



## **Part IV Magnetic Properties of Materials**

Chap. 14 Foundations of Magnetism Chap. 15 Magnetic Phenomena and Their Interpretation- Classical Approach Chap. 16 Quantum Mechanical Considerations Chap. 17 Applications



Different types of magnetism are characterized by the magnitude and the sign of the susceptibility

**KINDS OF** 

**MAGNETISM** 



### 15.1.1 Diamagnetism

#### What is diamagnetism?

**Diamagnetism** may then be explained by postulating that the external magnetic field induces a change in the magnitude of inneratomic currents in order that their magnetic moment is in then opposite direction from the external magnetic field.

A more accurate and quantitative explanation of diamagnetism replaces the induced currents by precessions the electron orbits about the magnetic field direction. (Larmor precession)

#### Lenz's law :

The induced current will appear in such a direction that it opposes change that produce it.



### Larmor frequency



$$dL = L\sin\theta d\phi$$
 and  $d\phi = \omega_L dt$ 



It has been observed that superconducting materials expel the magnetic flux lines when in the superconducting state (Meissner effect).





### 15.1.2 Paramagnetism

#### What is paramagnetism?

**Paramagnetism** in solids is attributed, to a large extent, to a magnetic moment that results from electrons which spin around their own axes.

In Curie Law, Susceptibility is inversely proportional to the absolute temperature T

In Curie-Weiss Law,

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





Figure 15.2. (a) Schematic representation of electrons which spin around their own axes. A (para)magnetic moment  $\mu_m$  results; its direction depends on the mode of rotation. Only two spin directions are shown (called "spin up" and "spin down"). (b) An orbiting electron is the source of *electron-orbit paramagnetism*.



Figure 15.3. Schematic representation of (a) the Curie law and (b) and (c) the Curie-Weiss law. (d) The diamagnetic behavior is also shown for comparison.



#### Hund's rule

- 1. Quantum states are filled so as to maximize  $s = \sum m_s$ . This rule forces electrons into different orbital states thereby tending to minimize their Coulomb repulsion. The energies here can be up to a few electronvolts (eV).
- 2. If rule 1 does not determine the occupancy, the state filling is such that  $l = \sum m_l$  is maximized. This also keeps electrons in orbits which circulate in the same sense and have lower probability near the nucleus, again tending to minimize their Coulomb repulsion. This correlation among the motions of different electrons is particularly strong for atomic (as opposed to molecular orbital or free electron) wavefunctions. The energies involved can be up to 0.5 eV.
- 3. Finally, l and s combine by subtraction when an energy level is less than half filled, j = |l s|, and by addition if more than half filled. This condition tends to minimize the spin-orbit energy, ζl<sub>i</sub>·s<sub>i</sub>, specifically, ζ > 0 for first-half shell and ζ < 0 for second-half shell. The spin-orbit interaction energy can be of order of 10<sup>-4</sup> eV. The understanding of the spin-orbit interactions that partially lift the 2(2l + 1)-fold degeneracy of the *l*th orbital came long after Hund's rules empirically outlined their implications.

Ref. Modern Magnetic Materials (R.C. O Hand

#### Hund's rules

(1) are based primarily on Coulomb repulsion and secondarily on spin-orbit interactions and

(2) account for the existence of atomic magnetic moments, even in some atoms with an even number of valance electrons

# $\bigstar \checkmark \bigstar \bigstar \bigstar \bigstar \bigstar \bigstar \bigstar$

Figure 15.4. Schematic representation of the spin alignment in a *d*-band which is partially filled with eight electrons (Hund's rule).

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### 15.1.3 Ferromagnetism

-Spontaneous magnetization

-transition metals : Fe, Co, Ni, rare-earth : Gd, Dy

-alignment of an appreciable fraction of molecular magnetic

moment in some favorable direction in crystal

-related o the unfilled 3d and 4f shells

-ferromagnetic transition temperature (Curie)





Figure 15.6. Schematic representation of a hysteresis loop of a ferromagnetic material. The dashed curve is for virgin material.

Figure 15.5. A ring-shaped solenoid with primary and secondary windings. The magnetic flux lines are indicated by a dashed circle. Note, that a current can flow in the secondary circuit only if the current (and therefore the magnetic flux) in the primary winding changes with time. An on-off switch in the primary circuit may serve for this purpose.

