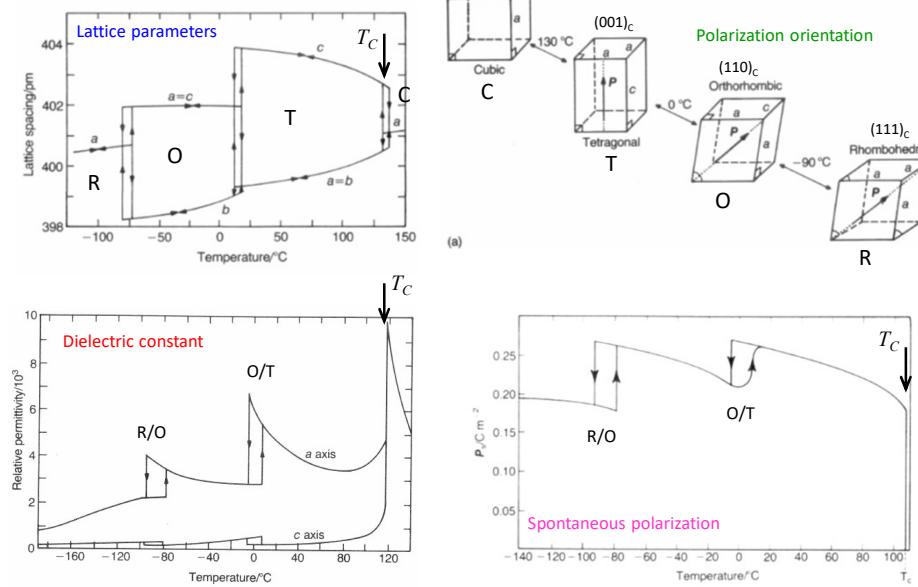


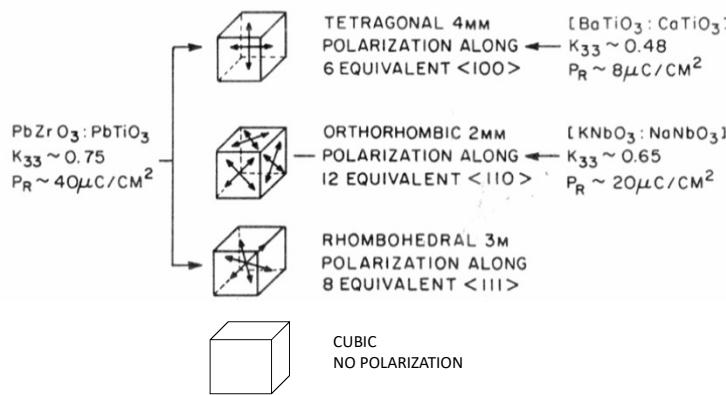
### Phase transitions in barium titanate



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### Phase transitions in ferroelectric perovskites

#### POSSIBLE ORIENTATION STATES IN PEROVSKITES



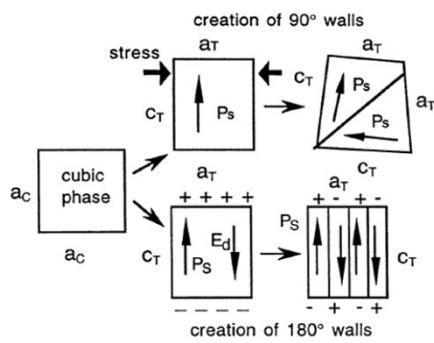
Polymorphic phase transition (PPT) in ferroelectrics are determined by:

- temperature change;
- external electric field;
- external stress;

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### Ferroelectric domains      Governed by “no bound space charges” principle

Non poled FE crystals spontaneously split in domains. A domain is a region with a uniform orientation of polarization. Domains are separated by **domain walls**. Ferroelectric domains form to minimize the **electrostatic energy** and the **elastic energy** associated with mechanical constraints to which the ferroelectric material is subjected as it is cooled through the Curie temperature.



Domains with perpendicular orientation of polarization (90° walls) minimize the elastic energy and reduce the depolarizing field ( $E_d$ ) associated to the surface charges. Formation of 90° domain walls is determined by mechanical stresses. These domain walls differ for both the orientation of polarization (ferroelectric domains) and the orientation of spontaneous strain (ferroelastic domains)

Domains with oppositely oriented polarization (180° walls) minimize the depolarizing field ( $E_d$ ) associated to the surface charges and are purely ferroelectric domains.

#### FE domains in tetragonal BaTiO<sub>3</sub>

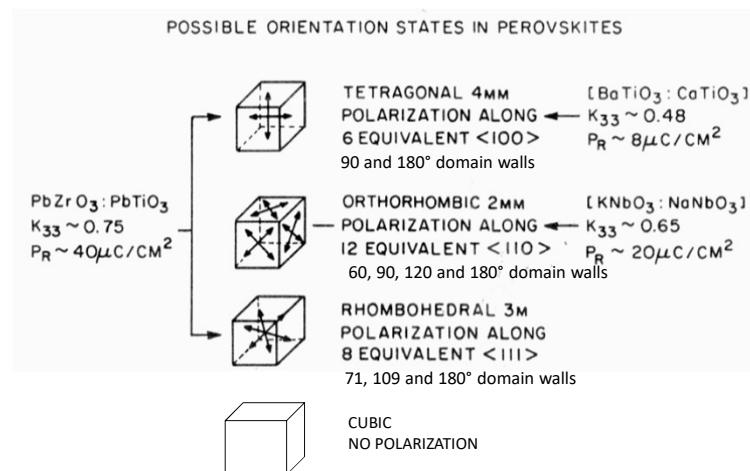
In tetragonal BaTiO<sub>3</sub> ceramics formation of complex domain structures with both 180° and 90° walls is observed due to the distribution of stresses and electrostatic boundary conditions to which each grain is subjected.

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### Ferroelectric domains

#### Domain wall configurations

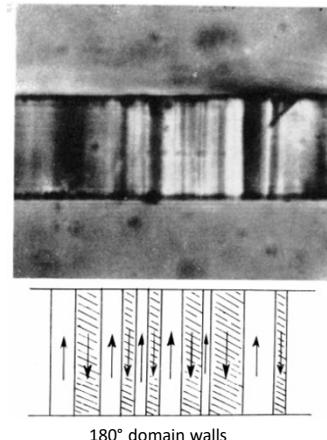
The number of possible orientations of  $P_s$  as well as the number of domain wall configurations increase with decreasing the crystal symmetry.



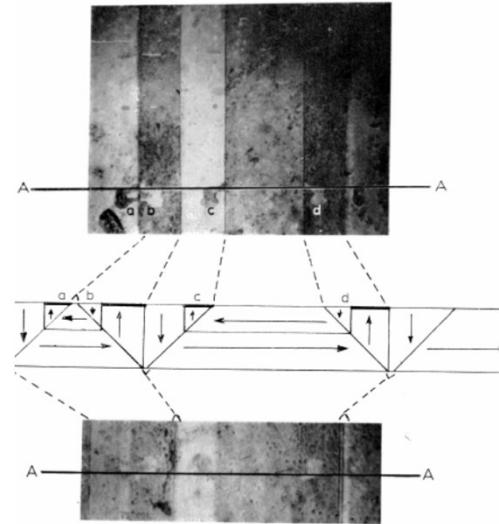
110

### Ferroelectric domains

The “no bound space charges” principle (  $\text{div } \mathbf{P} = 4\pi Q = 0$  in the bulk ) rules the formation of domain structures.

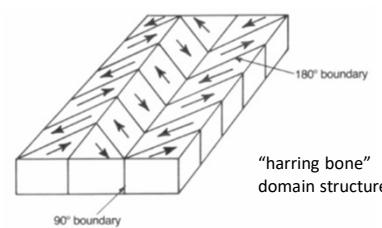
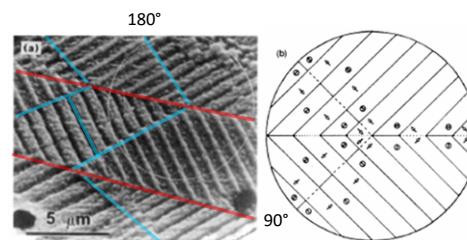
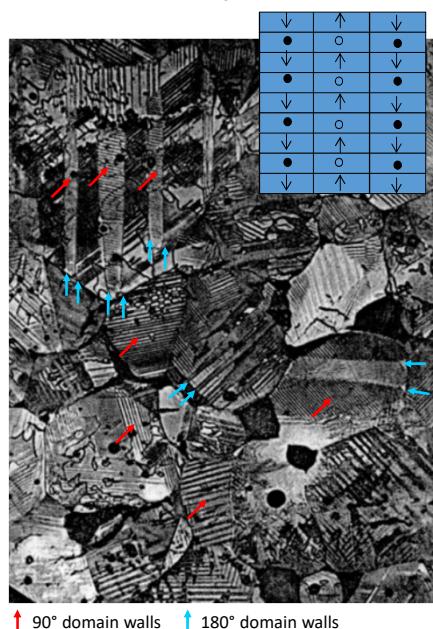


FE domains in single crystal BaTiO<sub>3</sub>.



111

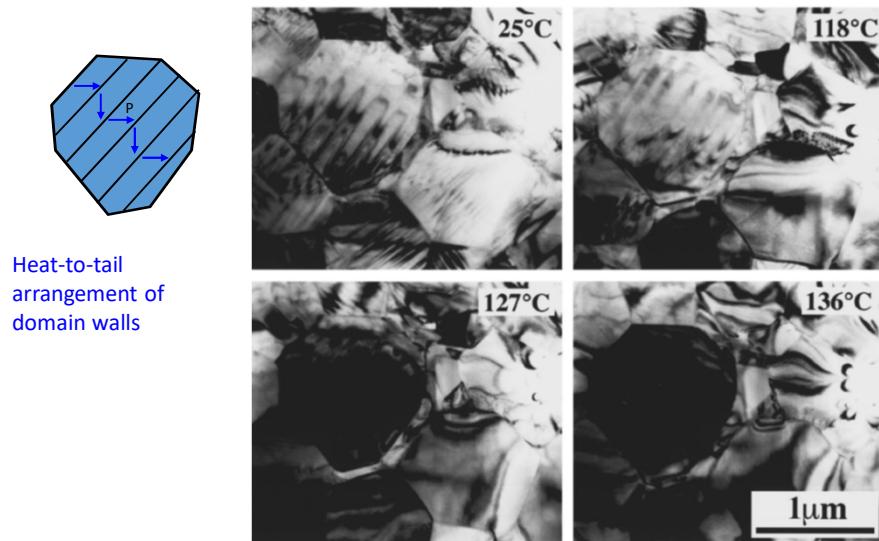
### FE domains in BaTiO<sub>3</sub> ceramics



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### FE domains in BaTiO<sub>3</sub> ceramics

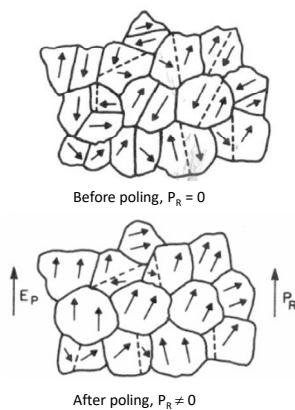
Fine grained ceramics (0.5-few  $\mu\text{m}$ ) show a simpler domain structure with 90° domain walls.  
The domains disappear above  $T_c$



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### Poling of ferroelectric ceramics

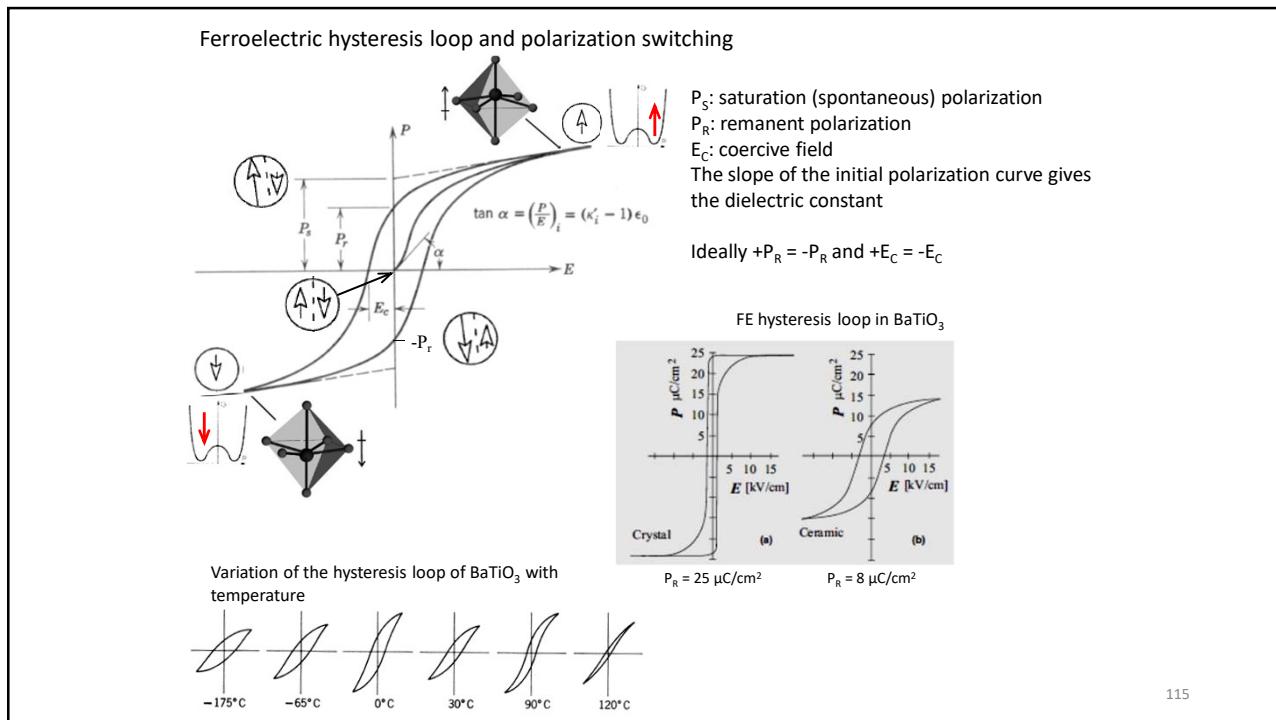
If the direction of the spontaneous polarization through the ceramic is random or distributed in such a way as to lead to zero net polarization, the pyroelectric and piezoelectric effects of individual domains will cancel and such material is neither pyroelectric nor piezoelectric. Polycrystalline ferroelectric materials may be brought into a polar state by applying a strong electric field (10–100 kV/cm), usually at elevated temperatures. This process, called **poling**, cannot orient grains, but **can reorient domains within individual grains in the direction of the field**. A poled polycrystalline ferroelectric exhibits pyroelectric and piezoelectric properties, even if many domain walls are still present. Poling is only possible in FE ceramics. Ceramics of purely piezoelectric compounds do not exhibit ferroelectric properties (examples: quartz).



