Atomic magnetism

- Larmor diamagnetism
- The ground state of an ion, Hund's rules
- Van Vleck paramagnetism
- Crystal field splitting
- The quenching of the orbital angular momentum
- The Kramers theorem
- The Jahn-Teller effect
- Curie's law, adiabatic demagnetization

Magnetism is a quantum phenomenon.

Теорема Бора — ван Лёвен : вещество в классической физике может быть намагничено только в термодинамически неравновесном состоянии: при его переходе в состояние равновесия, намагничивание исчезает.

Грубое объяснение полученного Бором и ван Леувен результата заключается в том, что магнитное поле не может производить работу над частицей. Конкретнее доказательство строится на преобразовании сдвига импульса всех заряженных частиц на величину eA/c (где e - заряд частицы, A - векторный потенциал поля, e - скорость света). Поскольку в классический гамильтониан, описывающий динамику системы, импульс входит только в комбинации p-eA/c, то при такой замене статистическая сумма не изменяется, то есть она не зависит от наличия магнитного поля. Отсюда следует, что магнитный момент системы также не зависит от наличия магнитного поля и потому всегда равен нулю, как и в отсутствии поля.

Magnetism is a quantum mechanical phenomenon.

A classical system in thermal equilibrium cannot display any magnetic moment, even in an external applied magnetic field.

A free atom – sources of the magnetic moment:

1. the spin;
2. the orbital angular momentum;
3. the change in the orbital moment in an external applied magnetic field.

Contibutions to the magnetization:

(1) and (2) – paramagnetic, (3) – diamagnetic.

Examples:

Hydrogen atom in the ground 1*s* state – the orbital moment is zero, the magnetic moment: the electron spin and a small induced diamagnetic moment.

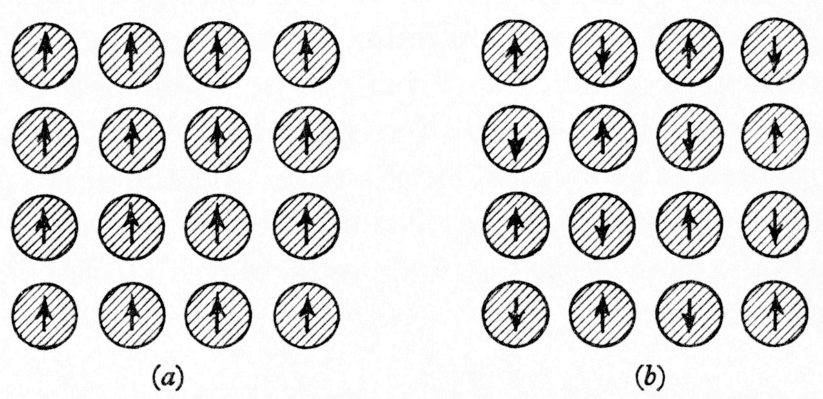
Helium atom in the $1s^2$ state – both the spin and orbital moments are zero, only an induced moment.

Atoms with filled electron shells – zero spin and zero orbital moment.

Periodically ordered arrays of magnetic moments will be considered later. These arrays may be ferromagnetic, antiferromagnetic, ferrimagnetic, helical, or of more complex varieties.

Examples:

(a) – ferromagnetic ordering, (b) – aniferromagnetic ordering

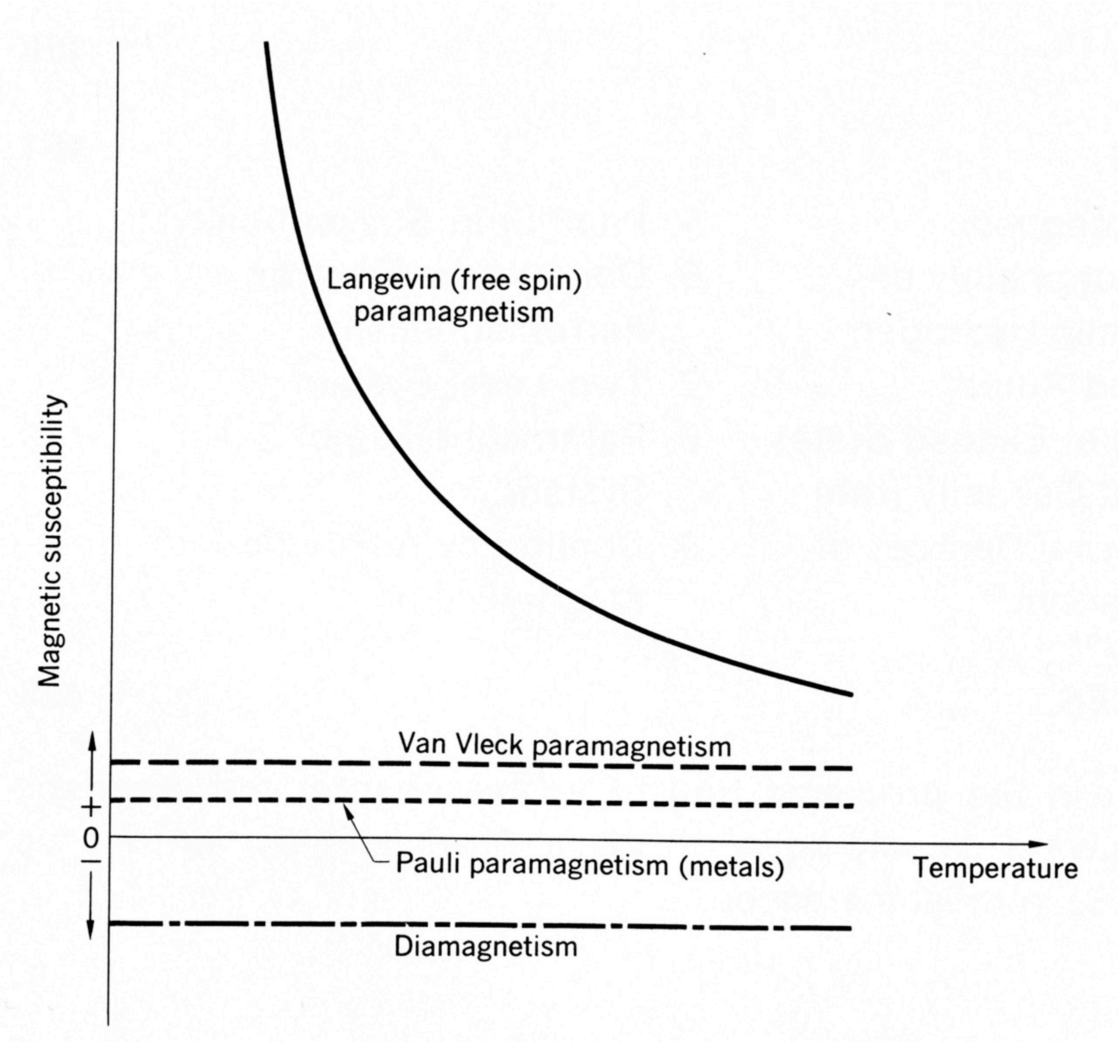


[from J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, 1979)]

Nuclear magnetism: magnetic moments of nuclei are about 10^{-3} times smaller than the magnetic moment of the electron.

Nuclear demagnetization.

Diamagnetic and paramagnetic media – magnetic susceptibilities



[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

Larmor diamagnetism

Magnetic susceptibility of insulators with all shells filled

Analogy with the Lentz law: if magnetic flux is changed, a current is induced in such a direction to oppose the flux change.

An electron orbit – "the induced current" persists as long as the external magnetic field $\mathbf{B}$ is present.

Diamagnetic moment – since the magnetic field of the induced current is opposite to the external field $\mathbf{B}$, the magnetic susceptibility is reduced.

The diamagnetic susceptibility is

$$\chi = -\frac{\mu_0 n Z e^2}{6m}\left\langle r^2 \right\rangle$$

Important: both the quantum mechanical and classical derivations of the Larmor diamagnetism are possible.

The usual treatment of the diamagnetism of atoms and ions employs the Larmor theorem: in a magnetic field the motion of the electrons around a central nucleus is, to the first order in B, the same as a possible motion in the absence of B except for the superposition of a precession of the electrons with Larmor angular frequency. The Larmor precession of Z electrons is equivalent to an electric current

Van Vleck paramagnetism

In the case of $L \neq 0$ and $S \neq 0$ the van Vleck term to the energy shift of the ground state induced by an external magnetic field $\mathbf{B}$ contributes to the magnetization even if the total angular momentum $J = 0$.

In this case the magnetic susceptibility χ is proportional to the van Vleck term:

$$\chi \sim \sum_n \frac{\left|\left\langle 0 \middle| L_z + g_0 S_z \middle| n \right\rangle\right|^2}{E_n^0 - E_0^0} \; .$$

The van Vleck paramagnetic contribution to χ can exceed the diamagnetic contribution.

Microscopic origin of atomic diamagnetism and of Van Vleck paramagnetism

Hamiltonian of a charged particle in electromagnetic field is given by

$$\mathcal{H} = \frac{1}{2M}\left(\boldsymbol{p} - \frac{Q}{c}\boldsymbol{A}\right)^2 + Q\varphi,$$

The additional term due to electromagnetic field is

$$\mathcal{H}' = \frac{ie\hbar}{2mc}\left(\boldsymbol{\nabla}\cdot\boldsymbol{A} + \boldsymbol{A}\cdot\boldsymbol{\nabla}\right) + \frac{e^2}{2mc^2}A^2,$$

In magnetic field only one can choose

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

Then the additional Hamiltonian term is

$$\mathcal{H}' = \underbrace{\frac{ie\hbar B}{2mc}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)}_{\text{paramagnetic (Van Vleck)}} + \underbrace{\frac{e^2B^2}{8mc^2}(x^2 + y^2)}_{\text{diamagnetic}}.$$

Diamagnetic term has diagonal matrix elements and gives energy correction in the first order:

$$E' = \frac{e^2B^2}{12mc^2}\langle r^2\rangle$$

The induced magnetic moment originating from this perturbation is

$$\mu = -\frac{\partial E'}{\partial B} = -\frac{e^2\langle r^2\rangle}{6mc^2}B.$$

Temperature-independent Van Vleck paramagnetism

Предположим, что недиагональный матричный элемент $\langle s|\mu_z|0\rangle$ оператора μ_z, связывающий основное состояние 0 с возбужденным состоянием s, соответствует энергии $\Delta = E_s - E_0$, отсчитываемой вверх от уровня энергии основного состояния (E_0). Тогда стандартная теория возмущений в случае слабых полей ($\mu_z B \ll \Delta$) дает для волновой функции основного состояния следующее выражение:

$$\psi_0' = \psi_0 + \frac{B}{\Delta}\langle s \mid \mu_z \mid 0\rangle\, \psi_s,$$

and for the wave function of excited state

$$\psi_s' = \psi_s - \frac{B}{\Delta}\langle 0 \mid \mu_z \mid s\rangle\, \psi_0$$

Hence, the new ground state has the magnetic moment

$$\langle 0' \mid \mu_z \mid 0'\rangle \approx 2B \mid \langle s \mid \mu_z \mid 0\rangle \mid^2/\Delta,$$

while the new excited state has the magnetic moment

$$\langle s' \mid \mu_z \mid s'\rangle \approx -2B \mid \langle s \mid \mu_z \mid 0\rangle \mid^2/\Delta.$$

At low temperature T<<Δ all particles are in the ground state, and magnetization is

$$M = \frac{2NB \mid \langle s \mid \mu_z \mid 0\rangle \mid^2}{\Delta}$$

The corresponding susceptibility is

$$\chi = \frac{2N \mid \langle s \mid \mu_z \mid 0\rangle \mid^2}{\Delta}$$

Van Vleck paramagnetism at high temperature

а) Случай $\Delta \ll k_B T$. Относительный избыток частиц на основном уровне (по сравнению с возбужденным) приближенно равен $N\Delta/2k_B T$, а для соответствующей намагниченности получим:

$$M = \frac{2B\,|\langle s\,|\,\mu_z\,|\,0\rangle|^2}{\Delta} \cdot \frac{N\Delta}{2k_B T}$$

and the corresponding susceptibility

$$\chi = \frac{N\,|\langle s\,|\,\mu_z\,|\,0\rangle|^2}{k_B T}$$

The total molecular magnetic susceptibility at low T can be positive or negative:

