

Calculations of optical properties of transition metal and rare-earth ions

Mikhail G. Brik

Institute of Physics, University of Tartu, Riia 142, Tartu, 51014, Estonia



LUMINET winter school, Costa Adeje, Tenerife, December 2-6, 2013

Outline

- **Introduction: impurities in crystals and glasses**
- **Transition metal and rare earth ions**
 - Energy level schemes of free ions
 - Correlation between the Racah parameters, spin-orbit constant and atomic number for isovalent ions
- **Basic foundations of crystal field theory**
 - Splitting of free ion energy levels in crystal field
 - Tanabe-Sugano diagrams for d ions
- **Conclusions**

Introduction: crystals, glasses, phosphor powders



Azurite



Quartz



Emerald



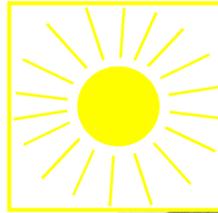
Diamond



Ice -
snowflake



Amethyst



Phosphor powders

Where does the color
come from?..



Introduction: crystals, glasses, phosphor powders

Impurities (imperfections) in crystals



Corundum Al_2O_3

If pure - colorless or grey



Ruby: corundum Al_2O_3

with a few percent of chromium



Sapphire: corundum Al_2O_3

with a few percent of titanium

Even a small amount of impurities (added either artificially or in a natural way) can drastically change optical properties of a crystal !!

Introduction: crystals, glasses, phosphor powders



Corundum Al_2O_3

+



Chromium

=



Ruby

Corundum:

<http://www.kaycircle.com/What-Is-The-Average-Cost-Of-Corundum-Per-Gram-Pound-Ton-Average-Corundum-Price>

~ 50 \$ per pound

+

Chromium:

<http://www.metalprices.com/FreeSite/metals/cr/cr.asp>

~1.6 - 2.6 \$/kg

≠

Ruby:

<http://www.ruby-sapphire.com/r-s-bk-prices.htm> “good quality” (on a scale “poor – fair – good – very good - exceptional”)

from 50 to 13,000 \$ per carat
1 carat = 0.2 gram

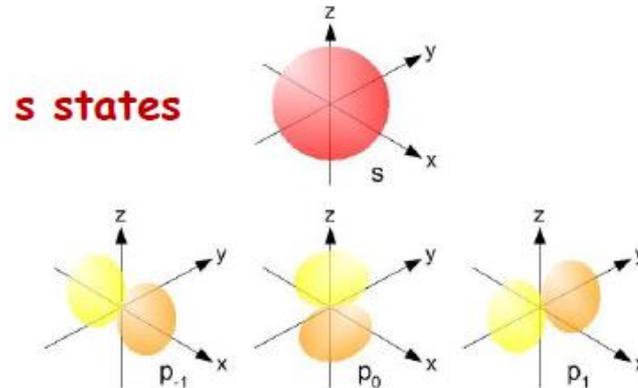
Math properties of addition cease to work, when it comes to gemstones ...

Outline

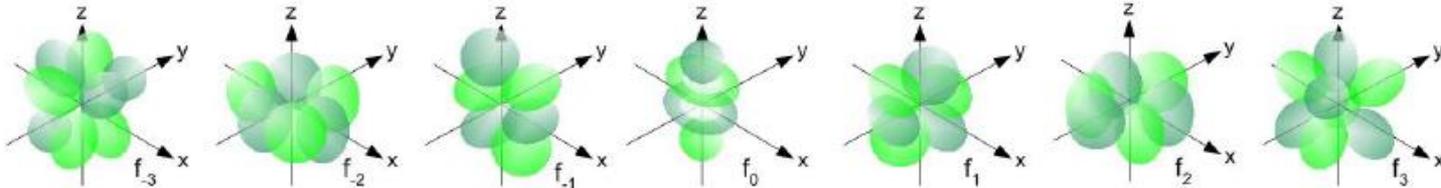
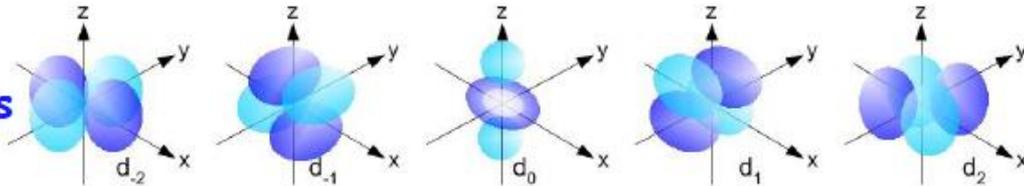
- **Introduction: impurities in crystals and glasses**
- **Transition metal and rare earth ions**
 - Energy level schemes of free ions
 - Correlation between the Racah parameters, spin-orbit constant and atomic number for isovalent ions
- **Basic foundations of crystal field theory**
 - Splitting of free ion energy levels in crystal field
 - Tanabe-Sugano diagrams for d ions
- **Conclusions**

Electron configurations

Impurities (3d, 4f ions) – MULTI-ELECTRON systems



d states



f states

Electron states of free ions

3d, 4f ions – MULTI-ELECTRON systems

d electrons quantum numbers:

Principal quantum number $n=3$, or 4, or 5

Orbital quantum number $l=2$

Magnetic quantum number $m_l=-2,-1,0,1,2$

Spin quantum number $m_s=-1/2, +1/2$

10 states in total

f electrons quantum numbers:

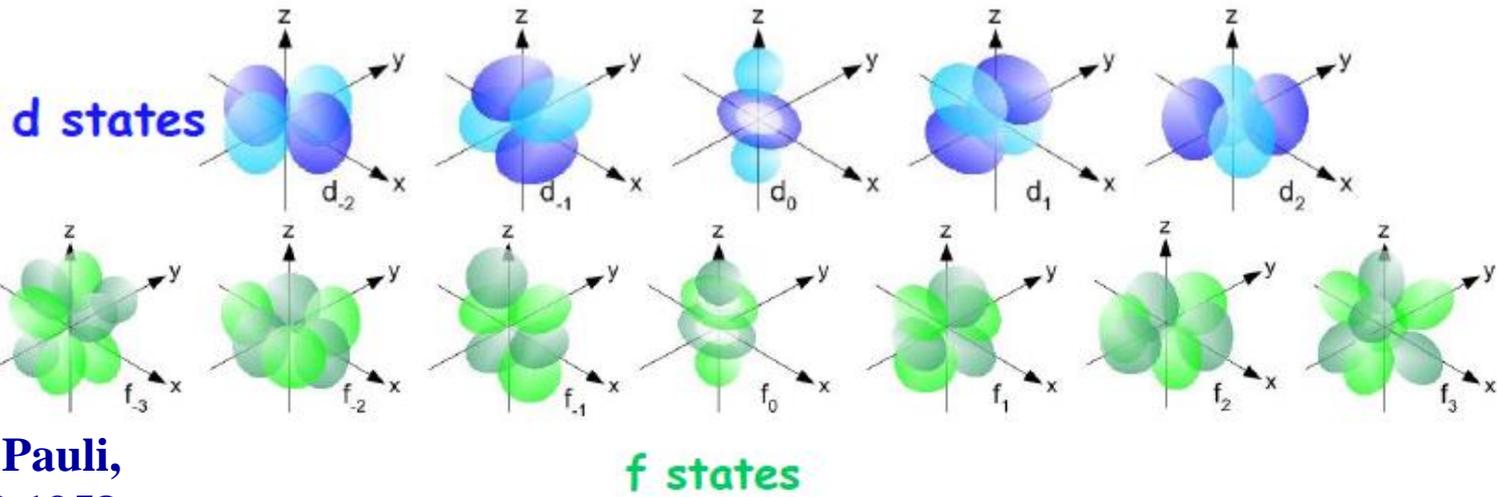
Principal quantum number $n=4$, or 5

Orbital quantum number $l=3$

Magnetic quantum number $m_l=-3,-2,-1,0,1,2,3$

Spin quantum number $m_s=-1/2, +1/2$

14 states in total



Wolfgang Ernst Pauli,

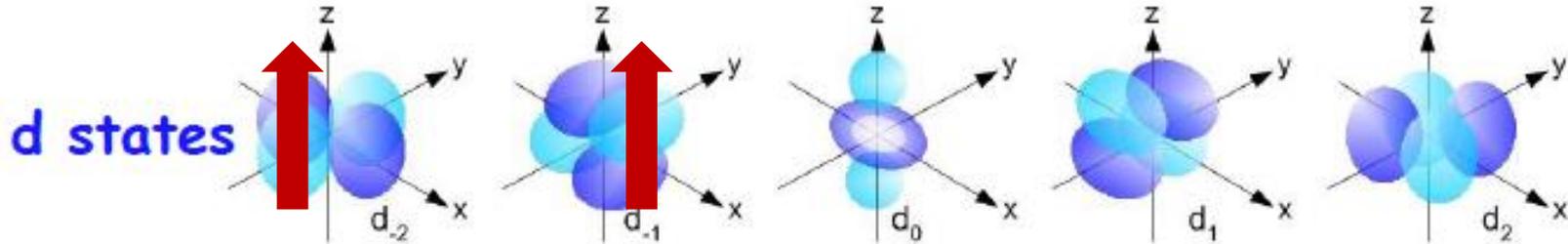
25.04.1900-15.12.1958

Nobel prize in physics 1945

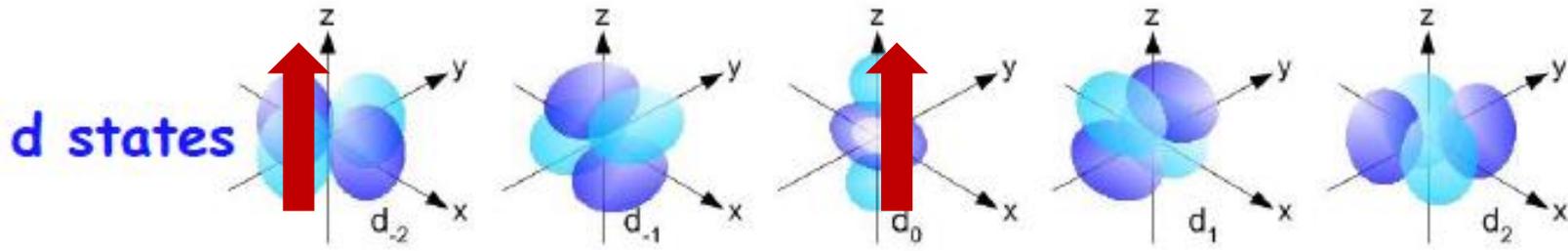
Pauli exclusion principle: no electrons with identical quantum numbers!

Electron states of free ions

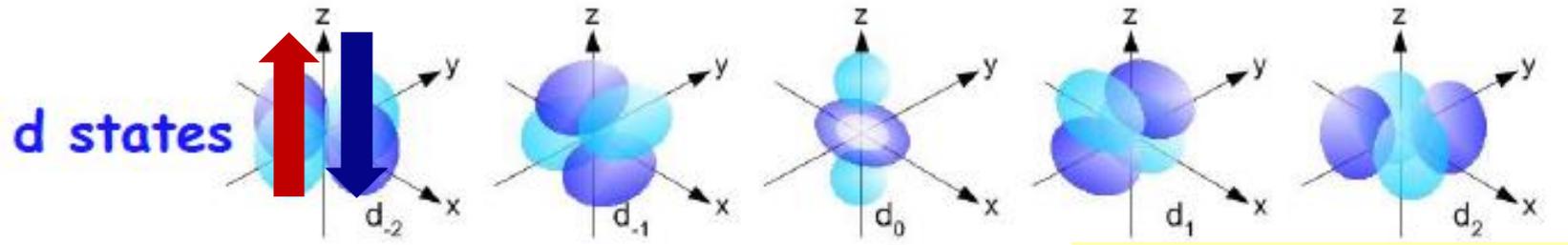
d² configuration (V³⁺, Cr⁴⁺, Mn⁵⁺, Fe⁶⁺)



OR:



OR:



OR...

d² configuration: q=10, k=2

$$N = \frac{q!}{k!(q-k)!}$$

Number of permutations of k electrons through q orbitals

$$N = \frac{10!}{2!(10-2)!} = 45$$

Electron states of free ions

$$N = \frac{q!}{k!(q-k)!}$$

Number of permutations of k electrons through q orbitals

Increase of the number of states

Electron configuration	Number of states	Number of energy levels
p^1, p^5	6	?
p^2, p^4	15	?
p^3	20	?

Electron configuration	Number of states	Number of energy levels
d^1, d^9	10	?
d^2, d^8	45	?
d^3, d^7	120	?
d^4, d^6	210	?
d^5	252	?

Electron configuration	Number of states	Number of energy levels
f^1, f^{13}	14	?
f^2, f^{12}	91	?
f^3, f^{11}	364	?
f^4, f^{10}	1001	?
f^5, f^9	2002	?
f^6, f^8	3003	?
f^7	3432	?

How can we find the number of energy levels for each of these configurations?..

How can we calculate the energies of those levels?..

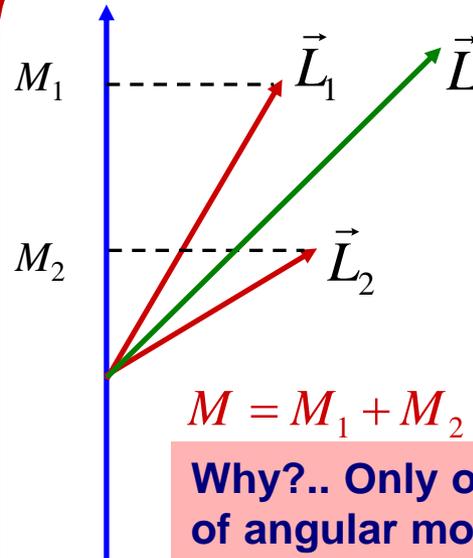


Electron states of free ions

$$\varphi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi) \quad \text{One-electron wave function}$$

$$R_{nl}(r) = -\sqrt{\frac{(n-l-1)!}{(n+l)!^3 2n}} \left(\frac{2Z}{na_0}\right)^{3/2} \exp\left(-\frac{Zr}{na_0}\right) \left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right) \quad \text{General form of the radial wave functions}$$

Wave function of a particular state can be obtained from the one-electron functions using the angular momenta addition rules and (again!) Pauli exclusion principle.



In quantum mechanics 2+2 is not always 4! ☺

The rule of addition of two momenta L_1 and L_2

$$|L_1 - L_2| \leq L \leq L_1 + L_2$$

For example, $L_1=2, L_2=2, L=0, 1, 2, 3, 4$

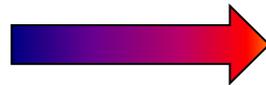
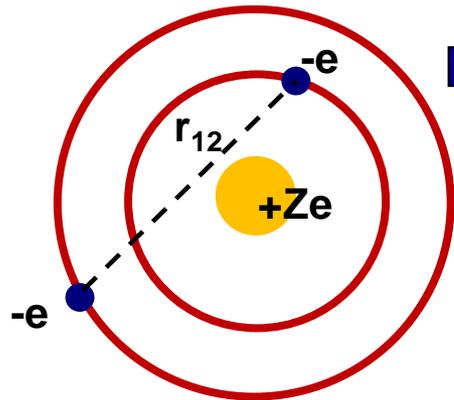
$$M = M_1 + M_2$$

Why?.. Only one out of three components of angular momentum operator can be determined at the same time

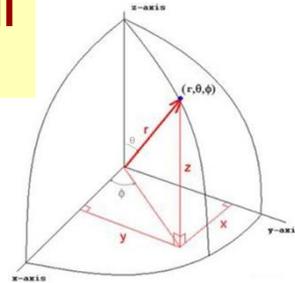
$$[\hat{L}_i, \hat{L}_j] \equiv i\hbar\hat{L}_k, \quad i, j, k = x, y, z$$

Spectral terms of free ions

Electrostatic (Coulomb) interaction between electrons of the unfilled shell is mainly responsible for the formation of the energy level schemes

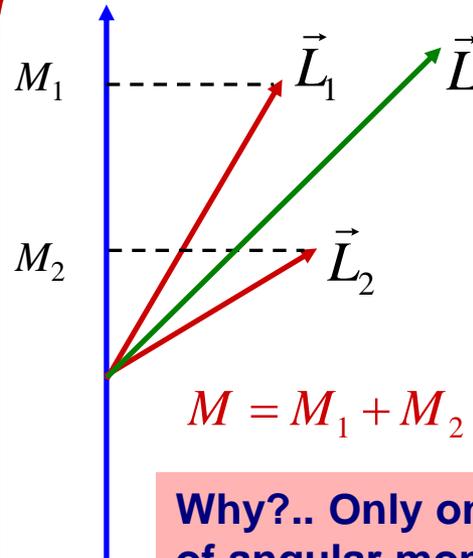


Spherical system of coordinates



$$\int \Psi^* \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \Psi r_1^2 r_2^2 \sin \theta_1 \sin \theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2$$

Ψ stands for the wave function of a particular state; it can be obtained from the one-electron functions using the angular momenta addition rules and (again!) Pauli exclusion principle.