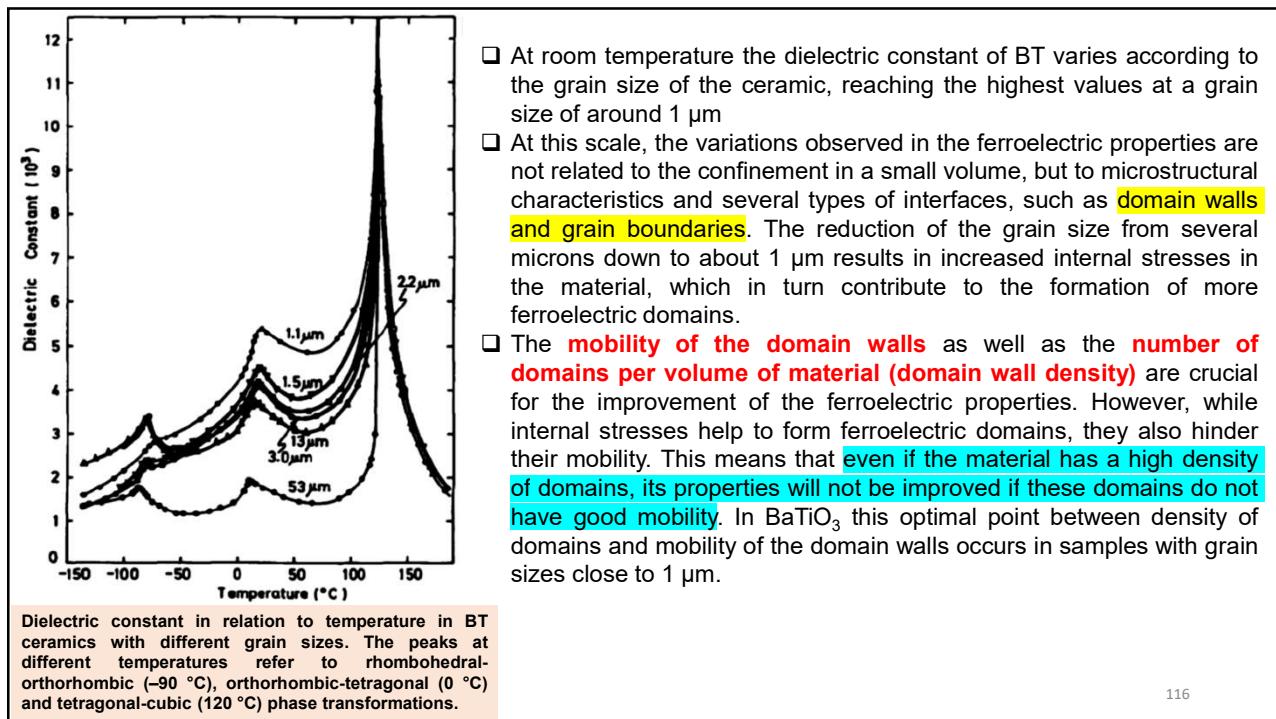
Due to the random orientation of the crystallites, the maximum polarization attainable in a ceramic ( $P_R$ ) is always smaller than in a single crystal and dependent on the number of available domain states:  
 $P_R = 0.83 P_S$  in tetragonal BT  
 $P_R = 0.87 P_S$  in rhombohedral BT  
 $P_R = 0.91 P_S$  in orthorhombic BT

In practice  $P_R$  is much smaller (less than  $0.5P_S$  in tetragonal BT) because switching of 90° domain walls is hindered by the large mechanical stress exerted on each grain by the adjacent grains. Only displacement of the 90° domain walls is observed.

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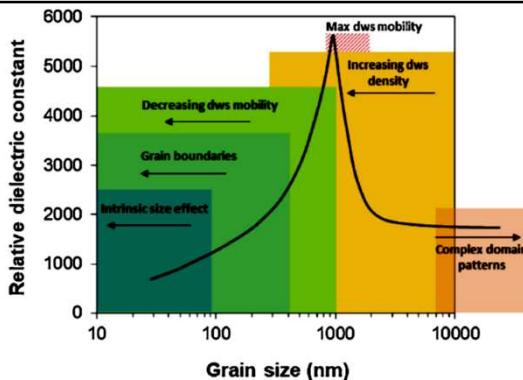
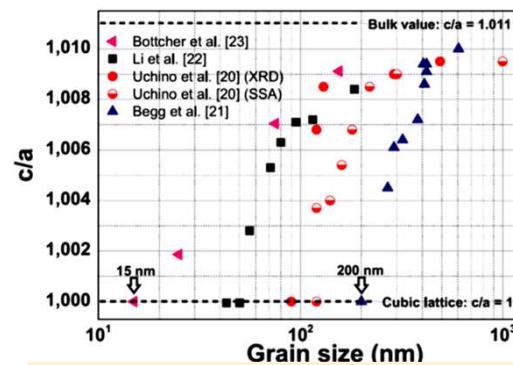


Fig. 14. The different mechanisms affecting the dielectric constant of BaTiO<sub>3</sub> ceramics. The black line is a guide to the eye and does not refer to a specific data set. The boundaries of the different regions are purely indicative.



Evolution of c/a ratio of lattice parameters as a function of particle size for powders prepared using different synthesis methods

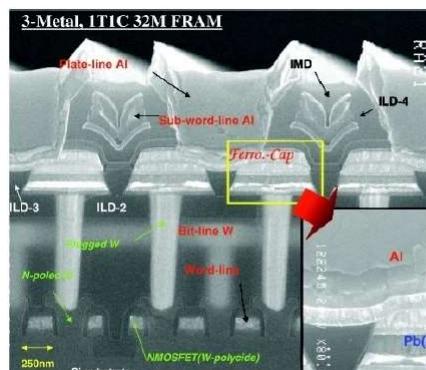
Buscaglia & Randall, Journal of the European Ceramic Society 40 (2020) 3744–3758

By reducing the grain size below this optimal point to around 400 nm the mobility of the domain walls is drastically compromised. Frey et al. [1] suggest in their work that the regions near the grain boundary are ferroelectrically inactive. In coarse-grained samples this effect is not very relevant, but in fine-grained BT (100–400 nm) where the volume of interfaces is extremely high, a drastic dilution of the ferroelectric properties occurs. By further reducing the grain size to the nanometer level, the intrinsic size effect dominates and a barium titanate bulk of 10 nm grain size loses its ferroelectric effect at room temperature.

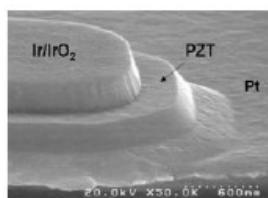
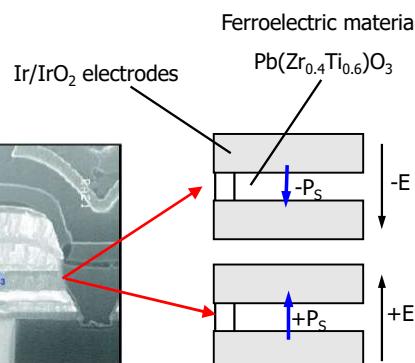
1. Frey, Role of interfaces on an apparent grain size effect on the dielectric properties for ferroelectric barium titanate ceramics. *Ferroelectrics* 206–207(1–4; 1–2), 337–353 (1998)

### Ferroelectric memories (FERAMs)

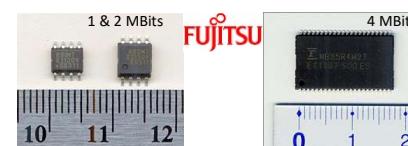
Non-volatile memories, no need for refresh as opposite to DRAMs



Samsung 32 Mb ferroelectric random access memories



Ferroelectric nanocapacitor



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### Pyroelectricity and ferroelectricity

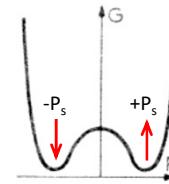
**Pyroelectric** or **polar** materials exhibit an electrical dipole even in the absence of an external electric field. The polarization associated to this electrical dipoles is called spontaneous polarization,  $P_s$  ( $C/m^2$ ). The variation of  $P_s$  with temperature determines a variation of the surface charge density and originates a pyroelectric current.

$$i = \frac{dP_s}{dt} = \left( \frac{dP_s}{dT} \right) \left( \frac{dT}{dt} \right)$$

**Ferroelectric** crystals are polar crystals in which there are at least two equilibrium orientations of the spontaneous polarization vector in the absence of an external electric field, and in which the spontaneous polarization vector may be switched between those orientations by an electric field.

"Fingerprints" of ferroelectric behaviour are:

- very high dielectric constant ( $\epsilon_r > 100$ , often  $> 1000$ );
- sharp peak or anomaly of  $\epsilon_r$  around a critical temperature  $T_c$ ;
- permittivity obeys the Curie-Weiss law above  $T_c$ ;
- **hysteresis loop** for polarization;

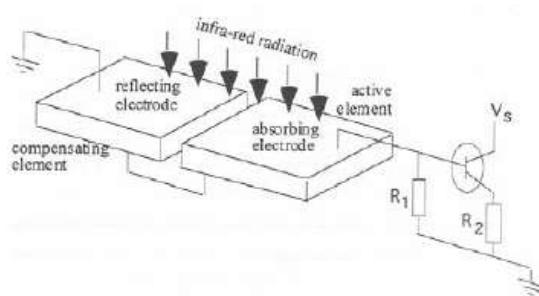


Not all polar crystals are ferroelectrics, examples are tourmaline and hexagonal CdS. Quartz is only piezoelectric; polarization is induced by the electric field. Antiparallel alignment of elementary dipoles can lead to **antiferroelectricity**.

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## Applications

- **Ferroelectric materials**, as dielectrics for capacitors: the capacitors can be made 100-1000 smaller than with conventional dielectrics.
- **Pyroelectric materials**, very sensitive to small changes in temperature. They can be used as infrared radiation detectors, for instance, for night vision goggles, anti-burglar detectors (capable of detecting the infrared radiation emitted by a person), etc...



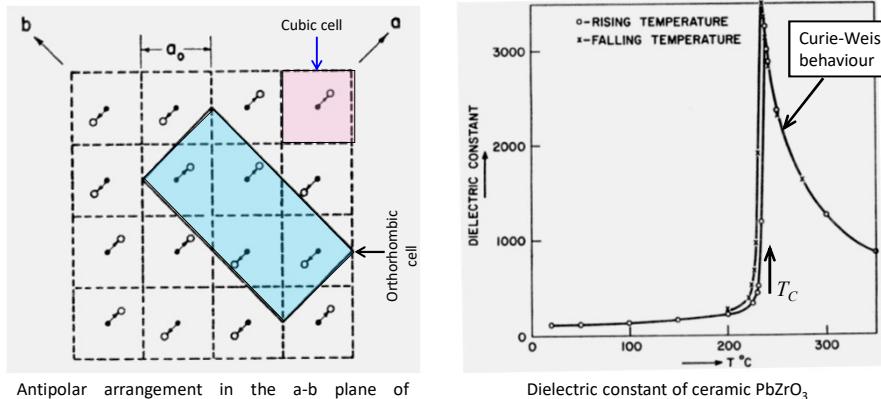
Ferroelectric materials are used for binary information storage in FeRAM (Ferroelectric Random Access Memory). The zeroes and ones in each ferroelectric capacitor correspond to a polarization that is up or down. The polarization state is set up or down by applying a positive or negative voltage, and the polarization stays up or down after removing this voltage. FeRAM therefore offers non-volatile data storage. However, to read FeRAM data, the polarization must be electrically cycled, which takes time and erases the data (destructive read). FeRAM was used in the Sony Playstation 2, and it has also been used in smart cards for Japanese railways.

<https://www.doitpoms.ac.uk/tplib/ferroelectrics/why.php>

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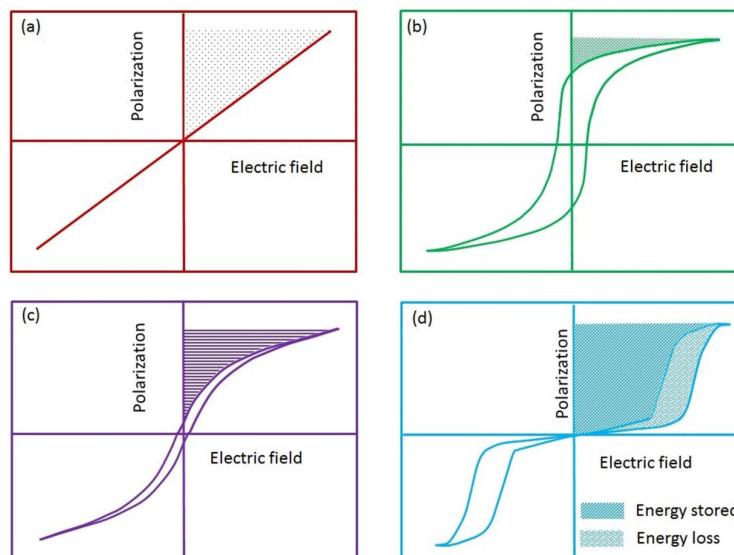
### Antiferroelectrics

In FEs, the off-center displacement occurs in the same direction in all unit cells and results in a macroscopic polarization. In contrast, in some compounds such as  $\text{PbZrO}_3$  and  $\text{NaNbO}_3$ , the unit cell has a spontaneous electrical dipole but with opposite orientation in adjacent cells, giving a net zero polarization. Like FEs, the AFE compound shows a sharp permittivity peak corresponding to transition from a cubic paraelectric phase. The transition temperature is again denoted as Curie temperature.