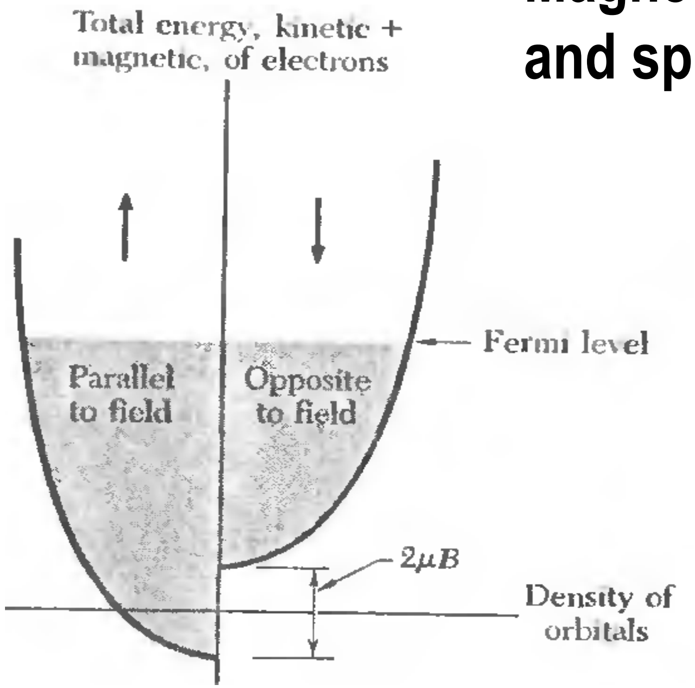
$$\chi_M = -\frac{N_0 e^2}{6mc^2} \sum \langle r^2 \rangle + 2N_0 \sum_s \frac{|\langle s\,|\,\mu_z\,|\,0\rangle|^2}{E_s - E_0},$$

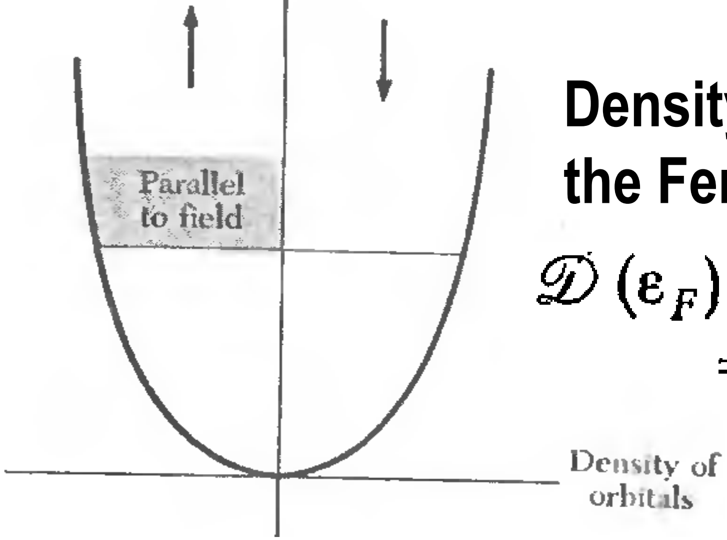
diamagnetic

paramagnetic (Van Vleck)

Pauli paramagnetism of metals

Magnetization is given by the difference of spin-up and spin-down electrons: $M = \mu (N_+ - N_-)$





Density of states at the Fermi level is

$$\mathcal{D}(\varepsilon_F) = 3N/2\varepsilon_F$$
$$= 3N/2k_BT_F$$

$$N_- = \frac{1}{2}\int_{\mu B}^{\varepsilon_F} d\varepsilon\, f(\varepsilon)\,\mathcal{D}(\varepsilon - \mu B) = \frac{1}{2}\int_0^{\varepsilon_F} d\varepsilon\, f(\varepsilon)\,\mathcal{D}(\varepsilon) - \frac{1}{2}\mu B\mathcal{D}(\varepsilon_F).$$

$$N_+ = \frac{1}{2}\int_{-\mu B}^{\varepsilon_F} d\varepsilon\, f(\varepsilon)\,\mathcal{D}(\varepsilon + \mu B) \approx \frac{1}{2}\int_0^{\varepsilon_F} d\varepsilon\, f(\varepsilon)\,\mathcal{D}(\varepsilon) + \frac{1}{2}\mu B\mathcal{D}(\varepsilon_F);$$

As a result spin magnetization of metals is $M \approx \mu^2\mathcal{D}(\varepsilon_F)\,B = \dfrac{3N\mu^2}{2k_BT_F}B$

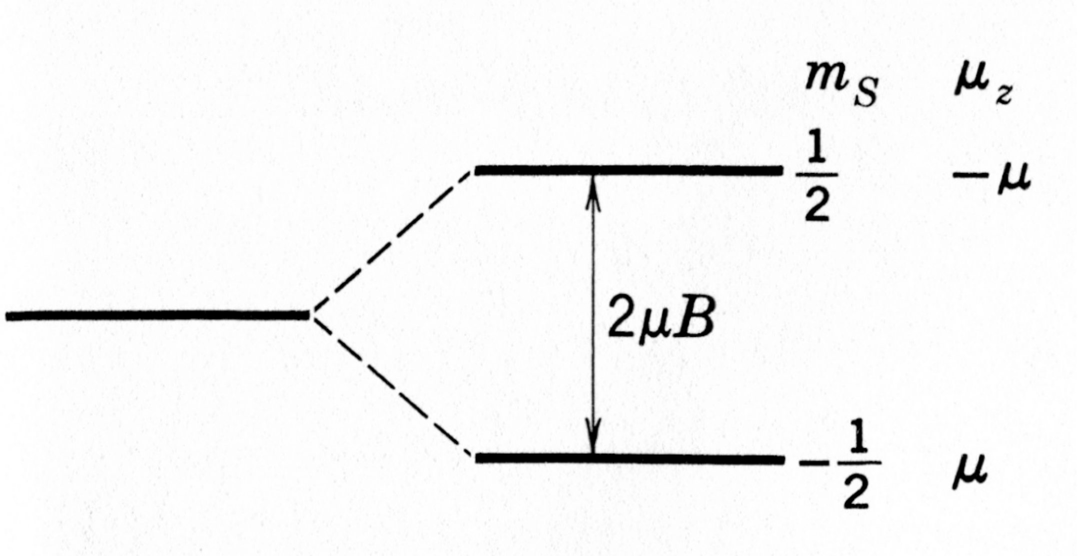
Comparison of Curie law (for localized spins) with magnetization in metals

The diamagnetic susceptibility of metals is -1/3 of paramagnetic, and originates from the change of electron wave functions in magnetic field (Landau levels -> Landau diamagnetism). The total magnetization is a sum of paramagnetic (spin) and diamagnetic contributions:

$$M = \frac{N\mu_B^2}{k_B T_F} B.$$

This is smaller than the Curie magnetization $M = \frac{N\mu_B^2}{k_B T} B$ by a factor $k_B T/E_F \ll 1$.

Energy level splitting for one electron in a magnetic field $\mathbf{B}$ directed along the positive z axis.

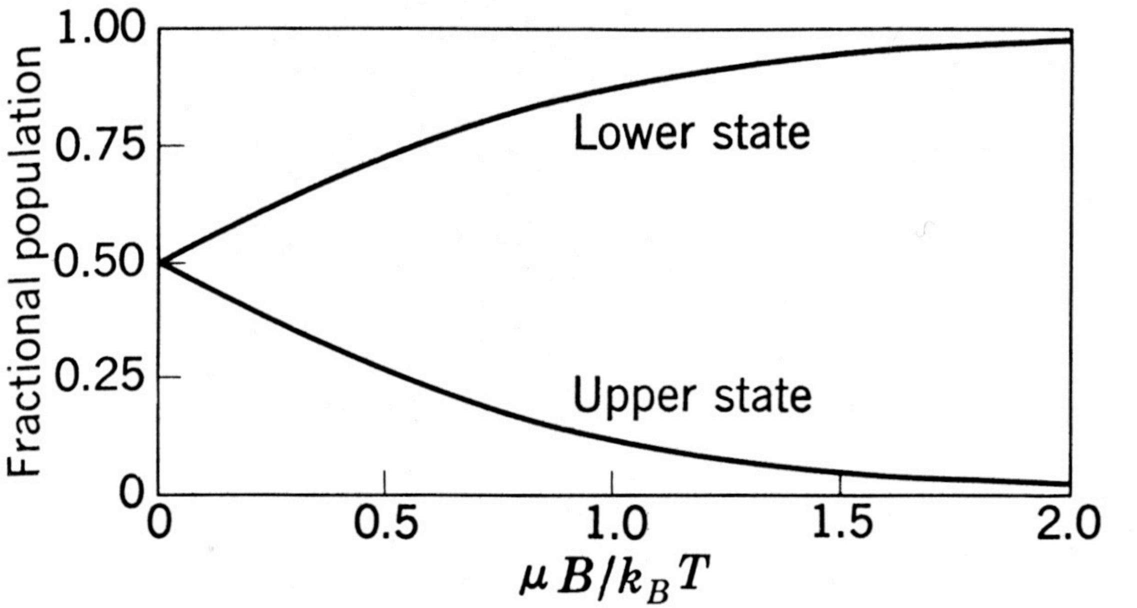


[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

The magnetic moment μ of an electron is opposite in sign to the spin S, so that $\mu = -g\mu_B S$.

In the low energy state the magnetic moment $\boldsymbol{\mu} \parallel \mathbf{B}$.

A two-level system in thermal equilibrium at temperature T in a magnetic field $\mathbf{B}$ – fractional populations:



[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

The magnetic moment is proportional to the difference between the two curves.

Comparison of (classical) Langevin formula and quantum formula for magnetization

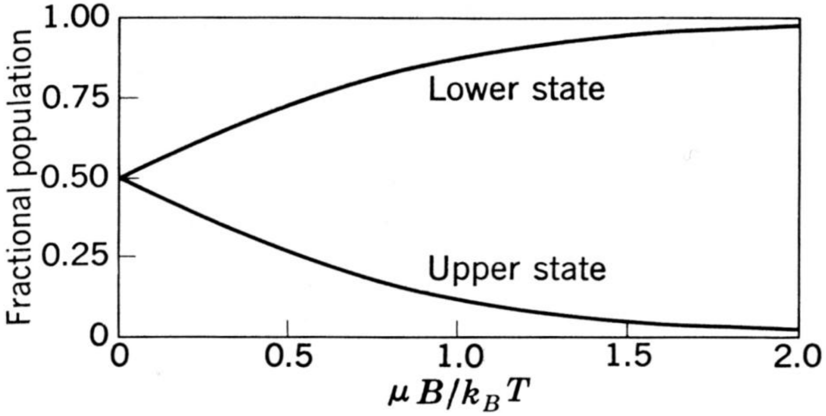
Langevin formula for magnetization M is derived by averaging the angle θ of classical magnetic moment μ with potential energy $U=-\mu B\cos\theta$:

$$\langle\cos\theta\rangle = \left(\int e^{-\beta U}\cos\theta \, d\Omega\right)\cdot\left(\int e^{-\beta U}\, d\Omega\right)^{-1} = \operatorname{cth} x - \frac{1}{x} \equiv L(x).$$

