Ch. 11. Diamagnetism and Paramagnetism

* Magnetization: magnetic moment per unit volume of the material

* Magnetic susceptibility (per unit volume): $\chi = \frac{M}{B}$ (CGS)

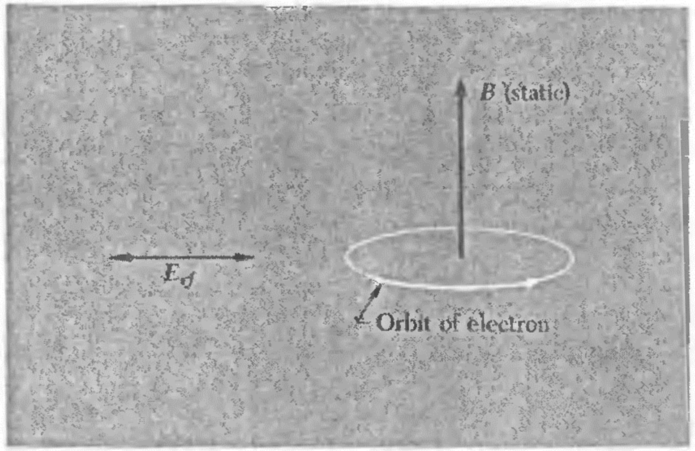
dimensionless quantity in CGS

(in MKS $\chi = \frac{\mu_0 M}{B}$)

$\chi > 0$: paramagnetic

$\chi < 0$: diamagnetic

(e.g., superconductors)



* Langevin diamagnetism equation

- Diamagnetism is associated with tendency of electrical charges to shield the interior of a body from external magnetic field

(e.g., Lenz's law)

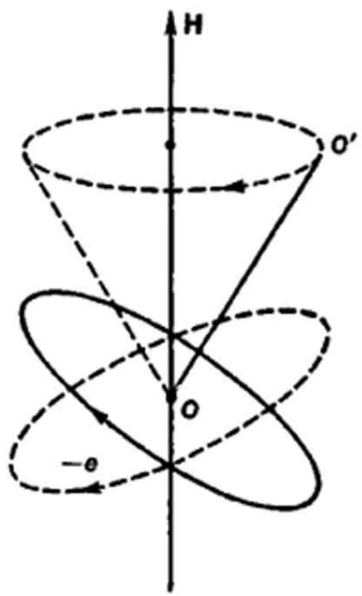
- treatment of diamagnetism in atoms and ions (& dielectric solids) employs the Larmor theorem
  : motion of electron under B field is a superposition of motion without B and precession with

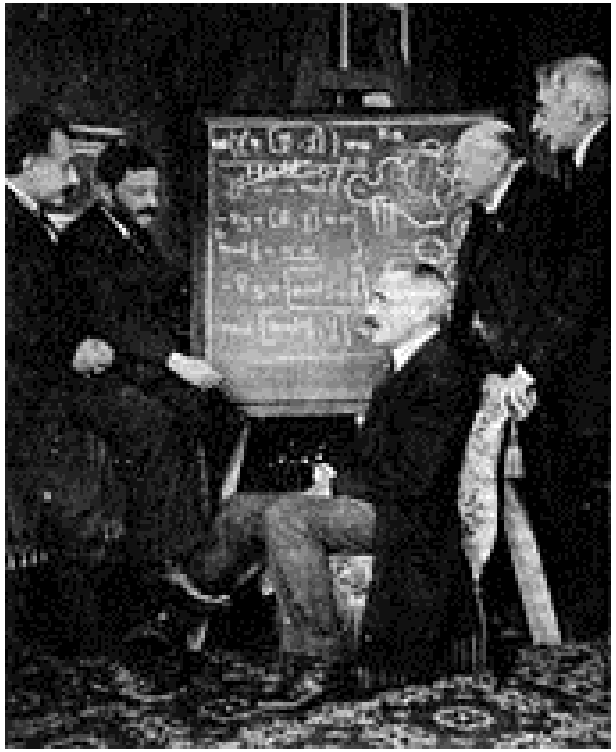
$$\omega = \frac{eB}{2mc}$$ (Larmor frequency)