Antipolar arrangement in the a-b plane of orthorhombic  $\text{PbZrO}_3$ . The arrows denote the Pb ions displacement.

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(P-E) hysteresis loops and energy storage characteristics of the four classes of solid dielectric materials namely (a) linear; (b) ferroelectric; (c) relaxor ferroelectric; (d) anti-ferroelectric

Anti-ferroelectric (AFE) materials possess relatively lower values of remnant polarization and coercive electric field and faster discharge rates for dissipating stored electrical energy, due to ferroelectric to anti-ferroelectric phase transition; see [Figure 1d](#). Due to the lack of ferroelectric domains at low electric field, AFE materials do not possess any considerable hysteresis and have low remnant polarization, coercive electric field, and dielectric loss. However, at higher electric fields, the anti-parallel dipoles are aligned to form a ferroelectric phase.

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# Piezoelectric Materials

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## Piezoelectric

- **Piezoelectricity** was discovered in 1880 by J & P Curie during studies into the effect of pressure on the generation of electrical charge by crystals (such as quartz).
- Described as the generation of electricity as a result of mechanical pressure, or
- "*electrical polarisation produced by mechanical strain in crystals belonging to certain classes*".
- The phenomenon can be attributed to a lack of centre of symmetry in the crystallographic unit cell - or the unit cell is described as **non-centrosymmetric**.

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## Piezoelectric

- For Piezoelectricity -
  - *the effect is linear and reversible,*
  - *the magnitude of the polarisation is dependant on the magnitude of the stress,*
  - *the sign of the charge produced is dependant on the type of stress (tensile or compressive).*

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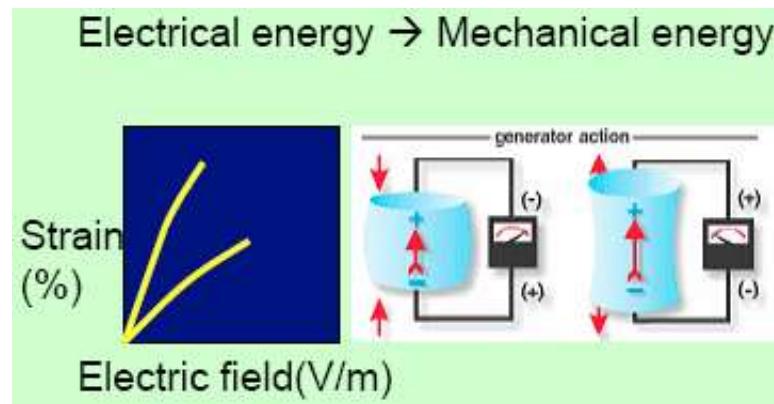
**Table 7.7** Piezoelectric materials and some typical values for  $d$  (piezoelectric coefficient) and  $k$  (electromechanical conversion factor).

Crystal	$d$ ( $\text{m V}^{-1}$ )	$k$	Comment
Quartz (crystal $\text{SiO}_2$ )	$2.3 \times 10^{-12}$	0.1	Crystal oscillators, ultrasonic transducers, delay lines, filters
Rochelle salt ( $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ )	$350 \times 10^{-12}$	0.78	
Barium titanate ( $\text{BaTiO}_3$ )	$190 \times 10^{-12}$	0.49	Accelerometers
PZT, Lead zirconate titanate ( $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$ )	$480 \times 10^{-12}$	0.72	Wide range of applications including earphones, microphones, spark generators(gas lighters, car ignition), displacement transducers, accelerometers.
Polyvinylidene fluoride (PVDF)	$18.2 \times 10^{-12}$		Must be poled; heated, put in an electric field and then cooled. Large area and inexpensive.

From *Principles of Electronic Materials and Devices, Second Edition*, S.O. Kasap (© McGraw-Hill, 2002)  
<http://Materials.Uask.Ca>

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# Piezoelectric Ceramics



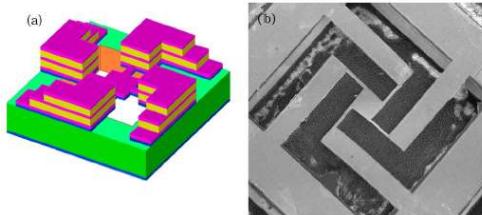
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- Piezoelectric materials can be divided into different classes, namely, ceramics, crystals, polymers, etc.; out of these materials, **piezoelectric ceramics** are the materials, which possess large piezoelectric coefficient compared to the other classes.
- There are 32 crystal classes, which are classified into the following seven groups: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, cubic. These groups are also related to the elastic behavior of the material taken where triclinic symbolizes an anisotropic material, **orthorhombic represents an orthotropic material**, and cubic are in most cases isotropic materials. **Only 20 of the 32 classes possess piezoelectric properties. Ten of these above classes are polar, i.e., it will show a spontaneous polarization without mechanical stress due to a nonvanishing electric dipole moment associated.**
- Quartz is the first naturally occurring piezoelectric material whose crystalline structure is made up of a continuous framework of  $\text{SiO}_4$  silicon-oxygen tetrahedral in which each oxygen atom is shared by two tetrahedrals. The entire structure is not polar until it is subjected to a pressure, which results in a polarized state.
- Rochelle Salt ( $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ) is one of the old materials that shows ferroelectricity between the two Curie temperatures  $T_{C_1} = 255$  K and  $T_{C_2} = 297$  K, which exhibits orthorhombic structure in the paraelectric phase and the monoclinic structure in the ferroelectric phase. It possesses a low decomposition temperature.

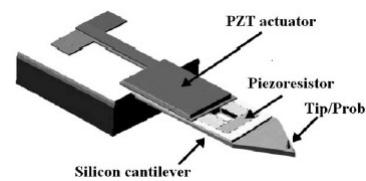
<b>Naturally existing piezoelectric crystals:</b>
(1) <b>Berlinite</b> (a rare phosphate mineral)
(2) <b>Quartz</b>
(3) <b>Cane sugar</b>
(4) <b>Rochelle</b>
(5) <b>Topaz</b>
(6) <b>Tourmaline</b>

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## Piezoelectric Microactuator Devices

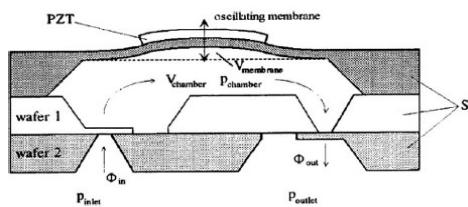


Schematic draw of optical scanning device with double layered PZT layer (a) and the fabricated device, (b) Mirror plate:  $300 \times 300 \mu\text{m}^2$ , DPZT beam:  $800 \times 230 \mu\text{m}^2$ .

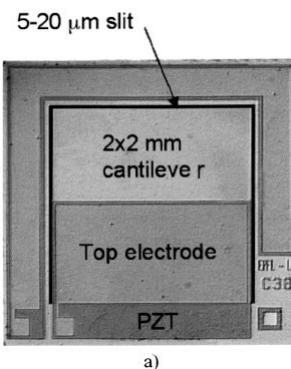


Schematic drawing of self-actuation cantilever with an integrated piezoresistor.

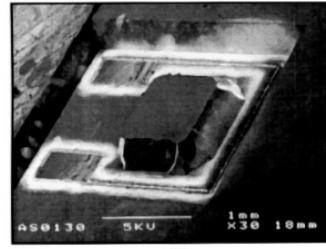
Micropump using screen-printed PZT actuator on silicon membrane. (Courtesy of Neil White, Univ. of Southampton, UK.)



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a)



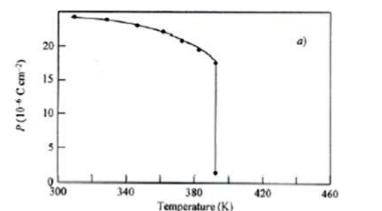
b)

Examples of piezoelectric microsensors on silicon: (a) microphone and (b) accelerometer. (OPA N.V., Taylor and Francis Ltd.)

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## Ferroelectricity, pyroelectricity and piezoelectricity

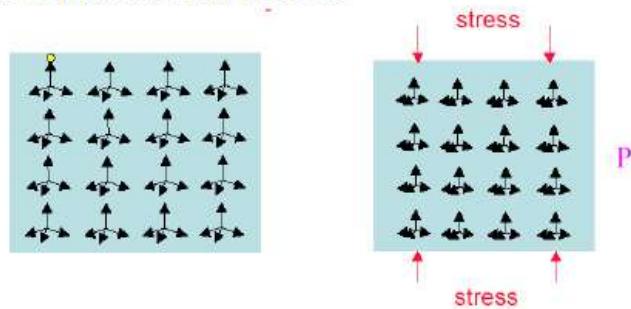
- A **ferroelectric material** shows an spontaneous polarization (in the absence of an electric field). Ex: BaTiO<sub>3</sub> at room temperature, due to the relative movement of the anions and the cations. The spontaneous polarization disappears at T higher than 130°C, due to the phase transformation to the cubic phase in which the positions of the cations and the anions is symmetric. As a consequence of the spontaneous polarisation, the dielectric constant is very high.
- A **pyroelectric material** is that in which a temperature variation induces a change in the spontaneous polarization of the material. Example: BaTiO<sub>3</sub>, the polarization depends on temperature because the movement of ions is also dependent on the temperature.



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## Ferroelectricity, pyroelectricity and piezoelectricity

- A **piezoelectric material** is that in which a pressure variation induces a change in the electrical polarization of the material. The applied pressure can induce the relative movement of anions and cations, and therefore, an spontaneous polarization. In the same way, an electric field can induce a movement of the anions and the cations, and therefore, a change in the shape of the crystal.
- That is, a piezoelectric material converts:  
Electric energy ↔ Mechanical energy
- Example: Quartz: it is not ferroelectric, but a pressure can induce an spontaneous polarization and viceversa.



1

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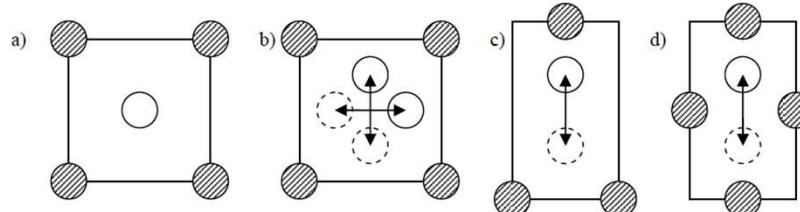
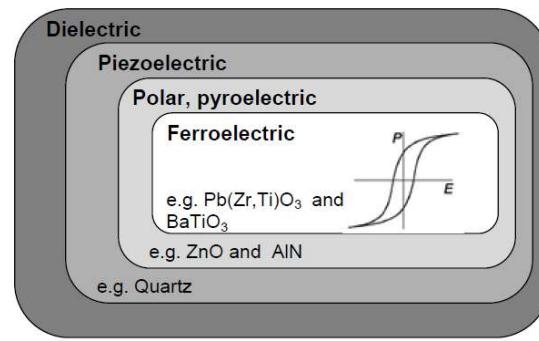
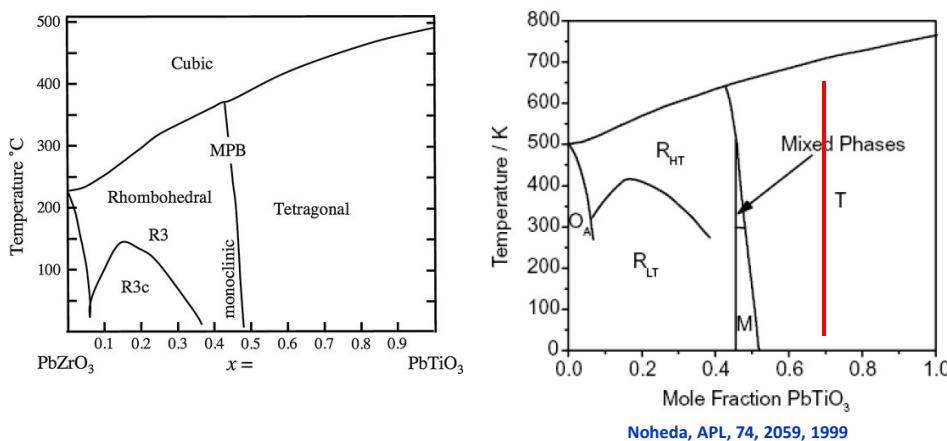


Figure 1-3 Examples of unit-cells in two dimensions with a) centro symmetry b) non centro symmetry with no unique polar axis, c) non centro symmetry with unique polarization axis with c) non centro symmetry with non-switchable polarization state (pyroelectric), and d) non centro symmetric with two switchable polarizations (ferroelectric)

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### PZT, Lead zirconium titanate, $\text{Pb}[\text{Zr}_{1-x}\text{Ti}_x]\text{O}_3$ ( $0 \leq x \leq 1$ )



Noheda, APL, 74, 2059, 1999

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**Table 1-1 – Property Comparison for BaTiO<sub>3</sub> and Pb(Zr,Ti)O<sub>3</sub> Ceramics:** A list of relevant dielectric, ferroelectric, piezoelectric, and pyroelectric properties for barium titanate and 52/48 PZT bulk ceramics at room temperature. Note that properties are quoted from the poled state. Data is compiled from references:[2, 13, 14, 21].

Property	BaTiO <sub>3</sub>	Pb(Zr <sub>0.52</sub> Ti <sub>0.48</sub> )O <sub>3</sub>
Curie Point (T <sub>c</sub> )	120°C	386°C
Dielectric Constant ( $\epsilon_r$ )	1620-1900	730-1180
Remanent Polarization (P <sub>r</sub> )	8 $\mu$ C/cm <sup>2</sup>	36 $\mu$ C/cm <sup>2</sup>
Piezoelectric Coefficient (d <sub>31</sub> )	-79 pC/N	-93.5 pC/N
Piezoelectric Coefficient (d <sub>33</sub> )	191 pC/N	223 pC/N
Electromechanical Coupling Coefficient (k)	0.21-0.44	0.31-0.69
Pyroelectric Coefficient (P)	-20 nC/cm <sup>2</sup> K	-27 nC/cm <sup>2</sup> K*

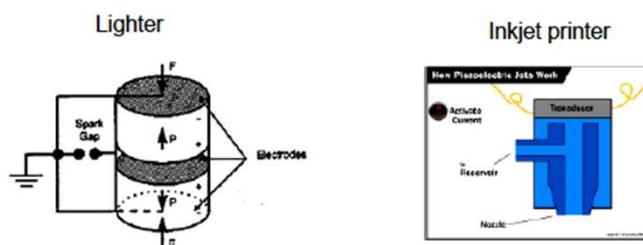
\*95/5 PZT composition.

