PYL102 Course
Lecture-16 on 13-09-2021

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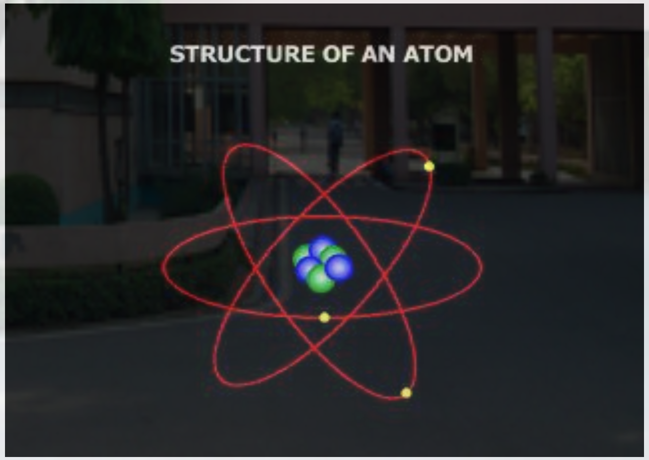
PYL102:
Principles of Electronic Materials

- Magnetic susceptibility….
- Ferro/antiferro-magnetism….
- Ferrimagnetism….
- Curie and Neel temperatures….



Ferromagnetism:

Certain materials like Fe, Co, Ni possess permanent magnetic moments in the absence of an external magnetic field. This is known as ferromagnetism.

Ferromagnetic materials are composed of atoms with a net magnetic moment, due to unpaired electrons in partially filled electron orbitals.

$\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$

Unlike paramagnetic materials, neighboring atomic moments in a ferromagnetic material exhibit very strong interactions

These interactions are produced by electronic exchange forces, couples neighboring atomic magnetic moments and result in a parallel alignment of atomic moments and therefore, in a large net positive magnetization.

The long-range ordering present in ferromagnetic materials, as a result of this exchange interaction, i.e., they exhibit a spontaneous magnetization even in the absence of an applied field.

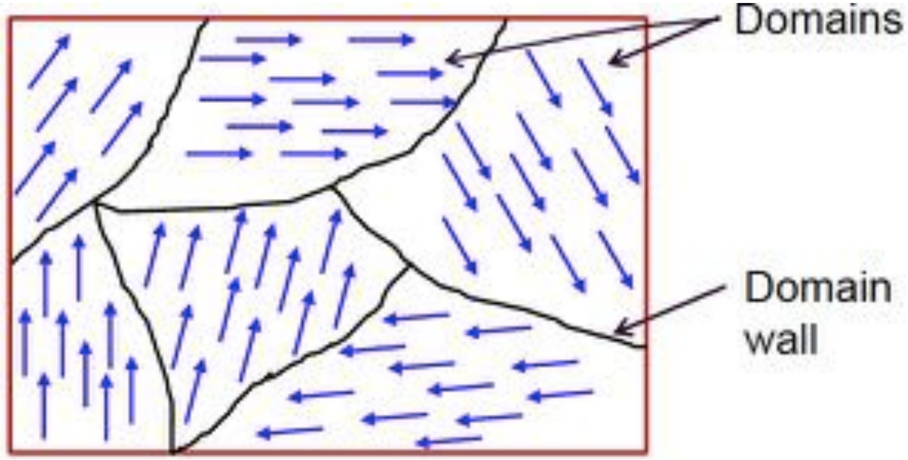
This spontaneous magnetization gives rise to the characteristic hysteretic behavior of ferromagnetic materials.

The applied field is not creating the magnetisation, it is rearranging the spontaneous magnetisation which is already in the sample…

Ferromagnetic materials:

FM materials exhibit a long-range ordering phenomenon at the atomic level which causes the unpaired e^- spins to align in the same direction in a region called a domain.

Pierre Weiss (1907) suggested that a ferromagnetic material consists of **small macroscopic regions** (called **domains**), which are already spontaneously magnetized.



When small externally imposed magnetic field, say from a solenoid, can cause the magnetic domains to line up with each other and the magnitude of magnetization is vector sum of all the domains….

The magnitude of the *magnetism of a sample*, is equal to the vector sum of the *magnetization of the domains*

The driving magnetic field will then be increased by a large factor which is usually expressed as a relative permeability for the material..

Antiferromagnetism and Ferrimagnetism:

Materials that exhibit antiferromagnet behavior are very similar to ferromagnetic materials in opposite direction.

The exchange interaction is negative and acts to align the magnetic moments of neighboring atoms antiparallel to one another.

Due to negative exchange interaction, the electron spins align antiparallel resulting in zero net magnetic moment.