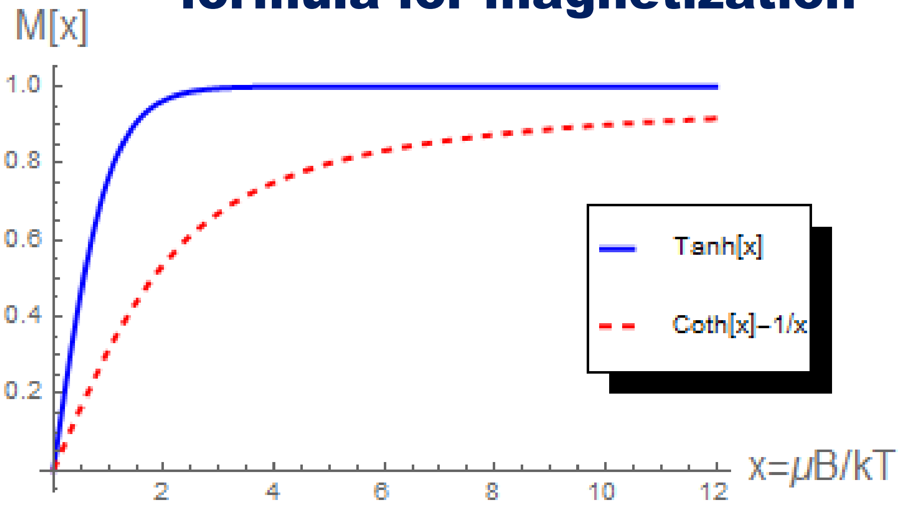
As a result one obtains $M=N\mu <\cos\theta>=N\mu\, L(\mu B/kT)$

Quantum formula for magnetization M is derived by the summation of magnetic moments of different energy levels weighted by the Gibbs distribution :

$$M=\Sigma_i\mu_i N_i=N\mu\tanh(\mu B/kT)$$



Comparison of Langevin formula with quantum formula for magnetization



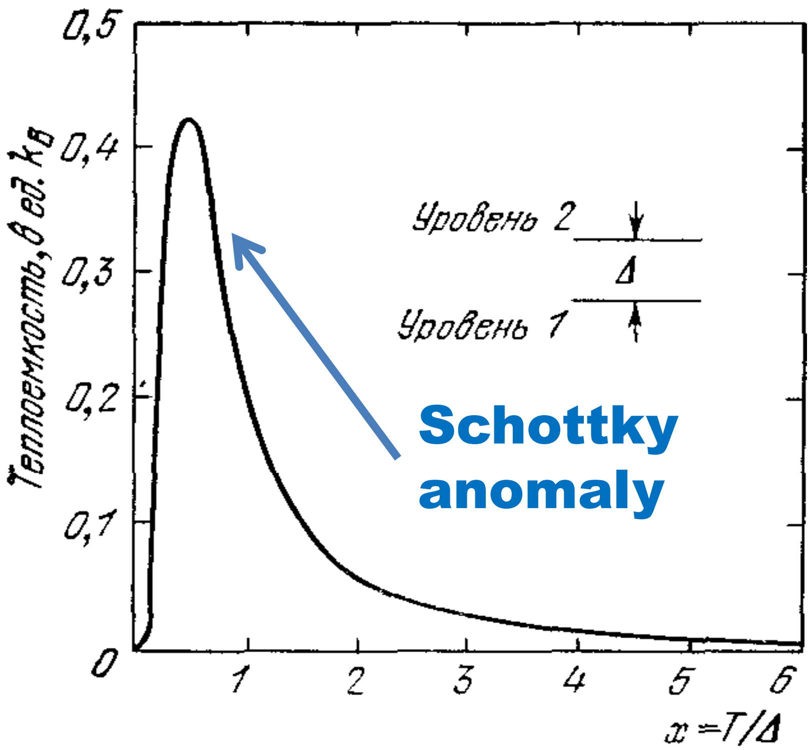
Heat capacity of two-level system (Schottky)

$$C = \left(\frac{\partial E}{\partial T}\right)_{\Delta} = k_B \frac{(\Delta/T)^2 e^{\Delta/T}}{(1+e^{\Delta/T})^2}$$

At high temperature T>>Δ

$$C \approx k_B (\Delta/2T)^2 + \ \ldots$$

Such a term in the heat capacity often allows the detection of low-energy splitting, e.g. nuclear spins or hyperfine splitting (Δ~0.001-0.1K).



Schottky anomaly

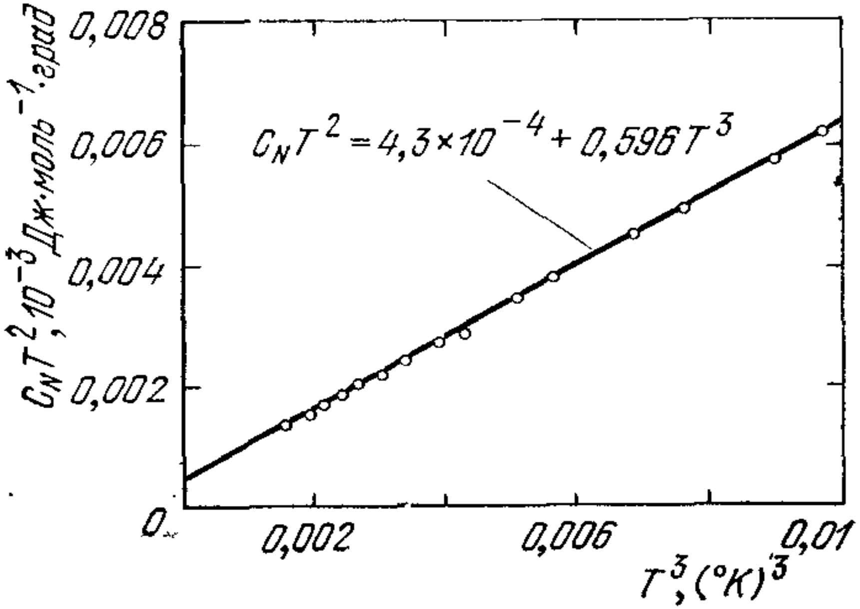


Рис. 15.15. Теплоемкость галлия в нормальном состоянии (при $T < 0{,}21$ °K). Вклады в теплоемкость, обусловленные квадрупольными моментами ядер ($C \sim T^{-2}$) и электронами проводимости ($C_{эл} \sim T$) при очень низких температурах, являются преобладающими. (Из

Curie's law: magnetization of a set of identical ions of angular momentum J.

$$M = \frac{N}{V} g\mu_B J B_J\left(\frac{g\mu_B J H}{k_B T}\right), \quad g = g(J,L,S) \ ,$$

where $g = g(J,L,S)$ and $B_J(x)$ is the Brillouin function

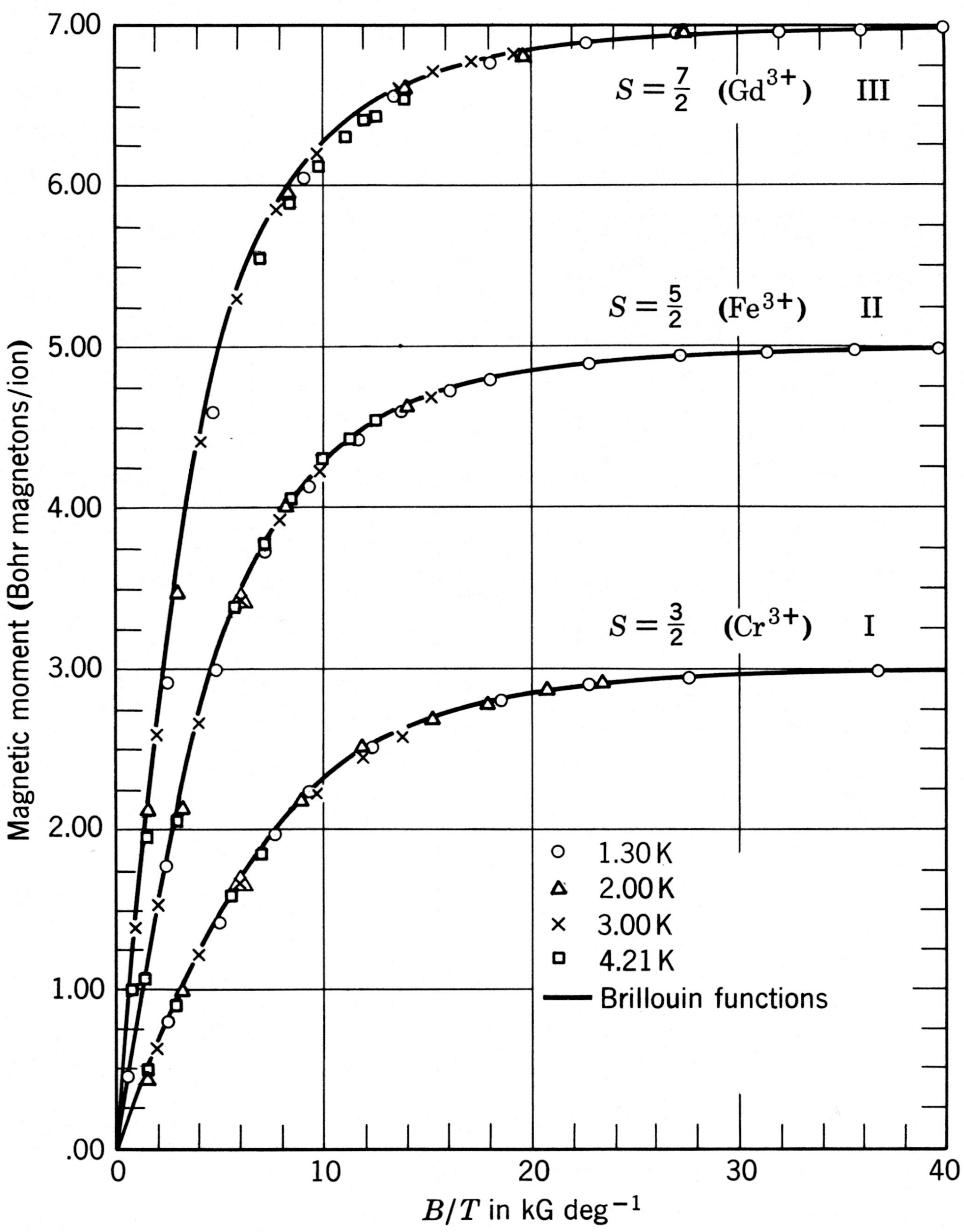
$$B_J(x) = \frac{2J+1}{2J}\coth\frac{2J+1}{2J}x - \frac{1}{2J}\coth\frac{1}{2J}x \ .$$

When $g\mu_B H \ll k_B T$ the series expansion gives Curie's law

$$\chi = \frac{N}{V}\frac{(g\mu_B)^2}{3}\frac{J(J+1)}{k_B T}.$$

Magnetic moment as a function of B/T for spherical samples of (I) potassium chromium alum, (II) ferric ammonium alum, and (III) gadolinium sulfate octahydrate.

