

# Diamagnetism and paramagnetism

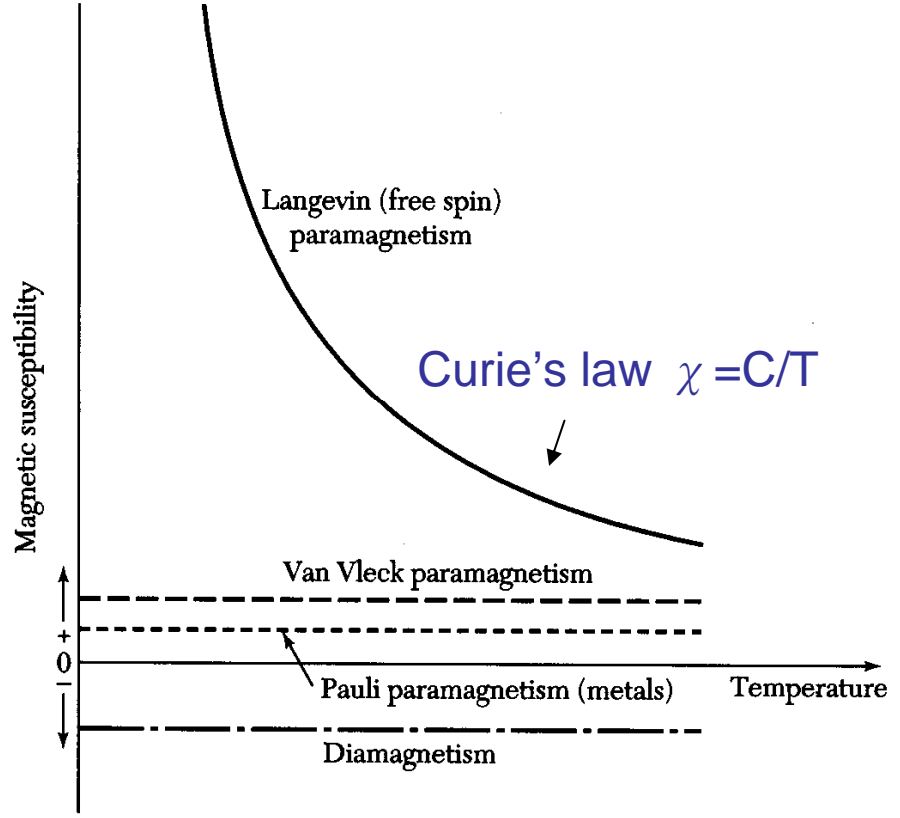
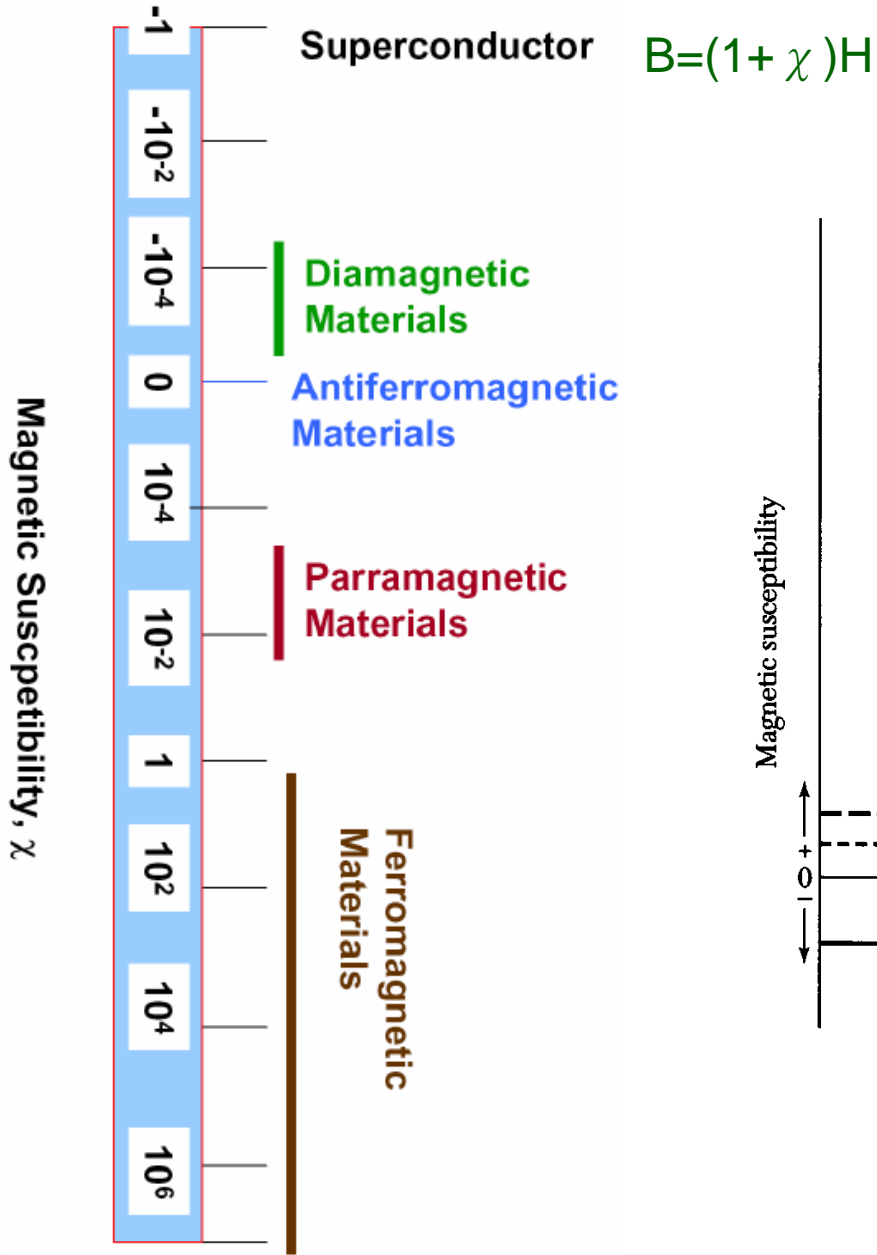
- Langevin diamagnetism
  - paramagnetism
    - Hund's rules
    - Lande g-factor
    - Brillouin function
  - crystal field splitting
    - quench of orbital angular momentum
- ) atom

- nuclear demagnetization
  - Pauli paramagnetism and Landau diamagnetism
- ) free electron gas

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## Basics

- System energy  $E(H)$  ( $E \rightarrow F = E - TS$  if  $T \neq 0$ )
- magnetization density  $M(H) = -\frac{1}{V} \frac{\partial E}{\partial H}$
- susceptibility  $\chi \equiv \frac{\partial M}{\partial H} = -\frac{1}{V} \frac{\partial^2 E}{\partial H^2}$

## Atomic susceptibility

$$H = \sum_i \left( \frac{p_i^2}{2m} + V_i \right) + \mu_B (\vec{L} + g\vec{S}) \cdot \vec{H} + \frac{e^2}{2mc} \sum_i A_i^2, \quad \mu_B = \frac{e\hbar}{2mc}$$

$$= H_0 + \Delta H$$

## Order of magnitude

- $\mu_B (\vec{L} + g\vec{S}) \cdot \vec{H} \approx \mu_B H \approx \hbar \omega_c$   
 $\approx 10^{-4} \text{ eV}$  when  $H = 1 \text{ T}$
- $\vec{A}_i = \frac{H}{2} (-y_i, x_i, 0)$   
 $\frac{e^2}{2mc} \sum_i A_i^2 \approx \left( \frac{eH}{mc} \right)^2 ma_0^2, \quad a_0 \equiv \frac{\hbar^2}{me^2}$   
 $\approx \frac{(\hbar \omega_c)^2}{e^2 / a_0} \approx 10^{-5}$  of the linear term at  $H = 1 \text{ T}$