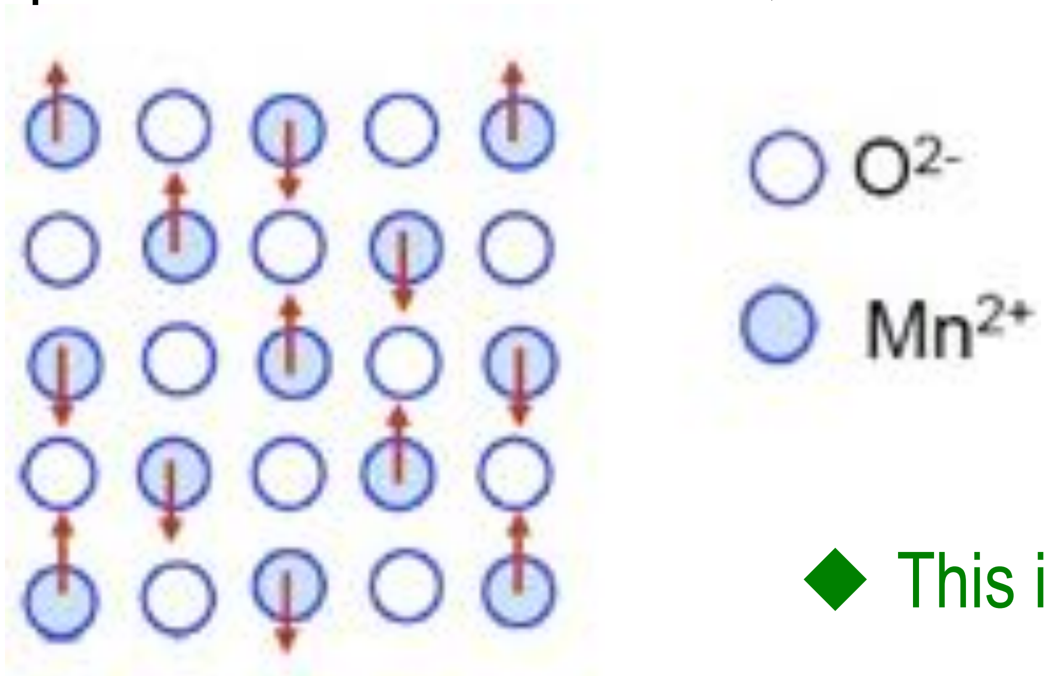
Ex: ***compounds like***. MnO, CoO, NiO, Cr_2O_3, MnS, MnSe, $CuCl_2$

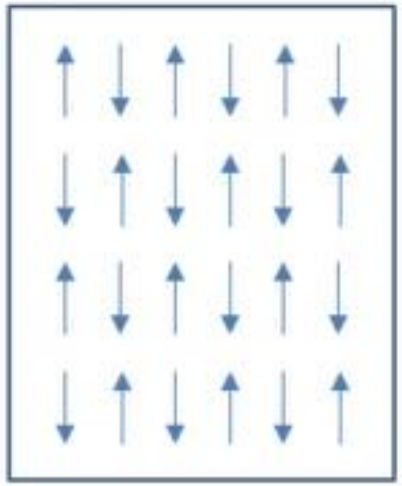
Ferrimagnetic materials consist of at least two nonequivalent sublattices.. If the coupling between the sublattices is ferromagnetic, means FM.. If sublattices interact antiferromagnetically, FiM…as the magnetic moments and on occasions the number of atoms on each sublattice are different, a net magnetization is observed.

Temperature dependent is more complex as each sublattice can behave differently. Ex.: ***Ferrites*** and ***magnetite***…

Antiferromagnetism:

If the coupling of electron spins results in antiparallel alignment, then spins will cancel each other, and no net magnetic moment will arise.



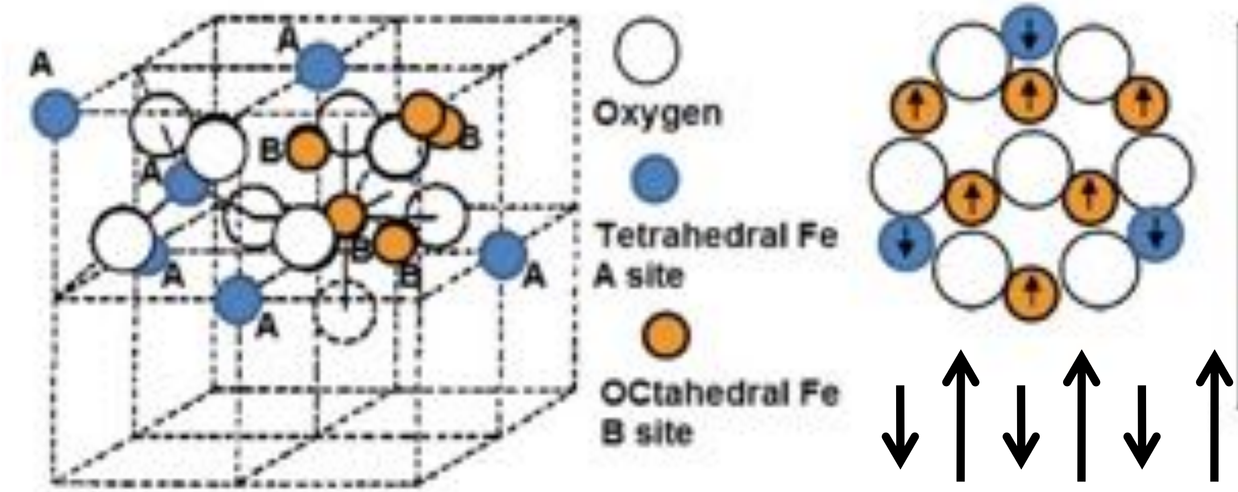


◆ This is known as antiferromagnetism.