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## Piezoelectricity

### Applications of piezoelectric materials:

- **Watches/computer clocks:** quartz (piezoelectric but not ferroelectric): an electrical signal induces the mechanical vibration of a quartz bar (to its resonance frequency). This frequency can be used to count time.
- **Lighters:** a pressure on a sheet of a (PbZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>) can induce an electric potential of 3 kV, enough to produce an arc discharge between two closely spaced sheets and ignite the gas.
- **Actuators:** a potential difference applied on a transducer can change its shape and actuate a mechanism, for instance, a inkjet printer.  
(<http://www.howstuffworks.com/inkjet-printer3.htm>)



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## Transducer

- Define?
- Many types of transducers exist
  - Pressure transducers
  - Air flow transducers, etc.
- What is function of transducer? convert electrical signals to sound waves, and vice versa.

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## Ultrasound Transducer Materials

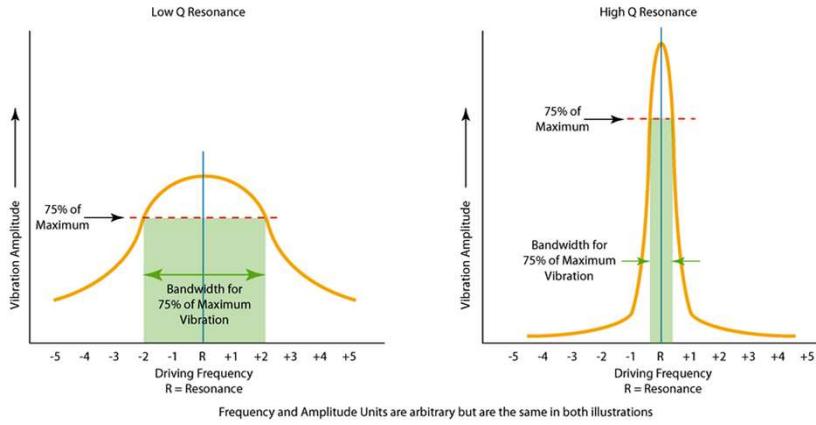
- Quartz (naturally piezoelectric)
  - First used as a stable resonator in time measurement devices
  - Used in some laboratory ultrasound applications
- Most current applications use piezoelectric ceramics (i.e., lead zirconate titanate; barium titanate)
  - Lower "Q" (good for short pulses)
  - Good sensitivity



Miniature quartz tuning fork; 32,768 Hz.

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An ultrasonic transducer must be driven at its resonant frequency to achieve optimum performance. The "Q" of a transducer defines the sensitivity of the transducer to changes in driving frequency.



Frequency and Amplitude Units are arbitrary but are the same in both illustrations

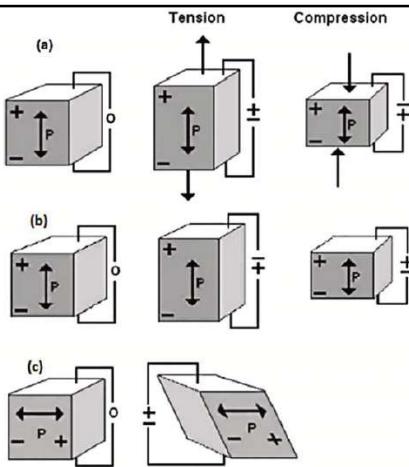
The vibrations of a transducer with a high "Q" are "damped" or significantly reduced once the driving frequency changes very slightly from its resonant frequency. The low "Q" transducer continues to vibrate with a considerable portion of its maximum amplitude even if the driving frequency deviates moderately from the resonant frequency. The width of the frequency range that will cause vibration of a particular scale is called the "Q" of the transducer.

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## Polarizing a Piezoelectric Element

- Most ultrasound transducer materials are not 'naturally' piezoelectric
  - Lead zirconate titanate
  - Microscopic crystals, randomly oriented
- Must be polarized
  - Heat to  $\sim 350^\circ\text{C}$  (Curie Temperature; Ref. to PZT)
  - Apply strong voltage across crystal
  - Cool while voltage is still applied

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A. Safari, E.K. Akdogan (eds.) *Piezoelectric and Acoustic Materials for Transducer Applications.. P.17*

Fig. 2.1 Schematic representation of the longitudinal direct (a), converse (b), and shear (c) piezoelectric effects

**Table 2.2** Physical properties of major piezoelectric materials together with their symmetries

Parameter	Quartz	BaTiO <sub>3</sub>	PbTiO <sub>3</sub> : Sm	PZT 5H	LF4T	PZN-8%PT [001]	PZN-8%PT [111]
Symmetry	32	4mm	4mm	3m/4mm	mm2/4mm	3m/4mm	3m/4mm
$d_{33}$ (pC/N)	2.3	190	65	593	410	2500	84
$d_{31}$ (pC/N)	0.09	0.38	0	-274	-154	-1400	-20
$\epsilon_{33}^T/\epsilon_0$	5	1700	175	3400	2300	7000	1000
$T_c$ (°C)	120	355	193	253	160	140	160

## Piezoelectric coupling coefficient, K

The piezoelectric coupling coefficient (sometimes referred to as the electromechanical coupling coefficient) is defined as the ratio of the mechanical energy accumulated in response to an electrical input or vice versa. The piezoelectric coupling coefficient can be expressed as

$$K = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}}$$

$$K = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}}$$

Under **dynamic DC conditions, as opposed to static DC conditions**, the behaviour of the piezoelectric materials is much more complex. It can be characterised in terms of an equivalent electrical circuit which exhibits both parallel and series resonance frequencies. To approximate these frequencies, the frequency of the minimum impedance ( $f_r$ ) and maximum impedance ( $f_a$ ) for the material are measured, since they differ from the actual values by a very small amount (< 0.1%). The planar coupling coefficient  $K_p$  for thin disc specimen then can be calculated from

$$K_p = \left( \frac{f_a^2 - f_r^2}{f_a^2} \right)^{1/2}$$

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## 2.2 Fundamentals of the Piezoelectric Effect in Single Crystals and Ceramics

Since the piezoelectric coupling is described by a linear relationship between the first-rank tensor or vector ( $\mathbf{D}$  or  $\mathbf{E}$ ) and the second-rank tensor ( $\sigma$  or  $S$ ), the corresponding coupling coefficients  $d_{kij}$  (also called charge piezoelectric coefficients) form a third-rank tensor. Hence, the piezoelectric equations may be written in the following form ( $i, j, k = 1, 2, 3$ ):

**electric displacement  $D$  that is directly proportional to an applied mechanical stress  $\sigma$ , strain  $S$  (elongation or contraction) changes to the opposite one if the direction of electric field  $E$  is reversed.**

$$S_{ij} = d_{kij}E_k, \quad (2.1)$$

$$D_k = d_{kij}\sigma_{ij}, \quad (2.2)$$

As mentioned earlier, it was understood from the very beginning that the crystallographic symmetry of materials plays a decisive role in the piezoelectric phenomena. According to the definition of the piezoelectric effect, all components of the piezoelectric tensor should vanish in crystals possessing the center of symmetry.

- It should be mentioned that statistically about 30% of all materials (from about several millions known by now) are noncentrosymmetric. However, the piezoelectric properties are revealed in only few thousands of them, with about several hundreds having piezoelectric activity valuable for the applications.

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- Therefore, it can be concluded that the absence of the center of symmetry represents the necessary but not sufficient requirement for a material to exhibit any sizeable piezoelectric effect. Though the symmetry does not determine the values of piezoelectric coefficients directly, the symmetry considerations, are indispensable for the design and fabrication of piezoelectric and acoustic devices. Table 2.1 lists the point groups that permit piezoelectricity for all crystallographic systems.

Table 2.1 Centrosymmetric and noncentrosymmetric point groups in crystals with different symmetries

Crystal system	Symmetry elements	Centro-symmetric	Noncentro-symmetric
Triclinic	Center	$\bar{1}$	1
Monoclinic	Center, axis, plane	$2/m$	$2, m$
Orthorhombic	Center, axis, plane	$mmm$	$222, mm2$
Tetragonal	Center, axis, plane	$4/m, 4/mmm$	$4, 4, 422, 4mm, 42m$
Trigonal	Center, axis, plane	$\bar{3}, \bar{3}m$	$3, 32, 3m$
Hexagonal	Center, axis, plane	$6/m, 6/mmm$	$6, \bar{6}, 622, 6mm, \bar{6}m2$
Cubic	Center, axis, plane	$m\bar{3}, m\bar{3}m$	$23, \bar{4}3m, 432$

Fig. 2.2 Matrix of the piezoelectric coefficients for crystals of the tetragonal symmetry (point group  $4mm$ )

$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$$

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The linear relationship between the applied stress X and the resulting polarization P:

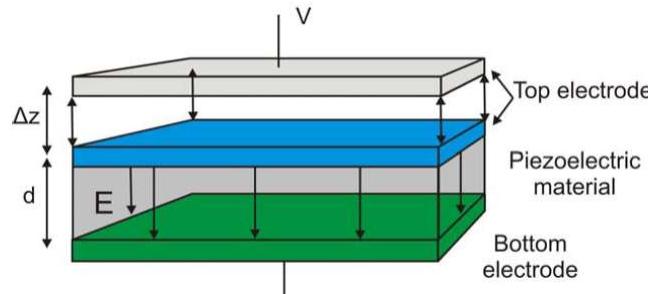
$$P = d^{\text{direct}} \cdot X \quad (1.9)$$

and  $d^{\text{direct}}$  is the piezoelectric coefficient.

Vice versa, when an external electric field E is applied to a crystal, this can cause a strain x in the material. This results in a physical contraction or expansion of the sample (see figure 1-5). This phenomenon is called the inverse piezoelectric effect:

$$x = d^{\text{inverse}} \cdot E \quad (1.10)$$

The piezoelectric constant  $d^{\text{direct}}$  can be expressed as a measured in Coulomb per Newton [C/N] for the inverse piezoelectric coefficient  $d^{\text{inverse}}$  and meter per Volt [m/V]. Typical sizes for useful piezoelectric materials range from about 1 pm/V for quartz materials to about 1000 pm/V for PZT ceramics<sup>3</sup>.



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In a realistic situation, a piezoelectric thin film consists of a top electrode, a bottom electrode and the piezoelectric material in between, see Figure 1-5. This situation can be thought of as an ideal capacitor, if electrode area A is bigger than the dielectric medium d ( $A \gg d$ ). A voltage is applied between the top and bottom electrode and generates an electrical field in the medium. The electrical field is:

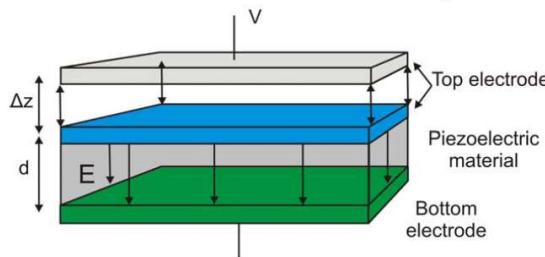
$$E = \frac{V}{d} \quad (1.11)$$

For a piezoelectric medium, the sample deformation will be perpendicular to the top electrode. Using the deformation-strain relation equation  $x = \frac{\Delta z}{d}$ , and the strain as a function of the deformation:

$$x = \frac{\Delta z}{d} \quad (1.12)$$

The following direct relation between piezoelectric deformation  $\Delta z$  and the applied voltage can be obtained:

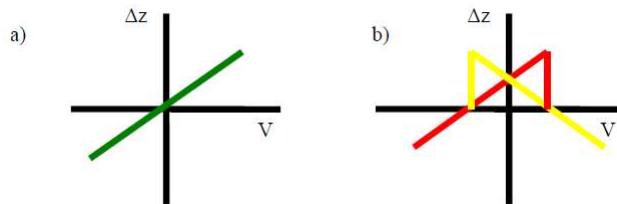
$$\Delta z = d_{33} \cdot V \quad (1.13)$$



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The subscripts of the piezoelectric coefficient denote the direction of the input electric field and the resulting deformation, which are in this case both out-of-plane. The  $d_{33}$ , or longitudinal piezoelectric coefficient, represents a deformation of the sample along the out-of-plane direction when the applied field is in the same direction. The  $d_{31}$ , or transverse piezoelectric coefficient, represents an expansion or contraction of the sample in the direction perpendicular to the applied field. The  $d_{15}$  coefficient describes shear deformation of the ferroelectric sample.

The piezoelectric displacement can be plotted as a function of voltage. Figure 1-6a shows a purely piezoelectric response, linear as a function of the voltage. Figure 1-6b shows a piezoelectric with a ferroelectric switching effect. At a certain coercive voltage, the polarization suddenly switches in direction. This reversal of the polarization will also generate a sudden reversal of the physical deformation of the material and thus the piezoelectric coefficient changes sign. Moreover, a hysteresis loop is obtained, which is usually called the piezoelectric 'butterfly loop', obviously named after its shape. Usually the first cycle will form start at zero and converge to the hysteresis loop.



1-6 a) Linear piezoelectric behavior b) 'Butterfly loop' in strain  $x(=\delta l/l)$  vs. voltage  $V$ , describing the response of a piezo actuator to a bipolar drive voltage. When a certain threshold voltage (negative to the polarization direction) is exceeded, reversion of polarization can occur.

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- Three piezoelectric modes,  $d_{31}$ ,  $d_{33}$  and  $d_{15}$ , the BEST choice of which influences the maximum output voltage and power.
- The  $d_{33}$  mode piezoelectric materials have advantage in generating higher output voltage while the  $d_{31}$  mode piezo-materials have potential in generating larger electric current.