For free electron $\omega = \frac{\omega_c}{2}$

(ω_c: cyclotron frequency)

$$\omega_c = \frac{eB}{mc}$$





Paul Langevin (1872 – 1946)
France

Larmor precession of Z electrons is equivalent to a current

I = (charge)/(revolutions per unit time) = $(-Ze)\left(\frac{1}{2\pi}\frac{eB}{2mc}\right)$

Magnetic moment of a current loop = (current)(loop area)/c

in CGS unit

$$\mu = -\frac{Ze^2 B}{4mc^2} < \rho^2 >$$

ρ : loop radius perpendicular to B field

$<\rho^2> = <x^2> + <y^2>$

From $<r^2> = <x^2> + <y^2> + <z^2>$ & $<x^2> = <y^2> = <z^2>$

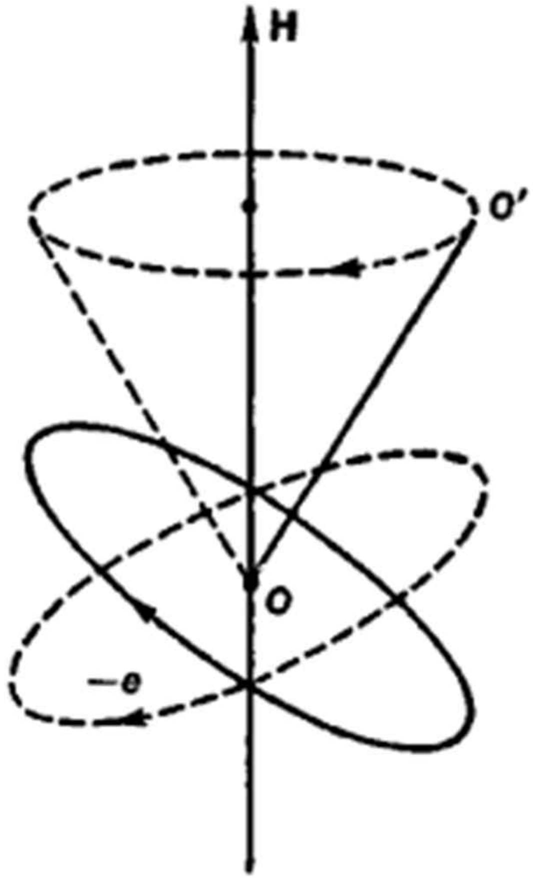
$$< \rho^2 > = \frac{2}{3} < r^2 >$$

$$\rightarrow \chi = \frac{M}{B} = \frac{N\mu}{B} = -\frac{NZe^2}{6mc^2} < r^2 >$$ N: # of atoms/unit volume

→ diamagnetic susceptibility of dielectric solids ∝ $<r^2>$

	He	Ne	Ar	Kr	Xe
χ_M in CGS in 10^{-6} cm^3/mole:	−1.9	−7.2	−19.4	−28.0	−43.0
Z =	2	10	18	36	54

Joseph Larmor (1857~1942) Ireland



* Quantum theory of diamagnetism of mononuclear system

Contribution of magnetic field to the Hamiltonian

$$H' = \frac{ie\hbar}{2mc}\left(\nabla \cdot \vec{A} + \vec{A} \cdot \nabla\right) + \frac{e^2}{2mc^2}A^2 \qquad (6)$$

(H′ can be treated perturbatively for an atomic electron)

In case $\vec{B} = B\hat{z}$ $\left(\vec{B} = \nabla \times \vec{A}\right)$

$$A_x = -\frac{1}{2}yB \ , \ A_y = \frac{1}{2}xB \ , \ A_z = 0$$

Then Eq.(6) becomes

$$H' = \frac{ie\hbar B}{2mc}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) + \frac{e^2B^2}{8mc^2}(x^2 + y^2)$$

1st term: proportional to orbital angular momentum (L_z) for mononuclear system, producing paramagnetism (probable for materials with unfilled p or d shells)

2nd term: diamagnetism

$$E' = \frac{e^2B^2}{12mc^2} < r^2 > \;\rightarrow\; \mu = -\frac{\partial E'}{\partial B} = -\frac{e^2 < r^2 >}{6mc^2}B$$

* Quantum theory of paramagnetism

Magnetic moment of an atom (or ion) in free space

$$\vec{\mu} = \gamma\hbar\vec{J} = -g\mu_B\vec{J}$$

$\hbar\vec{J} = \hbar\vec{L} + \hbar\vec{S}$ (total angular momentum = orbital + spin)