- Perturbation energy (to 2nd order)

$$\begin{aligned}\Delta E_n &= \langle n | \Delta H | n \rangle + \sum_{n' \neq n} \frac{|\langle n | \Delta H | n' \rangle|^2}{E_n - E_{n'}} \\ &= \mu_B \langle n | \vec{L} + g\vec{S} | n \rangle \cdot \vec{H} + \frac{e^2}{2mc^2} \langle n | \sum_i A_i^2 | n \rangle + \sum_{n'} \frac{|\langle n | \mu_B (\vec{L} + g\vec{S}) \cdot \vec{H} | n' \rangle|^2}{E_n - E_{n'}}\end{aligned}$$

- Filled atomic shell

(applies to noble gas, NaCl-like ions...etc)

Ground state  $|0\rangle$  :

$$\vec{L}|0\rangle = \vec{S}|0\rangle = 0$$

$$\therefore \Delta E = \frac{e^2}{8mc^2} H^2 \langle 0 | \frac{2}{3} \sum_i r_i^2 | 0 \rangle \quad (\text{for spherical charge dist})$$

For a collection of  $N$  ions,

$$\chi = -\frac{N}{V} \frac{\partial^2 \Delta E}{\partial H^2} = -\frac{e^2}{6mc^2} \frac{N}{V} \langle 0 | \sum_i r_i^2 | 0 \rangle < 0$$

Larmor (or Langevin) diamagnetism

## An atom with many electrons

- Without SO coupling

$$H = \sum_i \left( \frac{p_i^2}{2m} + V_i \right) + \frac{1}{2} \sum_{ij} V_{ij}$$

- Maximally mutually commuting set

$$H, L^2, S^2, L_z, S_z$$

- Eigenstates (including ground states)

$$|\alpha, L, S, m_L, m_S\rangle$$

- With SO coupling (weak)

$$H = \sum_i \left( \frac{p_i^2}{2m} + V_i \right) + \frac{1}{2} \sum_{ij} V_{ij} + \sum_i \lambda_i \vec{S}_i \cdot \vec{L}_i$$

- Maximally mutually commuting set

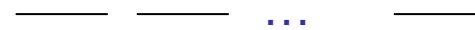
$$H, L^2, S^2, J^2, J_z$$

- Eigenstates (including ground states)

$$|\alpha, L, S, J, m_J\rangle$$

- single electron ground states

Degeneracy  $D=d$



- N-electron ground states

- Without e-e interaction

Degeneracy  $D=C_N^d$



- With e-e interaction



Ground states

w/o SO: labeled by L,S  $D=(2L+1)(2S+1)$

w/ SO: labeled by L,S,J  $D=(2J+1)$

Ground state of an atom with unfilled shell (no  $H$  field yet!):

non-interacting

- Atomic quantum numbers  $n, l, m_l, m_s$
- Energy of an electron depends on  $n, l$  (no  $m_l, m_s$ )
- Degeneracy of electron level  $\mathcal{E}_{n,l}$ :  $2(2l+1)$
- If an atom has  $N$  (non-interacting) valence electrons, then the degeneracy of the “atomic” ground state (with unfilled  $\mathcal{E}_{n,l}$  shell) is  $C_N^{2(2l+1)}$

interacting

**e-e interaction will lift this degeneracy partially, and then**

- the atom energy is labeled by the conserved quantities  $L$  and  $S$ , each is  $(2L+1)(2S+1)$ -fold degenerate
- SO coupling would split these states further, which are labeled by  $J$  (later).

What's the values of  $S$ ,  $L$ , and  $J$  for the atomic ground state?

Use the **Hund's rules** (1925),

1. Choose the max value of  $S$  that is consistent with the exclusion principle
2. Choose the max value of  $L$  that is consistent with the exclusion principle and the 1st rule

To reduce Coulomb repulsion, electron spins like to be parallel, electron orbital motion likes to be in high  $m_l$  state. Both help disperse the charge distribution.

Example: 2 e's in the  $p$ -shell ( $l_1 = l_2 = 1, s_1 = s_2 = 1/2$ )

(a) (1,1/2)                      (b) (0,1/2)                      (c) (-1,1/2)

(a') (1,-1/2)                      (b') (0,-1/2)                      (c') (-1,-1/2)

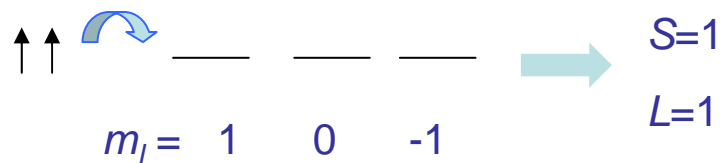
$C_2^6$  ways to put these 2 electrons in 6 slots

- Spectroscopic notation:

$^{2S+1}X_J$  ( $X = S, P, D...$ )

$^1S_0, ^3P_{0,1,2}, ^1D_2$  are o.k.;  $^3S_0, ^1P_1, ^3D_3$  are not.

(It's complicated. See Eisberg and Resnick App. K for more details)



- Ground state is  $^3P_{0,1,2}$ ,

$(2L+1) \times (2S+1) = 9$ -fold degenerate

- There is also the 3rd Hund's rule related to SO coupling (details below)

### Energy levels of Carbon atom

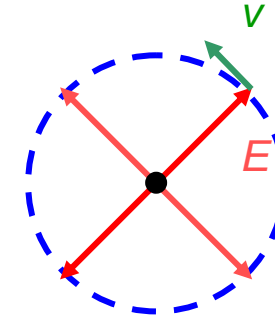
Configuration	Term	$J$	Level ( $\text{cm}^{-1}$ )
$2s^2 2p^2$	$^3P$	0	0.00000
		1	16.41671
		2	43.41350
$2s^2 2p^2$	$^1D$	2	10192.66
$2s^2 2p^2$	$^1S$	0	21648.02

[physics.nist.gov/PhysRefData/Handbook/Tables/carbontable5.htm](http://physics.nist.gov/PhysRefData/Handbook/Tables/carbontable5.htm)

## Review of SO coupling

- An electron moving in a static E field feels an effective B field

$$\vec{B}_{eff} = \vec{E} \times \frac{\vec{v}}{c}$$



- This B field couples with the electron spin

$$H_{SO} = -\vec{\mu} \cdot \vec{B}_{eff}$$

$$= -\left(\frac{q}{mc} \vec{S}\right) \cdot \left(\vec{E} \times \frac{\vec{v}}{c}\right), \quad \vec{E} = -\hat{r} \frac{d\phi}{dr} \quad \text{for central force, } \phi = +\frac{e}{r}$$

$$= \left(\frac{q}{m^2 c^2} \frac{d\phi}{r dr}\right) \vec{S} \cdot \vec{L}$$

(x 1/2 for Thomas precession, 1927)

$$\equiv \lambda \vec{S} \cdot \vec{L}$$

$\lambda > 0$  for less than half-filled (electron-like)

$\lambda < 0$  for more than half-filled (hole-like)

$$= \frac{\lambda}{2} (J^2 - L^2 - S^2)$$

Quantum states are now labeled by  $L, S, J$

(2L+1)x(2S+1) degeneracy is further lifted to become (2J+1)-fold degeneracy

### Hund's 3rd rule:

- if less than half-filled, then  $J=|L-S|$  has the lowest energy
- if more than half-filled, then  $J=L+S$  has the lowest energy