In quantum mechanics 2+2 is not always 4! 😊

The rule of addition of two momenta L_1 and L_2

$$|L_1 - L_2| \leq L \leq L_1 + L_2$$

For example, $L_1=2, L_2=2, L=0, 1, 2, 3, 4$

Why?.. Only one out of three components of angular momentum operator can be determined at the same time

Spectral terms of free ions

$$\varphi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi) \quad \text{One-electron wave function}$$

$$R_{nl}(r) = -\sqrt{\frac{(n-l-1)!}{(n+l)!}} \left(\frac{2Z}{na_0}\right)^{3/2} \exp\left(-\frac{Zr}{na_0}\right) \left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right) \quad \text{General form of the radial wave functions}$$

Ψ stands for the wave function of a particular state; it is a linear combination of products of one-electron wave functions

$$\Psi_{LM} = \sum_{M_1+M_2=M} C_{L_1M_1L_2M_2}^{LM} \varphi_{L_1M_1} \varphi_{L_2M_2}$$

The Clebsch-Gordan coefficients

They have the following physical meaning: the square of the absolute value of the $C_{L_1M_1L_2M_2}^{LM}$ coefficient is equal to the probability that two states (L_1, M_1) and (L_2, M_2) after addition produce the state (L, M) . If $M \neq M_1 + M_2$, the corresponding Clebsch-Gordan coefficient is **zero**.

Clebsch-Gordan coefficients and Wigner 3j-symbols

$$C_{j_1 m_1 j_2 m_2}^{j m} = (-1)^{j_1 - j_2 + m} \sqrt{2j+1} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix}$$

General definition
of the Wigner 3j-
symbol

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \sqrt{\frac{(j_1 + j_2 - j_3)!(j_1 - j_2 + j_3)!(-j_1 + j_2 + j_3)!}{(j_1 + j_2 + j_3 + 1)!}} \times \\ \times \sqrt{(j_1 + m_1)!(j_1 - m_1)!(j_2 + m_2)!(j_2 - m_2)!(j_3 + m_3)!(j_3 - m_3)!} \times \\ \times \sum_z \frac{(-1)^{z + j_1 - j_2 - m_3}}{z!(j_1 + j_2 - j_3 - z)!(j_1 - m_1 - z)!(j_2 + m_2 - z)!(j_3 - j_2 + m_1 + z)!(j_3 - j_1 - m_2 + z)!}$$

Not that difficult to write a computer program to calculate the 3j-symbols

Many standard packages (MAPLE, for example) have the built-in procedures for evaluation of the 3j-symbols

But in a “pre-computer era” one was supposed to calculate the 3j-symbols “by hands” (special tables were created...)

Spectral terms of free ions

After the wave functions of two electron configurations are built, one can repeat the procedure by adding the third electron to get the wave functions of three electron configuration etc ... (fractional parentage coefficients, seniority quantum number, 6j-, 9j-symbols)

It is a common practice to use the ^{2S+1}L notation for the multi-electron states where **S** is the **TOTAL** spin, and **L** is the **TOTAL** orbital momentum

<i>L</i>	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	<i>S</i>	<i>P</i>	<i>D</i>	<i>F</i>	<i>G</i>	<i>H</i>	<i>I</i>	<i>K</i>	<i>L</i>	<i>M</i>	<i>N</i>	<i>O</i>	<i>Q</i>	<i>R</i>	<i>T</i>

Each ^{2S+1}L spectral term is degenerated; the degree of degeneracy is $(2S+1)(2L+1)$. E.g. 4F term: $(2S+1)(2L+1) = 4(2 \times 3 + 1) = 28$ states

How to memorize the above-given sequence ... mnemonic rules?..

Sober Physicists Don't Find Giraffes Hiding In Kitchens Like My Nephew ☺

Spectral terms of free ions

Equivalent configurations for *p*-electrons:

p^1 and $p^5 - {}^2P$

p^2 and $p^4 - {}^1SD, {}^3P$

$p^3 - {}^2PD, {}^4S$

Equivalent configurations for *d*-electrons:

d^1 and $d^9 - {}^2D$

d^2 and $d^8 - {}^1SDG, {}^3PF$

d^3 and $d^7 - {}^2PD_{(2)}FGH, {}^4PF$

d^4 and $d^6 - {}^1S_{(2)}D_{(2)}FG_{(2)}I, {}^3P_{(2)}DF_{(2)}GH, {}^5D$

$d^5 - {}^2SPD_{(3)}F_{(2)}G_{(2)}HI, {}^4PDFG, {}^6S$

Equivalent configurations for *f*-electrons:

f^1 and $f^{13} - {}^2F$

f^2 and $f^{12} - {}^1SDGI, {}^3PFH$

f^3 and $f^{11} - {}^2PD_{(2)}F_{(2)}G_{(2)}H_{(2)}IKL, {}^4SDFGI$

f^4 and $f^{10} - {}^1S_{(2)}D_{(4)}FG_{(4)}H_{(2)}I_{(3)}KL_{(2)}N, {}^3P_{(3)}D_{(2)}F_{(4)}G_{(3)}H_{(4)}I_{(2)}K_{(2)}LM, {}^5SDFGI$

f^5 and $f^9 - {}^2P_{(4)}D_{(5)}F_{(7)}G_{(6)}H_{(7)}I_{(5)}K_{(5)}L_{(3)}M_{(2)}NO, {}^4SP_{(2)}D_{(3)}F_{(4)}G_{(4)}H_{(3)}I_{(3)}K_{(2)}LM, {}^6PFH$

f^6 and $f^8 - {}^1S_{(4)}PD_{(6)}F_{(4)}G_{(8)}H_{(4)}I_{(7)}K_{(3)}L_{(4)}M_{(2)}N_{(2)}Q, {}^3P_{(6)}D_{(5)}F_{(9)}G_{(7)}H_{(9)}I_{(6)}K_{(6)}L_{(3)}M_{(3)}NO, {}^5SPD_{(3)}F_{(2)}G_{(3)}H_{(2)}I_{(2)}KL, {}^7F$

$f^7 - {}^2S_{(2)}P_{(5)}D_{(7)}F_{(10)}G_{(10)}H_{(9)}I_{(9)}K_{(7)}L_{(5)}M_{(4)}N_{(2)}OQ, {}^4S_{(2)}P_{(2)}D_{(6)}F_{(5)}G_{(7)}H_{(5)}I_{(5)}K_{(3)}L_{(3)}MN, {}^6PDFGHI, {}^8S$

A subscript denotes a number of terms with the same *S* and *L*.

Hund's rule to find the ground term: i) max spin *S*; ii) max orbital momentum *L*



Friedrich Hund, 04.02.1896 – 31.03.1997

d^2 and $d^8 - {}^1SDG, {}^3PF$ - the ground term is 3F

Electron states and spectral terms of free ions

$$N = \frac{q!}{k!(q-k)!}$$

Number of permutations of k electrons through q orbitals

Increase of the number of states

Electron configuration	Number of states	Number of energy levels
p^1, p^5	6	1
p^2, p^4	15	3
p^3	20	3

Electron configuration	Number of states	Number of energy levels
d^1, d^9	10	1
d^2, d^8	45	5
d^3, d^7	120	8
d^4, d^6	210	16
d^5	252	16

Electron configuration	Number of states	Number of energy levels
f^1, f^{13}	14	1
f^2, f^{12}	91	7
f^3, f^{11}	364	17
f^4, f^{10}	1001	47
f^5, f^9	2002	73
f^6, f^8	3003	119
f^7	3432	119

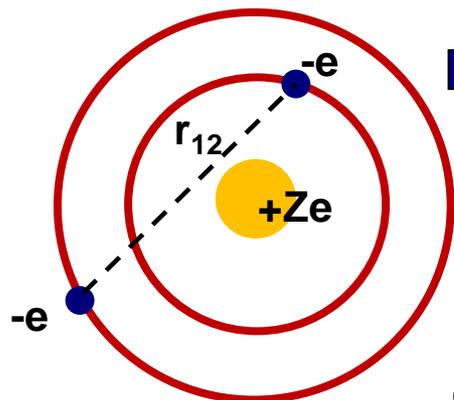
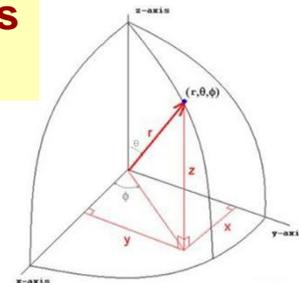
~~How can we find the number of energy levels for each of these configurations?..~~

How can we calculate the energies of those levels?..