γ : ratio of magnetic moment to total angular momentum (gyromagnetic ratio)

$g\mu_B = \gamma\hbar$ g : g-factor (= 2.0023) for electron spin

μ_B : Bohr magneton $\left(= \frac{e\hbar}{2mc}\right)$

spin magnetic moment of an electron

For a free atom

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} = 2 \quad (\because L = 0 \;\&\; J = S)$$

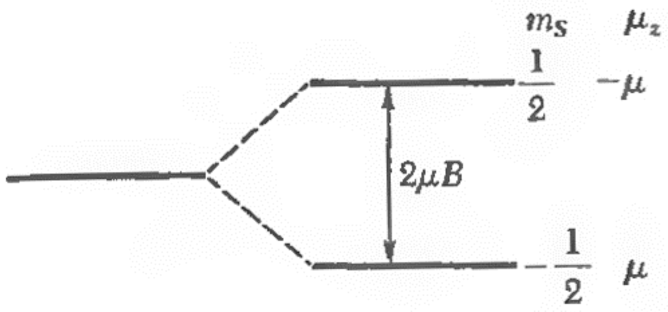
Energy levels of the system in a magnetic field

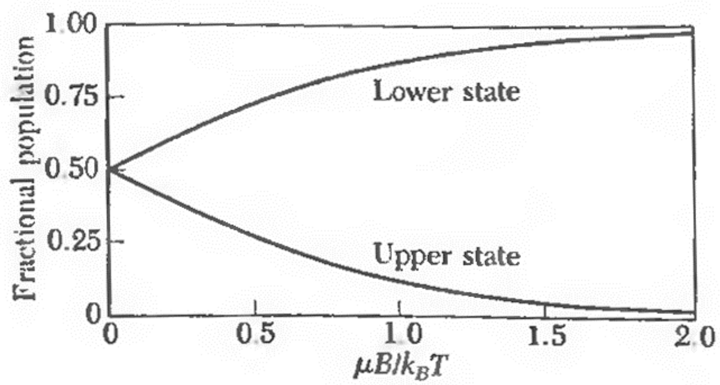
$$U = -\vec{\mu} \cdot \vec{B} = \mu_z B = m_J g \mu_B B$$

m_J = J, J-1, … -J : (2J+1) levels

For an electron with no orbital angular momentum (L = 0),

$$m_J = \pm\frac{1}{2} \quad \rightarrow \quad U = \pm\mu_B B$$





If a system has only two levels, the equilibrium populations are ($m_J \rightarrow J$) $x = -U/k_BT = \mu B/k_BT$

$$\frac{N_1}{N} = \frac{e^x}{e^x + e^{-x}} \qquad \frac{N_2}{N} = \frac{e^{-x}}{e^x + e^{-x}}$$

($\mu = Jg\mu_B = \mu_B$ for electron (L=0) $\because$ J = S = 1/2)

$N = N_1 + N_2$ (total number of spins)

The resultant magnetization (for N spins per unit volume)

$$M = (N_1 - N_2)\mu = N\mu \frac{e^x - e^{-x}}{e^x + e^{-x}} = N\mu \tanh(x) \qquad (17)$$