→  ${}^3P_0$  is the ground state in previous example



d-shell ( $l = 2$ )												
$n$	$l_z = 2,$	$1,$	$0,$	$-1,$	$-2$	$S$	$L =  \Sigma l_z $	$J$	SYMBOL			
1	↓					1/2	2	3/2	$J =  L - S $	${}^2D_{3/2}$		
2	↓	↓				1	3	2		${}^3F_2$		
3	↓	↓	↓			3/2	3	3/2		${}^4F_{3/2}$		
4	↓	↓	↓	↓		2	2	0		${}^5D_0$		
5	↓	↓	↓	↓	↓	5/2	0	5/2		${}^6S_{5/2}$		
6	↑	↑	↑	↑	↑	2	2	4	$J = L + S$	${}^3D_4$		
7	↑	↑	↑	↑	↑	3/2	3	9/2		${}^4F_{9/2}$		
8	↑	↑	↑	↑	↑	1	3	4		${}^3F_4$		
9	↑	↑	↑	↑	↑	1/2	2	5/2		${}^2D_{5/2}$		
10	↑	↑	↑	↑	↑	0	0	0		${}^1S_0$		
f-shell ( $l = 3$ )												
$n$	$l_z = 3,$	$2,$	$1,$	$0,$	$-1,$	$-2,$	$-3$	$S$	$L =  \Sigma l_z $	$J$	SYMBOL	
1	↓							1/2	3	5/2	$J =  L - S $	${}^2F_{5/2}$
2	↓	↓						1	5	4		${}^3H_4$
3	↓	↓	↓					3/2	6	9/2		${}^4I_{9/2}$
4	↓	↓	↓	↓				2	6	4		${}^5I_4$
5	↓	↓	↓	↓	↓			5/2	5	5/2		${}^6H_{5/2}$
6	↓	↓	↓	↓	↓	↓		3	3	0	${}^7F_0$	
7	↓	↓	↓	↓	↓	↓	↓	7/2	0	7/2	${}^8S_{7/2}$	
8	↑	↑	↑	↑	↑	↑	↑	3	3	6	$J = L + S$	${}^7F_6$
9	↑	↑	↑	↑	↑	↑	↑	5/2	5	15/2		${}^6H_{15/2}$
10	↑	↑	↑	↑	↑	↑	↑	2	6	8		${}^5I_8$
11	↑	↑	↑	↑	↑	↑	↑	3/2	6	15/2		${}^4I_{15/2}$
12	↑	↑	↑	↑	↑	↑	↑	1	5	6		${}^3H_6$
13	↑	↑	↑	↑	↑	↑	↑	1/2	3	7/2	${}^2F_{7/2}$	
14	↑	↑	↑	↑	↑	↑	↑	0	0	0	${}^1S_0$	

\*↑ = spin  $\frac{1}{2}$ ; ↓ = spin  $-\frac{1}{2}$ .

## Paramagnetism of an atom with unfilled shell

1) Ground state is nondegenerate ( $J=0$ )

$$\Delta E = \mu_B \langle 0 | \vec{L} + g\vec{S} | 0 \rangle \cdot \vec{H} + \frac{e^2}{2mc^2} \langle 0 | \sum_i A_i^2 | 0 \rangle + \sum_n \frac{|\langle 0 | \mu_B (\vec{L} + g\vec{S}) \cdot \vec{H} | n \rangle|^2}{E_0 - E_n}$$

(A+M, Prob 31.4)

Van Vleck PM

2) Ground state is degenerate ( $J \neq 0$ )

Then the 1<sup>st</sup> order term almost always  $\gg$  the 2nd order terms.

$$\vec{m} = -\mu_B (\vec{L} + 2\vec{S}) = -\mu_B (\vec{J} + \vec{S})$$

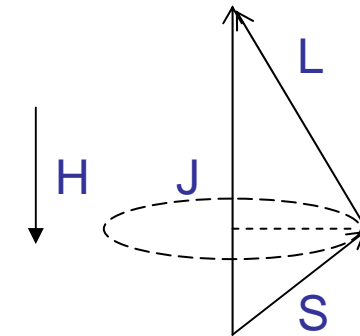
• Heuristic argument:  $J$  is fixed,  $L$  and  $S$  rotate around  $J$ , maintaining the triangle. So the magnetic moment is given by the component of  $L+2S$  parallel to  $J$ ,

$$\begin{aligned} \vec{S}_{\parallel} &= \frac{\vec{J} \cdot \vec{S}}{J^2} \vec{J} = \frac{\vec{J}}{2J^2} (J^2 - L^2 + S^2) \\ &= \frac{\vec{J}}{2J(J+1)} [J(J+1) - L(L+1) + S(S+1)] \end{aligned}$$

$$\therefore \vec{m}_{\text{eff}} = -g_J \mu_B \vec{J}$$

Lande g-factor  
(1921)

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$



•  $\Delta E(m_J) = g_J \mu_B m_J H$ , so  $\chi = 0$ ?

No! these  $2J+1$  levels are closely packed ( $< kT$ ), so  $F(H)$  is nonlinear (next page).

# Langevin paramagnetism

$$Z = \sum_{m_J=-J}^J e^{-E(m_J)/k_B T}, \quad \Delta E(m_J) = g_J \mu_B m_J H (\sim 1K \text{ at } H = 1 \text{ T})$$

$$F = E - TS = -k_B T \ln Z$$

$$M = -\frac{N}{V} \frac{\partial F}{\partial H} = \frac{N}{V} g_J \mu_B J B_J \left( \frac{g_J \mu_B J H}{k_B T} \right)$$

$$\text{where } B_J(x) \equiv \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$$

- $k_B T \ll g_J \mu_B J H \quad (x \gg 1)$

$$M = \frac{N}{V} g_J \mu_B J, \quad \chi = 0$$

- $k_B T \gg g_J \mu_B J H \quad (x \ll 1)$

$$M = \frac{N}{V} (g_J \mu_B)^2 \frac{J(J+1)}{3k_B T} H$$

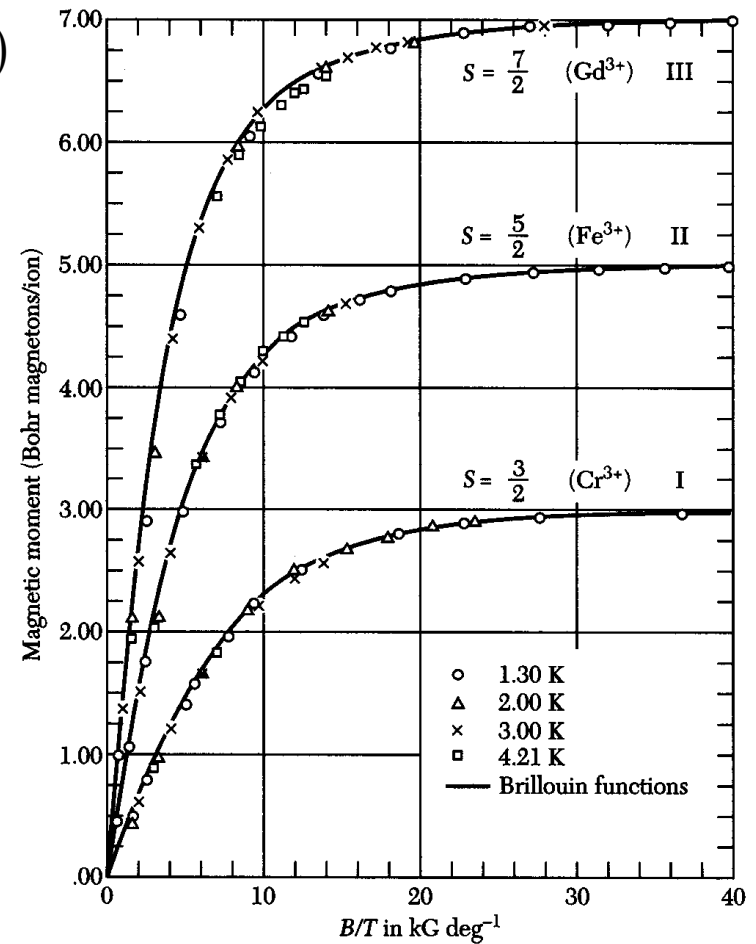
$\chi(T)$

**Brillouin function**

$$B_J(x) \sim \frac{J+1}{3J} x$$

- at room T,  $\chi$  (para)  $\sim 500 \chi$  (dia) calculated earlier
- Curie's law  $\chi = C/T$  (note: not good for  $J=0$ )

$$C = \frac{N}{V} \frac{(\mu_B p)^2}{3k}, \quad \text{where } p = g_J \sqrt{J(J+1)}$$



effective Bohr magneton number

f-shell (Lanthanides)  
 鑷系元素

In general (but not always), energy from low to high:  
 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d ...