[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

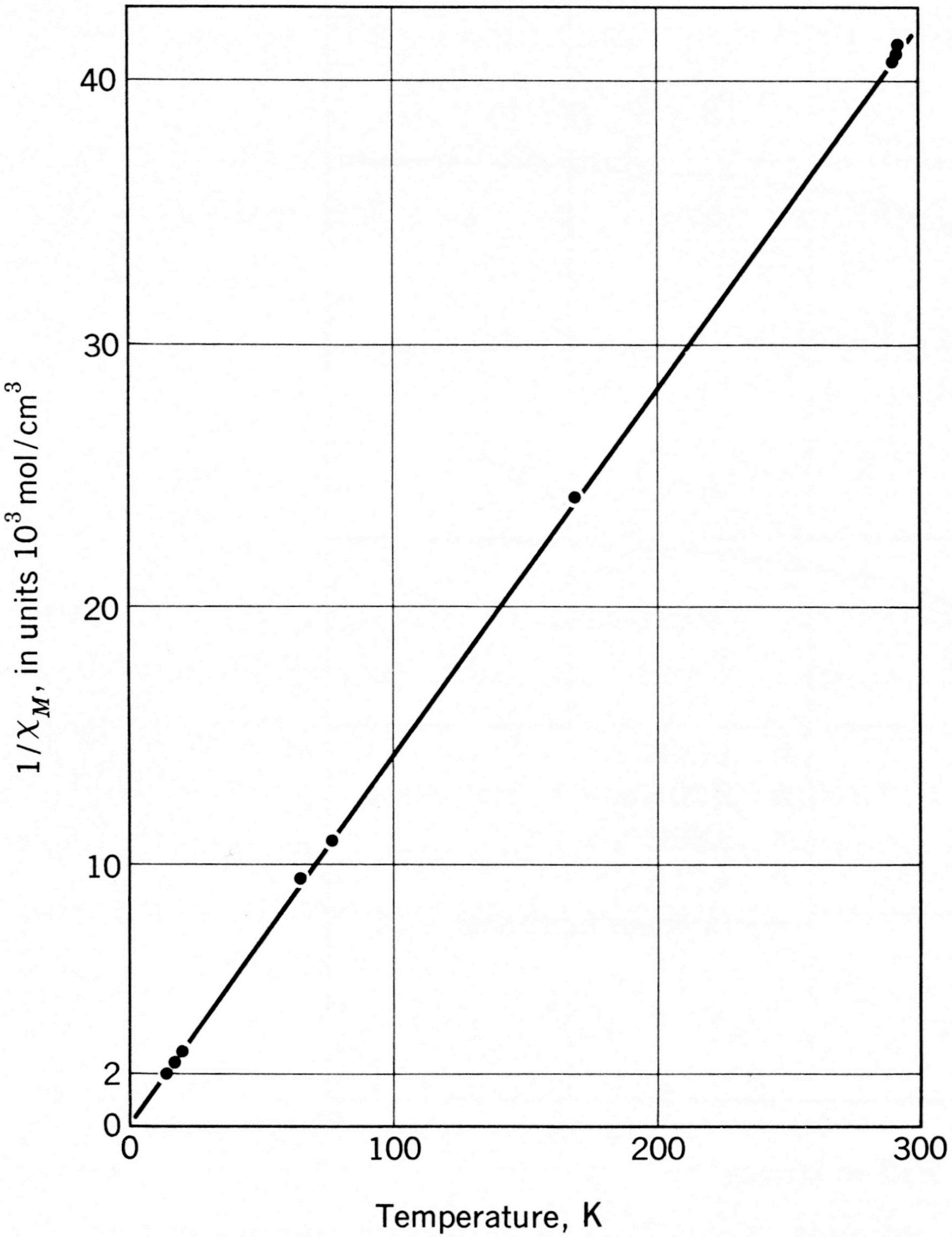


Plot of χ^{-1} vs T for $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$.

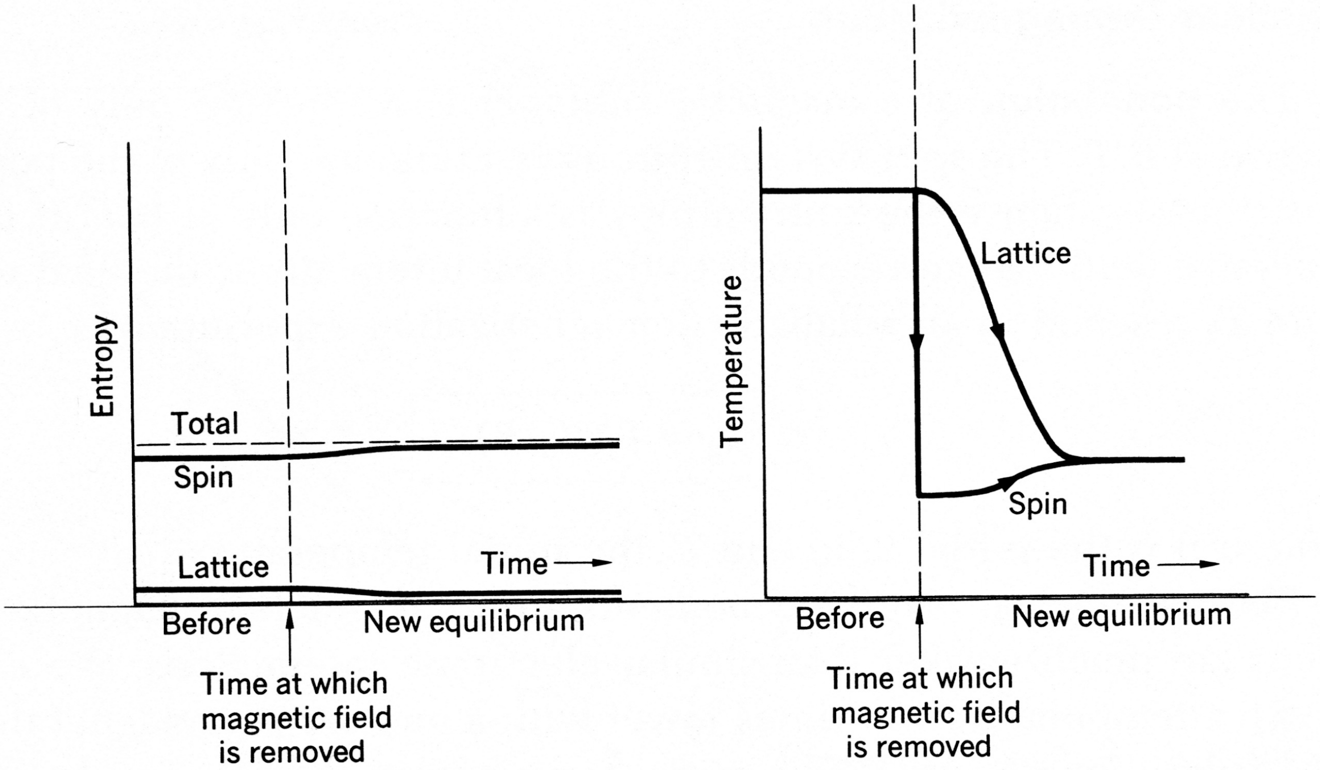
The straight line is the Curie law.

Curie's law: limits of applicability.

[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

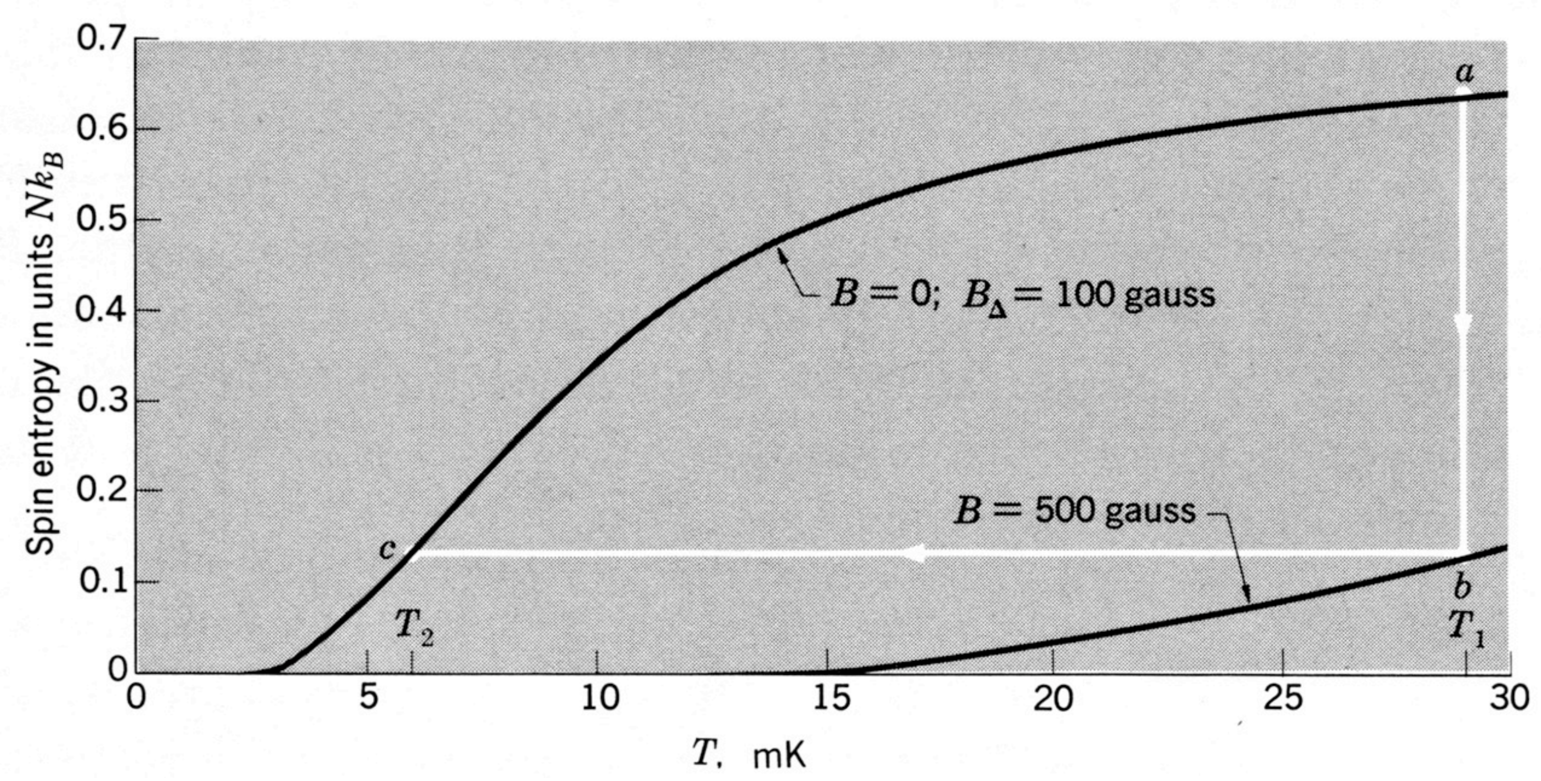


Adiabatic demagnetization: the total entropy is constant. The initial entropy of the lattice should be small compared with the entropy of the spin system.



[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

The spin ½ system is magnetized isothermally along *a–b,* and is then insulated. The external magnetic field is turned off along *b–a.* B_Δ – an internal random magnetic field of 100 G.



[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

The ground state of an ion, Hund's rules

The Hund rules – the way in which electrons occupy orbitals makes certain the following ground state of an ion:

1. The maximum value of the total spin S permitted by the exclusion principle.
2. The maximum value of the orbital angular momentum L compatible with the value of S as per rule no. 1.
3. The total angular momentum J is $\left|L-S\right|$ and $L+S$ when the shell is less than half full and more than half full, respectively. When the shell is exactly half full, rule no. 1 yields $L=0$ and, consequently, $J=S$.

Examples of Hund's rules:

Ce^{3+}: a single f electron with $l=3$ and $s=1/2$. Since the f shell is less than half full, $J=\left|L-S\right|=3-1/2=5/2$.

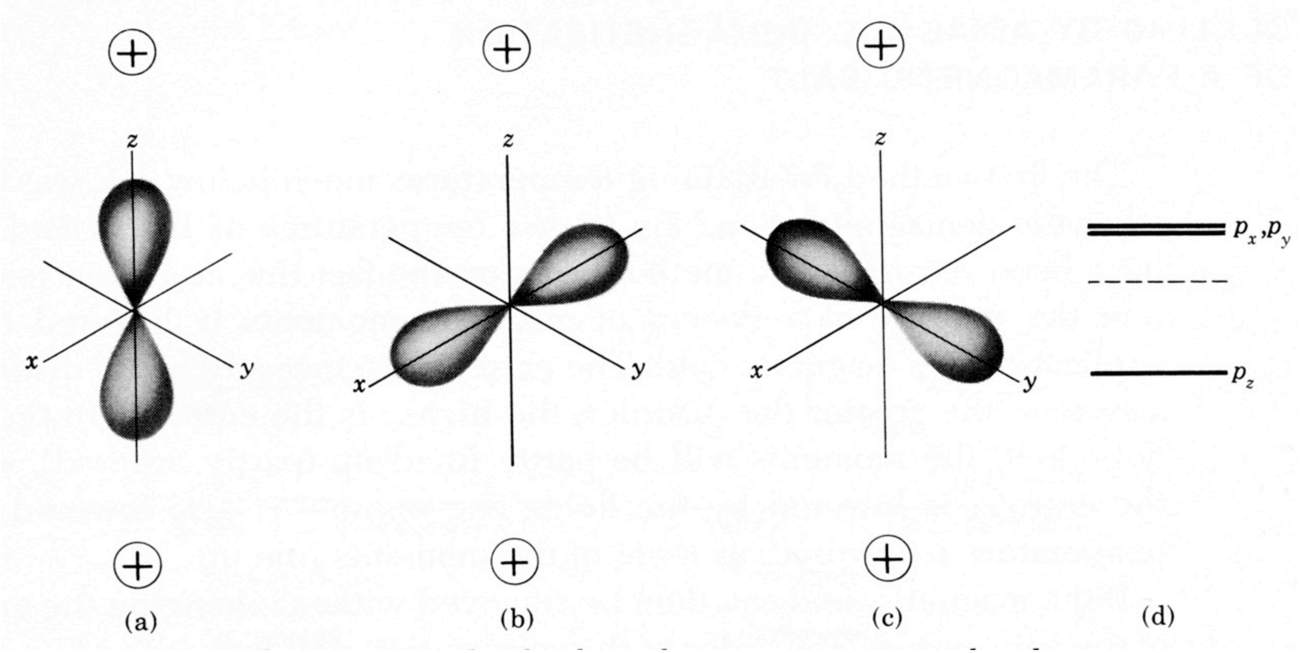
Pr^{3+}: two f electrons. Rule no. 1 (the maximum value of the total spin S permitted by the exclusion principle) yields $S=1/2+1/2=1$. The both f electrons cannot have $m_l=3$ (the Pauli exclusion principle would be violated), therefore, the maximum L consistent with the exclusion principle is only 5.

