## Lecture 11: *d*-block metals and magnetism

- Oxidation states in *d*-block metal compounds
- Ligand field theory
  - Jahn-Teller distortion
- Magnetism
  - Magnetic moments
  - Susceptibility
  - Temperature dependence





Figures: AJK

#### d-block metals

V•T•E						Р	eriodic	table of	electro	negativ	ity by P	auling s	cale					
	ightarrow Atomic radius decreases $ ightarrow$ Ionization energy increases $ ightarrow$ Electronegativity increases $ ightarrow$																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Group – ↓ Period	<b>&gt;</b>																	
1	H 2.20		Ma	any ox	idatio	on stat	tes, ve	ery ric	h chei	mistry	,							He
2	Li 0.98	Be 1.57	Ma	any m	agnet	ic con	npoun	ds (ui	npaire	d d-e	lectro	ns)	B 2.04	C 2.55	N 3.04	0 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31	Ma	Many colorful compounds due to <i>d-d</i> transitions						s	Al 1.61	Si 1.90	P 2.19	S 2.58	CI 3.16	Ar		
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	<mark>Sn</mark> 1.96	Sb 2.05	Te 2.1	ا 2.66	Xe 2.60
6	<mark>Cs</mark> 0.79	Ba 0.89	*	Hf 1.3	Та 1.5	W 2.36	Re 1.9	Os 2.2	lr 2.20	Pt 2.28	Au 2.54	Hg 2.00	TI 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	FI	Uup	Lv	Uus	Uuo
													· · · ·					
		*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27	
		**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3	

Figure: Wikipedia

#### Elemental *d*-block metals

21	22	23	24	25	26	27	28	29	30	Figure: Wikipedia
Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	
HCP	HCP	BCC	BCC	BCC	BCC	HCP	FCC	FCC	HCP	
39	40	41	42	43	44	45	46	47	48	
Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	
HCP	НСР	BCC	BCC	HCP	HCP	FCC	FCC	FCC	НСР	
	72	73	74	75	76	77	78	79	80	
	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	
	HCP	BCC/TETR	BCC	HCP	HCP	FCC	FCC	FCC	RHO	
	104	105	106	107	108	109	110	111	112	
	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	
	[HCP]	[BCC]	[BCC]	[HCP]	[HCP]	[FCC]	[BCC]	[BCC]	[HCP]	













Cu (fcc)

Fe (bcc)

#### Electron configurations (3d metals)

Ref: chem.libretexts.org

Element Name and Symbol	Atomic Number	Common Oxidation States	Е	lectron Configuration (for the free atom
Scandium (Sc)	21	+3	Sc: [Ar] 4s <sup>2</sup> 3d <sup>1</sup>	Sc: [Ar] 1 1
Titanium (Ti)	22	+4	Ti: [Ar] 4s <sup>2</sup> 3d <sup>2</sup>	Ti: [Ar] 1 1
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] 4s <sup>2</sup> 3d <sup>3</sup>	V: [Ar] $1_{4s}$ 1 1 1
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] 4s <sup>1</sup> 3d <sup>5</sup>	Cr: [Ar] $1_{4s}$ $1_{1}$ $1_{1}$ $1_{3d}$
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] 4s <sup>2</sup> 3d <sup>5</sup>	$Mn: [Ar] \stackrel{1}{\underset{4s}{\amalg}} \stackrel{1}{\underset{3d}{\amalg}} \stackrel{1}{\underset{3d}{\amalg}} \stackrel{1}{\underset{3d}{\amalg}} \stackrel{1}{\underset{3d}{\amalg}} \stackrel{1}{\underset{3d}{\amalg}} \stackrel{1}{\underset{3d}{\amalg}}$
Iron (Fe)	26	+2, +3	Fe: [Ar] 4s <sup>2</sup> 3d <sup>6</sup>	Fe: [Ar] $1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 $
Cobalt (Co)	27	+2,+3	Co: [Ar] 4s <sup>2</sup> 3d <sup>7</sup>	Co: [Ar] $1_{4s}$ $1_{4s}$ $1_{3d}$ $1_{3d}$
Nickel (Ni)	28	+2	Ni: [Ar] 4s <sup>2</sup> 3d <sup>8</sup>	Ni: [Ar] 1 1 1 1 1 1
Copper (Cu)	29	+1,+2	Cu: [Ar] 4s <sup>1</sup> 3d <sup>10</sup>	Cu: [Ar] $1$ $1$ $1$ $1$ $1$ $1$ $1$ $1$ $1$ $1$
Zinc (Zn)	30	+2	Zn: [Ar] 4s <sup>2</sup> 3d <sup>10</sup>	Zn: [Ar] 1 1 1 1 1 1