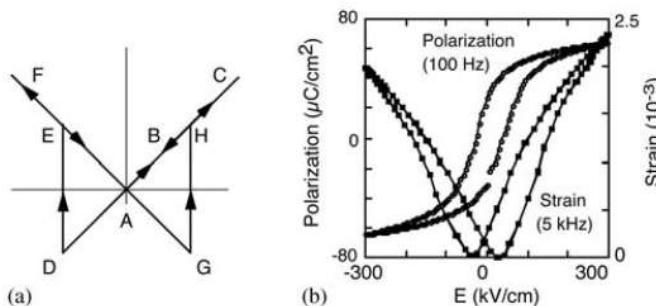
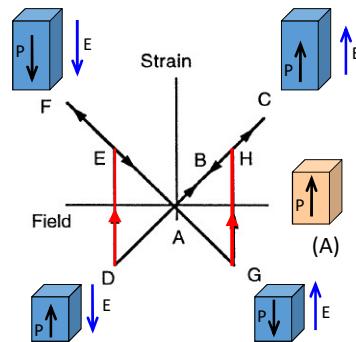


FIGURE 4.7 Strain–electric field ( $x$ - $E$ ) hysteresis loop (butterfly loop) in ferroelectrics: (a) idealized loop in a crystal in which polarization reverses only by  $180^\circ$ , and (b) the polarization and strain loops measured on a (111)-oriented, 322 nm thick, sol-gel  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  thin film (Courtesy of David V. Taylor).

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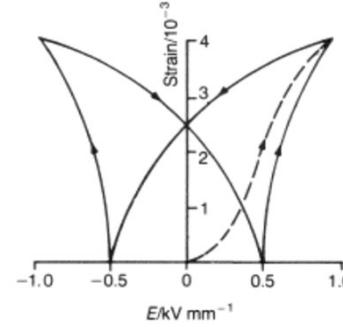
### Strain-field loops in ferroelectrics

In addition to the polarization–electric field hysteresis loop, polarization switching by an electric field in ferroelectric materials leads to strain–electric field hysteresis (butterfly loops).



**Ideal ferroelectric** with only 180° domain walls  
(pure piezoelectric response - intrinsic)

ABC: elongation (piezoelectric effect  $S=dE$ )  
CD: strain changes from positive to negative  
DE: switching  
EF: elongation  
FG: strain changes from negative to positive  
GH: switching



**Real ferroelectric (PZT)**  
Intrinsic (lattice) + extrinsic (dws)  
contributions

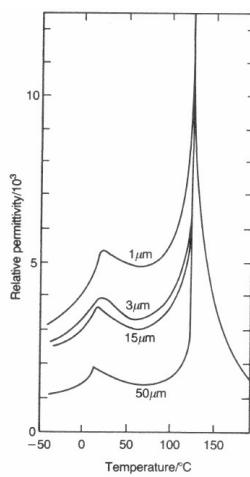
Multidomain (90 + 180° dws) structure.  
Contribution (non-linear and hysteretic) to strain from movement and switching of non-180° domain walls in addition to pure piezoelectric response. Can be comparable or even greater than the pure piezoelectric response.

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### Domain-wall contribution to the properties of ferroelectric materials

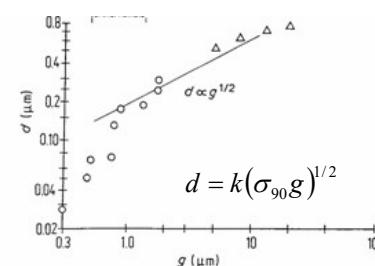
Movement of domain walls (vibration, bending, jump) at weak to moderate fields (subswitching fields) is one of the most important so-called extrinsic (nonlattice) contributions to the dielectric, elastic and piezoelectric properties of ferroelectric materials and may be comparable to the intrinsic effect of the lattice.

- Movement of all types of DWs affect polarization and permittivity
- Movement of non-180° DWs affect polarization and piezoelectric properties (strain)



The dielectric constant of BaTiO<sub>3</sub> ceramics decreases with decreasing grain size down to a grain size of about 1 μm. This is ascribed to the increasing density of 90° DWs with decreasing grain size. Similar behaviour observed in PZT ceramics.

$$\epsilon_r' = \epsilon_{r,lattice}' + \epsilon_{r,dw}' = \epsilon_{r,lattice}' + A g^{-\frac{1}{2}} \quad g: \text{grain size}$$



Thickness of domain walls  
as a function of grain size  
 $\sigma_{90}$ : domain wall energy

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# Magnetic Properties

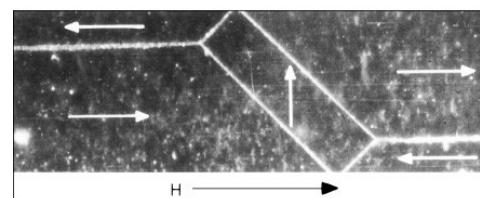
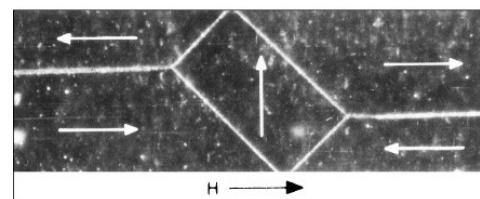
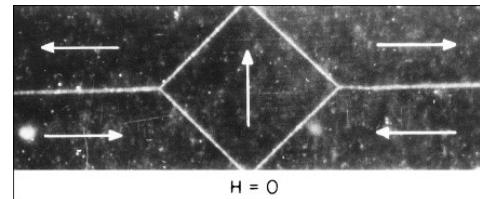
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## Magnetic Properties

Iron single crystal photomicrographs

magnetic domains change shape as a magnetic field ( $H$ ) is applied.

domains favorably oriented with the field grow at the expense of the unfavorably oriented domains.



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# Magnetic Properties



a) Transmission electron micrograph showing the microstructure of the perpendicular magnetic recording medium used in hard-disk drives.

b) Magnetic storage hard disks used in laptop (left) and desktop (right) computers.

c) Inside of a hard disk drive.

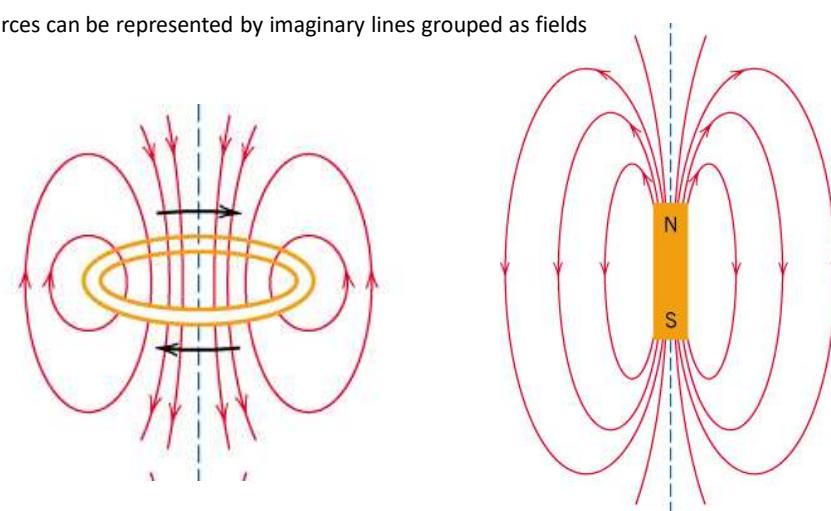
d) Laptop computer

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## Basic Concepts

Magnetic forces appear when moving charges

Forces can be represented by imaginary lines grouped as fields

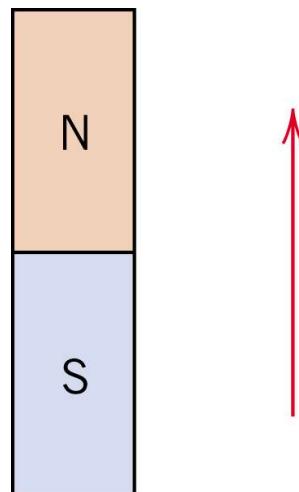


Magnetic field lines of force around a current loop and a bar magnet.

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## MAGNETIC DIPOLES

The magnetic moment represented by a vector



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## History on magnetism

### 1. Discovery of functionality of the magnet

Loadstone compass : China (BC 3)

### 2. Discovery of electromagnetic field

Oersted (Denmark, 1820): Current gives a force on a loadstone compass

- Establishment of Electromagnetism
- Maxwell's equations

### 3. Relation between the substance and magnetism

Ampere : Magnetism is based on the special molecular field (1821)

Langgvin : Angular momentum by electron orbital motion (1905)

Dirac : Discovery of spin angular momentum (1928)

Heisenberg: The origin of ferromagnetism is in the exchange interaction (1933)

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### Magnetic Field Vectors

**magnetic field strength ( $H$ ) & magnetic flux density ( $B$ )**

**Magnetic field strength**

$$H = \frac{NI}{l}$$

**Magnetic flux density**

$$B = \mu H$$

$$B_0 = \mu_0 H$$

**relative permeability**

$$\mu_r = \frac{\mu}{\mu_0}$$

**magnetization**

$$B = \mu_0 H + \mu_0 M$$

$$M = \chi_m H$$

**magnetic susceptibility**

$$\chi_m = \mu_r - 1$$

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## Behavior of Substances in a Magnetic Field

Behaviour	Typical $\chi$ value	Change of $\chi$ with increasing temperature	Field dependence?
Diamagnetism	$-8 \times 10^{-6}$ for Cu	None	No
Paramagnetism		Decreases	No
Pauli paramagnetism	$8.3 \times 10^{-4}$ for Mn	None	No
Ferromagnetism	$5 \times 10^3$ for Fe	Decreases	Yes
Antiferromagnetism	0 to $10^{-2}$	Increases	(Yes)

Magnetic behavior may be distinguished by the values of  $\chi$  and  $\mu$  and by their **temperature** and **field** dependence

1. **Positive vs. negative value:** only diamagnetic materials show negative  $\chi$
2. **Absolute value:** ferromagnetic materials show huge positive value
3. **Temperature dependence:** diamagnetism is not temp. dependence, antiferromagnetic materials increase with increasing temp, and para- and ferromagnetic materials decrease with increasing temp
4. **Field dependence:** only ferro- and antiferromagnetic materials show field dependence

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**Table 18.2 Room-Temperature Magnetic Susceptibilities for Diamagnetic and Paramagnetic Materials**

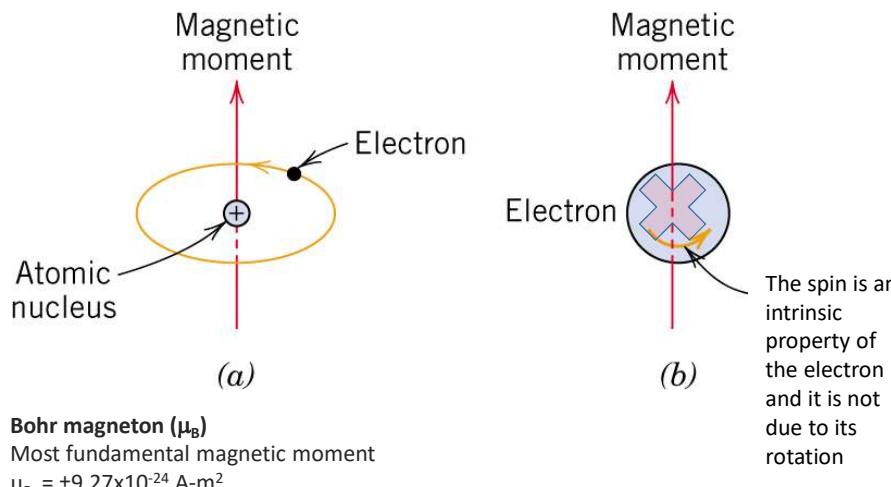
<i>Diamagnetics</i>		<i>Paramagnetics</i>	
<i>Material</i>	<i>Susceptibility <math>\chi_m</math> (volume) (SI units)</i>	<i>Material</i>	<i>Susceptibility <math>\chi_m</math> (volume) (SI units)</i>
Aluminum oxide	$-1.81 \times 10^{-5}$	Aluminum	$2.07 \times 10^{-5}$
Copper	$-0.96 \times 10^{-5}$	Chromium	$3.13 \times 10^{-4}$
Gold	$-3.44 \times 10^{-5}$	Chromium chloride	$1.51 \times 10^{-3}$
Mercury	$-2.85 \times 10^{-5}$	Manganese sulfate	$3.70 \times 10^{-3}$
Silicon	$-0.41 \times 10^{-5}$	Molybdenum	$1.19 \times 10^{-4}$
Silver	$-2.38 \times 10^{-5}$	Sodium	$8.48 \times 10^{-6}$
Sodium chloride	$-1.41 \times 10^{-5}$	Titanium	$1.81 \times 10^{-4}$
Zinc	$-1.56 \times 10^{-5}$	Zirconium	$1.09 \times 10^{-4}$

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### Origins of Magnetic Moments:

Responds to quantum mechanics laws

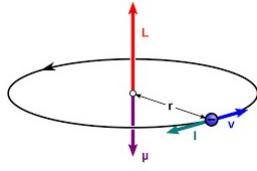
Two main contributions: (a) an orbiting electron and (b) electron spin.



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## Origin of Atomic Moment

### What is the microscopic origin of magnetism in materials ?



Now consider a magnetic dipole moment as a charge  $q$  moving in a circle with radius  $r$  with speed  $v$ . The current is the charge flow per unit time. Since the circumference of the circle is  $2\pi r$ , and the time for one revolution is  $2\pi r/v$ , one has the current as  $I = qv/2\pi r$ . The magnitude of the dipole moment is  $|\mu| = I \cdot (\text{area}) = (qv/2\pi r)\pi r^2 = qrp/2m$ , where  $p$  is the linear momentum. Since the radial vector  $\mathbf{r}$  is perpendicular to  $\mathbf{p}$ , we have

$$\mu = \frac{qr \times p}{2m} = \frac{q}{2m} \mathbf{L},$$

where  $\mathbf{L}$  is the angular momentum.