The resulting value of the total angular momentum J is $\left|L-S\right|=5-1=4$.

Crystal field splitting (results to quenching of magnetic moment)

An atom with $L = 1$ in the uniaxial crystalline electric field of the two positive ions along the z axis.

The states $m_l = \pm 1, 0$ of the free atom are degenerate.

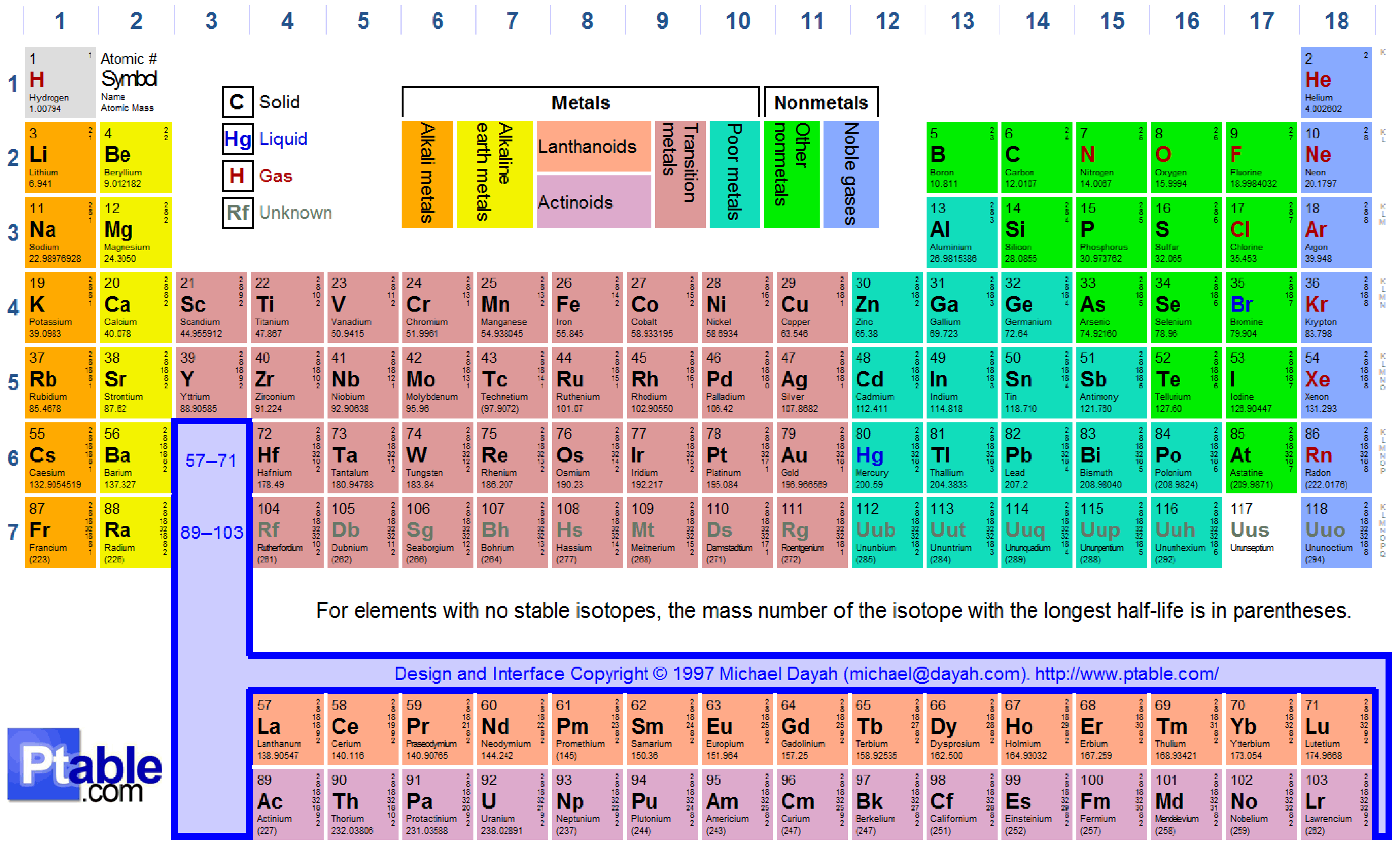


[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

In a crystal the atom has a lower energy when the electron orbital is close to positive ions (a) than when it is oriented between them (b, c).

(d) – The energy levels;
if the symmetry of the electric field is lower than axial, the energies of all three states are different.

Periodic Table of Elements



C Solid
Hg Liquid
H Gas
Rf Unknown

Metals: Alkali metals; Alkaline earth metals; Lanthanoids; Actinoids; Transition metals; Poor metals
Nonmetals: Other nonmetals; Noble gases

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	1 **H** Hydrogen 1.00794 1	Atomic # Symbol Name Atomic Mass																2 **He** Helium 4.002602 2	K
2	3 **Li** Lithium 6.941 2 1	4 **Be** Beryllium 9.012182 2 2											5 **B** Boron 10.811 2 3	6 **C** Carbon 12.0107 2 4	7 **N** Nitrogen 14.0067 2 5	8 **O** Oxygen 15.9994 2 6	9 **F** Fluorine 18.9984032 2 7	10 **Ne** Neon 20.1797 2 8	K L
3	11 **Na** Sodium 22.98976928 2 8 1	12 **Mg** Magnesium 24.3050 2 8 2											13 **Al** Aluminium 26.9815386 2 8 3	14 **Si** Silicon 28.0855 2 8 4	15 **P** Phosphorus 30.973762 2 8 5	16 **S** Sulfur 32.065 2 8 6	17 **Cl** Chlorine 35.453 2 8 7	18 **Ar** Argon 39.948 2 8 8	K L M
4	19 **K** Potassium 39.0983 2 8 8 1	20 **Ca** Calcium 40.078 2 8 8 2	21 **Sc** Scandium 44.955912 2 8 9 2	22 **Ti** Titanium 47.867 2 8 10 2	23 **V** Vanadium 50.9415 2 8 11 2	24 **Cr** Chromium 51.9961 2 8 13 1	25 **Mn** Manganese 54.938045 2 8 13 2	26 **Fe** Iron 55.845 2 8 14 2	27 **Co** Cobalt 58.933195 2 8 15 2	28 **Ni** Nickel 58.6934 2 8 16 2	29 **Cu** Copper 63.546 2 8 18 1	30 **Zn** Zinc 65.38 2 8 18 2	31 **Ga** Gallium 69.723 2 8 18 3	32 **Ge** Germanium 72.64 2 8 18 4	33 **As** Arsenic 74.92160 2 8 18 5	34 **Se** Selenium 78.96 2 8 18 6	35 **Br** Bromine 79.904 2 8 18 7	36 **Kr** Krypton 83.798 2 8 18 8	K L M N
5	37 **Rb** Rubidium 85.4678 2 8 18 8 1	38 **Sr** Strontium 87.62 2 8 18 8 2	39 **Y** Yttrium 88.90585 2 8 18 9 2	40 **Zr** Zirconium 91.224 2 8 18 10 2	41 **Nb** Niobium 92.90638 2 8 18 12 1	42 **Mo** Molybdenum 95.96 2 8 18 13 1	43 **Tc** Technetium (97.9072) 2 8 18 14 1	44 **Ru** Ruthenium 101.07 2 8 18 15 1	45 **Rh** Rhodium 102.90550 2 8 18 16 1	46 **Pd** Palladium 106.42 2 8 18 18 0	47 **Ag** Silver 107.8682 2 8 18 18 1	48 **Cd** Cadmium 112.411 2 8 18 18 2	49 **In** Indium 114.818 2 8 18 18 3	50 **Sn** Tin 118.710 2 8 18 18 4	51 **Sb** Antimony 121.760 2 8 18 18 5	52 **Te** Tellurium 127.60 2 8 18 18 6	53 **I** Iodine 126.90447 2 8 18 18 7	54 **Xe** Xenon 131.293 2 8 18 18 8	K L M N O
6	55 **Cs** Caesium 132.9054519 2 8 18 18 8 1	56 **Ba** Barium 137.327 2 8 18 18 8 2	57–71	72 **Hf** Hafnium 178.49 2 8 18 32 10 2	73 **Ta** Tantalum 180.94788 2 8 18 32 11 2	74 **W** Tungsten 183.84 2 8 18 32 12 2	75 **Re** Rhenium 186.207 2 8 18 32 13 2	76 **Os** Osmium 190.23 2 8 18 32 14 2	77 **Ir** Iridium 192.217 2 8 18 32 15 2	78 **Pt** Platinum 195.084 2 8 18 32 17 1	79 **Au** Gold 196.966569 2 8 18 32 18 1	80 **Hg** Mercury 200.59 2 8 18 32 18 2	81 **Tl** Thallium 204.3833 2 8 18 32 18 3	82 **Pb** Lead 207.2 2 8 18 32 18 4	83 **Bi** Bismuth 208.98040 2 8 18 32 18 5	84 **Po** Polonium (208.9824) 2 8 18 32 18 6	85 **At** Astatine (209.9871) 2 8 18 32 18 7	86 **Rn** Radon (222.0176) 2 8 18 32 18 8	K L M N O P
7	87 **Fr** Francium (223) 2 8 18 32 18 8 1	88 **Ra** Radium (226) 2 8 18 32 18 8 2	89–103	104 **Rf** Rutherfordium (261) 2 8 18 32 32 10 2	105 **Db** Dubnium (262) 2 8 18 32 32 11 2	106 **Sg** Seaborgium (266) 2 8 18 32 32 12 2	107 **Bh** Bohrium (264) 2 8 18 32 32 13 2	108 **Hs** Hassium (277) 2 8 18 32 32 14 2	109 **Mt** Meitnerium (268) 2 8 18 32 32 15 2	110 **Ds** Darmstadtium (271) 2 8 18 32 32 17 1	111 **Rg** Roentgenium (272) 2 8 18 32 32 18 1	112 **Uub** Ununbium (285) 2 8 18 32 32 18 2	113 **Uut** Ununtrium (284) 2 8 18 32 32 18 3	114 **Uuq** Ununquadium (289) 2 8 18 32 32 18 4	115 **Uup** Ununpentium (288) 2 8 18 32 32 18 5	116 **Uuh** Ununhexium (292) 2 8 18 32 32 18 6	117 **Uus** Ununseptium	118 **Uuo** Ununoctium (294) 2 8 18 32 32 18 8	K L M N O P Q