◆ MnO is one of the examples.

◆ In MnO, the O^{2-} ions have no net magnetic moments and the spin moments of Mn^{2+} ions are aligned antiparallel to each other in adjacent atoms…..

Ferrimagnetism:



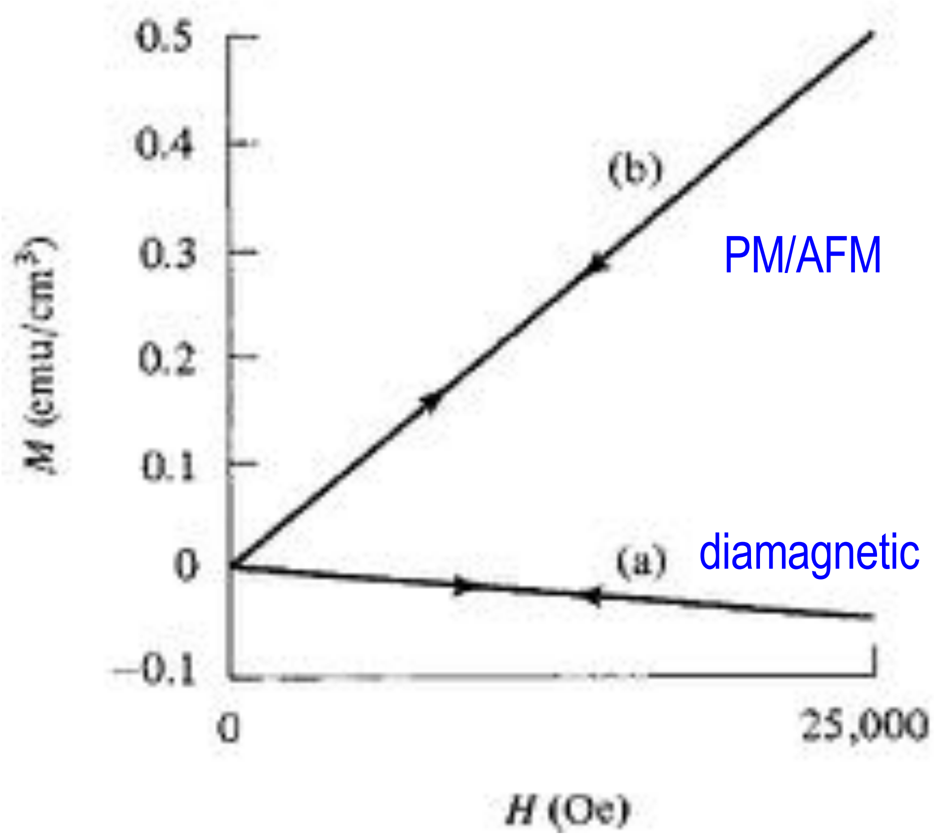
	Octahedral	Tetrahedral
Fe^{3+}	↑↑↑↑ ↑↑↑↑	↓↓↓↓ ↓↓↓↓
Fe^{2+}	↑↑↑↑ ↑↑↑↑	

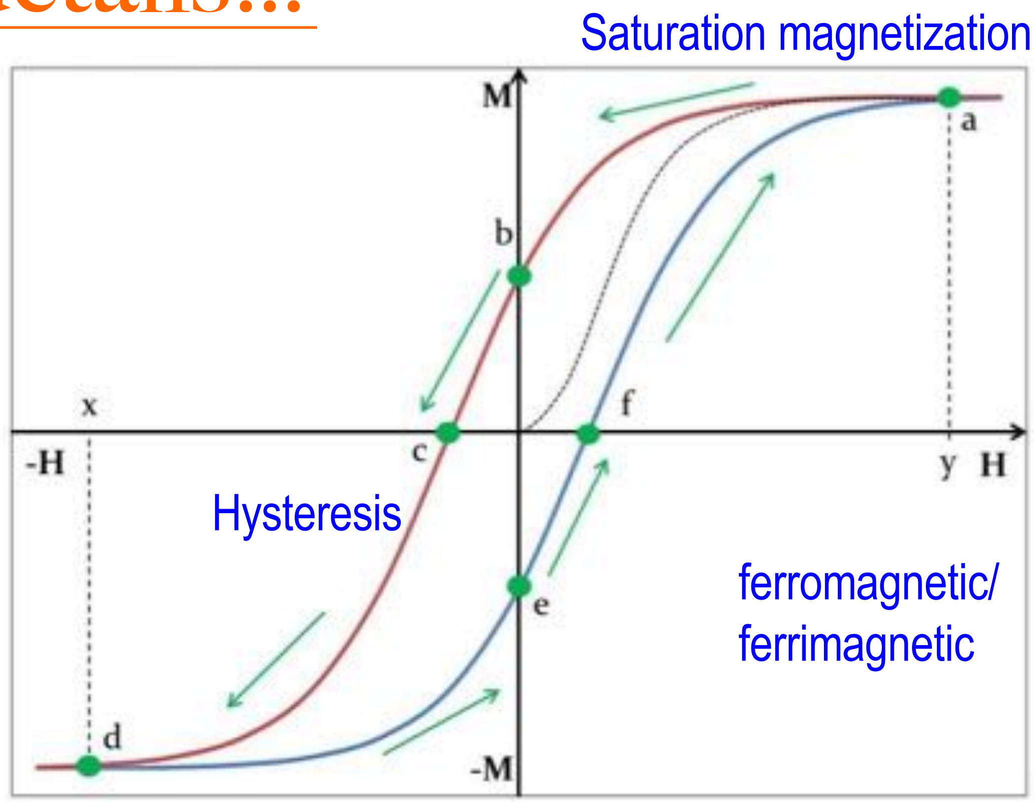
- Certain ionic solids having a general formula MFe_2O_4, where M is any metal, show permanent magnetism, termed ferrimagnetism, due to partial cancellation of spin moments.