In compounds where the metal is oxidized, consider that it only has *d*-electrons left <sub>4</sub>

#### Oxidation state (1)

- **Oxidation state** is a key concept for understanding the chemistry of *d*-block metals
- Indicates the degree of oxidation (*loss of electrons*) of an atom in a compound
- Let's see two iron chlorides as an example
- Electronegativities: Fe = 1.83, Cl = 3.16
- FeCl<sub>2</sub>
  - Formally Fe<sup>2+</sup> and 2 Cl<sup>-</sup>
  - $Fe^{2+} = Fe(II)$
  - Iron(II) chloride
- FeCl<sub>3</sub>
  - Formally Fe<sup>3+</sup> and 3 Cl<sup>-</sup>
  - $Fe^{3+} = Fe(III)$
  - Iron(III) chloride

One layer in FeCl<sub>3</sub> (*R*-3) 2-coordinate Cl



One layer in FeCl<sub>2</sub> (*R*-3*m*) 3-coordinate Cl

Both structures composed of 2D layers Top view along c-axis

### Oxidation state (2)

- The exact definition of an oxidation state is actually still debated
- IUPAC Technical Report *Toward a comprehensive definition of oxidation state:* 
  - P. Karen et al. Pure Appl. Chem. 2014, 86, 1017–1081
  - "The oxidation state of a bonded atom equals its charge after ionic approximation"
  - "In the ionic approximation, the atom that contributes more to the bonding molecular orbital (MO) becomes negative"
- The sum of oxidation states in a compound must be zero!
- The oxidation state of an atom in a compound is a useful concept, but it is really just a concept
- In particular, the formal charges such as Fe<sup>2+</sup> and Cl<sup>-</sup> in FeCl<sub>2</sub> are not real!

#### Known oxidation states for *d*-block



4 <i>d</i>				Y	+1	+2	+3					
		-2		Zr	+1	+2	+3	+4				
	-3		-1	Nb	+1	+2	+3	+4	+5			
-4		-2	-1	Мо	+1	+2	+3	+4	+5	+6		
	-3		-1	Тс	+1	+2	+3	+4	+5	+6	+7	
-4		-2		Ru	+1	+2	+3	+4	+5	+6	+7	+8
	-3		-1	Rh	+1	+2	+3	+4	+5	+6		
				Pd	+1	+2	+3	+4	+5	+6		
		-2	-1	Ag	+1	+2	+3	+4				
		-2		Cd	+1	+2						

*d*-block metals show a larger number of oxidation states in comparison to main group elements or *f*-block elements

#### The most common oxidation states are shown in bold

Ref: <u>https://en.wikipedia.org/wiki/</u> List of oxidation states of the elements (based on Greenwood and Earnshaw + recent literature)

5 <b>d</b>		-2		Hf	+1	+2	+3	+4						
	-3		-1	Та	+1	+2	+3	+4	+5					
-4		-2	-1	W	+1	+2	+3	+4	+5	+6				
	-3		-1	Re	+1	+2	+3	+4	+5	+6	+7			
-4		-2	-1	Os	+1	+2	+3	+4	+5	+6	+7	+8		
	-3		-1	Ir	+1	+2	+3	+4	+5	+6	+7	+8	+9	
	-3	-2	-1	Pt	+1	+2	+3	+4	+5	+6			Yea	ar
	-3	-2	-1	Au	+1	+2	+3		+5				20	14
		-2		Hg	+1	+2								-

#### LETTER Nature **2014**, *514*, 475.

#### Identification of an iridium-containing compound with a formal oxidation state of IX

Guanjun Wang<sup>1</sup>, Mingfei Zhou<sup>1</sup>, James T. Goettel<sup>2</sup>, Gary J. Schrobilgen<sup>2</sup>, Jing Su<sup>3</sup>, Jun Li<sup>3</sup>, Tobias Schlöder<sup>4</sup> & Sebastian Riedel<sup>4,5</sup>

