will tend to screen out the internal electric field. We will show later in transport theory how ε_r is large and negative in metals, so χ_e must do that too.

Important comments:

- One must be careful with this simple picture because solids usually have several dipole types, each having different α_j.

- Because ferroelectric state is singular (i.e., χ_e diverges), it is very sensitive to other macroscopic variables, such as temperature and stress.

- Normal dielectric (induced dipoles) *and* paraelectric (permanent dipoles) are similar in that for both types the solid responds in such a way that the electric polarization $\vec{P}_e$ *increases* with applied field.

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Types of ferroelectrics (to be augmented in lecture)

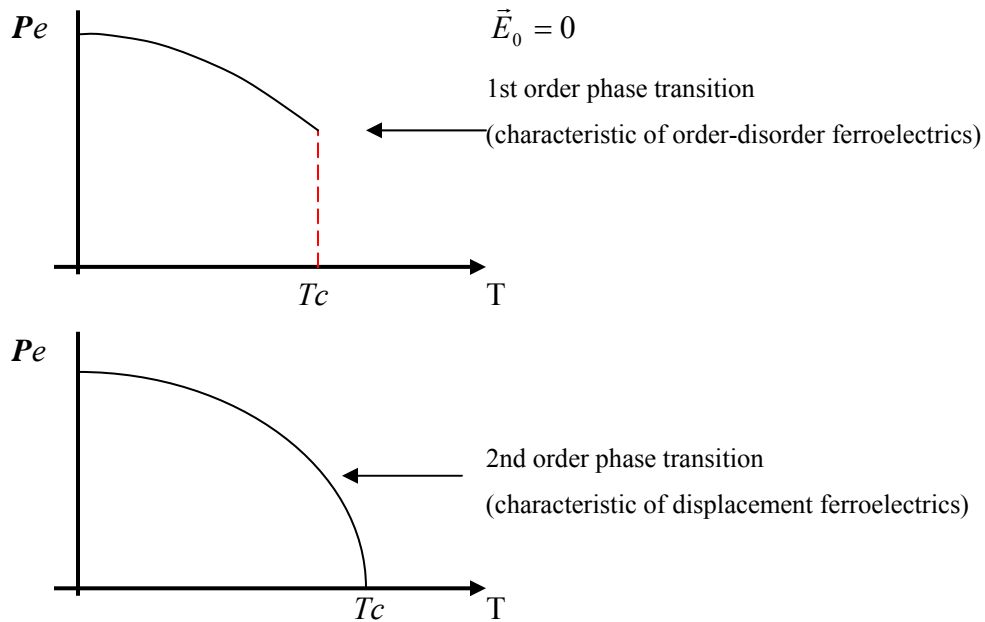1) order - disorder (e.g. KDP, KH_2PO_4)

$T > T_c$ $T < T_c$
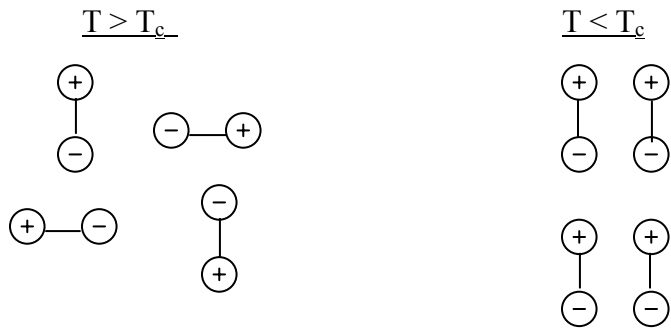
2) displacement e.g. Perovskites, $BaTiO_3$, $LiTiO_3$ (most important to engineering)

$T > T_c$ $T < T_c$
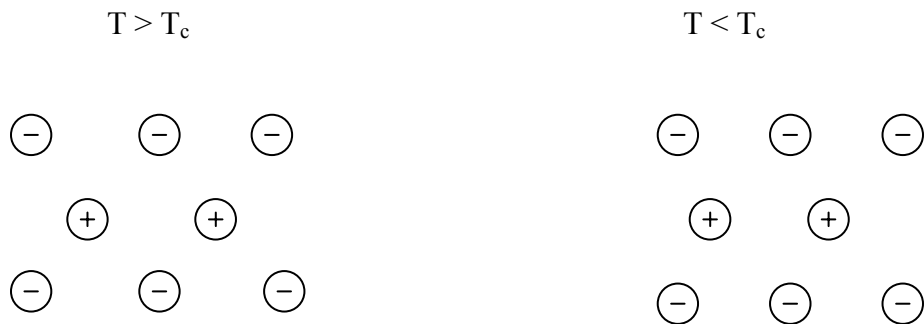
(e.g. Perovskites, $BaTiO_3$, $LiTiO_3$)

- Because of the critical dependence of $\mathbf{P}_e$ on the density and polarizability of atomic dipoles, many of the thermodynamic variables are also critical.