- In Fe_3O_4, Fe ions can exist in both 2+ and 3+ states as $Fe^{2+}O^{2-}(Fe^{3+})_2(O^{2-})_3$ in 1:2 ratio. The antiparallel coupling between Fe^{3+} (Half in A sites and half in B) moments cancels each other.

- Fe^{2+} moments are aligned in same direction and result in a net magnetic moment.

Magnetic materials: details...



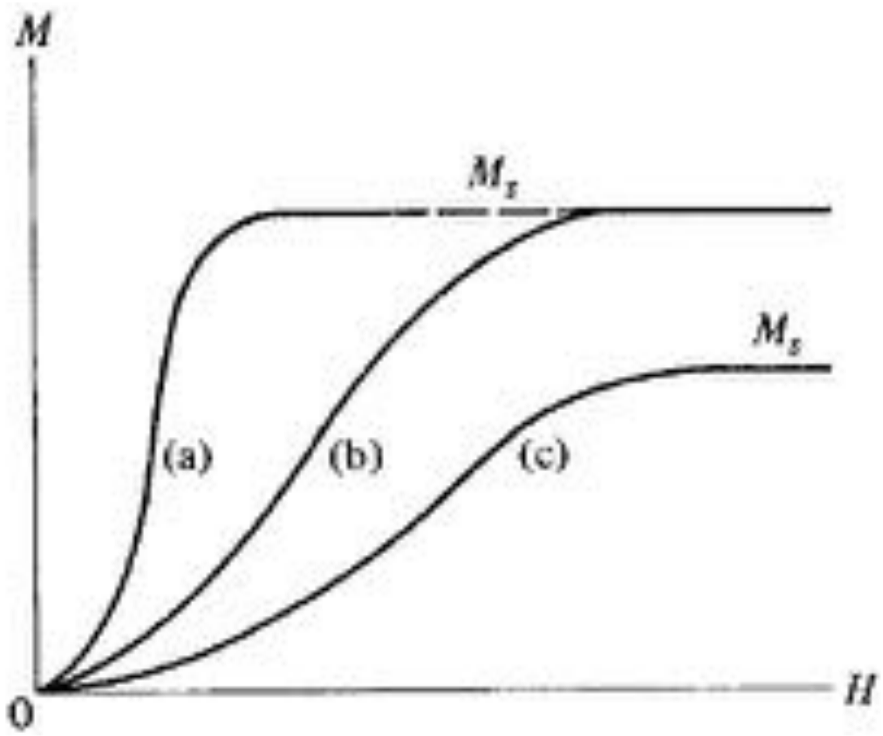


✧ Magnetization curves (M v/s H) of different types of materials…

✧ The atomic moments add up to produce a total magnetic moment for the permanent magnet,

✧ and the magnetization M is the total magnetic moment /volume.

Magnetization curves of different materials…



- Both ferro- and ferrimagnetic materials differ widely in the ease with which they can be magnetized.
- If a small applied field suffices to produce saturation, the material is said to be magnetically soft (a).
- Saturation of some other material, which will in general have a different value of Ms , may require very large fields, such a material is magnetically hard (c).
- Sometimes the same material may be either magnetically soft or hard, depending on its physical condition:
- thus curve (a) might relate to a well-annealed material, and curve (b) to the heavily cold-worked state.

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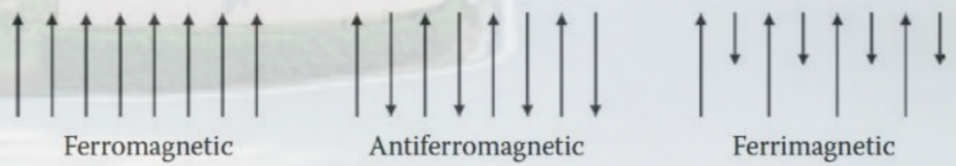
PYL102:
Principles of Electronic Materials

- Magnetic susceptibility….
- Curie and Neel temperatures….
- Magnetic anisotropy….
- Spin-orbit interactions….



FM and Curie temperature:

Manganic Susceptibility is a measure how a magnetic material respond to external magnetic field.. $\chi = M/H$, which is unitless quantity and can vary depending on the applied magnetic field in a material due to anisotropy and temperature.

Paramagnetism is temperature dependent since with increase of temperature the direction of magnetic moments gets randomized.