One of the most important classifications in chemistry and within the periodic table is the concept of formal oxidation states<sup>1-4</sup>. The preparation and characterization of compounds containing elements with unusual oxidation states is of great interest to chemists<sup>5</sup>. The highest experimentally known formal oxidation state of any chemical element is at present VIII<sup>2-4</sup>, although higher oxidation states have been postulated<sup>6,7</sup>. Compounds with oxidation state VIII include several xenon compounds<sup>8</sup> (for example XeO<sub>4</sub> and XeO<sub>3</sub>F<sub>2</sub>) and the wellcharacterized species RuO<sub>4</sub> and OsO<sub>4</sub> (refs 2-4). Iridium, which has nine valence electrons, is predicted to have the greatest chance of being oxidized beyond the VIII oxidation state<sup>1</sup>. In recent matrix-isolation experiments, the IrO4 molecule was characterized as an isolated molecule in rare-gas matrices<sup>9</sup>. The valence electron configuration of iridium in  $IrO_4$  is  $5d^1$ , with a formal oxidation state of VIII. Removal of the remaining d electron from IrO<sub>4</sub> would lead to the iridium tetroxide cation ( $[IrO_4]^+$ ), which was recently predicted to be stable<sup>10</sup> and in which iridium is in a formal oxidation state of IX. There has been some speculation about the formation of  $[IrO_4]^+$  species<sup>11,12</sup>, but these experimental observations have not been structurally confirmed. Here we report the formation of  $[IrO_4]^+$  and its identification by infrared photodissociation spectroscopy. Quantum-chemical calculations were carried out at the highest level of theory that is available today, and predict that the iridium tetroxide cation, with a T<sub>d</sub>-symmetrical structure and a  $d^0$  electron configuration, is the most stable of all possible  $[IrO_4]^+$  isomers.



**Figure 1** | Mass spectra of the iridium oxide cations. The cations are produced by pulsed-laser vaporization of an iridium metal target in an expansion of helium (**a**) or argon (**b**) seeded by dioxygen. The isotopic splitting of iridium can clearly be resolved with the relative peak areas matching the natural abundance isotopic distribution (<sup>191</sup>Ir, 37.3%; <sup>193</sup>Ir, 62.7%). *m/z*, mass/ charge ratio; intensity is shown in arbitrary units.

#### Non-bonding *d*-electrons

- The mutual interaction between *bonding* electron pairs is the same for *d*-block metal and main group compounds
- However, *d*-metals can possess *nonbonding d*-electrons in their five *d* orbitals.
- *d* electron configurations can be determined with *ligand field theory* (LFT)
  - 1. Attain a minimum repulsion with other *d*-electrons
  - 2. Attain a minimum repulsion with the bonding electron pairs (ligands)
- In its original version by Hans Bethe, it was formulated as crystal field theory (CFT)
  - Ligands are treated as point-like ions
  - Only consider electrostatic repulsion between the *d*-electrons and the ligands
- LFT is in principle superseded by the *molecular orbital theory* 
  - LFT is still is a convenient and simple tool to understand the bonding and magnetism of *d*-metal compounds



## Ligand field theory (1)

- In ligand field theory, the ligands are not just considered as negative point charges, but the covalent nature of the σ-bonding is also taken into account
- The basic concept of the *d*-orbital splitting remains



## Ligand field theory (2)

Ref: Müller p. 74

- In an octahedral geometry, the  $t_{2g}$  and  $e_g$  orbitals are separated by energy  $\Delta_0$ 
  - $-\Delta_0$  depends on the repulsion between the bonding electron pairs and *d* electrons
- $\Delta_0$  decreases when the ligand electronegativity increases
  - Bonding electrons are pulled further from the metal *d* electrons -> less repulsion
- $\Delta_0$  decreases when the size of the ligand atom increases
  - Bonding electrons are distributed over a larger space -> less repulsion
- $\Delta_0$  is large for ligands that form multiple bonds with the metal atom (e.g. CO, CN<sup>-</sup>)
  - More bonding electrons -> more repulsion with the d electrons
- $\Delta_0$  can be measured with spectroscopic methods and the *spectrochemical series* is obtained by ordering different ligands according to decreasing  $\Delta_0$ :
  - − CO (strong field, large  $\Delta_0$ ) > CN<sup>-</sup> > PR<sub>3</sub> > NO<sub>2</sub><sup>-</sup> > NH<sub>3</sub> > NCS<sup>-</sup> > H<sub>2</sub>O > RCO<sub>2</sub><sup>-</sup> ≈ OH<sup>-</sup> > F<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> ≈ SCN<sup>-</sup> > S<sub>2</sub><sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> (weak field, small  $\Delta_0$ )
- 4*d* and 5*d* orbitals have larger overlap with ligand orbitals and larger  $\Delta_0$  than 3*d*

$$\Delta_{O} = \begin{bmatrix} & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & &$$