    For example P_e is observed to depend critically on T

$\vec{E}_0 = 0$

1st order phase transition
(characteristic of order-disorder ferroelectrics)

2nd order phase transition
(characteristic of displacement ferroelectrics)

Charateristics of phase transitions (from Thermodynamic theory):

1st order	2nd order
1) Entropy discontinuous across T_c because of latent heat)	1) Entropy continuous across T_c (no latent heat)
2) Derivatives of entropy are continuous (e.g. heat capacity)	2) Derivatives of entropy are singular
3) Other thermodynamic derivatives are continuous	3) Other thermodynamic derivatives are singular

1st order derivatives

Dielectric susceptibility

Heat capacity
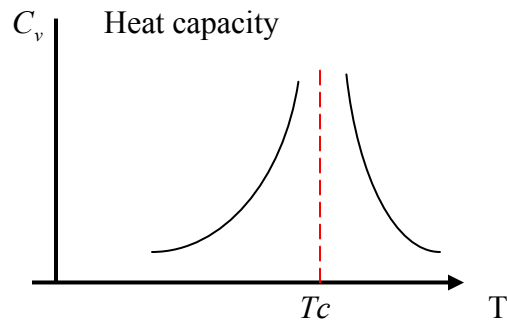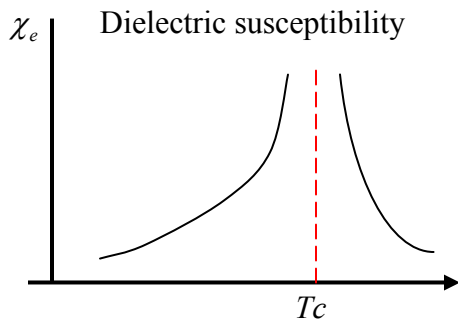
- Many of the common ferroelectrics, such as LiN_bO_3 and other Perovskites, display these characteristics. The sensitive nature of Thermodynamic variables leads to many useful effects in ferroelectric solids.

$\frac{dPe}{dT}$ → pyroelectric coefficient

Pyroelectric Effect

(Room temperature infrared detectors)

Tc T

d_{ik} $d_{ik} \equiv \frac{\partial e_x}{\partial E_1}\Big|_P$ (Piezoelectric constant)

Piezoelectric effect

(acoustic transducers;

electromechanical

transducers)
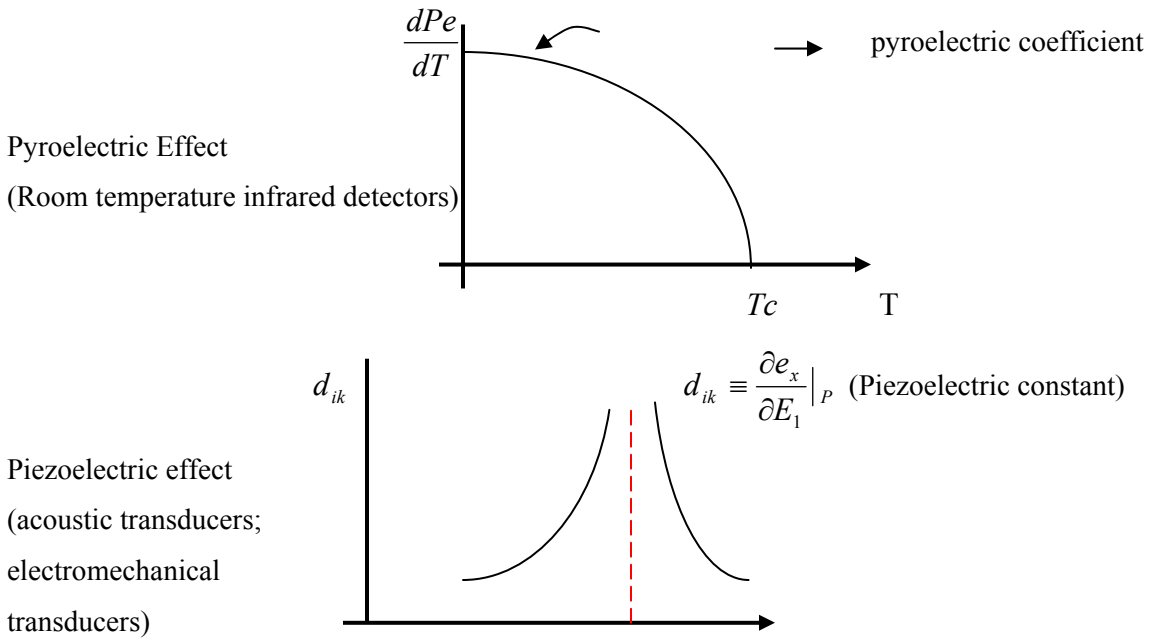
Important comments about ferroelectrics: At $T > T_C$, the ferroelectric goes into a *paraelectric state* whereby there are still permanent dipoles in the solid, but they all cancel in the absence of an external electric field. But the electric susceptibility can still be very high in magnitude because we still have $\sum_j n_j \alpha_j / 3\varepsilon_0 \approx 1$. But note that in this state, χ_e is still positive !