ELEMENT (TRIPLY IONIZED)	BASIC ELECTRON CONFIGURATION	GROUND-STATE TERM	CALCULATED <sup>b</sup> <i>p</i>	MEASURED <sup>c</sup> <i>p</i>
La	4f <sup>0</sup>	<sup>1</sup> S	0.00	diamagnetic
Ce	4f <sup>1</sup>	<sup>2</sup> F <sub>5/2</sub>	2.54	2.4
Pr	4f <sup>2</sup>	<sup>3</sup> H <sub>4</sub>	3.58	3.5
Nd	4f <sup>3</sup>	<sup>4</sup> I <sub>9/2</sub>	3.62	3.5
Pm	4f <sup>4</sup>	<sup>5</sup> I <sub>4</sub>	2.68	—
Sm	4f <sup>5</sup>	<sup>6</sup> H <sub>5/2</sub>	0.84	1.5
Eu	4f <sup>6</sup>	<sup>7</sup> F <sub>0</sub>	0.00	3.4 <i>J=0</i>
Gd	4f <sup>7</sup>	<sup>8</sup> S <sub>7/2</sub>	7.94	8.0
Tb	4f <sup>8</sup>	<sup>7</sup> F <sub>6</sub>	9.72	9.5
Dy	4f <sup>9</sup>	<sup>6</sup> H <sub>15/2</sub>	10.63	10.6
Ho	4f <sup>10</sup>	<sup>5</sup> I <sub>8</sub>	10.60	10.4
Er	4f <sup>11</sup>	<sup>4</sup> I <sub>15/2</sub>	9.59	9.5
Tm	4f <sup>12</sup>	<sup>3</sup> H <sub>6</sub>	7.57	7.3
Yb	4f <sup>13</sup>	<sup>2</sup> F <sub>7/2</sub>	4.54	4.5
Lu	4f <sup>14</sup>	<sup>1</sup> S	0.00	diamagnetic

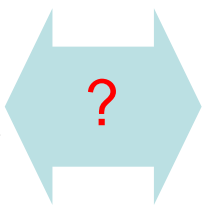
• Before ionization, La: 5p<sup>6</sup> 6s<sup>2</sup> 5d<sup>1</sup>; Ce: 5p<sup>6</sup> 6s<sup>2</sup> 4f<sup>2</sup> ...

PERIODS	s		d										p					
	GROUP I	GROUP II	Transition elements										GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII
1	1 <b>H</b> 1.01 1s <sup>1</sup>																	2 <b>He</b> 4.00 1s <sup>2</sup>
2	3 <b>Li</b> 6.94 2s <sup>1</sup>	4 <b>Be</b> 9.01 2s <sup>2</sup>											5 <b>B</b> 10.81 2p <sup>1</sup>	6 <b>C</b> 12.01 2p <sup>2</sup>	7 <b>N</b> 14.01 2p <sup>3</sup>	8 <b>O</b> 16.00 2p <sup>4</sup>	9 <b>F</b> 19.00 2p <sup>5</sup>	10 <b>Ne</b> 20.18 2p <sup>6</sup>
3	11 <b>Na</b> 22.99 3s <sup>1</sup>	12 <b>Mg</b> 24.31 3s <sup>2</sup>											13 <b>Al</b> 26.98 3p <sup>1</sup>	14 <b>Si</b> 28.09 3p <sup>2</sup>	15 <b>P</b> 30.97 3p <sup>3</sup>	16 <b>S</b> 32.07 3p <sup>4</sup>	17 <b>Cl</b> 35.45 3p <sup>5</sup>	18 <b>Ar</b> 39.95 3p <sup>6</sup>
4	19 <b>K</b> 39.10 4s <sup>1</sup>	20 <b>Ca</b> 40.08 4s <sup>2</sup>	21 <b>Sc</b> 44.96 3d <sup>1</sup> 4s <sup>2</sup>	22 <b>Ti</b> 47.88 3d <sup>2</sup> 4s <sup>2</sup>	23 <b>V</b> 50.94 3d <sup>3</sup> 4s <sup>2</sup>	24 <b>Cr</b> 52.00 3d <sup>5</sup> 4s <sup>1</sup>	25 <b>Mn</b> 54.94 3d <sup>5</sup> 4s <sup>2</sup>	26 <b>Fe</b> 55.85 3d <sup>6</sup> 4s <sup>2</sup>	27 <b>Co</b> 58.93 3d <sup>7</sup> 4s <sup>2</sup>	28 <b>Ni</b> 58.69 3d <sup>8</sup> 4s <sup>2</sup>	29 <b>Cu</b> 63.55 3d <sup>10</sup> 4s <sup>1</sup>	30 <b>Zn</b> 65.39 3d <sup>10</sup> 4s <sup>2</sup>	31 <b>Ga</b> 69.72 4p <sup>1</sup>	32 <b>Ge</b> 72.61 4p <sup>2</sup>	33 <b>As</b> 74.92 4p <sup>3</sup>	34 <b>Se</b> 78.96 4p <sup>4</sup>	35 <b>Br</b> 79.90 4p <sup>5</sup>	36 <b>Kr</b> 83.80 4p <sup>6</sup>
5	37 <b>Rb</b> 85.47 5s <sup>1</sup>	38 <b>Sr</b> 87.62 5s <sup>2</sup>	39 <b>Y</b> 88.96 4d <sup>1</sup> 5s <sup>2</sup>	40 <b>Zr</b> 91.22 4d <sup>2</sup> 5s <sup>2</sup>	41 <b>Nb</b> 92.91 4d <sup>4</sup> 5s <sup>1</sup>	42 <b>Mo</b> 95.94 4d <sup>5</sup> 5s <sup>1</sup>	43 <b>Tc</b> (98) 4d <sup>5</sup> 5s <sup>2</sup>	44 <b>Ru</b> 101.07 4d <sup>7</sup> 5s <sup>1</sup>	45 <b>Rh</b> 102.91 4d <sup>8</sup> 5s <sup>1</sup>	46 <b>Pd</b> 106.42 4d <sup>10</sup> 5s <sup>0</sup>	47 <b>Ag</b> 107.87 4d <sup>10</sup> 5s <sup>1</sup>	48 <b>Cd</b> 112.41 4d <sup>10</sup> 5s <sup>2</sup>	49 <b>In</b> 114.82 5p <sup>1</sup>	50 <b>Sn</b> 118.71 5p <sup>2</sup>	51 <b>Sb</b> 121.76 5p <sup>3</sup>	52 <b>Te</b> 127.60 5p <sup>4</sup>	53 <b>I</b> 126.90 5p <sup>5</sup>	54 <b>Xe</b> 131.29 5p <sup>6</sup>
6	55 <b>Cs</b> 132.91 6s <sup>1</sup>	56 <b>Ba</b> 137.33 6s <sup>2</sup>	57 <b>La</b> 138.91 5d <sup>1</sup> 6s <sup>2</sup>	* 72 <b>Hf</b> 178.49 5d <sup>2</sup> 6s <sup>2</sup>	73 <b>Ta</b> 180.95 5d <sup>3</sup> 6s <sup>2</sup>	74 <b>W</b> 183.85 5d <sup>4</sup> 6s <sup>2</sup>	75 <b>Re</b> 186.21 5d <sup>5</sup> 6s <sup>2</sup>	76 <b>Os</b> 190.2 5d <sup>6</sup> 6s <sup>2</sup>	77 <b>Ir</b> 192.22 5d <sup>7</sup> 6s <sup>2</sup>	78 <b>Pt</b> 195.08 5d <sup>9</sup> 6s <sup>1</sup>	79 <b>Au</b> 196.97 5d <sup>10</sup> 6s <sup>1</sup>	80 <b>Hg</b> 200.59 5d <sup>10</sup> 6s <sup>2</sup>	81 <b>Tl</b> 204.36 6p <sup>1</sup>	82 <b>Pb</b> 207.2 6p <sup>2</sup>	83 <b>Bi</b> 208.98 6p <sup>3</sup>	84 <b>Po</b> (209) 6p <sup>4</sup>	85 <b>At</b> (210) 6p <sup>5</sup>	86 <b>Rn</b> (222) 6p <sup>6</sup>
7	87 <b>Fr</b> (223) 7s <sup>1</sup>	88 <b>Ra</b> 226.03 7s <sup>2</sup>	89 <b>Ac</b> 227.03 6d <sup>1</sup> 7s <sup>2</sup>	+ 104 <b>Rf</b> (261) 6d <sup>2</sup> 7s <sup>2</sup>	105 <b>Db</b> (262) 6d <sup>3</sup> 7s <sup>2</sup>	106 <b>Sg</b> (263) 6d <sup>4</sup> 7s <sup>2</sup>	107 <b>Bh</b> (264) 6d <sup>5</sup> 7s <sup>2</sup>	108 <b>Hs</b> (265) 6d <sup>6</sup> 7s <sup>2</sup>	109 <b>Mt</b> (268) 6d <sup>7</sup> 7s <sup>2</sup>	110 (269)	111 (272)	112 (277)						