## Ligand field theory (3)

- LFT can be used to explain the magnetism of transition metal compounds
- Because of the splitting of the *d*-orbitals, there is an energetical competition between *high-spin* and *low-spin* configuration of the *d*-orbitals
- The first three *d* electrons occupy the  $t_{2q}$  orbitals in accordance to *Hund's rule*
- When four *d* electrons are present, there are two alternatives for the fourth electron
  - The energy for putting a second electron in an already occupied orbital is called the electron pairing energy P
  - If  $P > \Delta_0$ , the fourth electron will occupy an  $e_q$  orbital (high-spin)
  - If  $P < \Delta_0$ , the fourth electron will occupy a  $t_{2q}$  orbital (low-spin)



#### Jahn-Teller effect (1)

Ref: Müller p. 76

- In a high-spin  $d^4$  complex only one of the two  $e_a$  orbitals is occupied
- If  $d_z^2$  is occupied -> repulsion on the bonding electrons of the ligands on the z axis
- The ligands are pushed outwards and the octahedron elongates along the z axis
  - This effect is known as the Jahn–Teller effect
- The  $d_{x-y}^{2-2}$  orbital could have been occupied, elongating bonds along x and y axes
  - However, more energy would be needed to stretch four bonds
- The J-T effect occurs when degenerate orbitals are unevenly occupied
- **Strong** J-T effect is observed for the following electronic configurations:



14

#### Jahn-Teller effect (2)

• Illustration of tetragonal distortion (elongation) for an octahedral *d*<sup>9</sup> complex



#### Other coordination geometries

- The splitting of the *d*-orbitals is different for other coordination geometries
- The figure below shows the most typical geometries for *d*-metals



The 'centers of gravity' (mean values of the energy levels) for all term sequences were positioned on the dotted line