The magnitude of the orbital magnetic momentum of an electron with orbital-angular momentum quantum  $l$  is

$$\mu = \frac{e\hbar}{2m_e} [l(l+1)]^{1/2} = \mu_B [l(l+1)]^{1/2}.$$

Here,  $\mu_B$  is a constant called Bohr magneton, and is equal to

$$\mu_B = \frac{e\hbar}{2m_e} = \frac{(1.6 \times 10^{-19} \text{C}) \times (6.626 \times 10^{-34} \text{J} \cdot \text{s}/2\pi)}{2 \times 9.11 \times 10^{-31} \text{kg}} = 9.274 \times 10^{-24} \text{J/T}$$

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- i. According to Bohr's theory, an electron in an atom can revolve only in certain stationary orbits in which angular momentum ( $L$ ) of the electron is an integral multiple ( $n$ ) of  $\frac{\hbar}{2\pi}$ , where  $\hbar$  is Planck's constant.

$$\therefore L = m_e vr = \frac{n\hbar}{2\pi} \quad \dots(1)$$

- ii. The orbital magnetic momentum of an electron is given as,  $m_{\text{orb}} = \frac{eL}{2m_e} \quad \dots\dots(2)$

- iii. Substituting equation (1) and (2), we have,

$$m_{\text{orb}} = n \left( \frac{e\hbar}{4\pi m_e} \right)$$

- iv. For the 1<sup>st</sup> orbit,  $n = 1$ ,

$$\therefore m_{\text{orb}} = \frac{e\hbar}{4\pi m_e}$$

- v. The quantity  $\frac{e\hbar}{4\pi m_e}$  is called Bohr Magneton and its value is  $9.274 \times 10^{-24} \text{ Am}^2$ .

### Significance of Bohr Magnetons

1. It is a physical constant and the natural unit for describing the magnetic moment (in atomic scale) of an electron induced by either its orbital or spin angular momentum.
2. It is the magnitude of the magnetic dipole moment of an orbiting electron with an orbital angular momentum of  $\hbar$ .

On the other hand, magnetic moment by electron spin is given using spin angular momentum number s from the Dirac equation

$$\mu_s = -(\mu_0 e/m) \mathbf{P}_s = -(\mu_0 e/m) \hbar s = -2 \mu_B s \quad (1.8)$$

where  $\mathbf{P}_s = \hbar s$ ,  $s = \pm 1/2$ .

Thus, the total magnetic moment by an electron is

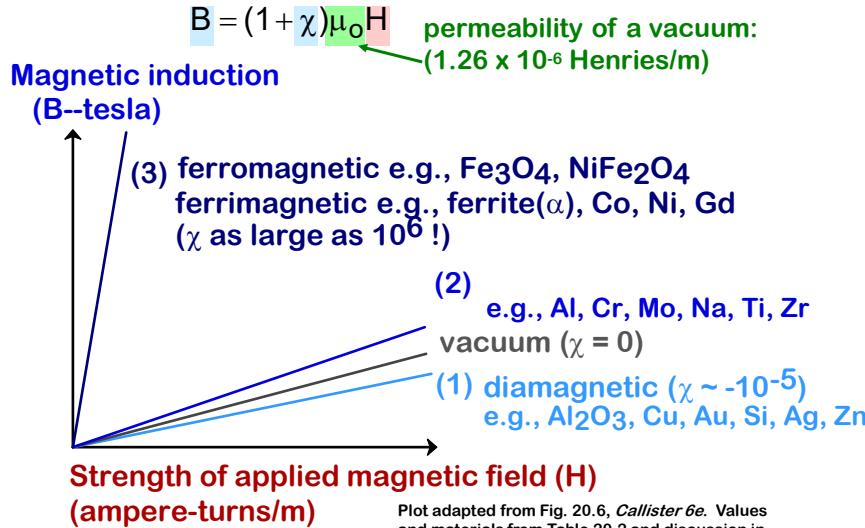
$$\mu = \mu_l + \mu_s = -(1 + 2s) \mu_B = -g_j \mu_B \quad (1.9)$$

$j = l + s$  : total angular momentum

$g$ : g factor  $g = 2$  for  $l = 0$

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### 3 TYPES OF MAGNETISM



Plot adapted from Fig. 20.6, *Callister 6e*. Values and materials from Table 20.2 and discussion in Section 20.4, *Callister 6e*.

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### PERMANENT MAGNETS

- Process:
  - initial (unmagnetized state)
  - apply  $H$ , cause alignment
  - remove  $H$ , alignment stays!  
 $\rightarrow$  permanent magnet!

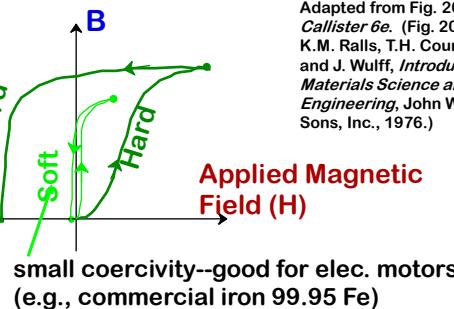
Adapted from Fig. 20.14, *Callister 6e*.

- Coercivity,  $H_c$ :  
Negative  $H$  needed to demagnetize!

Adapted from Fig. 20.16, *Callister 6e*. (Fig. 20.16 from K.M. Ralls, T.H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*, John Wiley and Sons, Inc., 1976.)

- Hard vs Soft Magnets

large coercivity  
--good for perm magnets  
--add particles/voids to make domain walls hard to move (e.g., tungsten steel:  
 $H_c = 5900$  amp-turn/m)



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## Magnetic Properties of Materials

1. Magnetisation of materials due to a set of isolated atoms (or ions)

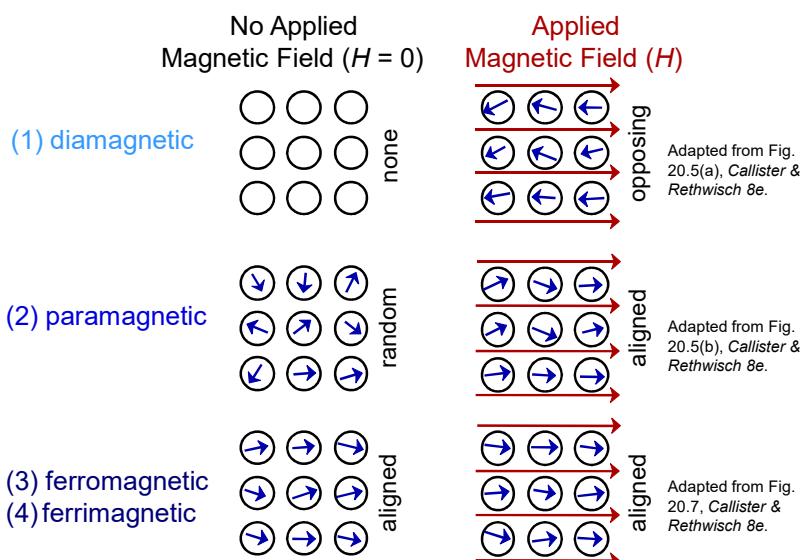
a) Diamagnetism - magnetic moment of filled shells of atoms. Induced moment opposes applied field

b) Paramagnetism - unfilled shells have a finite magnetic moment (orbital angular momentum) which aligns along the magnetic field direction.

2. Collective magnetisation - magnetic moments of adjacent atoms interact with each other to create a spontaneous alignment - Ferromagnetism, Ferrimagnetism, Antiferromagnetism

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## Magnetic Responses for 4 Types

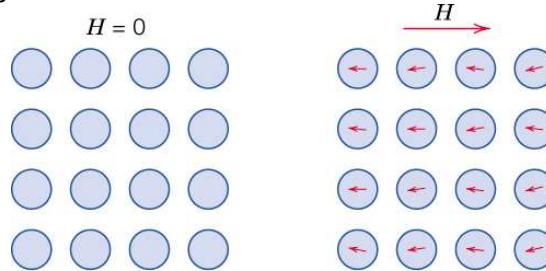


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### 18.3 Diamagnetism and Paramagnetism

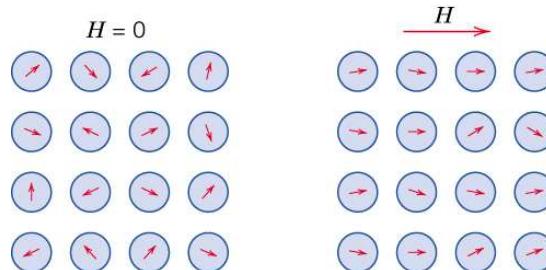
#### Diamagnetic material

in the presence of a field, dipoles are induced and aligned opposite to the field direction.



(a)

#### Paramagnetic material



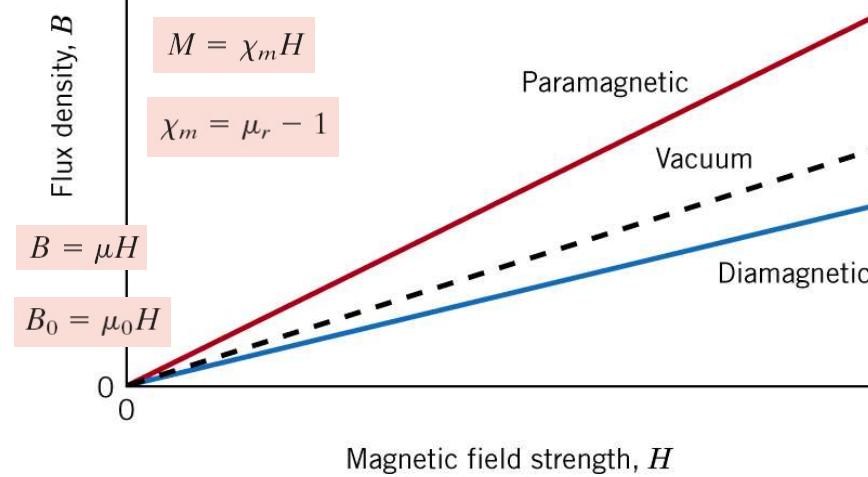
(b)

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$$B = \mu_0 H + \mu_0 M = \mu_0 H + \mu_0 \chi_m H \quad \mu = \mu_0(1 + \chi_m)$$

The flux density  $B$  versus the magnetic field strength  $H$  for diamagnetic and paramagnetic materials.

$$\mu_r = \frac{\mu}{\mu_0}$$



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**Table 18.2 Room-Temperature Magnetic Susceptibilities for Diamagnetic and Paramagnetic Materials**

Diamagnetics		Paramagnetics	
Material	Susceptibility $\chi_m$ (volume) (SI units)	Material	Susceptibility $\chi_m$ (volume) (SI units)
Aluminum oxide	$-1.81 \times 10^{-5}$	Aluminum	$2.07 \times 10^{-5}$
Copper	$-0.96 \times 10^{-5}$	Chromium	$3.13 \times 10^{-4}$
Gold	$-3.44 \times 10^{-5}$	Chromium chloride	$1.51 \times 10^{-3}$
Mercury	$-2.85 \times 10^{-5}$	Manganese sulfate	$3.70 \times 10^{-3}$
Silicon	$-0.41 \times 10^{-5}$	Molybdenum	$1.19 \times 10^{-4}$
Silver	$-2.38 \times 10^{-5}$	Sodium	$8.48 \times 10^{-6}$
Sodium chloride	$-1.41 \times 10^{-5}$	Titanium	$1.81 \times 10^{-4}$
Zinc	$-1.56 \times 10^{-5}$	Zirconium	$1.09 \times 10^{-4}$

Element	Electronic configuration	Crystal structure	Magnetization at 0 K (Amp/m)	Ferromagnetic curie temp. $T_c$ (K)	Melting temp. (K)
Fe	$3d^6 4s^2$	bcc	$1.7 \times 10^6$	1043	1810
Co	$3d^7 4s^2$	hcp	$1.4 \times 10^6$	1404	1750
Ni	$3d^8 4s^2$	fcc	$0.48 \times 10^6$	632	1732
Gd	$4f^7 5d^1 6s^2$	hcp	$5.66 \times 10^6$	290	1586

**Selected Physical properties of ferromagnetic systems**

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**Magnetic units and conversion factors for the SI, CGS and emu systems**

Quantity	Symbol	SI units		CGS-emu unit	Conversion
		Derived	Primary		
• Magnetic induction (flux density)	B	tesla ( $\text{Wb}/\text{m}^2$ )	$\text{kg}/\text{s}\cdot\text{C}$	gauss	$1 \frac{\text{Wb}}{\text{m}^3} = 10^4 \text{ gauss}$
• Magnetic Field Strength	H	$\frac{\text{amp-turn}}{\text{m}}$	$\text{C}/\text{m}\cdot\text{s}$	oersted	$\frac{1 \text{ amp-turn}}{n} = 4\pi \times 10^{-3} \text{ oersted}$
• Magnetization	M (SI)	$\frac{\text{amp-turn}}{\text{m}}$	$\text{C}/\text{m}\cdot\text{s}$	$\text{maxwell}/\text{cm}^2$	$\frac{1 \text{ amp-turn}}{m} = 10^{-3} \text{ maxwell}/\text{cm}^2$
• Permeability of a vacuum	$\mu_0$	henry/m	$\text{kg}\cdot\text{m}/\text{C}^2$	unitless	$4\pi \times 10^{-7} \text{ henry}/\text{m} = 1 \text{ emu}$
• Relative permeability	$\mu_r$ (SI) $\mu'$ (CGS-emu)	unitless	unitless	unitless	$\mu_r = \mu'$
• Susceptibility	$\chi$ (SI) $\chi'$ (CGS-emu)	unitless	unitless	unitless	$\chi = 4\pi\chi'$

Note: units of Weber (Wb) are volt-seconds, units of Henry are Webers per ampere

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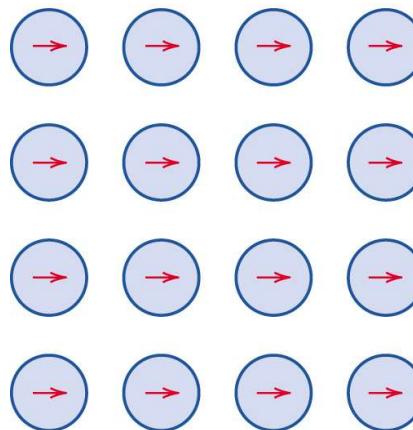
## 18.4 FERROMAGNETISM

$$H = 0$$

mutual alignment of atomic dipoles

even in the absence of an external magnetic field.

coupling forces align the magnetic spins



$$B = \mu_0 H + \mu_0 M$$

$$B \approx \mu_0 M$$

Domains with mutual spin alignment

$B$  grows up to a saturation magnetization  $M_s$  with a saturation flux

$B_s = M_{\text{atom}} \times N_{\text{atoms}}$  (average moment per atom times density of atoms)