 $M_r$  = remanent magnetization  $M_s$  = saturation magnetization  $H_c$  = coercive field



#### **TEMPERATURE-DEPENDENCE OF SATURATION MAGNETIZATION**



**Figure 15.7** (a) Temperature dependence of the saturation magnetization of ferromagnetic materials. (b) Enlarged area near the Curie temperature showing the paramagnetic Curie point (see Fig. 15.3) and the ferromagnetic Curie temperature .

Above **Curie Temperature** T<sub>c</sub>, ferromagnetics become paramagnetic.

For ferromagnetics, the **Curie temperature**  $T_c$  and the constant  $\theta$  in the Curie-Weiss law are nearly identical.

However a small difference exists because the transition from ferromagnetism to paramagnetism is gradual.



#### Piezomagnetism

The magnetization of ferromagnetics is stress dependent



Figure 15.8. Schematic representation of the effect of tensile and compressive stresses on the magnetization behavior of (a) nickel and (b) iron. (Piezomagnetism.)



#### Magnetostriction

When a substance is exposed to a magnetic field, its dimensions change. This effect Called *magnetostriction*. (inverse of piezomagnetism)



$$\lambda = \frac{\Delta l}{l}$$
$$|\lambda| = 10^{-5} \sim 10^{-6}$$



M orientation => change in dimension

### DOMAIN

Minimization of magnetostatic energy with changing domain shape



Figure 15.9. (a) Spontaneous alignment of all spins in a single direction. (b) Division into two magnetic domains having opposite spin directions. (c) Closure domains in a cubic crystal. (d) Growth of a domain whose spins are parallel to an external magnetic field. (The domain walls are *not* identical with the grain boundaries.)

#### 

### **15.1.4 Antiferromagnetism**

#### What is antiferromagnetism?

**Antiferromagnetic materials** exhibit just as ferromagnetics, a spontaneous alignment of moments below a critical temperature. However, the responsible neighboring atoms are aligned in an antiparallel fashion.



Figure 15.10. Schematic representation of spin alignments for antiferromagnetics at 0 K. (a) Display of a (100) plane of MnO. The gray (spin down) and black (spin up) circles represent the Mn ions. The oxygen ions (open circles) do not contribute to the antiferromagnetic behavior. MnO has a NaCl structure. (b) Three-dimensional representation of the spin alignment of manganese ions in  $MnF_2$ . (The fluorine ions are not shown.) This figure demonstrates the interpenetration of two manganese sublattices, A and B, having antiparallel aligned moments.



#### Antiferromagnetic ordering







#### **TEMPERATURE-DEPENDENCE OF ANTIFERROMAGNETIC MATERIAL**



 $T_N$  = Nėel temperature  $\chi = \frac{C}{T - (-\theta)} = \frac{C}{T + \theta}$ 







ferromagnetic

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

Antiferromagnetic

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

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Table 5.1         Some Antiferromagnetic Substances*							
Substance	Metal ion arrangement†	<i>Т<sub>N</sub></i> (°К)	θ(°K)††	$\frac{\theta}{T_N}$	$\frac{\chi_p(0)}{\chi_p(T_N)}$		
MnO	FCC	122	610	5.0	0.69		
FeO	FCC	198	570	2.9	0.78		
CoO	FCC	293	280	1.0			
NiO	FCC	523	3000	5.7	0.67		
α-MnS	FCC	154	465	3.0	0.82		
$\beta$ -MnS	FCC	155	982	6.3	-		
a-Fe <sub>2</sub> O <sub>2</sub>	R	950	2000	2.1			
Cr <sub>2</sub> O <sub>2</sub>	R	307	1070	3.5	0.76		
$CuCl_2 \cdot 2H_2O$	R	4.3	5	1.2			
FeS	HL	613	857	1.4	Solid Tank		
FeCl,	HL	24	-48	-2.0	< 0.2		
CoCl,	HL	25	-38	-1.5	~0.6		
NiCl <sub>2</sub>	HL	50	-68	-1.4	Asterna State		
MnF,	BCT	67	80	1.2	0.76		
FeF,	BCT	79	117	1.5	0.72		
CoF,	BCT	40	53	1.3	in the template		
NiF,	BCT	78	116	1.5			
MnO <sub>2</sub>	BCT	84		sure The d	0.93		
Cr	BCC	310					
α-Mn	CC	100					