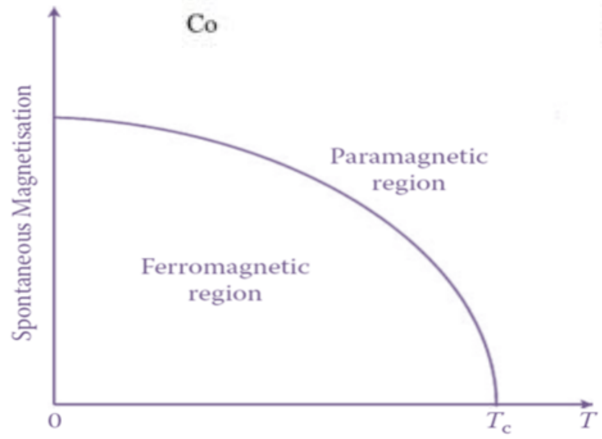
The paramagnetic Curie law is given as: $\chi = C/T$, here C is Curie constant, and T is the temperature.

Paramagnetic solid and liquid and ferromagnetic solid in their paramagnetic region follow Curie-Weiss (C-W) law: $\chi = C/(T - \theta)$
Here θ is Weiss constant which is either positive or negative

The spontaneous magnetization in a ferromagnet decreases as the temperature increases, becoming zero at the *ferromagnetic Curie temperature*, T_c.

Metal	Curie Temperature (K)
Gd	289
Ni	631
Tungsten steel	1033
Fe	1043
Co	1404

This is because thermal energy opposes the exchange interaction, and once the temperature is as high as T_c or above it, the ferromagnetism disappears completely



Above the Curie temperature, ferromagnetic solids become paramagnetic and obey the C–W law

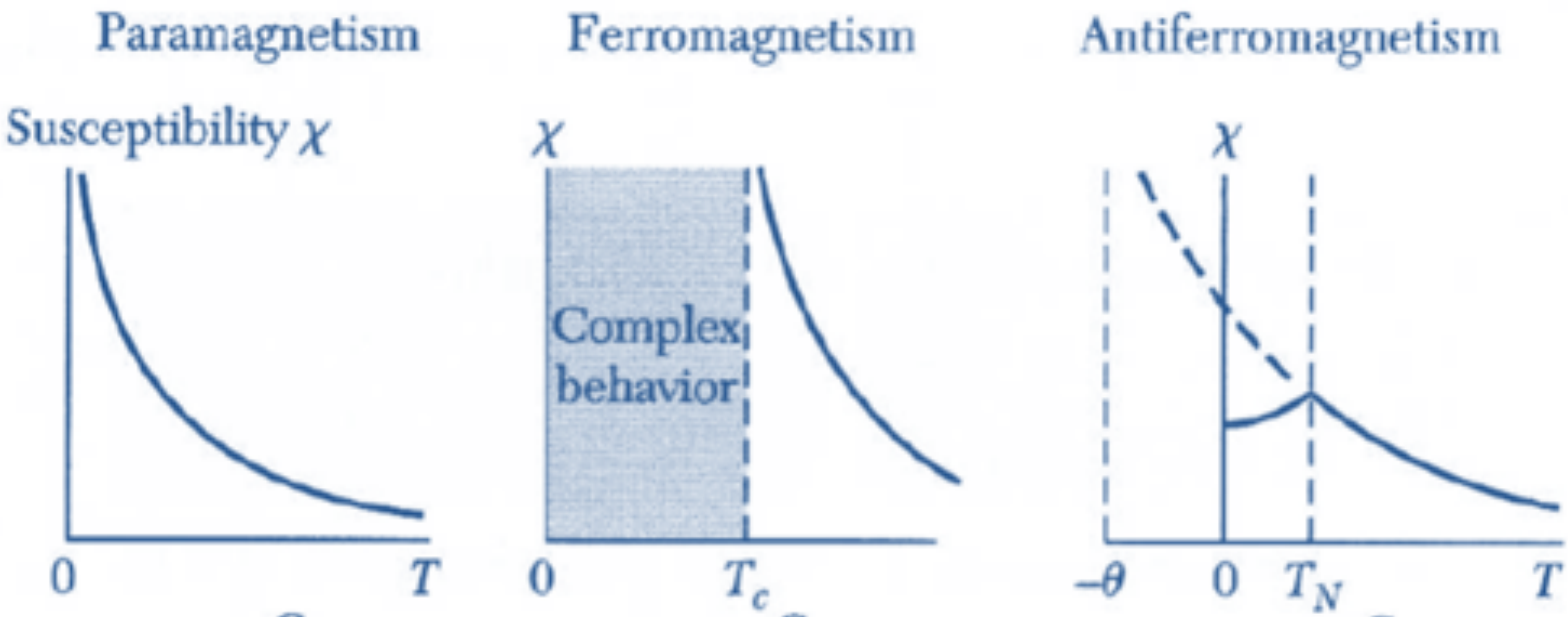
AFM and Neel temperature:

In an antiferromagnetic material the moments are only in an ordered (antiparallel) arrangement below a critical temperature known as the Neel temperature (T_N)

Antiferromagnetic materials become paramagnetic above T_N.

The susceptibility of an antiferromagnet is not infinite at T_N but has a weak cusp.

Now let's see the comparison….