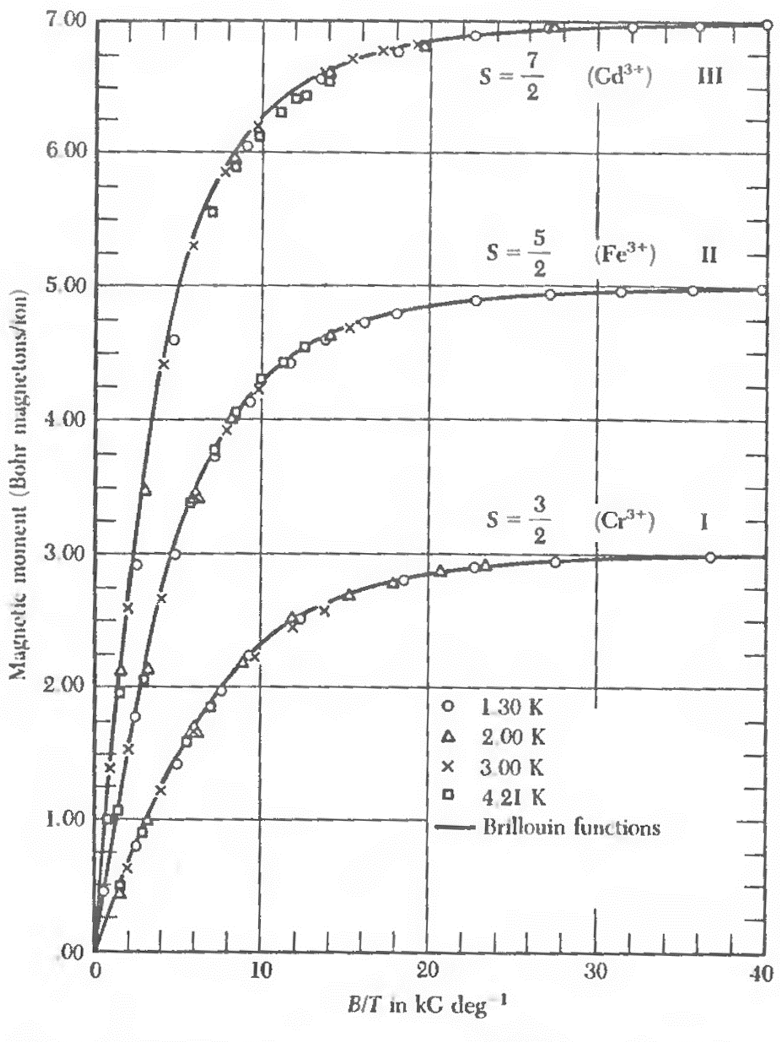
For x << 1, tanh(x) ≈ x

$$\rightarrow \; M \approx N\mu\left(\frac{\mu B}{k_B T}\right) \qquad (18)$$

In a magnetic field, an atom with angular momentum quantum number J has (2J+1) equally spaced energy levels

$$M = NgJ\mu_B B_J(x) \qquad \left(x = \frac{gJ\mu_B B}{k_B T}\right)$$

$$B_J(x) = \frac{2J+1}{2J}\operatorname{ctnh}\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\operatorname{ctnh}\left(\frac{1}{2J}x\right)$$



For x << 1

$$\rightarrow \quad B_J(x) \approx \frac{J+1}{3J}x$$

$$\rightarrow \quad M \approx \frac{NJ(J+1)g^2\mu_B^2 B}{3k_B T}$$

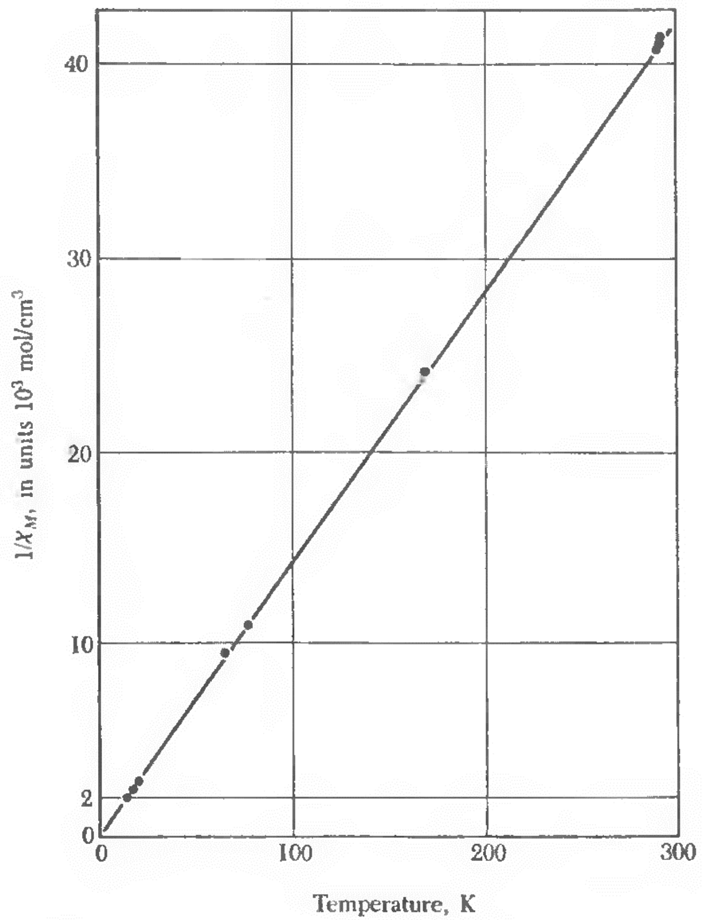
Magnetic susceptibility

$$\chi = \frac{M}{B} \approx \frac{NJ(J+1)g^2\mu_B^2}{3k_B T} = \frac{Np^2\mu_B^2}{3k_B T} = \frac{C}{T} \quad (22)$$