\*\*\*\*







### **15.1.5 Ferrimagnetism**

Different elements, different moments



#### Ionic bonding, localized field theory

- Cubic:  $MO \cdot Fe_2O_3$   $M = Mn^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  etc. (ferrite) soft magnet except Co  $\cdot Fe_2O_3$
- Hexagonal: BaO •6Fe<sub>2</sub>O<sub>3</sub> hard magnet



Ferrimagnetic substances consist of self-saturated domains, and they exhibit the phenomena of magnetic saturation and hysteresis. Their spontaneous magnetization disappears above a certain critical temperature,  $T_c$  also called Curie temperature and they become paramagnetic



Different elements, different moments



lons										Number of 3d electrons	Spin-only moment in $\mu_{\rm B}$
Sc3+	Ti4 *									0	0
	Ti3+	V4 *								1	1
	Ti2 *	V3 +	Cr4+							2	2
		V <sup>2</sup> *	Cr3+	Mn <sup>4</sup> *						3	3
			Cr2+	Mn <sup>3+</sup>	Fe4+					4	4
				Mn <sup>2+</sup>	Fe <sup>3+</sup>	Co4+				5	5
					Fe <sup>2+</sup>	Co3+	Ni <sup>4+</sup>			6	4
						Co <sup>2+</sup>	Ni <sup>3+</sup>			7	3
							Ni <sup>2+</sup>			8	2
								Cu <sup>2+</sup>		9	1
								Cu+	Zn2+	10	0

Table 6.1 Spin-Only Moments of Ions of First Transition Series (after Smit and Wijn [G.10])









Example : NiO  $\bullet$ Fe<sub>2</sub>O<sub>3</sub>

 $12 \mu_B$  if ferromagnetic ordering (5 Bohr magnetrons for Fe<sup>+3</sup> and 2 for Ni<sup>+2</sup>) but experimental value is  $2.3 \mu_B$  (56 emu/g) at 0 K

Table 6.2	Arrangements of	Metal Ions in the	Unit Cell of a	Ferrite MO · Fe,O,
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Kind of site	Number available	Number occupied	Normal spinel	Inverse spinel
Tetrahedral (A)	64	8	8 M <sup>2+</sup>	8 Fe <sup>3+</sup>
Octahedral (B)	32	16	16 Fe <sup>3+</sup>	$8 \text{ Fe}^{3+}$ $8 \text{ M}^{2+}$

A sites; (b) octahedral or B sites; and (c) one-fourth of the unit cell of a cubic ferrite. A tetrahedron and an octahedron are marked. Adapted from J. Smit, and H.P.J. Wijn, *Ferrites*, Wiley, New York (1959).









Oxygen



A site: 8a

Octahedral interstice (32 per unit cell)



Tetrahedral interstice (64 per unit cell)







➢ 15.1 Overview



Normal spinel:  $AO(B_2O_3)$ 

A<sup>2+</sup> on tetrahedral sites, B<sup>3+</sup> on octahedral sites (e.g.) ZnFe2O4, CdFe2O4, MgAl2O4, CoAl2O4, MnAl2O4

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MO \cdot Fe_2O_3 (M = Zn, Cd)
non-magnetic (paramagnetic)
8M^{2+}: A site, 16Fe<sup>3+</sup>: B site
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Inverse spinel:  $B(AB)O_4$ 