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

Curie law

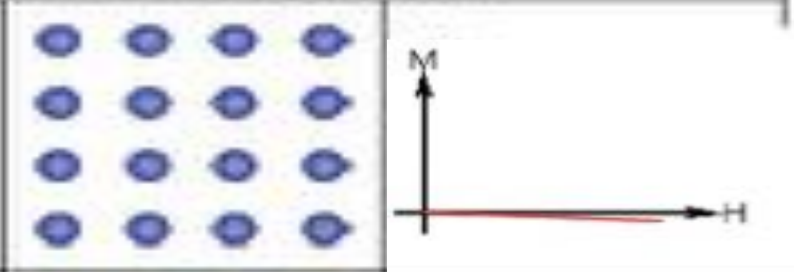
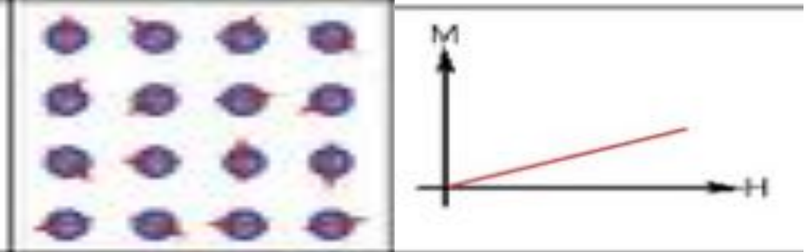
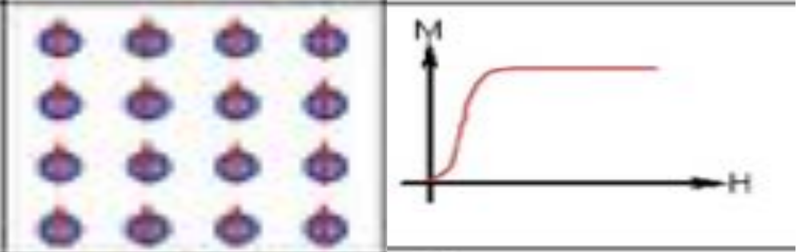
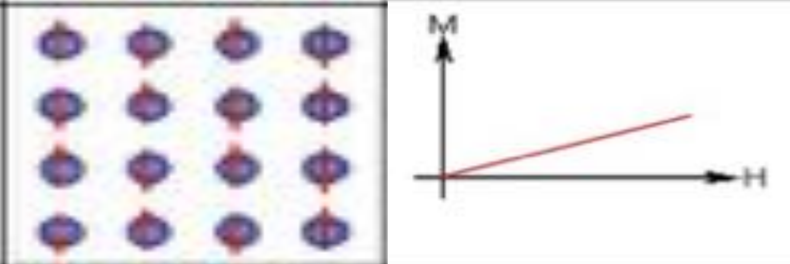
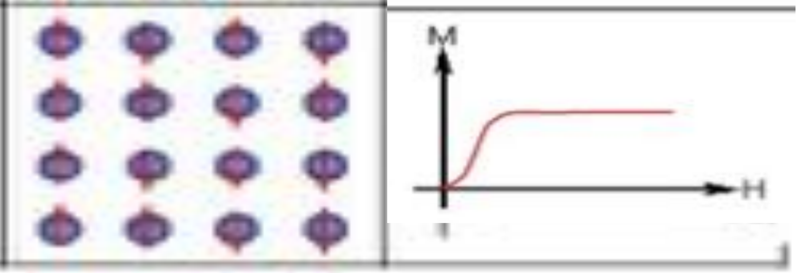
$$\chi = \frac{C}{T - T_c}$$

Curie-Weiss law ($T > T_c$)

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

($T > T_N$)

Magnetic materials: classification…

Type	Example	Atomic/Magnetic Behaviour	
Diamagnetism	Inert gases; many metals eg Au, Cu, Hg; non-metallic elements e.g. B, Si, P, S; many ions e.g. Na^+, Cl^- & their salts; diatomic molecules e.g. H_2, N_2; H_2O; most organic compounds	Atoms have no magnetic moment. Susceptibility is small & negative, -10^{-6} to -10^{-5}	
Paramagnetism	Some metals, e.g. Al; some diatomic gases, e.g. O_2, NO; ions of transition metals and rare earth metals, and their salts; rare earth oxides.	Atoms have randomly oriented magnetic moments. Susceptibility is small & positive, $+10^{-5}$ to $+10^{-3}$	
Ferromagnetism	Transition metals Fe, Ni, Co, Ni; rare earths with $64 \le Z \le 69$; alloys of ferromagnetic elements; some alloys of Mn, e.g. MnBi, Cu_2MnAl	Atoms have parallel aligned magnetic moments. Susceptibility is large (below T_C)	
Antiferromagnetism	Transition metals Mn, Cr & many of their compound, e.g. MnO, CoO, NiO, Cr_2O_3, MnS, MnSe, $CuCl_2$	Atoms have anti-parallel aligned magnetic moments. Susceptibility is small & positive, $+10^{-5}$ to $+10^{-3}$	
Ferrimagnetism	Fe_3O_4 (magnetite); γ-Fe_2O_3 (maghemite); mixed oxides of iron and other elements such as Sr ferrite	Atoms have mixed parallel and anti-parallel aligned magnetic moments. Susceptibility is large (below T_C)	