#### Most common coordination polyhedra for coordination numbers 2-6

polyhedronc.n.config.central atomexampleslinear2 $d^{10}$ Cu(I), Ag(I),Cu_2O, Ag(CN)_2^-,arrangementAu(I)He(II)Au(C)^* Au(CI^-, II)	gCl <sub>2</sub> , HgO*
linear 2 $d^{10}$ Cu(I), Ag(I), Cu <sub>2</sub> O, Ag(CN) <sub>2</sub> <sup>-</sup> , Au(I) Ha(II) Au(I) $d^{10}$ Au(I) $d^{10}$ Cu <sub>2</sub> O, Ag(CN) <sub>2</sub> <sup>-</sup> , Au(I) $d^{10}$ Au(I) $d^{10}$ Au(I) $d^{10}$ Cu <sub>2</sub> O, Ag(CN) <sub>2</sub> <sup>-</sup> , Au(I) $d^{10}$	gCl <sub>2</sub> , HgO*
$A_{\rm H}({\rm I}) = A_{\rm H}({\rm I})$ $A_{\rm H}({\rm I})$	lgCl <sub>2</sub> , HgO*
arrangement $Au(1), Hg(11)$ $AuCIN, AuCI2, H$	
triangle 3 $d^{10}$ Cu(I), Ag(I), Cu(CN) <sub>3</sub> <sup>2-</sup> , Ag <sub>2</sub> Cl	3— 5 ,
Au(I), Hg(II) Au(PPh <sub>3</sub> ) $^+_3$ , HgI $^3$	
square 4 $d^8$ Ni(II), Pd(II), Ni(CN) <sub>4</sub> <sup>2-</sup> , PdCl <sub>2</sub> <sup>*</sup>	,
Pt(II), Au(III) $PtH_4^{2-}$ , Pt(NH <sub>3</sub> ) <sub>2</sub> C	$l_2, AuCl_4^-$
tetrahedron 4 $d^0$ Ti(IV), V(V), TiCl <sub>4</sub> , VO <sub>4</sub> <sup>3-</sup> ,	
$Cr(VI), Mo(VI), CrO_3^*, CrO_4^{2-}, Mo$	$O_4^{2-}, WO_4^{2-}$
$Mn(VII), Re(VII) Mn_2O_7, ReO_4^-$	
$Ru(VIII), Os(VIII) RuO_4, OsO_4$	
$d^1$ V(IV), Cr(V), VCl <sub>4</sub> , CrO <sub>4</sub> <sup>3-</sup> ,	
Mn(VI), Ru(VII) $MnO_4^{2-}$ , Ru $O_4^{-}$	
$d^5$ Mn(II), Fe(III) MnBr <sub>4</sub> <sup>2-</sup> , Fe <sub>2</sub> Cl <sub>6</sub>	
$d^6$ Fe(II) FeCl <sub>4</sub> <sup>2-</sup>	
$d^7$ Co(II) CoCl <sub>4</sub> <sup>2-</sup>	
$d^8$ Ni(II) NiCl <sub>4</sub> <sup>2-</sup>	
$d^9$ Cu(II) CuCl <sub>4</sub> <sup>2-†</sup>	
$d^{10}$ Ni(0), Cu(I), Ni(CO) <sub>4</sub> , Cu(CN) <sup>3</sup> <sub>4</sub>	}
$Zn(II), Hg(II)$ $Zn(CN)_4^{2-}, HgI_4^{2-}$	
square 5 $d^0$ Ti(IV), V(V), TiOCl <sub>4</sub> <sup>2-</sup> , VOF <sub>4</sub> <sup>-</sup> ,	
pyramid $Nb(V)$ , $NbSCl_4^-$ ,	
Mo(VI), W(VI), MoNCl <sub>4</sub> <sup>-</sup> , WNCl <sub>4</sub> <sup>-</sup>	
$d^1$ V(IV), Cr(V), VO(NCS) <sub>4</sub> <sup>2-</sup> , CrOO	$Cl_4^-$ ,
$Mo(V), W(V), MoOCl_4^-, WSCl_4^-,$	
Re(VI) ReOCl <sub>4</sub>	
$d^2$ Os(VI) OsNCl <sub>4</sub>	
$d^4$ Mn(III), Re(III) MnCl <sub>5</sub> <sup>2-</sup> , Re <sub>2</sub> Cl <sub>8</sub>	
$d^7$ Co(II) Co(CN) <sub>5</sub> <sup>3-</sup>	
trigonal 5 $d_2^2$ V(IV) VCl <sub>3</sub> (NMe <sub>3</sub> ) <sub>2</sub>	
bipyramid $d^8$ Fe(0) Fe(CO) <sub>5</sub>	
octahedron 6 nearly all; rarely Pd(II), Pt(II), Au(III), C	u(I)

endless chain Jahn–Teller distorted

#### Magnetic moments (1)

- Unpaired electrons of *d*-block metal complexes give rise to magnetic properties
- Magnetic properties are often expressed in terms of the **magnetic moment**  $\mu$ , which is directly related to the number of unpaired electrons
- $\mu$  arises from electron spin ( $\mu_s$ ) and electron orbital motion ( $\mu_L$ )
- Electron may be considered as a bundle of negative charge spinning on its axis.
- The magnitude of the resulting spin moment,  $\mu_s$ , is 1.73 BM, Bohr Magneton (SI units):  $1 \text{ BM} = \frac{e\hbar}{2m_s}$

where e is the electron charge,  $\hbar$  is the reduced Planck constant,  $m_e$  is the electron rest mass

• Spin magnetic moment  $\mu_s$  for a single electron can be calculated with

$$\mu_S = g\sqrt{s(s+1)}$$

where s is the spin quantum number,  $\frac{1}{2}$ , and g is the gyromagnetic ratio (~2.00). Substituting for s and g gives  $\mu_s = 1.73$  BM for one electron

#### Magnetic moments (2)

• For atoms or ions that contain more than one unpaired electron, the overall spin moment is given by

$$u_S = g\sqrt{S(S+1)}$$

where *S* is the sum of the spin quantum numbers of the individual unpaired electrons

• For high-spin Fe<sup>3+</sup> with five unpaired electrons,  $S = 5 * \frac{1}{2} = \frac{5}{2}$  and  $\mu_s = 5.92$  BM.