Energy of spectral terms of free ions

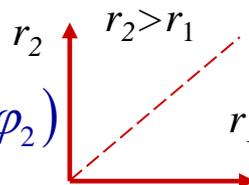
Coulomb interaction between electrons of the unfilled shell is mainly responsible for the formation of the energy level schemes



Spherical system of coordinates

$$\int \Psi^* \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \Psi r_1^2 r_2^2 \sin \theta_1 \sin \theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\varphi_1 d\varphi_2$$

$$\frac{1}{r_{12}} = \sum_k \sum_{m=-k}^k \frac{4\pi}{2k+1} \frac{r_{<}^k}{r_{>}^{k+1}} Y_{km}(\theta_1, \varphi_1) Y_{km}^*(\theta_2, \varphi_2)$$



$$r_1 > r_2 \iint \frac{r_{<}^k}{r_{>}^{k+1}} dr_1 dr_2 = \int_0^\infty dr_1 \left(\int_0^{r_1} \frac{r_2^k}{r_1^{k+1}} dr_2 + \int_{r_1}^\infty \frac{r_1^k}{r_2^{k+1}} dr_2 \right)$$

$$\Psi \sim \varphi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi)$$

Eventually we have the integrals from the product of three spherical functions

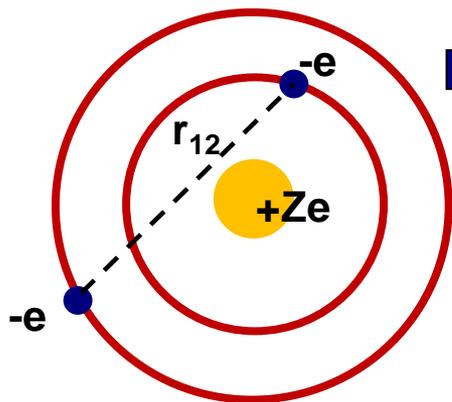
This integral is expressed in terms of the Wigner 3j-symbols:

$$\int_0^\pi \int_0^{2\pi} Y_{l_1 m_1}^* Y_{l_2 m_2} Y_{l_3 m_3} \sin \theta d\varphi d\theta = (-1)^{m_1} \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix}$$

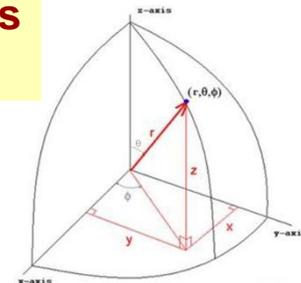
Not zero, if l_1+k+l_2 is an even number. $k=0, 2, 4$ for d-electrons
 $k=0, 2, 4, 6$ for f-electrons

Energy of spectral terms of free ions

Coulomb interaction between electrons of the unfilled shell is mainly responsible for the formation of the energy level schemes



Spherical system of coordinates



$$\int \Psi^* \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \Psi r_1^2 r_2^2 \sin \theta_1 \sin \theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2$$

The energy of the LS terms will be a combination of the F^k parameters (Slater integrals) defined as:

$$F^k = e^2 \int \int \frac{r_{<}^k}{r_{>}^{k+1}} R_1(r_1)^2 R_2(r_2)^2 r_1^2 r_2^2 dr_1 dr_2$$

$R(r)$ – radial parts of the wave functions

The integrals can be found numerically
 $k=0, 2, 4$ for the d-electrons
 $k=0, 2, 4, 6$ for the f-electrons

It is a common practice to express the energy of the LS terms for 3d ions in the so called Racah parameters A, B, C :

$$A = F^0 - \frac{49}{441} F^4; B = \frac{1}{49} F^2 - \frac{5}{441} F^4; C = \frac{5}{63} F^4$$

Energy of spectral terms of free ions

Equivalent configurations for d -electrons:

d^1 and $d^9 - {}^2D$

d^2 and $d^8 - {}^1SDG, {}^3PF$

d^3 and $d^7 - {}^2PD_{(2)}FGH, {}^4PF$

d^4 and $d^6 - {}^1S_{(2)}D_{(2)}FG_{(2)}I, {}^3P_{(2)}DF_{(2)}GH, {}^5D$

$d^5 - {}^2SPD_{(3)}F_{(2)}G_{(2)}HI, {}^4PDFG, {}^6S$

$3d^n$ electron configurations and corresponding ions from the periodic table

d^1 Ti^{3+}

d^2 $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}, Fe^{6+}$

d^3 $V^{2+}, Cr^{3+}, Mn^{4+}, Fe^{5+}$

d^4 $Cr^{2+}, Mn^{3+}, Fe^{4+}$

d^5 Mn^{2+}, Fe^{3+}

d^6 Fe^{2+}, Co^{3+}

d^7 Co^{2+}, Ni^{3+}

d^8 Ni^{2+}

d^9 Cu^{2+}

d^2 and $d^8 - {}^1SDG, {}^3PF$	
1S	$A + 14B + 7C$
3P	$A + 7B$
1D	$A - 3B + 2C$
3F	$A - 8B$
1G	$A + 4B + 2C$
d^3 and $d^7 - {}^2PD_{(2)}FGH, {}^4PF$	
2P	$3A - 6B + 3C$
4P	$3A$
${}^2D_1, {}^2D_2$	A can be omitted (a shift of all terms)
2F	$3A + 9B + 3C$
4F	$3A - 15B$
2G	$3A - 11B + 3C$
2H	$3A - 6B + 3C$

Typical values of the Racah parameters for some free 3d ions

Ion	B (cm ⁻¹)	C (cm ⁻¹)
Ti ²⁺	718	2629
V ³⁺	861	4165
Cr ⁴⁺	1039	4238
V ²⁺	766	2855
Cr ³⁺	918	3850
Mn ³⁺	965	3675
Fe ⁴⁺	1144	4459
Mn ²⁺	960	3325
Fe ³⁺	1015	4800
Co ²⁺	971	4366
Ni ²⁺	1041	4831
Cu ²⁺	1238	4659

Cr⁴⁺ – ¹SDG, ³PF	
³F	– 8312 cm⁻¹
¹D	5359 cm⁻¹
³P	7273 cm⁻¹
¹G	12632 cm⁻¹
¹S	44212 cm⁻¹

Electron states and spectral terms of free ions

$$N = \frac{q!}{k!(q-k)!}$$

Number of permutations of k electrons through q orbitals

Increase of the number of states

Electron configuration	Number of states	Number of energy levels
p^1, p^5	6	1
p^2, p^4	15	3
p^3	20	3

Electron configuration	Number of states	Number of energy levels
d^1, d^9	10	1
d^2, d^8	45	5
d^3, d^7	120	8
d^4, d^6	210	16
d^5	252	16

Electron configuration	Number of states	Number of energy levels
f^1, f^{13}	14	1
f^2, f^{12}	91	7
f^3, f^{11}	364	17
f^4, f^{10}	1001	47
f^5, f^9	2002	73
f^6, f^8	3003	119
f^7	3432	119

How can we find the number of energy levels for each of these configurations?..

How can we calculate the energies of those levels?..

Outline

- **Introduction: impurities in crystals and glasses**
- **Transition metal and rare earth ions**
 - Energy level schemes of free ions
 - Correlation between the Racah parameters, spin-orbit constant and atomic number for isovalent ions
- **Basic foundations of crystal field theory**
 - Splitting of free ion energy levels in crystal field
 - Tanabe-Sugano diagrams for d ions
- **Conclusions**

Electronic states: Hamiltonian for free d-ions

Coulomb interaction

Spin-orbit interaction

Tree's correction

$$H_{FI} = \sum_{k=2,4} F^{(k)} h_k + \zeta \sum_{i=1}^N \mathbf{l}_i \cdot \mathbf{s}_i + \alpha L(L+1)$$

Slater integrals

C.A. Morrison, *Crystal Fields for Transition-Metal Ions in Laser Host Materials*, Springer-Verlag, 1992

$$F^{(2)} = 7(7B + C)$$

$$F^{(4)} = 63C/5$$

Racah parameters

Is there any trend between these parameters and a number of d-electrons (or atomic number)?