Atomic number — 26 **Fe** — Symbol  
 Atomic mass — 58.85 — Atomic mass  
 Outer electron configuration — 3d<sup>6</sup>4s<sup>2</sup>

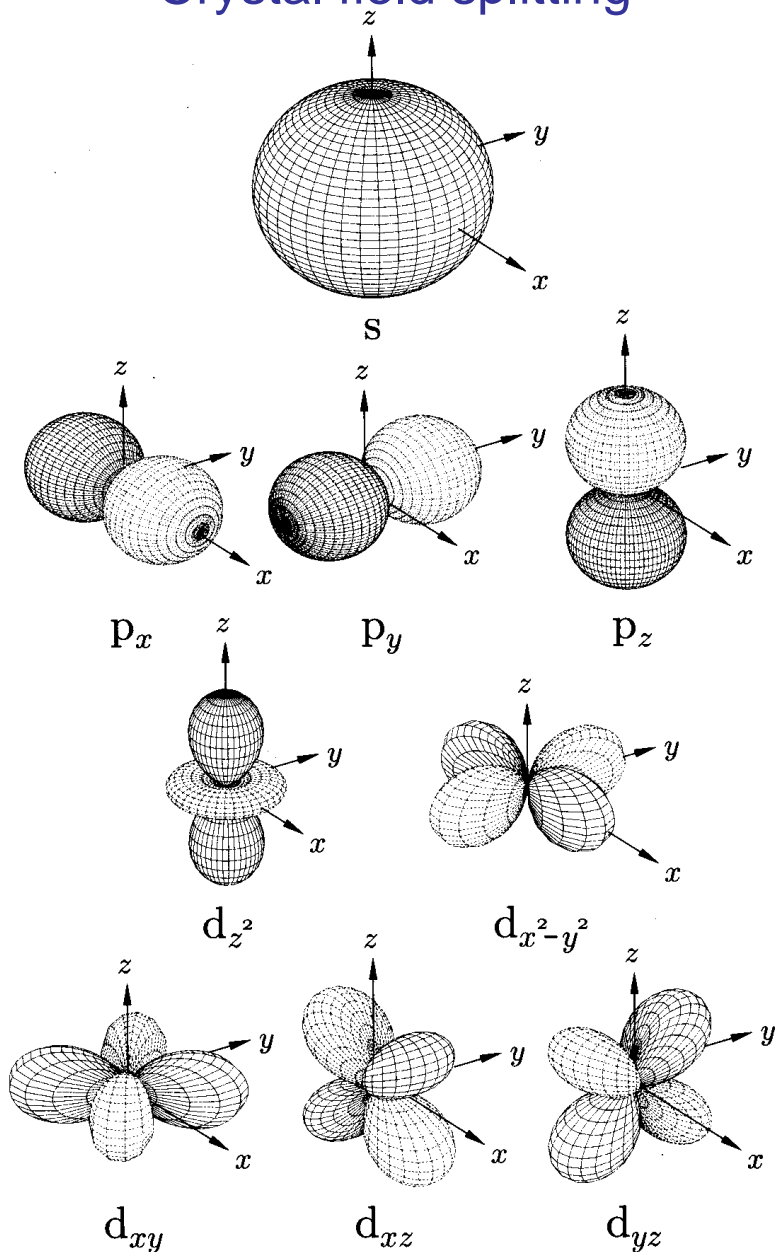
	f														
*	58 <b>Ce</b> 140.12 5d <sup>1</sup> 4f <sup>1</sup> 6s <sup>2</sup>	59 <b>Pr</b> 140.91 4f <sup>3</sup> 6s <sup>2</sup>	60 <b>Nd</b> 144.24 4f <sup>4</sup> 6s <sup>2</sup>	61 <b>Pm</b> (145) 4f <sup>5</sup> 6s <sup>2</sup>	62 <b>Sm</b> 150.36 4f <sup>6</sup> 6s <sup>2</sup>	63 <b>Eu</b> 151.96 4f <sup>7</sup> 6s <sup>2</sup>	64 <b>Gd</b> 157.25 5d <sup>1</sup> 4f <sup>7</sup> 6s <sup>2</sup>	65 <b>Tb</b> 158.93 5d <sup>1</sup> 4f <sup>8</sup> 6s	66 <b>Dy</b> 162.50 4f <sup>10</sup> 6s <sup>2</sup>	67 <b>Ho</b> 164.93 4f <sup>11</sup> 6s <sup>2</sup>	68 <b>Er</b> 167.26 4f <sup>12</sup> 6s <sup>2</sup>	69 <b>Tm</b> 168.93 4f <sup>13</sup> 6s <sup>2</sup>	70 <b>Yb</b> 173.04 4f <sup>14</sup> 6s <sup>2</sup>	71 <b>Lu</b> 174.97 5d <sup>1</sup> 4f <sup>14</sup> 6s <sup>2</sup>	(Lanthanides)
+	90 <b>Th</b> 232.04 6d <sup>2</sup> 7s <sup>2</sup>	91 <b>Pa</b> 231.04 5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	92 <b>U</b> 238.03 5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	93 <b>Np</b> 237.05 5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	94 <b>Pu</b> (244) 5f <sup>6</sup> 6d <sup>0</sup> 7s <sup>2</sup>	95 <b>Am</b> (243) 5f <sup>7</sup> 6d <sup>0</sup> 7s <sup>2</sup>	96 <b>Cm</b> (247) 5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	97 <b>Bk</b> (247) 5f <sup>8</sup> 6d <sup>1</sup> 7s <sup>2</sup>	98 <b>Cf</b> (251) 5f <sup>10</sup> 6d <sup>0</sup> 7s <sup>2</sup>	99 <b>Es</b> (252) 5s <sup>1</sup> 16d <sup>0</sup> 7s <sup>2</sup>	100 <b>Fm</b> (257) 5f <sup>12</sup> 6d <sup>0</sup> 7s <sup>2</sup>	101 <b>Md</b> (258) 5f <sup>13</sup> 6d <sup>0</sup> 7s <sup>2</sup>	102 <b>No</b> (259) 5f <sup>14</sup> 6d <sup>0</sup> 7s <sup>2</sup>	103 <b>Lr</b> (260) 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>	(Actinides)