lon	No. of unpaired electrons	$\mu_{S( ext{calc})}$	$\mu_{S+L(calc)}$	$\mu_{( ext{observed})}$
V <sup>4+</sup>	1	1.73	3.00	~1.8
V <sup>3+</sup>	2	2.83	4.47	$\sim 2.8$
Cr <sup>3+</sup>	3	3.87	5.20	$\sim 3.8$
Mn <sup>2+</sup>	5 (high spin)	5.92	5.92	$\sim 5.9$
Fe <sup>3+</sup>	5 (high spin)	5.92	5.92	$\sim 5.9$
Fe <sup>2+</sup>	4 (high spin)	4.90	5.48	5.1-5.5
Co <sup>3+</sup>	4 (high spin)	4.90	5.48	$\sim$ 5.4
Co <sup>2+</sup>	3 (high spin)	3.87	5.20	4.1-5.2
Ni <sup>2+</sup>	2	2.83	4.47	2.8-4.0
Cu <sup>2+</sup>	1	1.73	3.00	1.7-2.2

Table 9.3 Calculated and observed magnetic moments (BM) for some transition metal ions

Source: data taken from F. A. Cotton and G. Wilkinson (1966), Advanced Inorganic Chemistry: a Comprehensive Text, 2nd edn, John Wiley & Sons, Inc., New York.

#### Magnetic moments (3)

• The motion of an electron around the nucleus may give rise to an orbital moment (the expression is applicable to free atoms or ions):

$$\mu_{S+L} = g\sqrt{4S(S+1) + L(L+1)}$$

where *L* is the orbital angular momentum quantum number for the metal ion:

$$L = \hbar \sqrt{l(l+1)}$$

where *I* is the azimuthal quantum number ( $s \rightarrow 0$ ,  $p \rightarrow 1$ ,  $d \rightarrow 2$ ,  $f \rightarrow 3$ , ...)

- In practice, *L* is often completely or partially quenched in cases where the electric fields on the surrounding atoms or ions restrict the orbital motion
  - In such cases, the observed moments are similar to predicted spin-only values

lon	No. of unpaired electrons	$\mu_{S( ext{calc})}$	$\mu_{S+L(calc)}$	$\mu_{( ext{observed})}$
V <sup>4+</sup>	1	1.73	3.00	~1.8
V <sup>3+</sup>	2	2.83	4.47	$\sim 2.8$
Cr <sup>3+</sup>	3	3.87	5.20	$\sim 3.8$
$Mn^{2+}$	5 (high spin)	5.92	5.92	$\sim$ 5.9
Fe <sup>3+</sup>	5 (high spin)	5.92	5.92	$\sim 5.9$
$Fe^{2+}$	4 (high spin)	4.90	5.48	5.1-5.5
Co <sup>3+</sup>	4 (high spin)	4.90	5.48	$\sim$ 5.4
Co <sup>2+</sup>	3 (high spin)	3.87	5.20	4.1-5.2
Ni <sup>2+</sup>	2	2.83	4.47	2.8-4.0
Cu <sup>2+</sup>	1	1.73	3.00	1.7-2.2

 Table 9.3
 Calculated and observed magnetic moments (BM) for some transition metal ions

Source: data taken from F. A. Cotton and G. Wilkinson (1966), Advanced Inorganic Chemistry: a Comprehensive Text, 2nd edn, John Wiley & Sons, Inc., New York.

#### Magnetism





#### Magnetic susceptibility

• When a substance is placed in a magnetic field *H* (units A m<sup>-1</sup>), the magnetic induction *B* (units T, tesla) is

$$B = \mu H = \mu_0 H + \mu_0 M$$

Where  $\mu$  is *permeability*,  $\mu_0$  is the permeability of free space (4 $\pi$  \* 10<sup>-7</sup> H m<sup>-1</sup>, H = henry) and *M* is the magnetic moment or magnetization of the sample

Magnetization = magnetic moment per unit volume or mass

- $\mu_0 H$  is the induction generated by the field alone and  $\mu_0 M$  is the additional induction contributed by the sample
- The magnetic susceptibility,  $\chi$ , is defined as the ratio of magnetization M to field H:

$$\chi = \frac{M}{H}$$

- In other words: high magnetization M means high susceptibility  $\chi$
- Susceptibility  $\chi$  is the most important measurable quantity for the characterization of magnetic properties
  - Provides a measure of the **response of a sample to an applied magnetic field**
  - Somewhat analogous to polarizability (response to an applied electric field)