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

57 **La** Lanthanum 138.90547 2 8 18 18 9 2	58 **Ce** Cerium 140.116 2 8 18 19 9 2	59 **Pr** Praseodymium 140.90765 2 8 18 21 8 2	60 **Nd** Neodymium 144.242 2 8 18 22 8 2	61 **Pm** Promethium (145) 2 8 18 23 8 2	62 **Sm** Samarium 150.36 2 8 18 24 8 2	63 **Eu** Europium 151.964 2 8 18 25 8 2	64 **Gd** Gadolinium 157.25 2 8 18 25 9 2	65 **Tb** Terbium 158.92535 2 8 18 27 8 2	66 **Dy** Dysprosium 162.500 2 8 18 28 8 2	67 **Ho** Holmium 164.93032 2 8 18 29 8 2	68 **Er** Erbium 167.259 2 8 18 30 8 2	69 **Tm** Thulium 168.93421 2 8 18 31 8 2	70 **Yb** Ytterbium 173.054 2 8 18 32 8 2	71 **Lu** Lutetium 174.9668 2 8 18 32 9 2
89 **Ac** Actinium (227) 2 8 18 32 18 9 2	90 **Th** Thorium 232.03806 2 8 18 32 18 10 2	91 **Pa** Protactinium 231.03588 2 8 18 32 20 9 2	92 **U** Uranium 238.02891 2 8 18 32 21 9 2	93 **Np** Neptunium (237) 2 8 18 32 22 9 2	94 **Pu** Plutonium (244) 2 8 18 32 24 8 2	95 **Am** Americium (243) 2 8 18 32 25 8 2	96 **Cm** Curium (247) 2 8 18 32 25 9 2	97 **Bk** Berkelium (247) 2 8 18 32 27 8 2	98 **Cf** Californium (251) 2 8 18 32 28 8 2	99 **Es** Einsteinium (252) 2 8 18 32 29 8 2	100 **Fm** Fermium (257) 2 8 18 32 30 8 2	101 **Md** Mendelevium (258) 2 8 18 32 31 8 2	102 **No** Nobelium (259) 2 8 18 32 32 8 2	103 **Lr** Lawrencium (262) 2 8 18 32 32 9 2

Ptable.com

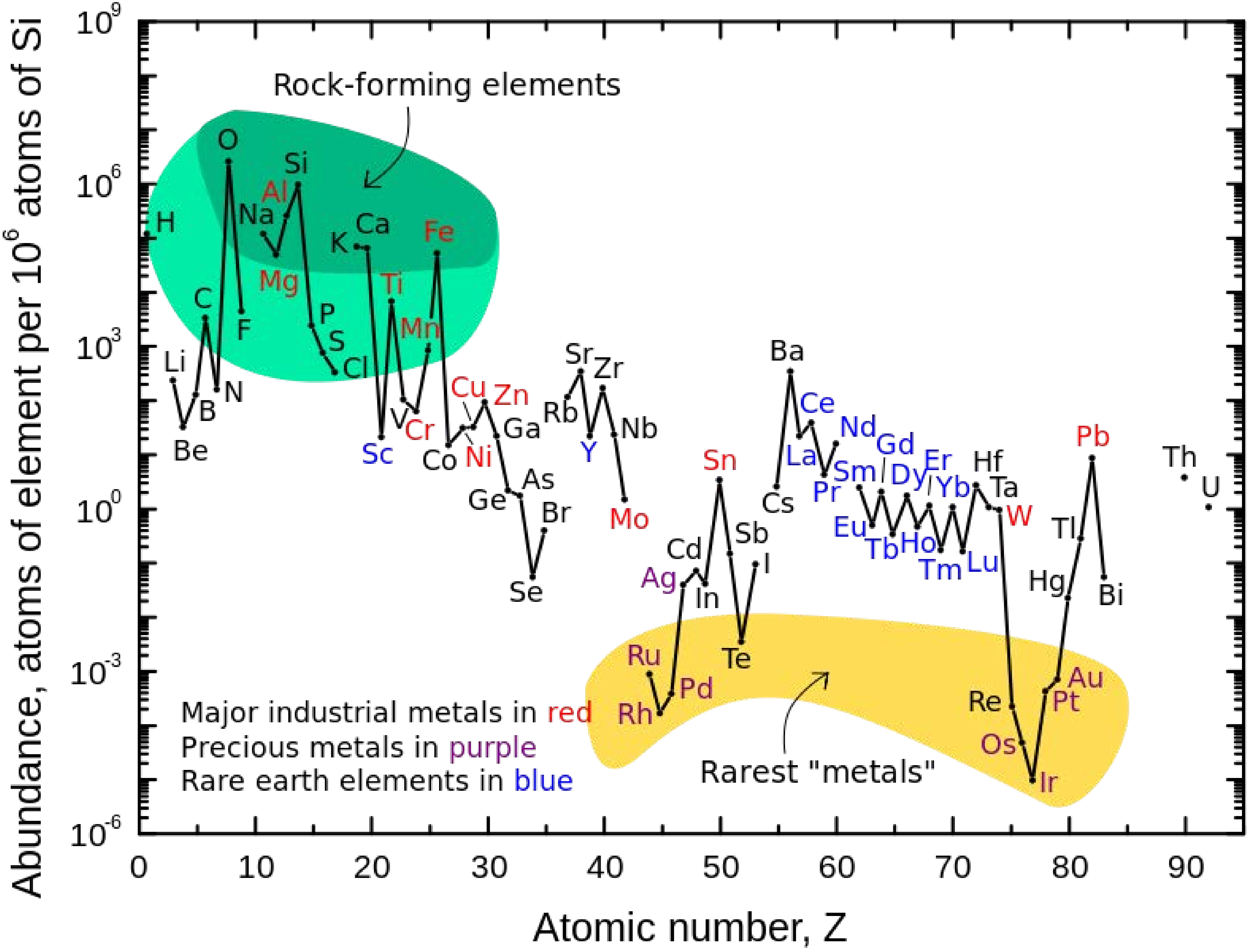
Rare earth elements (from Wikipedia)

A rare earth element (REE) or rare earth metal (REM), is one of a set of seventeen chemical elements in the periodic table, specifically the fifteen lanthanides, as well as scandium and yttrium.[2] Scandium and yttrium are considered rare earth elements because they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties.

Rare earth elements are cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lanthanum (La), lutetium (Lu), neodymium (Nd), praseodymium (Pr), promethium (Pm), samarium (Sm), scandium (Sc), terbium (Tb), thulium (Tm), ytterbium (Yb) and yttrium (Y).

Despite their name, rare earth elements are – with the exception of the radioactive promethium – relatively plentiful in Earth's crust, with cerium being the 25th most abundant element at 68 parts per million, or as abundant as copper. They are not especially rare, but they tend to occur together in nature and are difficult to separate from one another. However, because of their geochemical properties, rare earth elements are typically dispersed and not often found concentrated as rare earth minerals in economically exploitable ore deposits.[3] The first such mineral discovered was gadolinite, a mineral composed of cerium, yttrium, iron, silicon and other elements. This mineral was extracted from a mine in the village of Ytterby in Sweden; four of the rare earth elements bear names derived from this single location.

Rare-earth elements have large own magnetic moment because of partially filled atomic f-electron orbitals.



Abundance, atoms of element per 10^6 atoms of Si
Atomic number, Z
10^9
10^6
10^3
10^0
10^{-3}
10^{-6}
0
10
20
30
40
50
60
70
80
90
Rock-forming elements
Rarest "metals"
Major industrial metals in red
Precious metals in purple
Rare earth elements in blue
H
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

Rare-earth ions

The ions of the rare-earth elements have similar chemical properties.

The rare-earth ions display complex magnetic properties.

The trivalent ions are chemically similar. This is because the configurations of the outermost electron shells are the same ($5s^2 5p^6$), similar to neutral Xe.

In lanthanum the $4f$ shell is empty. In cerium, there is one $4f$ electron. The number of $4f$ electrons increases through the rare-earth group.

The configurations of ytterbium and lutetium are $4f^{13}$ at $4f^{14}$, respectively. The latter shell is filled.

Lanthanide contraction – the radii of the trivalent ions contract across the group from 1.11 Å (Ce) to 0.94 Å (Yb).

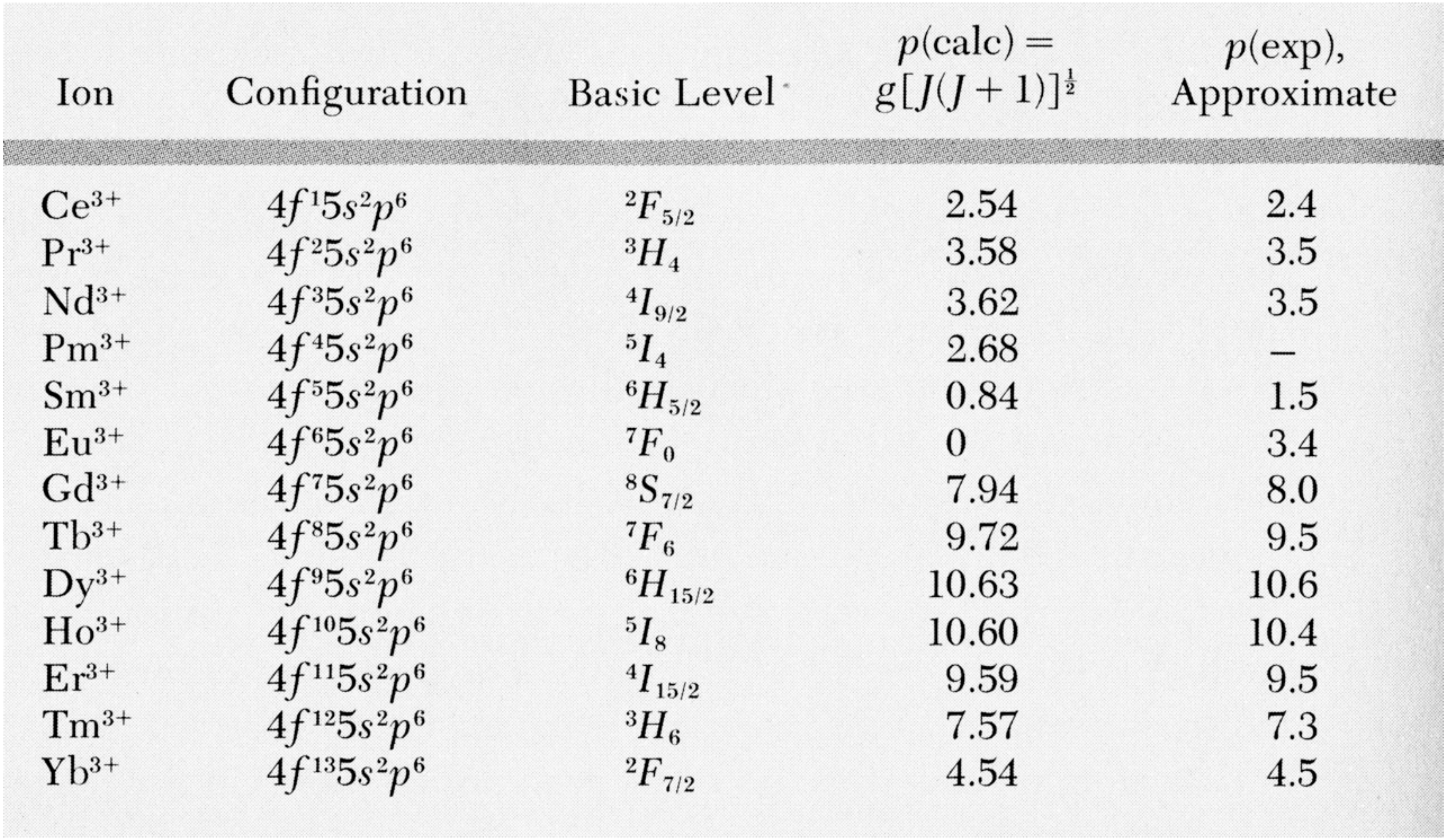
The magnetic behavior is determined by the number of $4f$ electrons in the inner shell (radius about 0.3 Å).

Interestingly, the $4f$ cores retain its atomic properties.

A $(2J+1)$ - fold degenerate ground state (a magnetic field lifts the degeneracy); higher energy states – neglected.

Many rare-earth ions satisfy these assumptions.