### 3d-shell (transition metal ions)

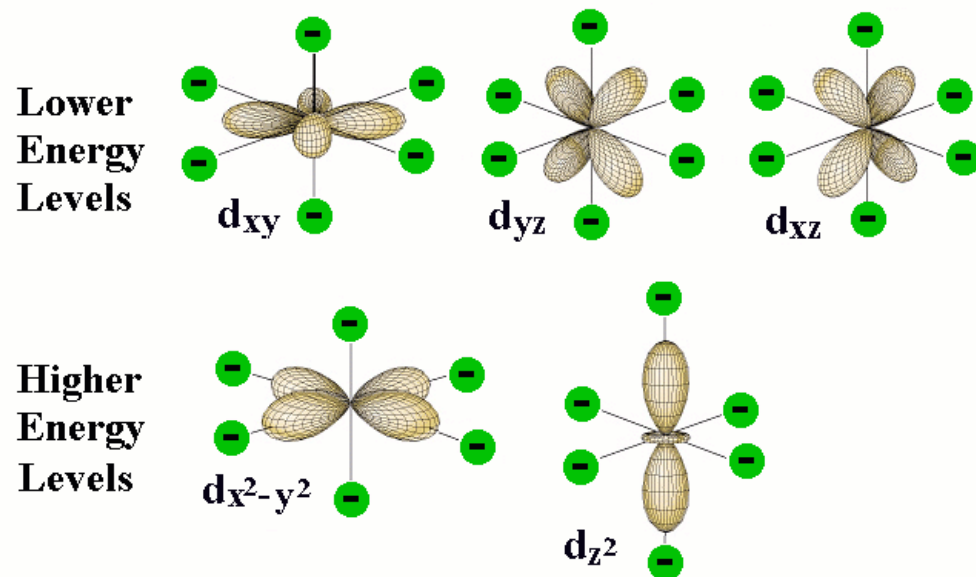
ELEMENT (AND IONIZATION)	BASIC ELECTRON CONFIGURATION	GROUND- STATE TERM	CALCULATED <sup>b</sup> $p$		MEASURED <sup>c</sup> $p$
			$(J = S)$	$(J =  L \pm S )$	
Ti <sup>3+</sup>	3d <sup>1</sup> 4s <sup>2</sup>	<sup>2</sup> D <sub>3/2</sub>	1.55		—
V <sup>4+</sup>	3d <sup>1</sup>	<sup>2</sup> D <sub>3/2</sub>	1.55		1.8
V <sup>3+</sup>	3d <sup>2</sup>	<sup>3</sup> F <sub>2</sub>	1.63		2.8
V <sup>2+</sup>	3d <sup>3</sup>	<sup>4</sup> F <sub>3/2</sub>	0.77		3.8
Cr <sup>3+</sup>	3d <sup>3</sup>	<sup>4</sup> F <sub>3/2</sub>	0.77		3.7
Mn <sup>4+</sup>	3d <sup>3</sup>	<sup>4</sup> F <sub>3/2</sub>	0.77		4.0
Cr <sup>2+</sup>	3d <sup>4</sup>	<sup>5</sup> D <sub>0</sub>	0		4.8
Mn <sup>3+</sup>	3d <sup>4</sup>	<sup>5</sup> D <sub>0</sub>	0		5.0
Mn <sup>2+</sup>	3d <sup>5</sup>	<sup>6</sup> S <sub>5/2</sub>	5.92		5.9
Fe <sup>3+</sup>	3d <sup>5</sup>	<sup>6</sup> S <sub>5/2</sub>	5.92		5.9
Fe <sup>2+</sup>	3d <sup>6</sup>	<sup>5</sup> D <sub>4</sub>	6.70		5.4
Co <sup>2+</sup>	3d <sup>7</sup>	<sup>4</sup> F <sub>9/2</sub>	6.54		4.8
Ni <sup>2+</sup>	3d <sup>8</sup>	<sup>3</sup> F <sub>4</sub>	5.59		3.2
Cu <sup>2+</sup>	3d <sup>9</sup>	<sup>2</sup> D <sub>5/2</sub>	3.55		1.9

- Curie's law is still good, but  $p$  is mostly wrong
- Much better improvement if we let  $J=S$

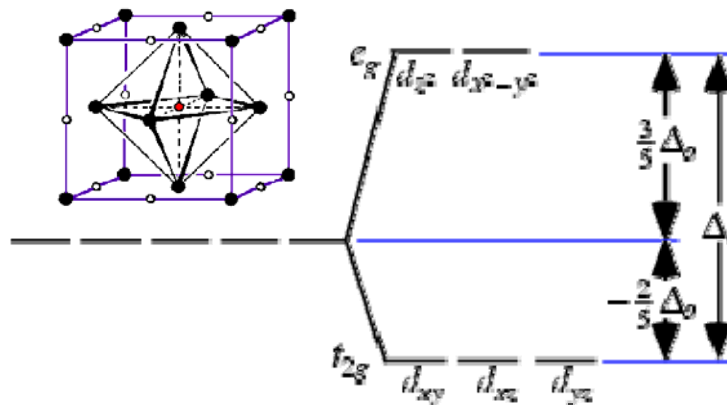
# Crystal field splitting



In a **crystal**, crystal field may be more important than the LS coupling



octahedral ( $O_h$ ) crystal field splitting



- Different symmetries would have different splitting patterns.

淬滅

## Quench of orbital angular momentum

- Due to crystal field, energy levels are now labeled by  $L$  (not  $J$ )
- Orbital degeneracy not lifted by crystal field may be lifted by  
1) LS coupling, or 2) Jahn-Teller effect, or both.
- The stationary state  $\psi$  of a non-degenerate level can be chosen as real

when  $t \rightarrow -t$ ,

$$\psi \rightarrow \psi^* (= \psi \text{ if nondegenerate})$$

- $\langle \psi | \vec{L} | \psi \rangle = \langle \psi | \vec{r} \times \frac{\hbar}{i} \nabla | \psi \rangle$  is purely imaginary

but  $\langle \psi | \vec{L} | \psi \rangle$  has to be real also

$$\therefore \langle \psi | \vec{L} | \psi \rangle = 0$$

( $\langle \psi | L^2 | \psi \rangle$  can still be non-zero)

- for 3d ions, crystal field > SO interaction
- for 4f ions, SO interaction > crystal field (because 4f is hidden inside 5p and 6s shells)
- for 4d and 5d ions that have stronger SO interaction, the 2 energies maybe comparable and it's more complicated.