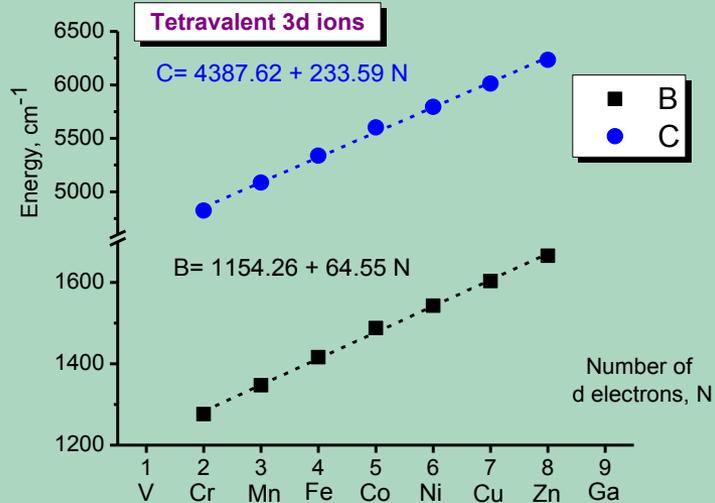
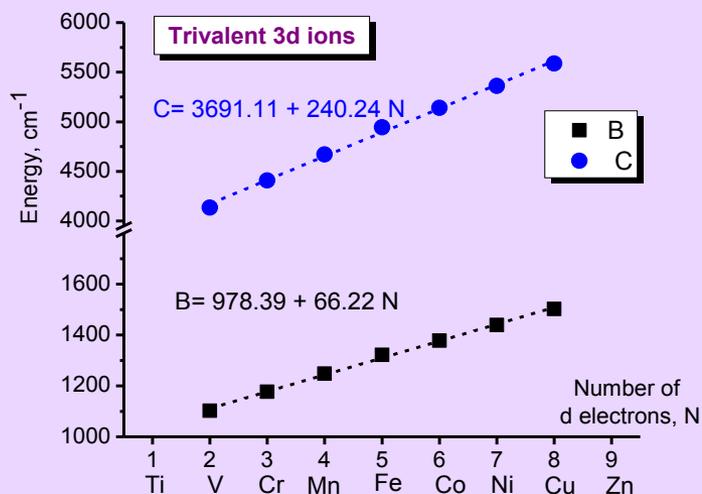
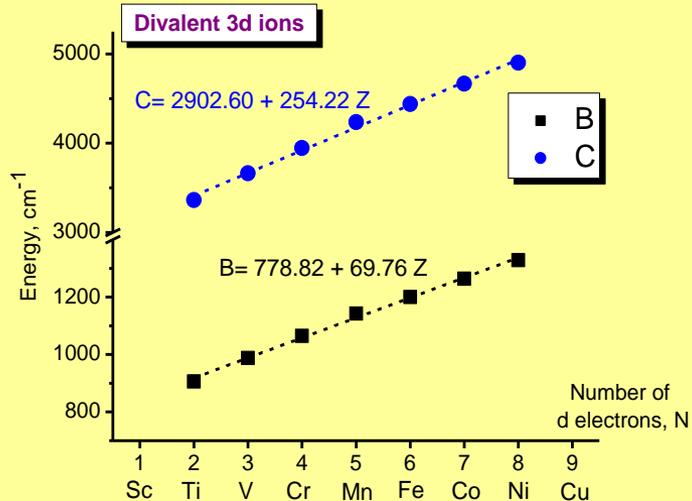
Systematic trends across the 3d ions series

Atomic numbers and electron configurations for the considered di-, tri- and tetravalent 3d ions.

Atomic number Z	Element's symbol	Electronic configuration $3d^N$		
		Divalent	Trivalent	Tetravalent
21	Sc	$3d^1$	$3d^0$	–
22	Ti	$3d^2$	$3d^1$	$3d^0$
23	V	$3d^3$	$3d^2$	$3d^1$
24	Cr	$3d^4$	$3d^3$	$3d^2$
25	Mn	$3d^5$	$3d^4$	$3d^3$
26	Fe	$3d^6$	$3d^5$	$3d^4$
27	Co	$3d^7$	$3d^6$	$3d^5$
28	Ni	$3d^8$	$3d^7$	$3d^6$
29	Cu	$3d^9$	$3d^8$	$3d^7$
30	Zn	$3d^{10}$	$3d^9$	$3d^8$
31	Ga	–	$3d^{10}$	$3d^9$

Is there any trend in behavior of the B , C parameters across these groups?..

Free di, tri-, tetravalent 3d ions: Racah parameters

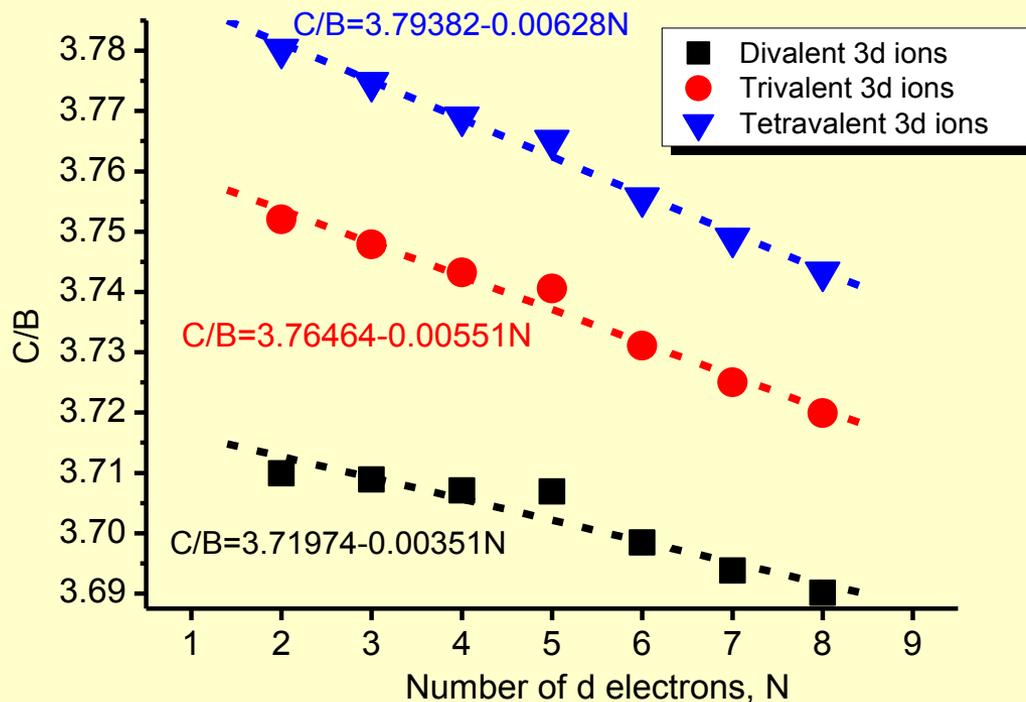


B and C – linear increasing functions of number of d-electrons (atomic number)

		a_1 (cm^{-1})	a_2 ($\text{cm}^{-1}/\text{electron}$)
Divalent ions	B	778.82 ± 10.31	69.76 ± 1.91
	C	2902.60 ± 42.06	254.22 ± 7.81
Trivalent ions	B	978.39 ± 7.88	66.22 ± 1.46
	C	3691.11 ± 33.06	240.24 ± 6.13
Tetravalent ions	B	1154.26 ± 6.78	64.55 ± 1.26
	C	4387.62 ± 28.89	233.59 ± 5.36

**M.G. Brik, A.M. Srivastava,
Opt. Mater. 35 (2013) 1776**

Free di, tri-, tetravalent 3d ions: C/B ratio



C.A. Morrison, *Crystal Fields for Transition-Metal Ions in Laser Host Materials*, Springer-Verlag, 1992