Magnetic anisotropy:

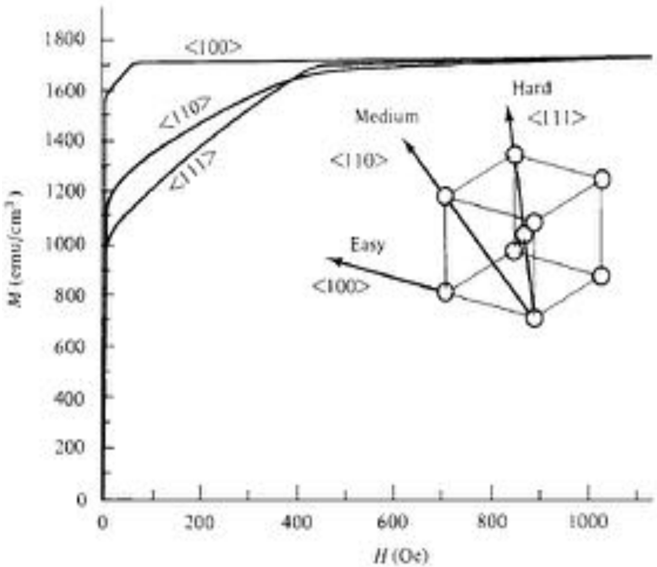
- When a physical property of a material is a function of the crystallographic direction, that physical property is said to exhibit anisotropy.
- The magnetic properties of crystalline ferromagnetic materials depend on the crystallographic direction in which an external field is applied, an effect which is called magnetic anisotropy.
- **Magnetic anisotropy** describes how an object's magnetic properties can be different depending on direction
- It turns out that depending on the orientation of the field with respect to the crystal lattice one would need a lower or higher magnetic field to reach the saturation magnetization.
- This means that magnetically anisotropic materials will be easier or harder to magnetize depending on which way the object is rotated.
- Ferromagnetic crystals characteristically exhibit magnetic anisotropy, which means that the magnetic properties are different along different crystal directions…
- **Easy axis** is the direction inside a crystal, along which small applied magnetic field is sufficient to reach the saturation magnetization.
- **Hard axis** is the direction inside a crystal, along which large applied magnetic field is needed to reach the saturation magnetization….

Magnetic anisotropy: example of Fe crystal…

The exchange interactions are such that spin magnetic moments are most easily aligned with each other if they all point in <100> direction. This means <100> direction in the iron crystal constitute the easy direction for magnetization.

When a magnetizing field **H** along a <100> direction is applied, magnetization rapidly increases and saturates with an applied field of less than 0.01 T.

In order to magnetize the crystal along the <111> direction by applying a field, then a stronger field is applied than that along <100>. The <111> direction in Fe crystal is consequently known as the hard direction.



The highest density of atoms is in the <111> direction, and consequently it is the hard axis. In contrast, the atom density is lowest in <100> directions and consequently it is the easy axis. Magnetization curves above show that the saturation magnetization in <100> direction requires significantly lower field than in the <111> direction.

So, the magnetization of the crystal along <100> needs the least energy, whereas that along <111> consumes the greatest energy.

The excess energy required to magnetize a unit volume of a crystal in a particular direction with respect to that in the easy direction is called the **magnetocrystalline anisotropy energy or simply crystal anisotropy….**

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Lecture-18 on 16-09-2021

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PYL102:

Principles of Electronic Materials

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- Magnetic anisotropy….
- Spin-orbit interactions….

Background:

- All magnetic moments are produced by the angular momentum of electrons in the atoms of solids…

- There are two types of angular momentum for electrons in atoms: spin and orbital

- In the Bohr's model of the atom, a single electron orbiting around the nucleus produces a magnetic moment at right angles to the plane of the orbit

- Since an electric current flowing in a closed loop of wire produces a magnetic moment at right angles to the plane of the loop

- The total magnetic moment of an atom is made up from vector sum of all the orbital and spin magnetic moments of the individual electrons that have not cancelled...

- There is possibility of coupling between spin and orbital moment of atoms.

- The magnetic moment from the electron's spin interacts with the magnetic field from its orbital motion. The resulting interaction is called the spin–orbit coupling….

- The different types of magnetism that a solid can possess are governed by how its atomic magnetic moments respond when a magnetic field applied to the solid.