Spontaneous  
lattice  
distortion



- Langevin diamagnetism
- paramagnetism
  - Hund's rules
  - Lande g-factor
  - Brillouin function
- crystal field splitting
  - quench of orbital angular momentum
- nuclear demagnetization
- Pauli paramagnetism and Landau diamagnetism

# Adiabatic demagnetization (proposed by Debye, 1926)

- The first method to reach below 1K

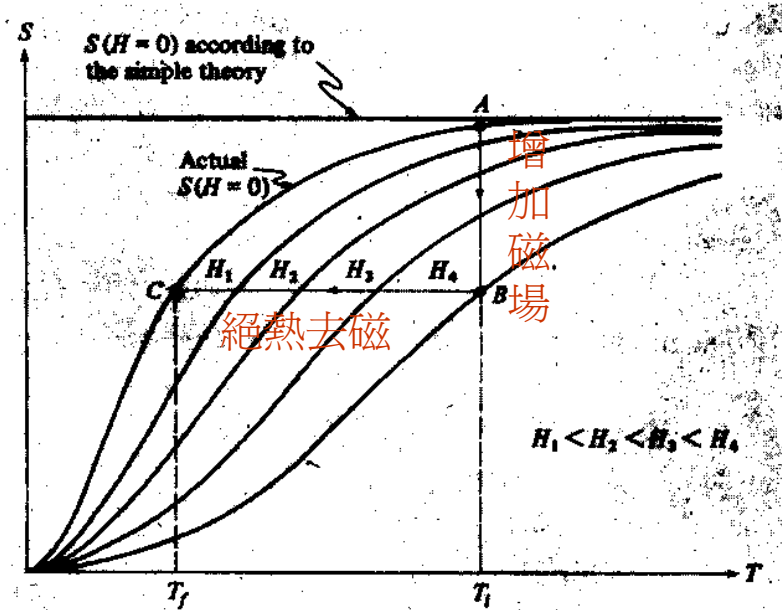
$$Z = \sum_{m_j=-J}^J e^{-E(m_j)/kT}, \quad \text{assume } E(m_j) \propto H$$

$$F = -kT \ln Z \left( \frac{H}{kT} \right)$$

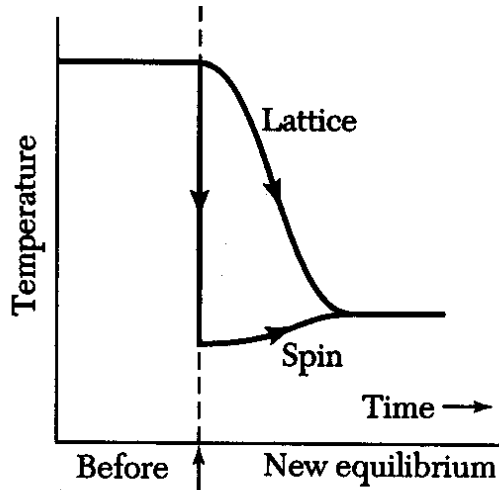
$$S = -\frac{\partial F}{\partial T} = S \left( \frac{H}{kT} \right)$$

- If  $S = \text{constant}$ , then  $kT \sim H \quad T_f = T_i \frac{H_f}{H_i}$
- $\therefore$  We can reduce  $H$  to reduce  $T$