Divalent: $C/B = (3.71974 \pm 0.00275) - (0.00351 \pm 0.00051)N$

Trivalent: $C/B = (3.76464 \pm 0.00187) - (0.00551 \pm 0.00035)N$

Tetravalent: $C/B = (3.79382 \pm 0.00145) - (0.00628 \pm 0.00027)N$

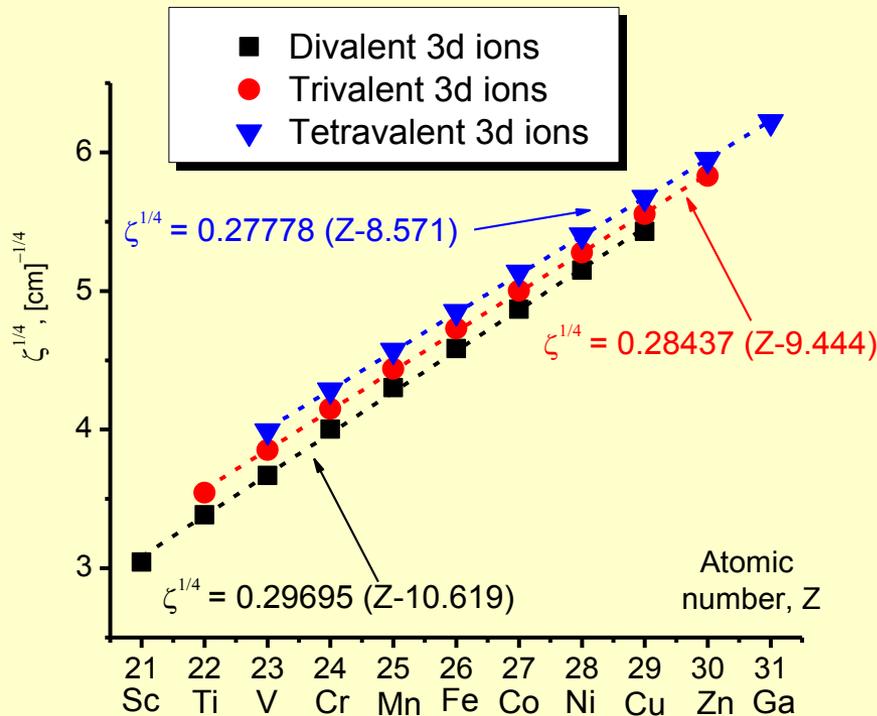
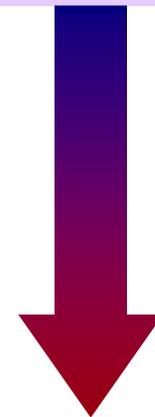
M.G. Brik, A.M. Srivastava, *Opt. Mater.* 35 (2013) 1776

Free di, tri-, tetravalent 3d ions: SO coupling

M.G. Brik, A.M. Srivastava,
Opt. Mater. 35 (2013) 1776

$$\zeta \sim Z^4; \text{ or } \zeta^{1/4} \sim Z$$

Increase of an effective
nuclear charge
with increasing oxidation
state

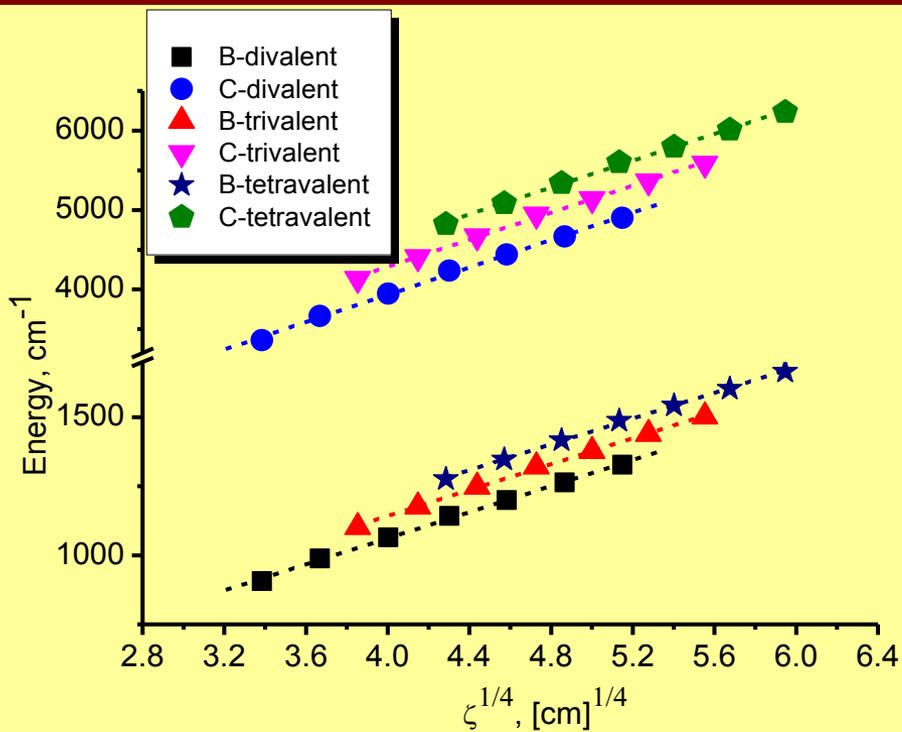


$$\zeta^{1/4} = 0.29695(Z - 10.619) = 0.29695Z^* \quad \text{Divalent}$$

$$\zeta^{1/4} = 0.28437(Z - 9.444) = 0.28437Z^* \quad \text{Trivalent}$$

$$\zeta^{1/4} = 0.27778(Z - 8.571) = 0.27778Z^* \quad \text{Tetravalent}$$

Free di-, tri-, tetravalent 3d ions: relation between B , C and SO constant



Divalent ions

$$B=117 + 236 \zeta^{1/4}; C=489 + 861 \zeta^{1/4}$$

Trivalent ions

$$B=205 + 234 \zeta^{1/4}; C=887 + 850 \zeta^{1/4}$$

Tetravalent ions

$$B=281 + 233 \zeta^{1/4}; C=1228 + 845 \zeta^{1/4}$$

M.G. Brik, A.M. Srivastava,
Opt. Mater. 35 (2013) 1776

Conclusion: if the value of any single parameter (B , C , or ζ) is known for one ion from the group of di-, tri- or tetravalent 3d ions, all parameters for all members in the considered isovalent ions can be estimated.

Free di, tri-, tetravalent 4d/5d ions

Atomic numbers and electron configurations for the considered di-, tri- and tetravalent 4d and 5d ions.

Atomic number Z	Symbol	Electron configuration 4d ^N		
		Divalent	Trivalent	Tetravalent
39	Y	4d ¹	4d ⁰	–
40	Zr	4d ²	4d ¹	4d ⁰
41	Nb	4d ³	4d ²	4d ¹
42	Mo	4d ⁴	4d ³	4d ²
43	Tc	4d ⁵	4d ⁴	4d ³
44	Ru	4d ⁶	4d ⁵	4d ⁴
45	Rh	4d ⁷	4d ⁶	4d ⁵
46	Pd	4d ⁸	4d ⁷	4d ⁶
47	Ag	4d ⁹	4d ⁸	4d ⁷
48	Cd	4d ¹⁰	4d ⁹	4d ⁸
49	In	–	4d ¹⁰	4d ⁹
		Electron configuration 5d ^N		
		Divalent	Trivalent	Tetravalent
71	Lu	5d ¹	5d ⁰	–
72	Hf	5d ²	5d ¹	5d ⁰
73	Ta	5d ³	5d ²	5d ¹
74	W	5d ⁴	5d ³	5d ²
75	Re	5d ⁵	5d ⁴	5d ³
76	Os	5d ⁶	5d ⁵	5d ⁴
77	Ir	5d ⁷	5d ⁶	5d ⁵
78	Pt	5d ⁸	5d ⁷	5d ⁶
79	Au	5d ⁹	5d ⁸	5d ⁷
80	Hg	5d ¹⁰	5d ⁹	5d ⁸
81	Tl	–	5d ¹⁰	5d ⁹

Similar behavior:

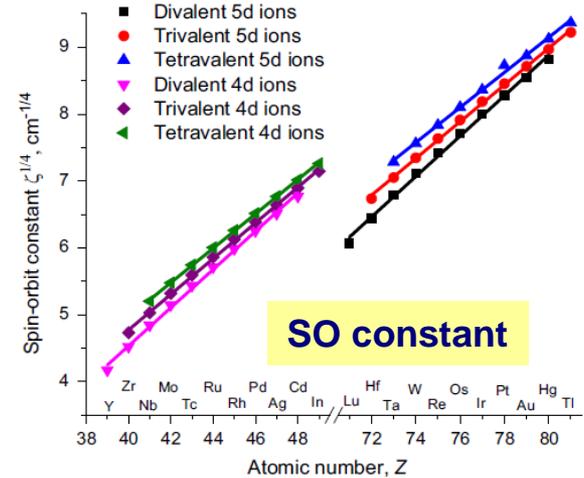
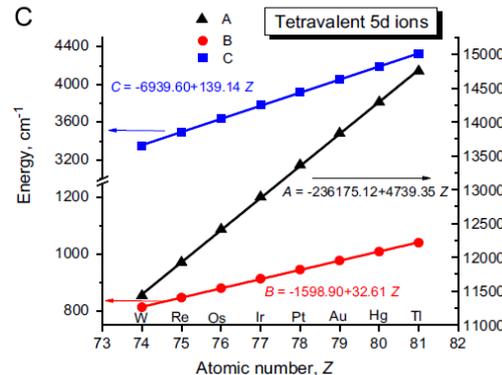
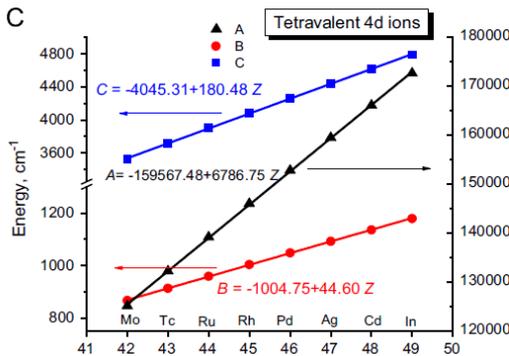
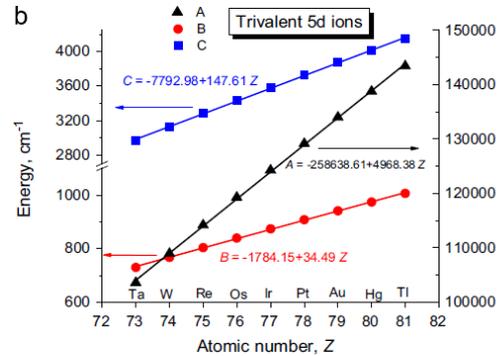
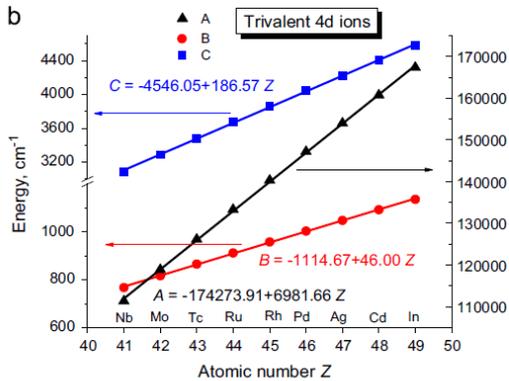
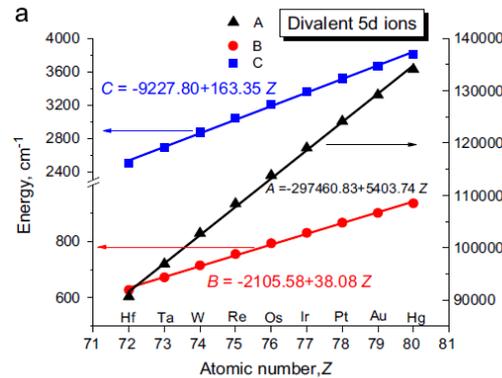
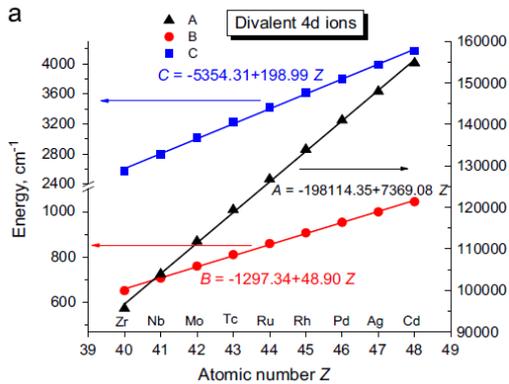
The Racah parameters **A**, **B**, **C**, and SO constant $\zeta^{1/4}$ all proportional to atomic number **Z**.

If one parameter is known for one ion from the group of di-, tri- or tetravalent 4d/5d ions, all parameters for all members in the considered isovalent ions can be estimated.

C.-G. Ma, M.G. Brik,
J. Lumin. 145 (2014) 402

Free di, tri-, tetravalent 4d/5d ions

Racah parameters



Similar behavior:

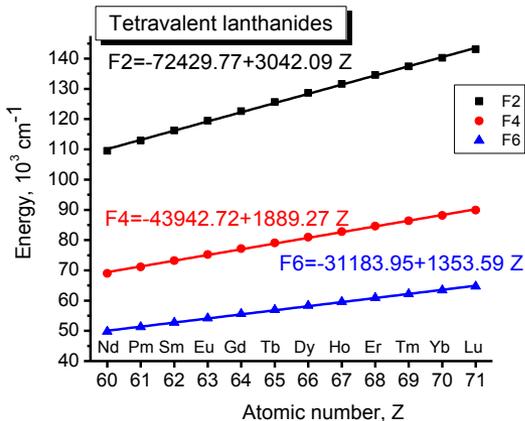
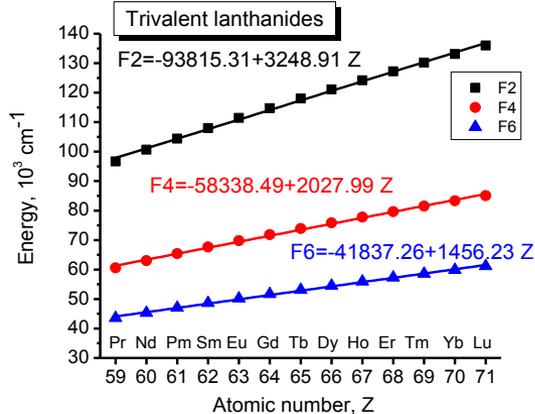
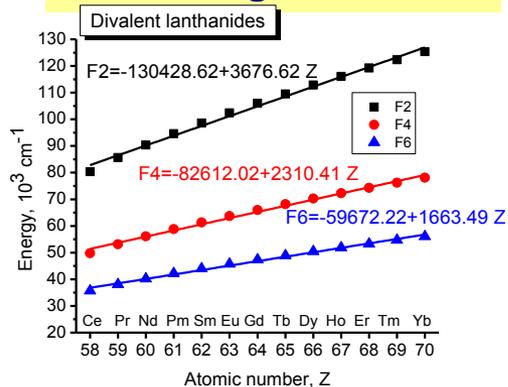
The Racah parameters A , B , C , and SO constant $\zeta^{1/4}$ all proportional to atomic number Z .

If one parameter is known for one ion from the group of di-, tri- or tetravalent 4d/5d ions, all parameters for all members in the considered isoivalent ions can be estimated.

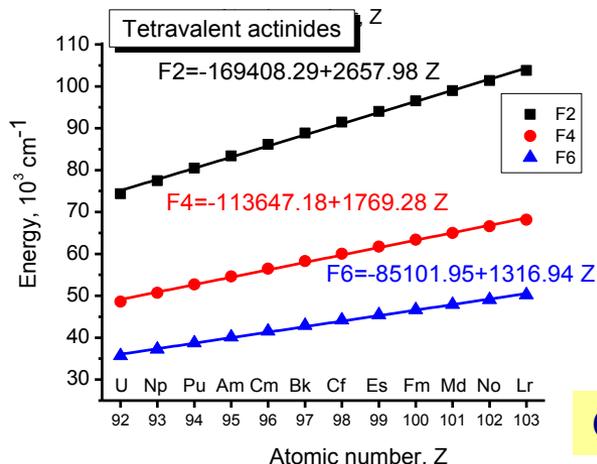
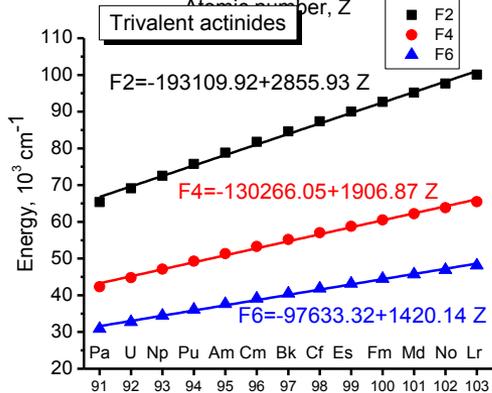
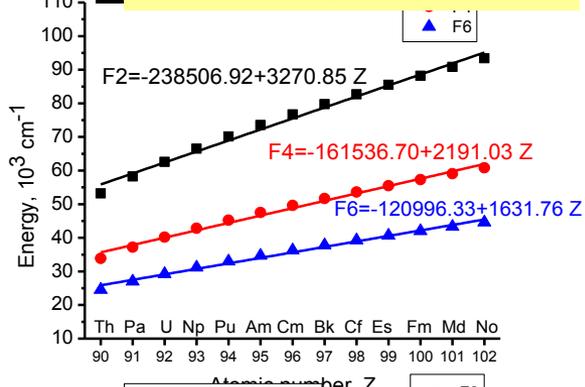
C.-G. Ma, M.G. Brik,
J. Lumin. 145 (2014) 402