#### Classification based on susceptibility $\chi$

- The different kinds of magnetic behavior may be distinguished by the values of  $\chi$ 
  - In *diamagnetic* materials,  $\chi$  is very small and slightly negative
  - In *paramagnetic* materials,  $\chi$  is small and positive
  - In *ferromagnetic* materials,  $\chi > 1$  and such materials are strongly attracted to a magnetic field.
  - In *antiferromagnetic* materials,  $\chi$  is positive and comparable to paramagnetic substances (or somewhat smaller).

Behaviour	Typical χ value	Change of χ with increase in temperature	Field dependence?
Diamagnetism	$-8 \times 10^{-6}$ for Cu; $-1$ for superconductors	None	No
Paramagnetism	0.1–0.001 for transition metal compounds	Decreases	No
Pauli paramagnetism	$8.3 \times 10^{-4}$ for Mn	None	Yes
Ferromagnetism	$5 \times 10^3$ for Fe	Decreases	Yes
Antiferromagnetism	0–10 <sup>–2</sup>	Increases	(Yes)

Table 9.1	Magnetic susce	otibilities
-----------	----------------	-------------

#### Dia- and paramagnetism

- Diamagnetism is a property of all materials
- When diamagnetism dominates, there is a slight repulsion by a magnetic field
  - Diamagnetism is associated with orbital motion of electrons in atoms.
  - This orbital motion generates a small electric field
  - In the presence of an external field, the orbital motion is modified slightly to give a magnetic moment that opposes the applied field leading to a slight repulsion effect which is explained by Lenz's law of electromagnetism.
  - Superconductors represent a special, extreme type of diamagnetism since they repel magnetic fields completely, leading in magnetic levitation
- Paramagnetic materials are attracted by a magnetic field



#### Paramagnetic



#### Pauli paramagnetism

• In addition to the strong ferro- or antiferromagnetic coupling shown by some metals, most metals display a weak *Pauli paramagnetism* in the presence of a magnetic field



 Figure 9.9
 Schematic splitting of 3d band into two sub-bands: (a) in the absence of a magnetic field; (b) in

 Pauli paramagnets, an energy difference develops in a magnetic field; (c) in ferromagnetic transition metals,<br/>the splitting occurs spontaneously.
 Ref: West p. 458

# Antiferromagnetic ordering: superexchange

• Superexchange is the mechanism of antiferromagnetism in, e.g. NiO



*Figure 9.5* Antiferromagnetic coupling of spins of d electrons on Ni<sup>2+</sup> ions through p electrons of oxide ions.<sup>27</sup>

#### **Curie and Néel temperatures**

- Ordered magnetic structures lose their ordered structures above a certain temperature
  - *Curie temperature*, T<sub>c</sub> for ferromagnets and ferrimagnets
  - *Néel temperature*,  $T_N$  for antiferromagnets
- The spins become disordered and the materials become paramagnetic



Temperature, K

Figure: Robert John Lancashire

Table 9.2	Some Curie and Néel temperatures						
Element	T <sub>c</sub> /K	T <sub>N</sub> /K					
Cr		308					
Mn		100					
Fe	1043						
Со	1404						
Ni	631						
Ce		12.5					
Pr		25					
Nd		19					
Sm		14.8					
Eu		90					
Gd	293						
Tb	222	229					
Dy	85	179					
Ho	20	131					
Er	20	84					
Tm	25	56					

# Experimental characterization of the magnetic ground state

- SQUID (Superconducting Quantum Interference Device)
  - Very sensitive magnetometer (measure susceptibility as a function of T)
- Neutron diffraction

χ

- Neutrons carry a spin and interact with magnetic moments



SQUID data for antiferromagnetic  $SrU_2F_{12}$  (Otto Mustonen / Aalto)

**Figure 5.26** Schematic neutron and powder XRD patterns for MnO for  $\lambda = 1.542$  Å. Peaks are assigned Miller indices for the cubic unit cells given. Neutron data adapted from Shull, Strauser and Wollan, Phys. Rev., 83, 333, © 1951 American Physical Society.