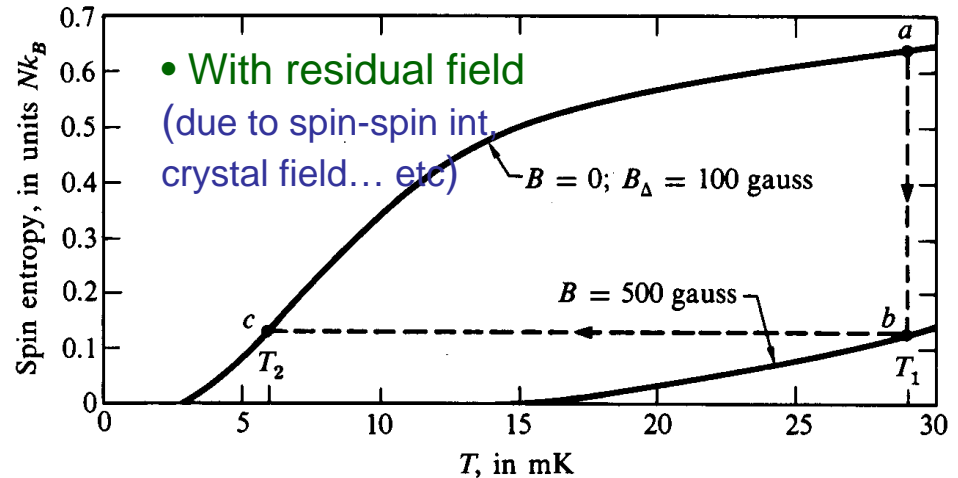
- Without residual field



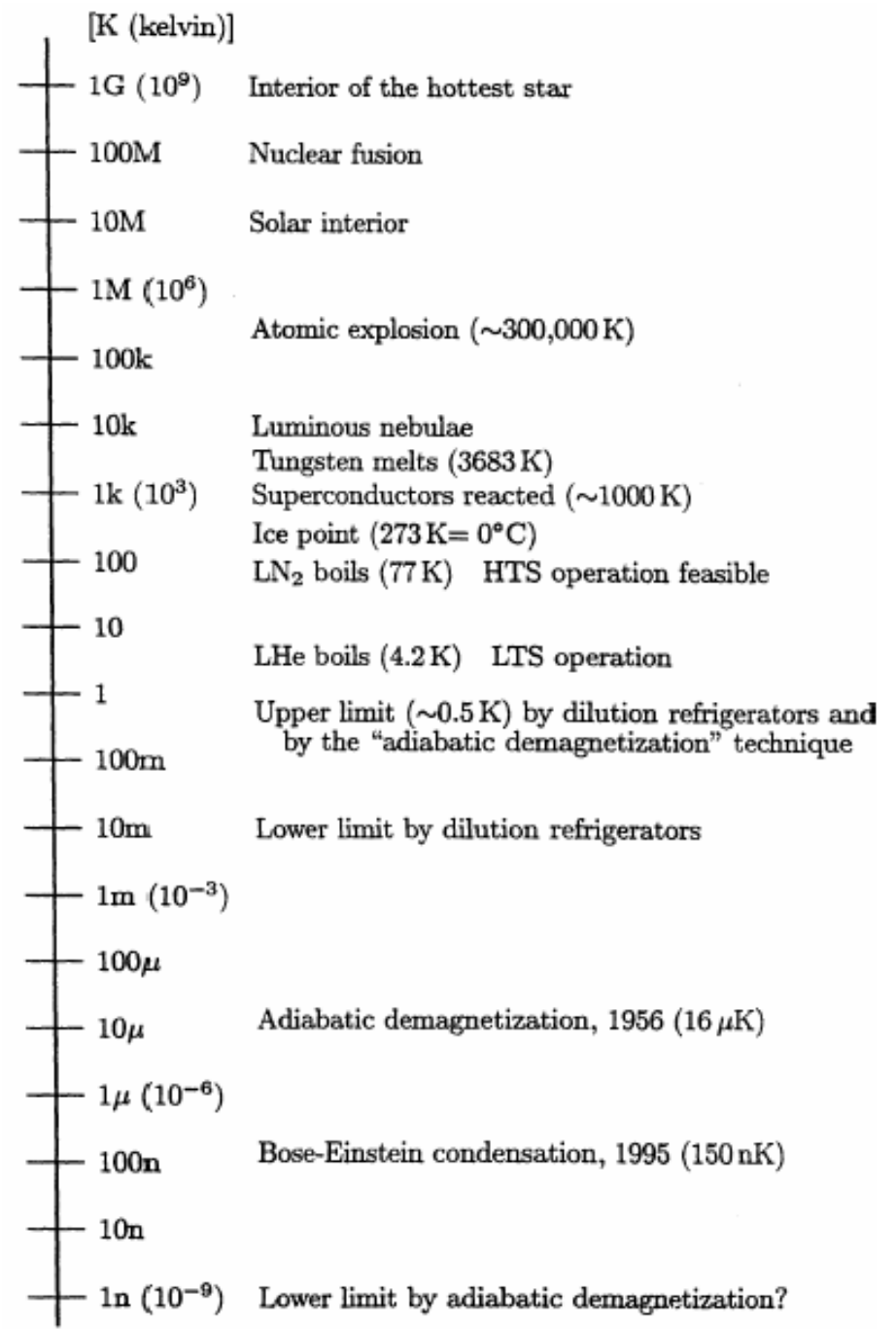
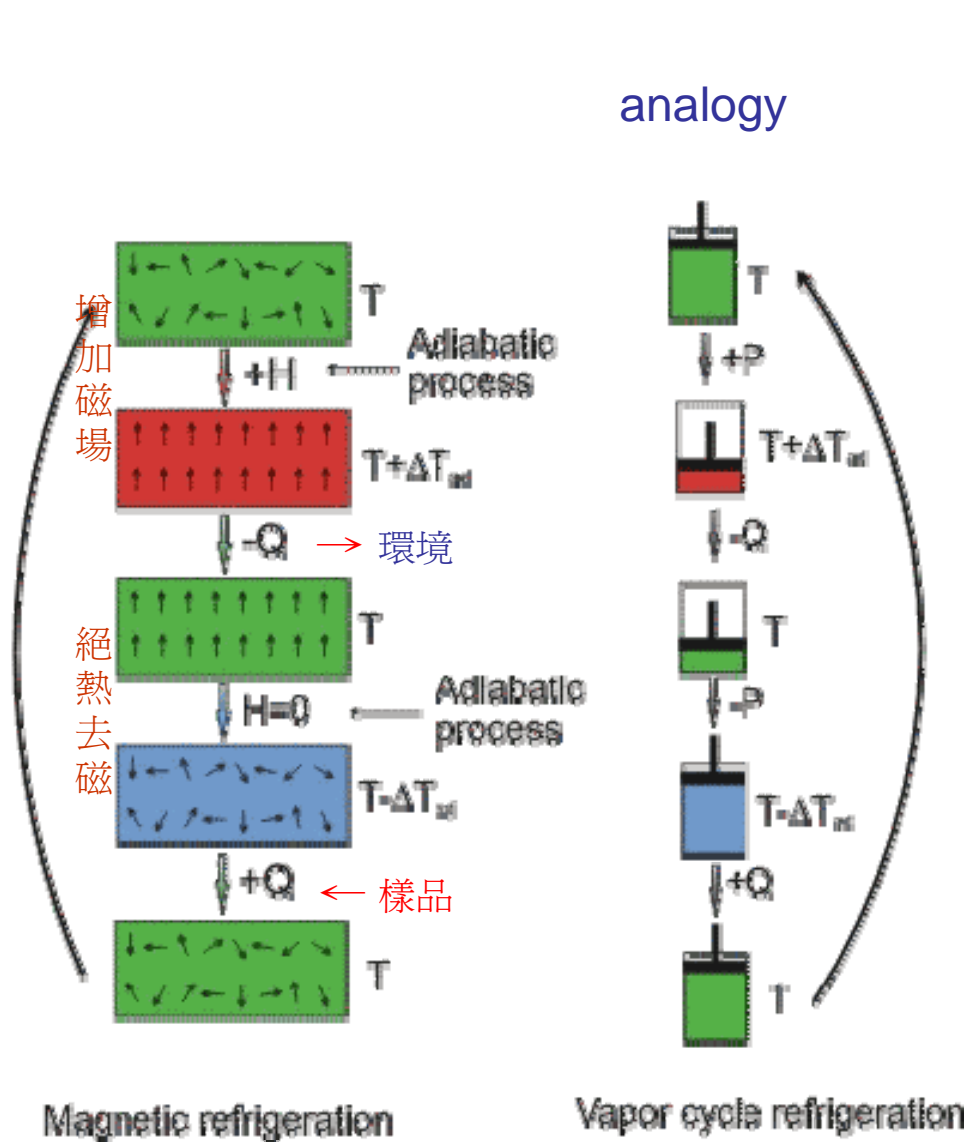
Freezing is effective only if spin specific heat is dominant (usually need  $T \ll T_D$ )



Time at which magnetic field is removed



Can reach  $10^{-6}$  K (dilution refrig only  $10^{-3}$  K)



## Pauli paramagnetism for free electron gas (1925)

- **Orbital** response to  $H$  neglected, consider only **spin** response
- One of the earliest application of the exclusion principle

$$N = N_{\uparrow} + N_{\downarrow}$$

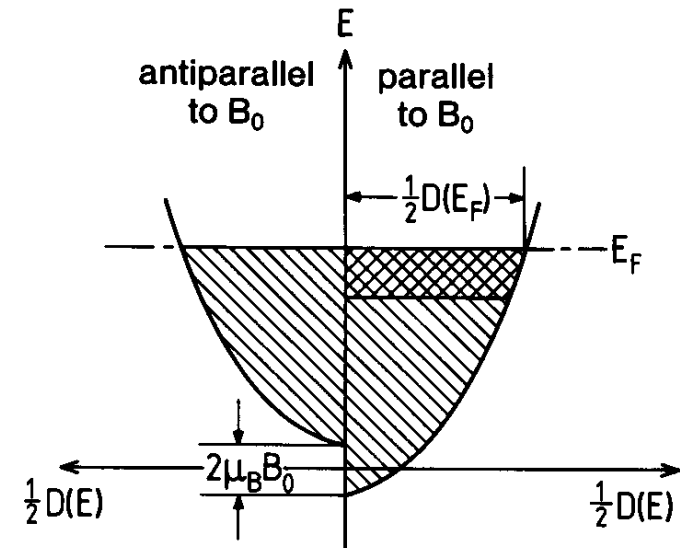
$$M = \frac{1}{V} (N_{\uparrow} - N_{\downarrow}) \mu_B$$

For  $T \ll T_F$ ,

$$n_{\uparrow} - n_{\downarrow} \cong g(\varepsilon_F) \mu_B H, \quad g = g_{\uparrow} + g_{\downarrow}$$

$$\therefore M = g(\varepsilon_F) \mu_B^2 H$$

$$\Rightarrow \chi_{Pauli} = g(\varepsilon_F) \mu_B^2 = \left( \frac{\alpha}{2\pi} \right)^2 (k_F a_0)^1 \sim 10^{-6}$$



$$g(\varepsilon) = \frac{m}{\pi^2 \hbar^3} \sqrt{2m\varepsilon} \quad a_0 = \frac{\hbar^2}{me^2}$$

$$\mu_B = \frac{e\hbar}{2mc} \quad \alpha = \frac{e^2}{\hbar c}$$

- unlike the PM of magnetic ions, here the magnitude  $\sim$  DM's (suppressed by Pauli exclusion principle)

## Landau diamagnetism for free electron gas (1930)

Landau began his paper with the remark, “It has until now been more or less quietly assumed that the magnetic properties of electrons, other than spin, originate exclusively from the binding of electrons in atoms.”

- The **orbital** response neglected earlier gives slight DM
- The calculation is not trivial. For free electron gas,

$$\begin{aligned}\chi_{Landau} &= -\frac{e^2 k_F}{12\pi^2 mc^2} \\ &= -\frac{1}{3} \chi_{Pauli}\end{aligned}$$

- So far we have learned PM and DM for a free electron gas. How do we separate these contributions in experiment?

X-ray magnetic circular dichroism (XMCD)