Effective magneton numbers p for trivalent lanthanide ions



Ion	Configuration	Basic Level	p(calc) = $g[J(J+1)]^{\frac{1}{2}}$	p(exp), Approximate
Ce^{3+}	$4f^1 5s^2 p^6$	$^2F_{5/2}$	2.54	2.4
Pr^{3+}	$4f^2 5s^2 p^6$	$^3H_4$	3.58	3.5
Nd^{3+}	$4f^3 5s^2 p^6$	$^4I_{9/2}$	3.62	3.5
Pm^{3+}	$4f^4 5s^2 p^6$	$^5I_4$	2.68	–
Sm^{3+}	$4f^5 5s^2 p^6$	$^6H_{5/2}$	0.84	1.5
Eu^{3+}	$4f^6 5s^2 p^6$	$^7F_0$	0	3.4
Gd^{3+}	$4f^7 5s^2 p^6$	$^8S_{7/2}$	7.94	8.0
Tb^{3+}	$4f^8 5s^2 p^6$	$^7F_6$	9.72	9.5
Dy^{3+}	$4f^9 5s^2 p^6$	$^6H_{15/2}$	10.63	10.6
Ho^{3+}	$4f^{10} 5s^2 p^6$	$^5I_8$	10.60	10.4
Er^{3+}	$4f^{11} 5s^2 p^6$	$^4I_{15/2}$	9.59	9.5
Tm^{3+}	$4f^{12} 5s^2 p^6$	$^3H_6$	7.57	7.3
Yb^{3+}	$4f^{13} 5s^2 p^6$	$^2F_{7/2}$	4.54	4.5

[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

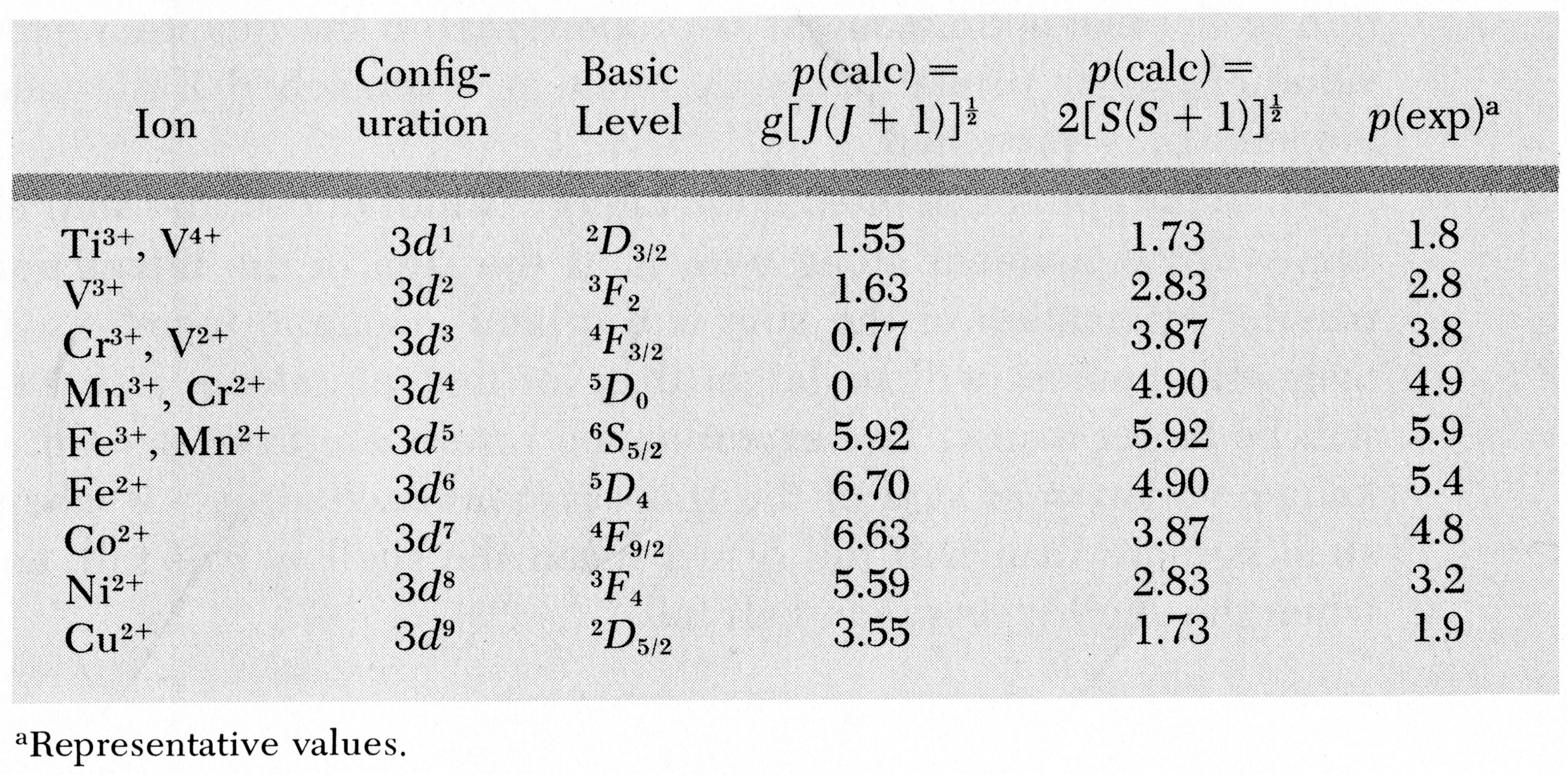
The calculated magneton numbers $p_{\text{calc}} = g[J(J+1)]^{1/2}$ are obtained using g values from the Landé result.

The ground state – Hund's theory of spectral terms.

The discrepancy between p_{exp} and p_{calc} for Eu^{3+} and Sm^{3+} – the high-energy states of the $L-S$ multiplet must be taken into account.

The quenching of the orbital angular momentum

Effective magneton numbers for iron group ions



Ion	Config-uration	Basic Level	$p(\text{calc}) = g[J(J+1)]^{\frac{1}{2}}$	$p(\text{calc}) = 2[S(S+1)]^{\frac{1}{2}}$	$p(\text{exp})$[a]
Ti^{3+}, V^{4+}	$3d^1$	$^2D_{3/2}$	1.55	1.73	1.8
V^{3+}	$3d^2$	$^3F_2$	1.63	2.83	2.8
Cr^{3+}, V^{2+}	$3d^3$	$^4F_{3/2}$	0.77	3.87	3.8
Mn^{3+}, Cr^{2+}	$3d^4$	$^5D_0$	0	4.90	4.9
Fe^{3+}, Mn^{2+}	$3d^5$	$^6S_{5/2}$	5.92	5.92	5.9
Fe^{2+}	$3d^6$	$^5D_4$	6.70	4.90	5.4
Co^{2+}	$3d^7$	$^4F_{9/2}$	6.63	3.87	4.8
Ni^{2+}	$3d^8$	$^3F_4$	5.59	2.83	3.2
Cu^{2+}	$3d^9$	$^2D_{5/2}$	3.55	1.73	1.9

[a] Representative values.

[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

The experimental magneton numbers for salts of the iron group are in poor agreement with theoretical expectations.

Instead, the experimental values often agree well with magneton numbers $p = 2[S(S+1)]^{1/2}$, i.e., calculated as if the orbital moment were reduced to zero.

The orbital moments are “quenched”.

The van Vleck arguments.

The Kramers theorem

The energy levels of a system with an odd number of electrons remain at least doubly degenerate in the presence of electric fields only (no magnetic fields).

The Kramers theorem is a consequence of the time reversal invariance of the electric field.

The rare-earth ions are classified as Kramers and non-Kramers ions depending on whether the number of $4f$ electrons is odd or even, respectively.

Due to the crystal field effects, the ground state of non-Kramers ions (Pr^{3+}, Tb^{3+}, Tm^{3+}, Ho^{3+}) is a singlet.

The Jahn–Teller effect

Molecular distortions due to a degenerate electronic ground state.

Any non-linear molecule with a degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy.

This is because the distortion lowers the overall energy.

The Jahn–Teller effect is often encountered in octahedral complexes of the transition metals.

Magnetism of the free-electron gas

- Pauli paramagnetism
- Landau levels
- Landau diamagnetism
- The Aharonov–Bohm effect
- The integer quantum Hall effect

Note: Pauli paramagnetism, Landau levels and Landau diamagnetism are discussed in “Theory of metals”

The Aharonov–Bohm effect

Y. Aharonov and D. Bohm, "Significance of electromagnetic potentials in quantum theory", Phys. Rev. **115**, 485 (1959).

N. Osakabe *et al.*, "Experimental confirmation of Aharonov-Bohm effect using a toroidal magnetic field confined by a superconductor", Phys. Rev. A **34**, 815 (1986).

The electromagnetic potential consists of the electric potential φ and magnetic vector potential $\mathbf{A}$.

The related electric and magnetic fields are:

$$\mathbf{E} = -\nabla\varphi - \frac{\partial \mathbf{A}}{\partial t} \quad \text{(SI)} \qquad\qquad \mathbf{E} = -\nabla\varphi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \quad \text{(cgs)}$$

$$\mathbf{B} = \nabla \times \mathbf{A}$$

Aharonov and Bohm predicted that an electron travelling along a closed curve C in an area with zero magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$, but non-zero magnetic vector potential $\mathbf{A}$, acquires a phase shift

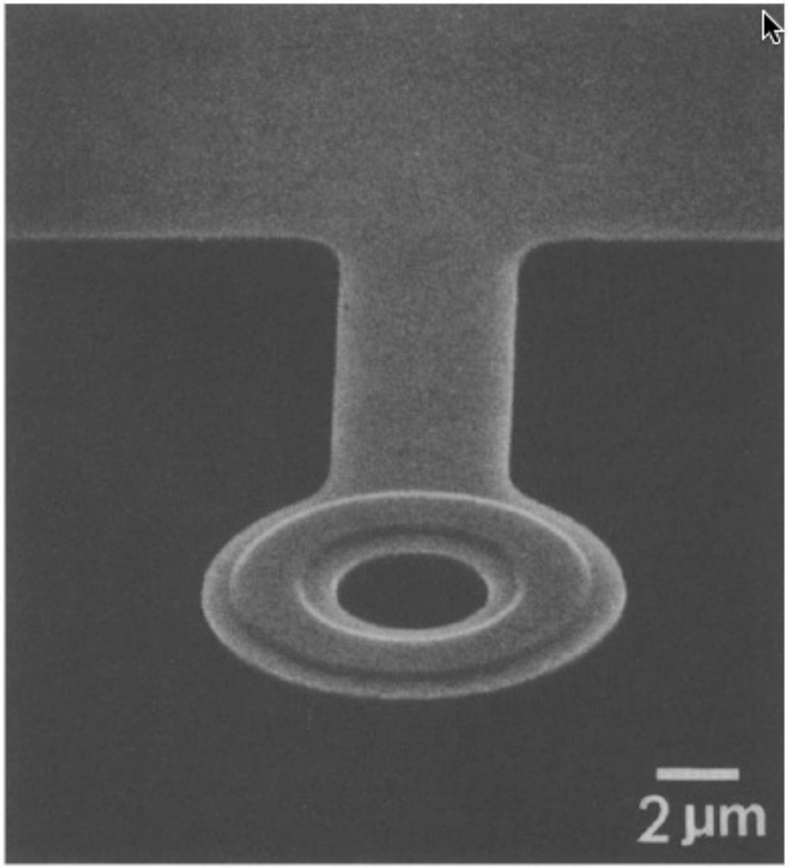
$$\Delta\phi = \frac{e}{\hbar} \oint_C \mathbf{A} \cdot d\mathbf{x} \quad . \qquad \text{(SI)}$$

The magnetic vector potential $\mathbf{A}$ is an example of a gauge field.

Therefore, the Aharonov–Bohm effect demonstrates that electromagnetism conforms to the theory of gauge fields.