half of the  $B^{3+}$  on tetrahedral sites,  $A^{2+}$  and remaining  $B^{3+}$  on octahedral sites (e.g.) FeMgFeO<sub>4</sub>, FeTiFeO<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>, FeNiFeO<sub>4</sub>

```
MO•Fe<sub>2</sub>O<sub>3</sub> (M = Fe, Co, Ni)
Ferrimagnetic
8M^{2+}: B site, 16Fe<sup>3+</sup>: A,B sites
(disordered state)
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Mixed ferrite: NiO·Fe<sub>2</sub>O<sub>3</sub> + ZnO·Fe<sub>2</sub>O<sub>3</sub>  $\rightarrow \rightarrow$  (Ni,Zn)O·Fe<sub>2</sub>O<sub>3</sub>



#### Classical model



- *e* : electron charge
- r : radius of the orbit
- s : length of the orbit (=  $2\pi r$ )
- *v* : velocity of the orbiting electron
- *t* : revolution time

*&* : electric field strength
 V<sub>e</sub> : induced voltage
 L : orbit Length

$$F = ma = \mathcal{E}e \qquad \therefore a = \frac{dv}{dt} = -\frac{d(\mu_0 HA)}{dt}$$
  
Induced field  
$$\mu_m = I \cdot A = \frac{evr}{2}$$

Thus, 
$$\frac{dv}{dt} = \frac{\mathcal{E}e}{m} = \frac{V_e e}{Lm} = -\frac{eA\mu_0}{Lm}\frac{dH}{dt} = -\frac{e\pi r^2\mu_0}{2\pi rm}\frac{dH}{dt} = -\frac{er\mu_0}{2m}\frac{dH}{dt}$$

A change in the magnetic field strength from 0 to  $V + \Delta V$  H yields a change in the velocity of the electrons :



Magnetic moment per electron

$$\Delta\mu_m = \frac{e\Delta vr}{2} = -\frac{e^2r^2\mu_0H}{4m}$$

Average value of magnetic moment per electron



#### Average value of magnetic moment per atom

 $\overline{\Delta \mu_m} = -\frac{e^2 Z \ \overline{r}^2 \mu_0 H}{6m} \qquad Z : \text{ atomic number} \\ \overline{r} : \text{ average radius of all electronic orbits}$ 

Magnetization caused by this change of magnetic moment

$$M = \frac{\mu_m}{V} \equiv -\frac{e^2 Z r^2 \mu_0 H}{6mV}$$

#### **Diamagnetic Susceptibility**

$$\chi_{dia} = \frac{M}{H} = -\frac{e^2 Z r^2 \mu_0}{6mV} = -\frac{e^2 Z r^2 \mu_0}{6m} \frac{N_0 \delta}{W}$$

 $N_0$ : Avogadro constant

 $\delta$  : density

W : atomic mass

\*\*\*\*



Magnetic susceptibility

$$\Delta m = -\frac{2}{3} \frac{\mu_0 e^2 r^2 H}{4m_e}$$

$$\Delta m_n = -\frac{\mu_0 e^2 H}{6m_e} \sum_i r_i^2$$

$$\Delta M = -(\frac{N_0\rho}{A})\frac{\mu_0 Z e^2 \overline{r}^2 H}{6m_e}$$

$$\Delta M / \Delta H = \chi_V = -\left(\frac{N_0\rho}{A}\right) \frac{\mu_0 Z e^2 \overline{r}^2}{6m_e}$$

$$\chi_V = -18.85 \times 10^{-6}$$

#### Assumptions: no interaction, only m , H interaction, and thermal agitation

In a state of thermal equilibrium at temperature T The probability of an atom having an energy E follows the Boltzmann distribution  $\overrightarrow{H}$ 

$$\propto \exp(-E_p/kT)$$

 $E_p = -\mu_m \mu_0 H \cos \alpha$ 

 $dn = K dA \exp(-E_p / k_B T)$  $dA = 2\pi R^2 \sin \alpha d\alpha$ 



If R=1 ( unit sphere )

Figure 15.16. Schematic representation of a unit sphere in whose center the electrons are thought to be located.

$$dn = \mathbf{K} \cdot 2\pi \sin \alpha d\alpha \exp(\frac{\mu_m \mu_0 H}{k_B T} \cos \alpha) \qquad \zeta = \frac{\mu_m \mu_0 H}{k_B T}$$

Intergrating "dn" to calculate the number of total atoms in a unit volume

$$n = 2\pi \mathbf{K} \cdot \int_0^{\pi} \sin \alpha \exp(\zeta \cos \alpha) d\alpha$$
  
$$\therefore \mathbf{K} = \frac{n}{2\pi \int_0^{\pi} \sin \alpha \exp(\zeta \cos \alpha) d\alpha}$$

The magnetization M is the magnetic moment per unit volume.