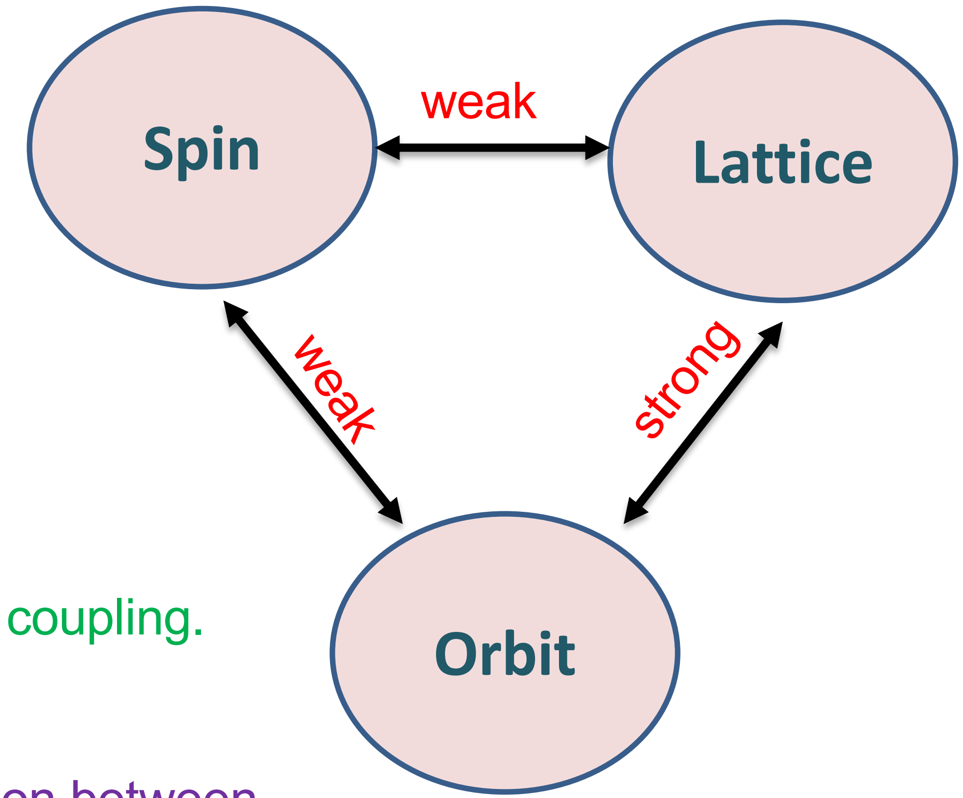
Physical origin of crystal anisotropy:

In FM materials, one factor which may strongly affect the shape of the M-H curve, or the shape of the hysteresis loop, is magnetic anisotropy.

This term simply means that the magnetic properties depend on the direction in which they are measured…

So now we need to understand the physical origin of this anisotropy….

Origin of anisotropy emerges from the interactions (coupling) between these three degrees of freedom.



Possible Interactions in the system are:

- Spin-Spin (up/down)
- Spin-Orbit
- Spin-Lattice
- Orbit-Lattice

Crystal anisotropy is due mainly to spin-orbit coupling.
By coupling is meant a kind of interaction.

Thus we can speak of the exchange interaction between two neighboring spins as a **spin–spin coupling**.

Physical origin of crystal anisotropy:

This coupling can be very strong, and acts to keep neighboring spins parallel or antiparallel to one another.

But the associated exchange energy is isotropic; it depends only on the angle between adjacent spins, not at all on the direction of the spin axis relative to the crystal lattice.

The spin–spin coupling therefore cannot contribute to the crystal anisotropy….

So, we need to consider other interactions….

The **orbit-lattice coupling** is also strong.

Orbital magnetic moments are quenched inside the crystal.

Orientation of the orbit is fixed w.r.t lattice strongly and this orientation can't be changed even with stronger fields as the crystal field has dominant effect.

So, orbit-lattice interaction also do not contribute to the crystal anisotropy.

There is also a coupling between the spin and the orbital motion of each electron.

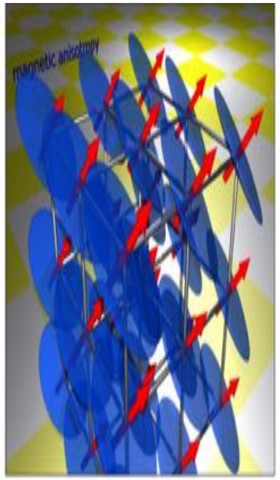
When an external field tries to reorient the spin of an electron, the orbit of that electron also tends to be reoriented. But the orbit is strongly coupled to the lattice and therefore resists the attempt to rotate the spin axis.

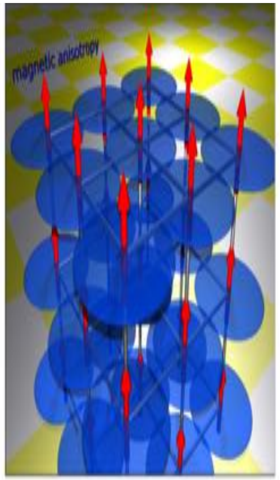
Crystal anisotropy: Spin-Orbit interactions….

The energy required to rotate the spin system of a domain away from the easy direction, which we call the anisotropy energy, is just the energy required to overcome the spin–orbit coupling.

This coupling is relatively weak, because fields of a few hundred Oe are usually strong enough to rotate the spins.

Inasmuch as the “lattice” consists of a number of atomic nuclei arranged in space, each with its surrounding cloud of orbital electrons, we can also speak of a spin–lattice coupling and conclude that it too is weak.





The spin of the electron interacts with crystal structure via spin orbit coupling.

Due to the spin-orbit coupling, different orientation of electron spins correspond to different orientations of atomic orbitals w. r. t. the crystal structure.

Resultant magnetic moments are obtained from the spin-orbit coupling

However, some of the orientations of the magnetic moments are energetically favourable known as Easy Axis

While the energetically unfavourable orientations are Hard Axis.

All the best