$M_{\text{atom}} = 2.22\mu_B, 1.72\mu_B, 0.60\mu_B$  for Fe, Co, Ni, respectively

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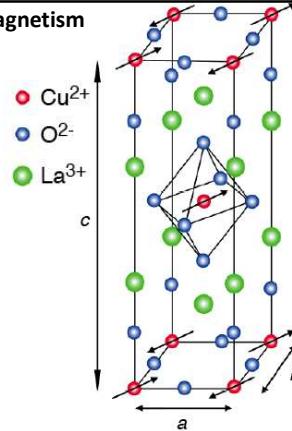
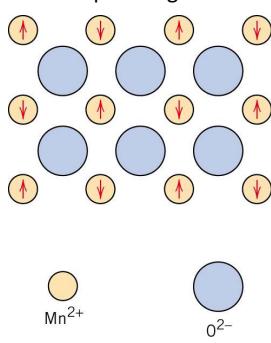
## 18.5 Antiferromagnetism & Ferrimagnetism

### ANTIFERROMAGNETISM

Antiparallel alignment of spin magnetic moments for antiferromagnetic manganese oxide ( $\text{MnO}$ )

At low T

Above the Neel temperature they become paramagnetic



1986: superconductivity discovered in layered compound  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  with a transition T much higher than expected. Little was known about copper oxides

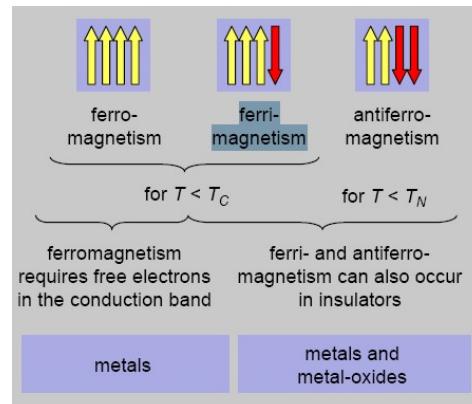
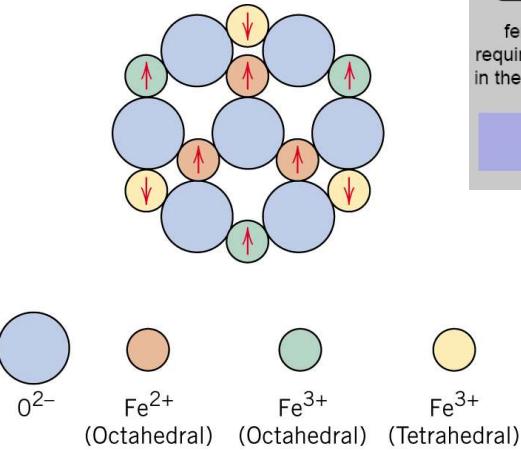
Parent materials,  $\text{La}_2\text{CuO}_4$ , and  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , demonstrated that the  $\text{CuO}_2$  planes exhibit antiferromagnetic order.

This work initiated a continuing exploration of magnetic excitations in copper-oxide superconductors, crucial to the mechanism of high-temperature superconductivity.

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## FERRIMAGNETISM

spin magnetic moment configuration for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in  $\text{Fe}_3\text{O}_4$ . Above the Curie temperature becomes paramagnetic



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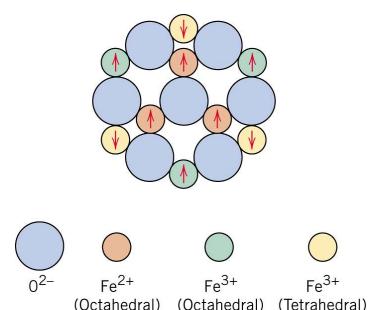
**Table 18.3** The Distribution of Spin Magnetic Moments for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  Ions in a Unit Cell of  $\text{Fe}_3\text{O}_4^a$

Cation	Octahedral Lattice Site	Tetrahedral Lattice Site	Net Magnetic Moment
$\text{Fe}^{3+}$	$\uparrow \uparrow \uparrow \uparrow$ $\uparrow \uparrow \uparrow \uparrow$	$\downarrow \downarrow \downarrow \downarrow$ $\downarrow \downarrow \downarrow \downarrow$	Complete cancellation
$\text{Fe}^{2+}$	$\uparrow \uparrow \uparrow \uparrow$ $\uparrow \uparrow \uparrow \uparrow$	—	$\uparrow \uparrow \uparrow \uparrow$ $\uparrow \uparrow \uparrow \uparrow$

<sup>a</sup> Each arrow represents the magnetic moment orientation for one of the cations.

**Table 18.4** Net Magnetic Moments for Six Cations

Cation	Net Spin Magnetic Moment (Bohr magnetons)
$\text{Fe}^{3+}$	5
$\text{Fe}^{2+}$	4
$\text{Mn}^{2+}$	5
$\text{Co}^{2+}$	3
$\text{Ni}^{2+}$	2
$\text{Cu}^{2+}$	1



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# Spinel structure

JCPDS File No.: 00-021-1152

**Mineral name:** Spinel

**Compound name:** Magnesium Aluminum Oxide

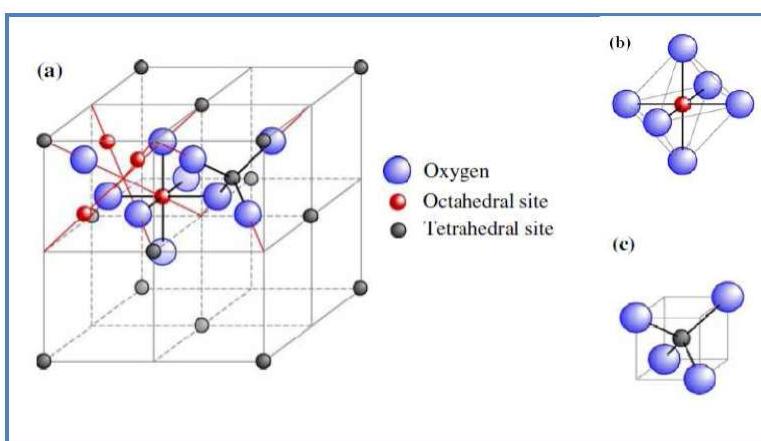
**Chemical formula:**  $\text{MgAl}_2\text{O}_4$

**Crystal system:** Cubic

**Space group:** Fd-3m

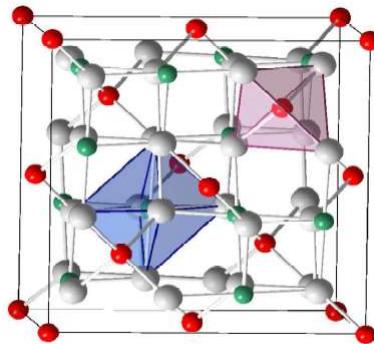
**Space group number:** 227

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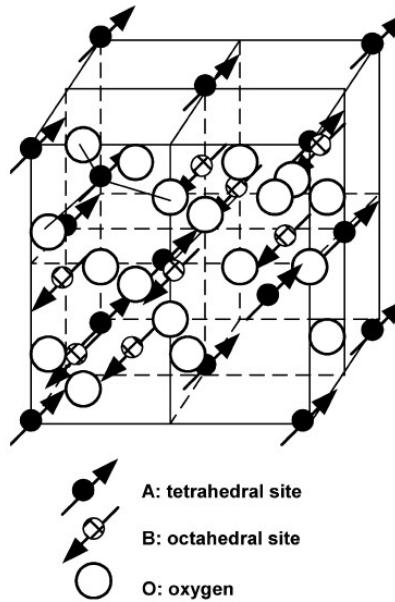


**Figure 2.1** (a) Spinel structure, (b) octahedral interstice (B site: 32 per unit cell, 16 occupied), and (c) tetrahedral interstice (A site: 64 per unit cell, 8 occupied)

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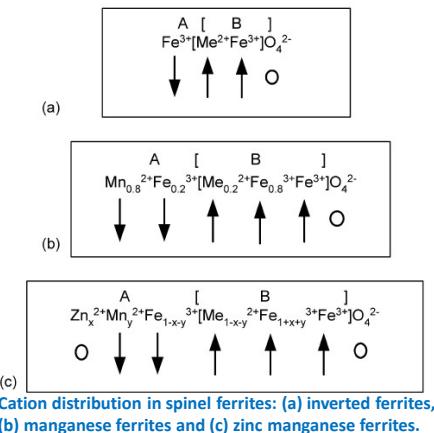
**Figure 2.2** Spinel unit cell structure

Spinel ferrite crystallizes in the cubic structure. The spinel lattice is composed of a close-packed oxygen anions arrangement in which 32 oxygen ions form the unit cell (the smallest repeating unit in the crystal network). These anions are packed in a face centred cubic (FCC) arrangement leaving two kinds of spaces between anions: tetrahedrally coordinated sites (A), surrounded by four nearest oxygen atoms, and octahedrally coordinated sites (B), surrounded by six nearest neighbour oxygen atoms (Figure 2.1). There are total 64 tetrahedral sites and 32 octahedral sites in the unit cell, of which only 8 tetrahedral sites and 16 octahedral sites are occupied, resulting in a structure that is electrically neutral



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- (1) Normal spinel structure, where all  $\text{M}^{2+}$  ions occupy A-sites; structural formula of such ferrites is  $\text{M}^{2+}[\text{Fe}^{3+}] \text{O}_4^{2-}$ . This type of distribution takes place in zinc ferrites  $\text{Zn}^{2+}[\text{Fe}^{2+}\text{Fe}^{3+}] \text{O}_4^{2-}$ .
- (2) Inversed spinel structure, where all  $\text{M}^{2+}$  are in B-positions and  $\text{Fe}^{3+}$  ions are equally distributed between A and B-sites: structural formula of these ferrites are  $\text{Fe}^{3+}[\text{M}^{2+}\text{Fe}^{3+}] \text{O}_4^{2-}$ . Magnetite  $\text{Fe}_3\text{O}_4$ , ferrites  $\text{NiFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  have inverted spinel structure.
- (3) Mixed spinel structure, when cations  $\text{M}^{2+}$  and  $\text{Fe}^{3+}$  occupy both A and B-positions; structural formula of this ferrite is  $\text{M}^{1-\delta}\text{Fe}_{\delta}^{3+}[\text{M}^{2+\delta}\text{Fe}_{2-\delta}^{3+}] \text{O}_4^{2-}$ , where  $\delta$  is the degree of inversion.  $\text{MnFe}_2\text{O}_4$  represent this type of structure and has an inversion degree of  $\delta=0.2$  and its structural formula therefore is  $\text{Mn}_{0.8}^{2+}\text{Fe}_{0.2}^{3+}[\text{Mn}_{0.2}^{2+}\text{Fe}_{1.8}^{3+}] \text{O}_4^{2-}$ . Mn-Zn ferrites also have a mixed spinel structure ( $\text{Zn}^{2+}$  prefers to occupy A-sites)  $\text{Zn}_x^{2+}\text{Mn}_{1-x}^{2+}\text{Fe}_{1-x-y}^{3+}[\text{Mn}_{1-x-y}^{2+}\text{Fe}_{1+x+y}^{3+}] \text{O}_4^{2-}$ , where  $\delta=1-x-y$ .

**Table 2.1** Various Ferrites with their structures and general formula

Sr. No.	Types	Crystal structure	General formula	Replacements
1	Spinel	Cubic	$\text{A}^{\text{II}}\text{Fe}_2\text{O}_4$	$\text{A}^{\text{II}}$ - Mn, Zn, Ni, Mg, Co
2	Garnet	Cubic	$\text{Ln}^{\text{III}}_3\text{Fe}_5\text{O}_{12}$	$\text{Ln}^{\text{III}}$ - Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Lu
3	Ortho ferrite	Perovskite	$\text{Ln}^{\text{III}}\text{FeO}_3$	$\text{Ln}^{\text{III}}$ - Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Lu
4	Magnetoplumbite	Hexagonal	$\text{A}^{\text{II}}\text{Fe}_{12}\text{O}_{19}$	$\text{A}^{\text{II}}$ - Ba, Sr, Pb

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**magnetic susceptibility  $\chi_m$** 

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H (-2,5)	Be 24																He (-1,1)
Li 24																	
Na 8.1	Mg 5.7																
K 5.7	Ca 21	Sc 264	Ti 181	V 383	Cr 267	Mn 828	Fe 2.16	Co 1.76	Ni 0.61	Cu -9.7	Zn -12	Ga -23	Ge -7.3	As -5.4	Se -18	Br -16	Kr (-16)
Rb 4.4	Sr 36	Y 122	Zr 109	Nb 236	Mo 119	Tc 373	Ru 66	Rh 170	Pd 783	Ag -25	Cd -19	In -8.2	Sn 2.4	Sb -67	Te -24	I -22	Xe (-24)
Cs 5.3	Ba 6.7	La 63	Hf 71	Ta 175	W 78	Re 96	Os 15	Ir 37	Pt 264	Au -34	Hg -28	Tl -36	Pb -16	Bi -153	Po At		Rn

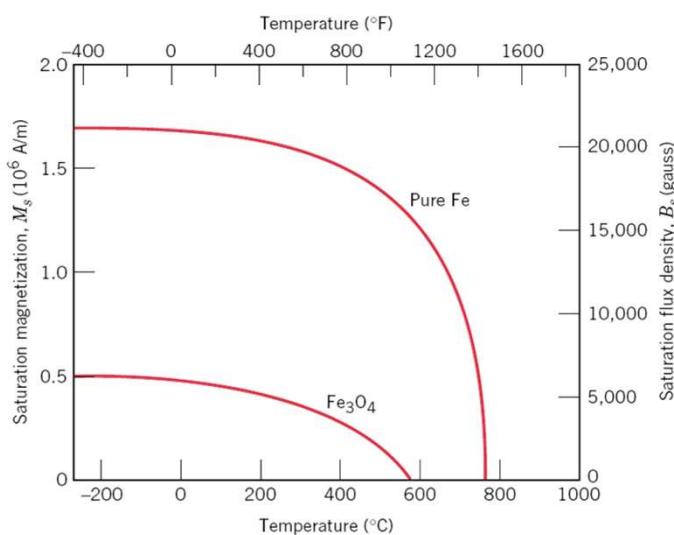
diamagnetic

paramagnetic

ferromagnetic

numbers without  $(\cdot) \cdot 10^{-6}$   
numbers with  $(\cdot) \cdot 10^{-9}$ 

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**18.6 The Influence of Temperature on magnetic Behavior** $T_c$ : Curie temperature (ferromagnetic, ferrimagnetic) $T_N$ : Neel temperature (antiferromagnetic)

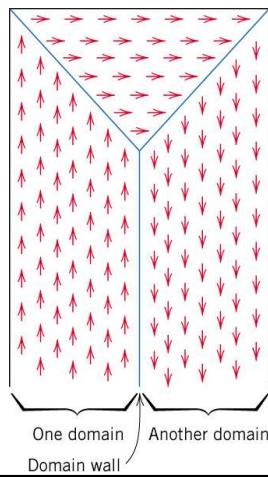
material become paramagnetic

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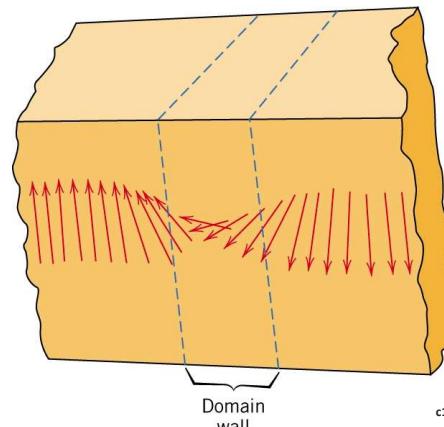
## 18.7 Domains and Hysteresis

Domains in a ferromagnetic or ferrimagnetic material; arrows represent atomic magnetic dipoles.