$$\therefore M = \int_0^n \mu_m \cos \alpha \, dn$$
$$= \mathbf{K} \cdot 2\pi \mu_m \int_0^\pi \cos \alpha \sin \alpha \exp(\zeta \cos \alpha) \, d\alpha = \frac{n \mu_m \int_0^\pi \cos \alpha \sin \alpha \exp(\zeta \cos \alpha) \, d\alpha}{\int_0^\pi \sin \alpha \exp(\zeta \cos \alpha) \, d\alpha}$$

This function can be brought into a standard form by setting

$$x = \cos \alpha \text{ and } dx = -\sin \alpha d\alpha$$
$$M = n\mu_m \left( \coth \zeta - \frac{1}{\zeta} \right) = n\mu_m \left( \frac{\zeta}{3} - \frac{\zeta^3}{45} - \frac{\zeta^5}{945} - \cdots \right)$$





\*\*\*\*

 $M_0 = n\mu_m$ : the maximum possible magnetization

Because  $\zeta = \frac{\mu_m \mu_0 H}{k_B T}$  is usually small,

$$\frac{M}{M_0} = \frac{\zeta}{3} \quad \Longrightarrow \quad \therefore \quad M = M_0 \frac{\zeta}{3} = \frac{n\mu_m^2 \mu_0 H}{3k_B T}$$

$$\chi_{para} = \frac{M}{H} = \frac{n\mu_m^2 \mu_0}{3k_B} \frac{1}{T} \equiv C \cdot \frac{1}{T}$$

$$C = \frac{n\mu_m^2 \mu_0}{3k_B}$$





A magnetization greater than P will spontaneously revert to P, in the absence of an applied field. The substance has therefore become spontaneously magnetized level P, which is the value of  $M_s$ 







Figure 15.18. Langevin function  $L(\zeta)$ , i.e., (15.28) and plot of (15.38) for three temperatures.



$$a = \frac{\mu H_m}{k_B T} = \frac{\mu \gamma M}{k_B T} = \frac{\mu \gamma M}{k_B T} \cdot \frac{M_0}{M_0}$$

$$\frac{M}{M_0} = \left(\frac{k_B T}{\mu \gamma M_0}\right) \cdot a \qquad \qquad \frac{k_B T}{\mu \gamma M_0} = \frac{1}{3} at T = T_c$$

$$\frac{k_B T_c}{\mu \gamma M_0} \left( \frac{T}{T_c} \right) = \frac{1}{3} \left( \frac{T}{T_c} \right) = f\left( \frac{T}{T_c} \right)$$

$$\frac{M_s}{M_0} \approx f(\frac{T}{T_c})$$

Law of corresponding states





# Saturation magnetization & Curie temperature







 $\frac{M}{M_{\odot}} = \frac{2J+1}{2J} \operatorname{coth} \left(\frac{2J+1}{2J}\right) a' - \frac{1}{2J} \operatorname{coth} \frac{a'}{2J} \quad \text{Brillouin function}$  $\operatorname{coth} x \approx \frac{1}{x} + \frac{x}{3}$  for small x  $B(J,a') = \left(\frac{J+1}{3I}\right)a'$  $\frac{M}{M_0} = \left(\frac{k_B T}{\mu \gamma M_0}\right) \cdot a' \qquad a' = \frac{\mu H_m}{k_B T} = \frac{\mu \gamma M}{k_B T} \qquad \frac{k_B T}{\mu \gamma M_0} = \frac{J+1}{3J} \quad \text{at } T = T_c$  $\frac{M}{M_o} = \left(\frac{J+1}{3J}\right)(T/T_c)a'$  $\frac{k_B T_c}{\mu \gamma M_c} \left(\frac{T}{T}\right) = \frac{J+1}{3J} \left(\frac{T}{T}\right)$ 



$$J \rightarrow \frac{1}{2}, \qquad \frac{M}{M_0} = \tanh a'$$

$$\frac{M}{M_0} = \left(\frac{J+1}{3J}\right)(T/T_c)a' \longrightarrow \frac{M}{M_0} = (T/T_c)a'$$
$$\frac{M}{M_0} = \tanh\left(\frac{M/M_0}{T/T_c}\right) \qquad \boxed{08}$$







$$\frac{\sigma}{\sigma_0} = \left(\frac{kT}{\mu_H \gamma \rho \sigma_0}\right) a^{-1} - \frac{H}{\gamma \rho \sigma_0}$$
$$\frac{\sigma}{\sigma_0} = \left(\frac{J+1}{3J}\right) a^{-1}$$
$$\chi = \frac{\sigma}{H} = \frac{\mu_H \sigma_0 (J+1)/3kJ}{T - [\mu_H \gamma \rho \sigma_0 (J+1)/3kJ]}$$
$$\chi = \frac{C}{(T-\theta)}$$

When a magnetic field is applied  $\mathbf{H} = \mathbf{H}_{appl} + \mathbf{H}_{m} = \mathbf{H}_{appl} + \gamma \mathbf{M}$ 

$$C = \frac{\mu_H \sigma_0(J+1)}{3kJ} \qquad \theta = \frac{\mu_H \gamma \rho \sigma_0(J+1)}{3kJ}$$



Short range order