Example: a toroidal solenoid is such a special current configuration – its magnetic induction is confined to the solenoid; outside the solenoid $\mathbf{A} \neq 0, \quad \mathbf{B} = \nabla \times \mathbf{A} = 0.$

Scanning electron micrograph of toroidal magnet covered by a superconductor:



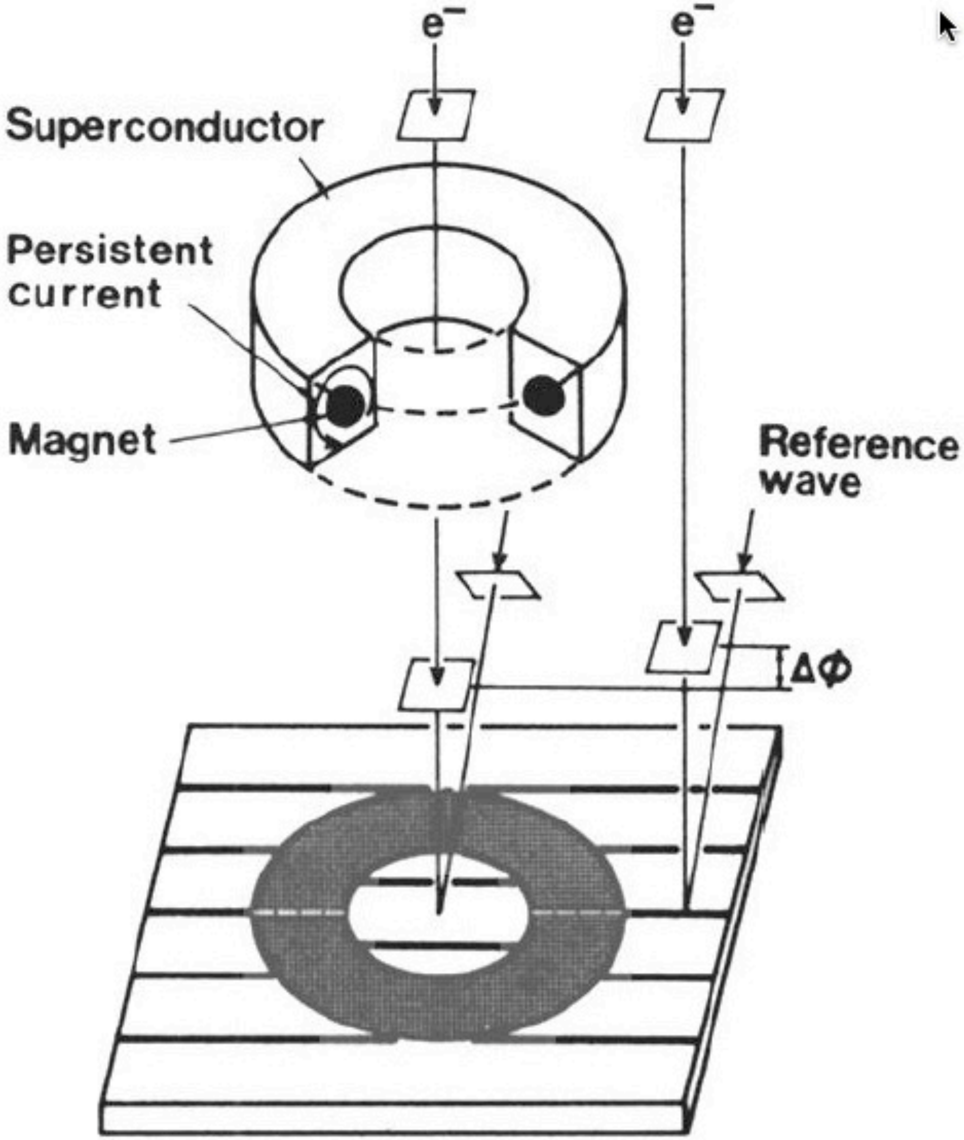
[from N. Osakabe *et al.*, Phys. Rev. A **34**, 815 (1986)]

Electrons travelling from point 1 to point 2 along two different routes will acquire a phase difference $\Delta\varphi = q\Phi/\hbar$, where Φ is the magnetic flux through the contour comprise the two routes.

In quantum mechanics, a particle can travel between two points along various routes.

The phase difference can be observed if a solenoid is placed between the slits of a double-slit-type experiment.

Outside the solenoid $\mathbf{A} \neq 0$, and the relative phase of particles passing through different slits is altered by turning on or off the solenoid current, leading to a shift of the interference fringes on the observation screen.



[from N. Osakabe *et al.*, Phys. Rev. A **34**, 815 (1986)]

Integer quantum Hall effect

First reported by von Klitzing, Dorda, and Pepper (1980).

Experiments – a two-dimensional electron gas formed by an inversion layer at a Si/SiO$_2$ interface.

At low temperatures and at high magnetic fields, the transverse conductivity σ_{xy} was quantized, with values

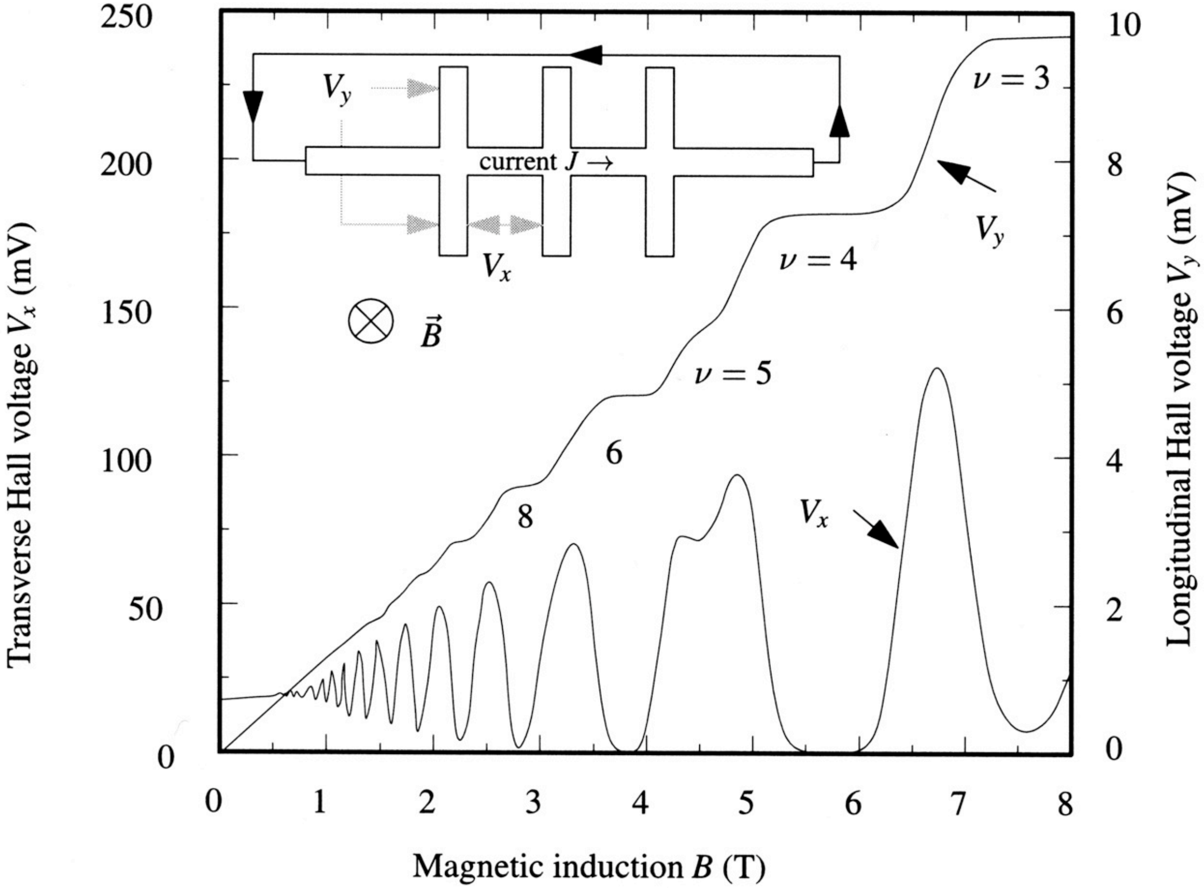
$$\sigma_{xy} = \frac{\nu}{R_H},$$

where ν is an integer and

$$R_H = \frac{h}{e^2} = 25\,813\ \Omega\ .$$

Experiment – a current $I = 28\,\mu\mathrm{A}$ runs in the upper loop.

The current between the vertical terminals is much smaller.



[from M. P. Marder, *Condensed Matter Physics* (Wiley, 2000)]

The plateaus are separated by steep rises correspond to Hall resistances of R_H / ν.

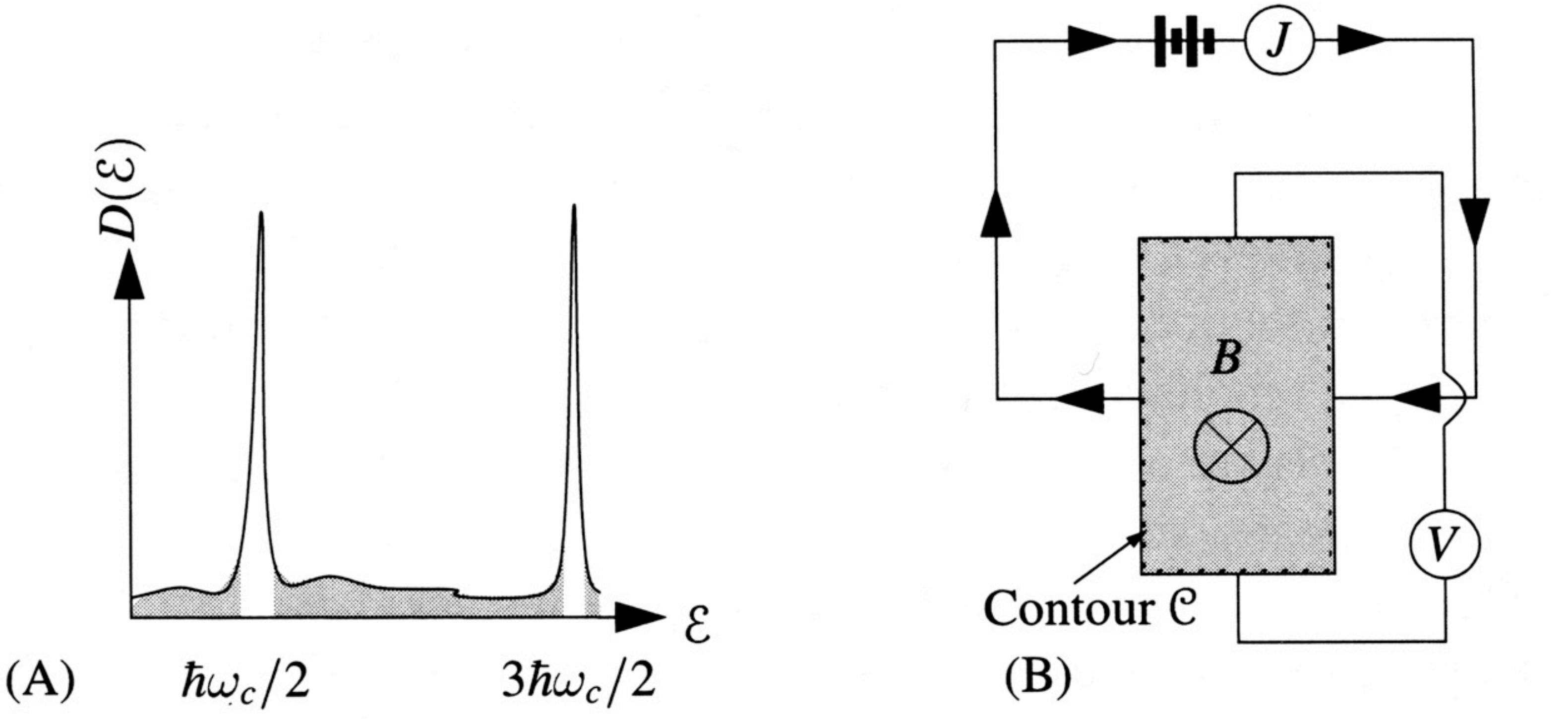
The value of σ_{xy} in the plateau coincides with its theoretical value to at least 1 part in 10^8, and reproducible to 1 part in 10^{10}.

The quantum Hall effect is currently employed in the international standards of electrical resistance.

Early explanation: current loops and moments.

(A) A quantum Hall device – DOS contains a lot of states at $\hbar\omega_c(\nu+1/2)$, and localized states in between these energies.

(B) The QHE – 2D electron gas in a high magnetic field $\mathbf{B}$.



[from M. P. Marder, *Condensed Matter Physics* (Wiley, 2000)]