Within each domain, all dipoles are aligned, whereas the direction of alignment varies from one domain to another.



Gradual change in magnetic dipole orientation across a domain wall.



c18f12

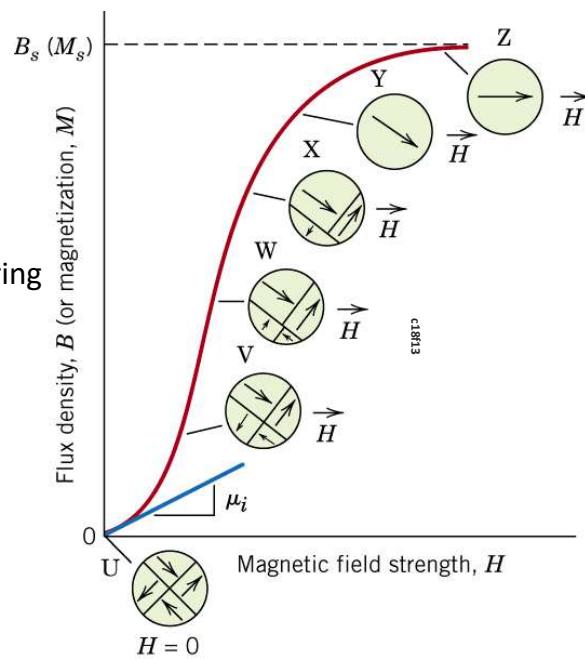
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### **B** versus **H**

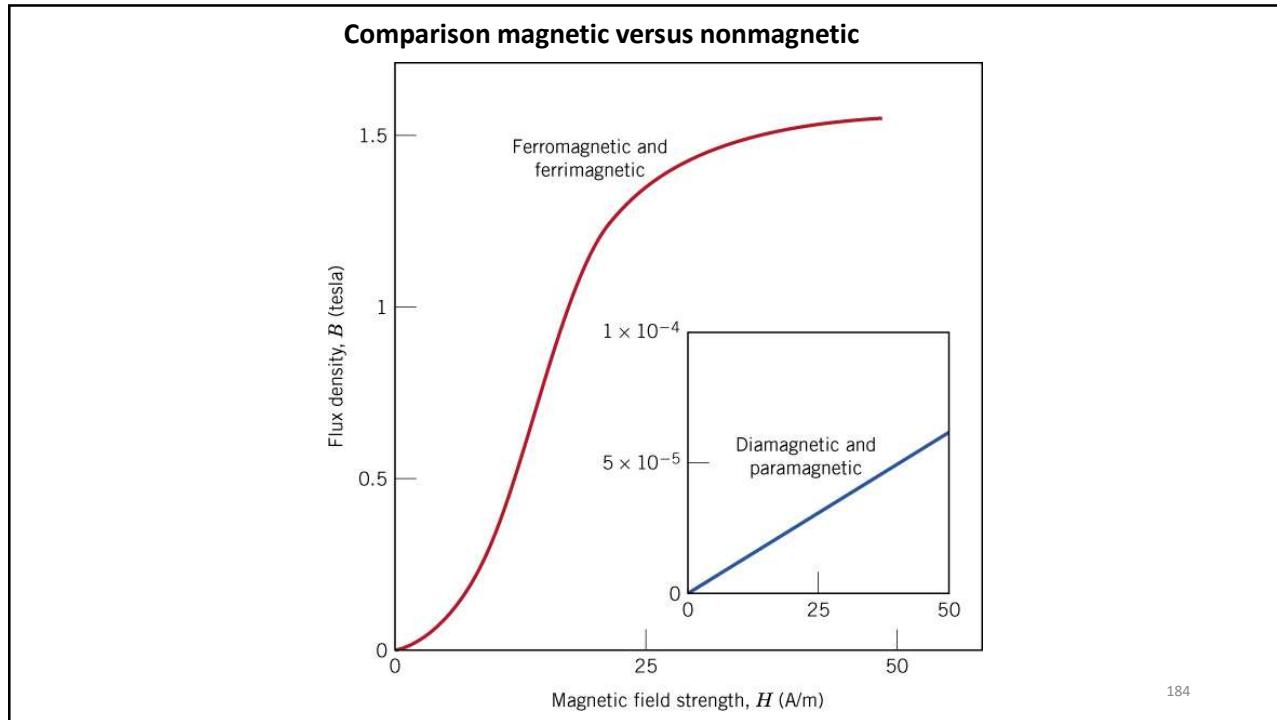
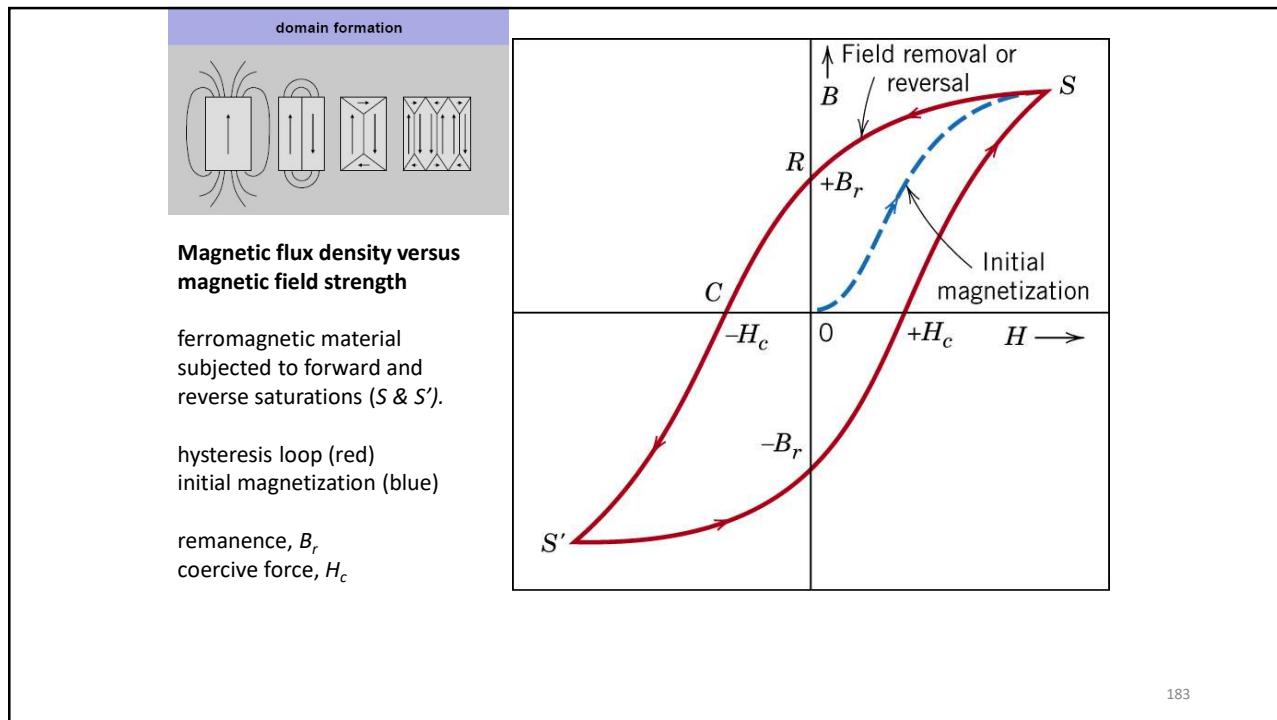
ferromagnetic or ferrimagnetic material initially unmagnetized

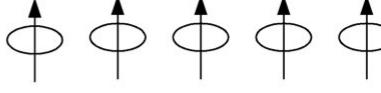
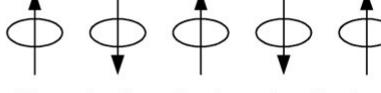
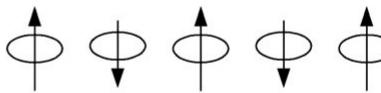
Domain configurations during several stages of magnetization

Saturation flux density,  $B_s$   
Magnetization,  $M_s$ ,  
initial permeability  $\mu_i$



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Spontaneous domain formation	<b>Ferromagnetism</b>		<b>Moments of individual atoms aligned</b>
	<b>Antiferromagnetism</b>		<b>Moments alternating from atom to atom</b>
	<b>Ferrimagnetism</b>		<b>Unequal moments alternate</b>
No domains	<b>Paramagnetism</b>	<b>No long-range order; alignment with applied field</b>	
	<b>Diamagnetism</b>	<b>No long-range order; alignment opposes field</b>	

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## Magnetic Properties

Materials → Magnetic (with unpaired electron)  
 Materials → Non-magnetic or diamagnetic (electrons all paired up)

(a)  → Paramagnetic

(b)  → Ferromagnetic

(c)  → Antiferromagnetic

(d)  → Ferrimagnetic

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## Magnetic Behavior

$$B = \mu H$$

$$B = \mu_0 H + \mu_0 M$$

Induction generated by the field      Induction generated by the sample

B: magnetic flux density  
 $\mu$ : permittivity ( $\mu_0$ : free space)  
 H: magnetic field  
 M: Magnetization

$$\chi = M/H \quad \chi: \text{magnetic susceptibility}$$

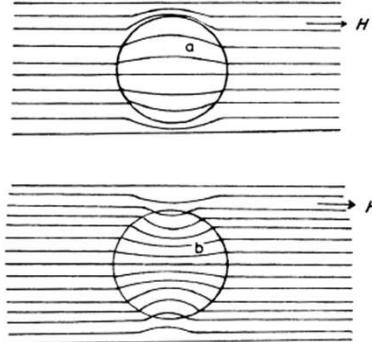
$$B = \mu_0 H + \mu_0 H \chi$$

$$B = \mu_0 H (1 + \chi) = \mu H$$

$$\mu_0 (1 + \chi) = \mu$$

$$(1 + \chi) = \mu / \mu_0 = \mu_r$$

$\mu_r$ : relative permittivity



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## Behavior of Substances in a Magnetic Field

Behaviour	Typical $\chi$ value	Change of $\chi$ with increasing temperature	Field dependence?
Diamagnetism	$-8 \times 10^{-6}$ for Cu	None	No
Paramagnetism		Decreases	No
Pauli paramagnetism	$8.3 \times 10^{-4}$ for Mn	None	No
Ferromagnetism	$5 \times 10^3$ for Fe	Decreases	Yes
Antiferromagnetism	0 to $10^{-2}$	Increases	(Yes)

Magnetic behavior may be distinguished by the values of  $\chi$  and  $\mu$  and by their *temperature* and *field* dependence

1. *Positive vs. negative value*: only diamagnetic materials show negative  $\chi$
2. *Absolute value*: ferromagnetic materials show huge positive value
3. *Temperature dependence*: diamagnetism is not temp. dependence, antiferromagnetic materials increase with increasing temp, and para- and ferromagnetic materials decrease with increasing temp
4. *Field dependence*: only ferro- and antiferromagnetic materials show field dependence

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## Effect of Temperature

Paramagnetic substance: obey Curie Law

$$\chi = \frac{C}{T}$$

C: Curie constant  
T: temperature

There is **no** spontaneous interaction between adjacent unpaired electrons.  
*With increasing temperature the alignment is more difficult and  $\chi$  decreases.*

Paramagnetic substance show some magnetic ordering (ferro- or antiferro):  
Curie-Weiss Law

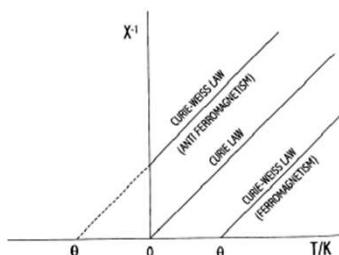
$$\chi = \frac{C}{T - \theta}$$

$\theta$ : Weiss constant

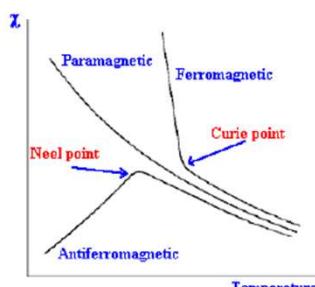
There is **some** spontaneous interaction between adjacent spins. A better fit to the high temperature behavior in the paramagnetic region is provided by Curie-Weiss Law (with additional Weiss constant).

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## Effect of Temperature



Paramagnetic: Curie law; T decrease, c increase (alignment easier)



Robert John Lancashire ([www.chem.uwimona.edu.jm](http://www.chem.uwimona.edu.jm))

Table 8.2 Some Curie and Néel temperatures

Material	$T_c$ (°C)	$T_N$ (°C)
Cr		35
Mn		-173
Fe	770	
Co	1131	
Ni	358	

$T_c$ : ferromagnetic Curie temperature (below  $T_c$ , sample is ferromagnetic)

$T_N$ : Néel Temperature (below  $T_N$ , sample is antiferromagnetic)

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