<u>Clarification of Energy Density</u>

• Earlier in discussions of dielectrics we had stated:

$$dU_e = \vec{E}_{in} \cdot d\left(\vec{P}_e V\right) + \tfrac{1}{2}\varepsilon_0 \vec{E}_{in}^{\,2} d\upsilon$$

potential energy from dipoles   potential energy of field alone

In the simple case of a parallel plate capacitor filled with dielectric material, this is easy to evaluate for energy $U(E_{in})$

$$U = \int_0^{E_{in}} \vec{E}_{in} \cdot d\left(\vec{P}_e \cdot V\right) + \frac{1}{2}\varepsilon_0 \vec{E}_{in}^{\,2} \cdot V$$

since for dielectric $\vec{P}_e = \chi_e \varepsilon_0 \vec{E}_{in}$, we find

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$$U = V \int_0^{E_{in}} \chi_e \varepsilon_0 E_{in} dE_{in} + \tfrac{1}{2} \varepsilon_0 E_{in}^2 \cdot V$$

$$= \frac{1}{2} V \varepsilon_0 \left(\chi_e + 1 \right) E_{in}^2 = \frac{V}{2} \varepsilon_0 \varepsilon E_{in}^2$$

But in the case of a ferroelectric, one must know the precise relationship of $\vec{P}$ vs. $\vec{E}_{in}$ because this may be *nonlinear*. Specifically, the dipole saturation effect makes the "small-signal" χ_e (and ε) of ferroelectrics optimistic in predicting energy density. Saturation is associated with a universal phenomenon in ferroelectric (and ferromagnetics) called hysteresis (origin Greek for "retardation" or "lagging behind"; in this case P will lag behind E).
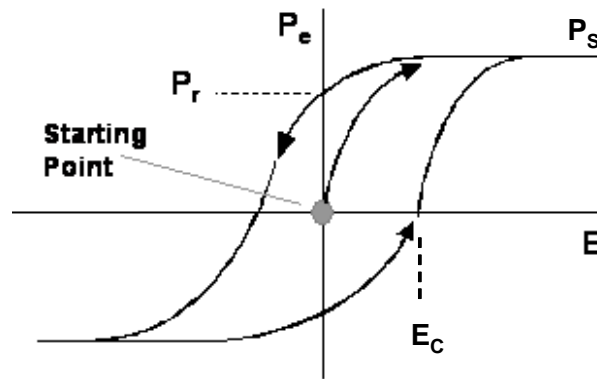

Fig. 3. Universal hysteresis curve

Most ferroelectric materials display the hysteresis curve shown in Fig. 3. P_S is associated with the fact that the greatest possible spontaneous polarization is with all dipoles aligned. Typically in best ferroelectrics (Perovskites)

$P_s \sim 30 \times 10^{-2}$ C/m^2 (Recall $P = \varepsilon_0 \chi E$ and $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m)

Energy density: $U' \approx P_s E_c$ and $E_c \approx 10^6$ V/m

$\Rightarrow U' \approx 0.3 \times 10^6$ J/m^3 or 0.3 J/cc (rather low !)

Good "rule-of-thumb" for all dielectric matter is: $U' < 1$ J/cc

Note also that 0.3 J/cc is about 6 times higher than U' in Si. (homework problem)