: Curie law

$$p \equiv g[J(J+1)]^{1/2}$$

: effective number of Bohr magnetons



* Rare-earth ions

- usually have trivalent ions (e.g., Ce^{3+} : $4f^1 5s^2 5p^6 5d^1 6s^2$)

  : chemical properties of the ions are similar because of identical outermost electron configuration ($5d^1 6s^2$)

- ionic radius gradually contracts as number of 4f electrons increases (from 0.111 nm for Ce to 0.094 nm for Yb)

- 4f electrons are compacted in inner shell within a radius ~0.03 nm (This property is retained even in atom and solid)

- due to well-localized nature of 4f electrons, spin-orbit interaction is strong

  → multiplet splitting in terms of total angular momentum (orbital + spin)

Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.

H^1 4K hcp 3.75 6.12																	He^4 2K hcp 3.57 5.83
Li 78K bcc 3.491	Be hcp 2.27 3.59											B rhomb.	C diamond 3.567	N 20K cubic 5.66 (N_2)	O complex (O_2)	F	Ne 4K fcc 4.46
Na 5K bcc 4.225	Mg hcp 3.21 5.21	← Crystal structure → ← a lattice parameter, in Å → ← c lattice parameter, in Å →										Al fcc 4.05	Si diamond 5.430	P complex	S complex	Cl complex (Cl_2)	Ar 4K fcc 5.31
K 5K bcc 5.225	Ca fcc 5.58	Sc hcp 3.31 5.27	Ti hcp 2.95 4.68	V bcc 3.03	Cr bcc 2.88	Mn cubic complex	Fe bcc 2.87	Co hcp 2.51 4.07	Ni fcc 3.52	Cu fcc 3.61	Zn hcp 2.66 4.95	Ga complex	Ge diamond 5.658	As rhomb.	Se hex. chains	Br complex (Br_2)	Kr 4K fcc 5.64
Rb 5K bcc 5.585	Sr fcc 6.08	Y hcp 3.65 5.73	Zr hcp 3.23 5.15	Nb bcc 3.30	Mo bcc 3.15	Tc hcp 2.74 4.40	Ru hcp 2.71 4.28	Rh fcc 3.80	Pd fcc 3.89	Ag fcc 4.09	Cd hcp 2.98 5.62	In tetr. 3.25 4.95	Sn (α) diamond 6.49	Sb rhomb.	Te hex. chains	I complex (I_2)	Xe 4K fcc 6.13
Cs 5K bcc 6.045	Ba bcc 5.02	La hex. 3.77 *ABAC*	Hf hcp 3.19 5.05	Ta bcc 3.30	W bcc 3.16	Re hcp 2.76 4.46	Os hcp 2.74 4.32	Ir fcc 3.84	Pt fcc 3.92	Au fcc 4.08	Hg rhomb.	Tl hcp 3.46 5.52	Pb fcc 4.95	Bi rhomb.	Po sc 3.34	At —	Rn —
Fr —	Ra —	Ac fcc 5.31															

Ce fcc 5.16	Pr hex. 3.67 *ABAC*	Nd hex. 3.66	Pm —	Sm complex	Eu bcc 4.58	Gd hcp 3.63 5.78	Tb hcp 3.60 5.70	Dy hcp 3.59 5.65	Ho hcp 3.58 5.62	Er hcp 3.56 5.59	Tm hcp 3.54 5.56	Yb fcc 5.48	Lu hcp 3.50 5.55
Th fcc 5.08	Pa tetr. 3.92 3.24	U complex	Np complex	Pu complex	Am hex. 3.64 *ABAC*	Cm —	Bk —	Cf —	Es —	Fm —	Md —	No —	Lr —