Free di, tri-, tetravalent 4f/5f ions

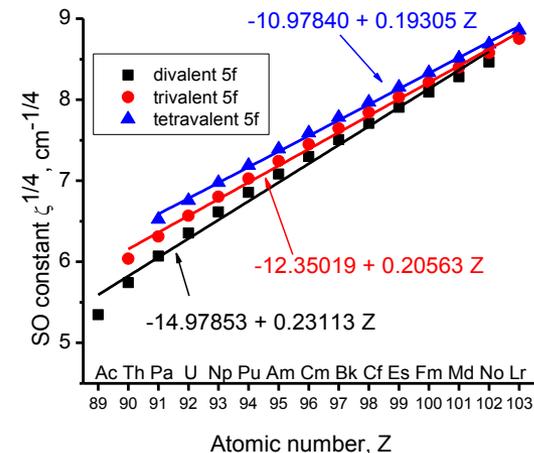
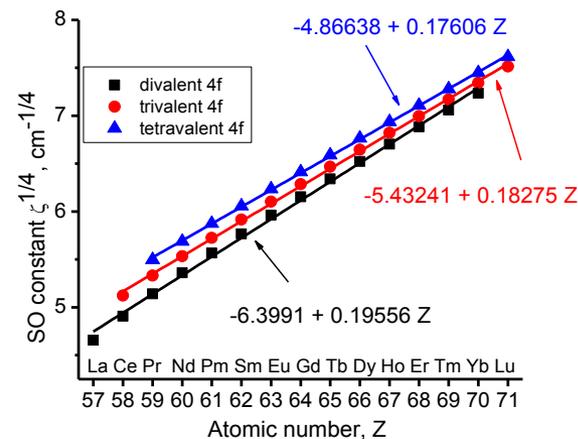
Slater integrals, 4f ions

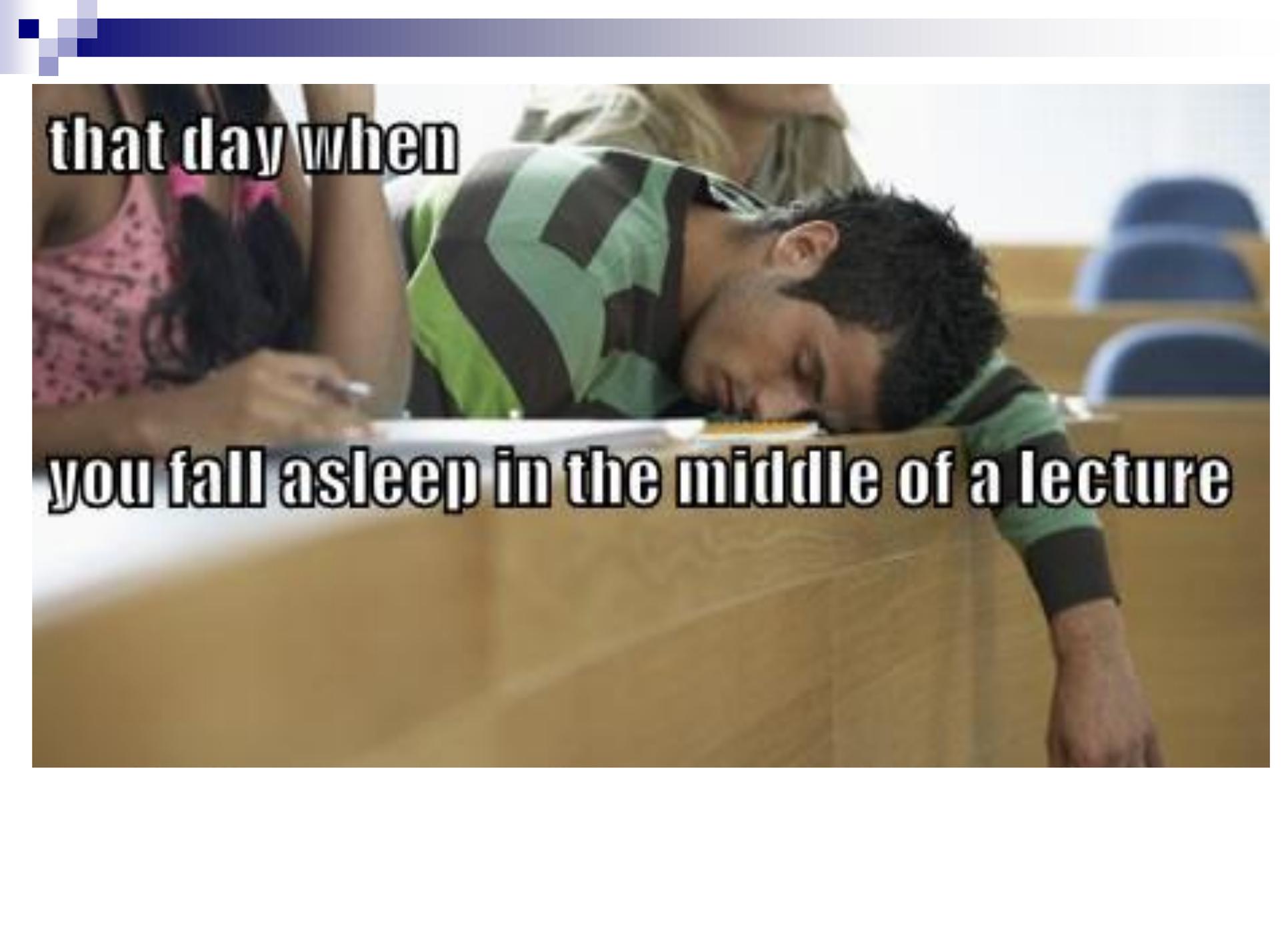


Slater integrals, 5f ions



SO constant



A photograph of a man in a green and black striped shirt falling asleep at a desk in a lecture hall. He is leaning his head on the desk, and his eyes are closed. To his left, a woman in a pink patterned top is writing on a piece of paper. The background shows rows of blue chairs in a lecture hall.

that day when

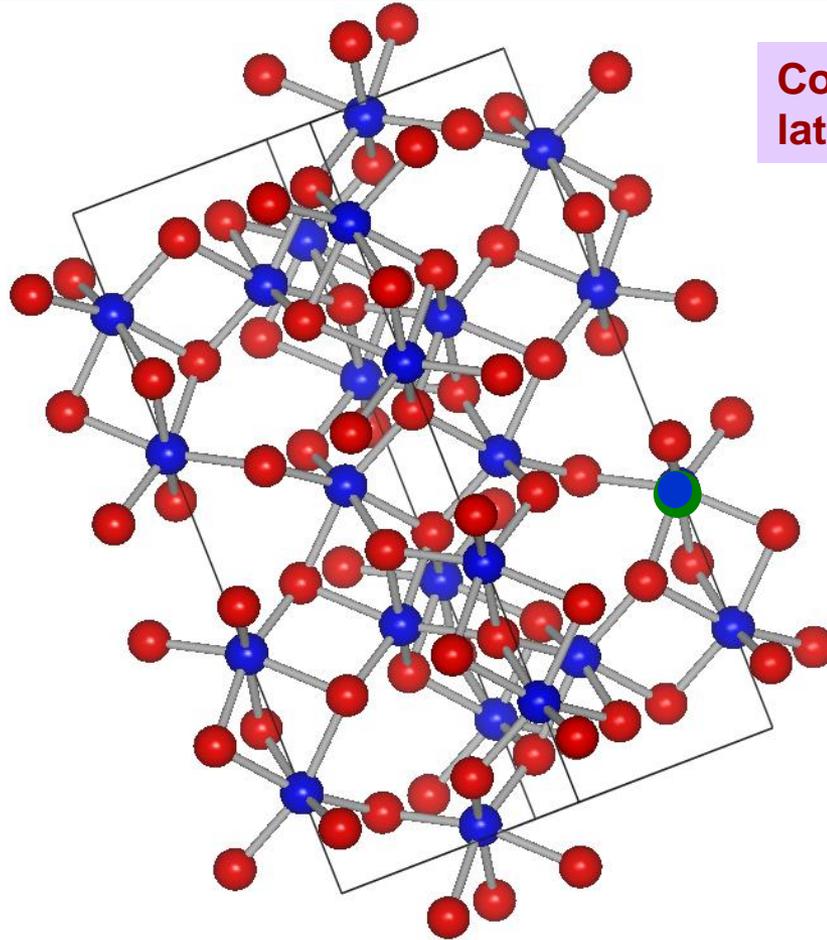
you fall asleep in the middle of a lecture

Outline

- **Introduction: impurities in crystals and glasses**
- **Transition metal and rare earth ions**
 - Energy level schemes of free ions
 - Correlation between the Racah parameters, spin-orbit constant and atomic number for isovalent ions
- **Basic foundations of crystal field theory**
 - Splitting of free ion energy levels in crystal field
 - Tanabe-Sugano diagrams for d ions
- **Conclusions**

Impurity ions in crystals: what happens to the energy levels?..

● Al
● O



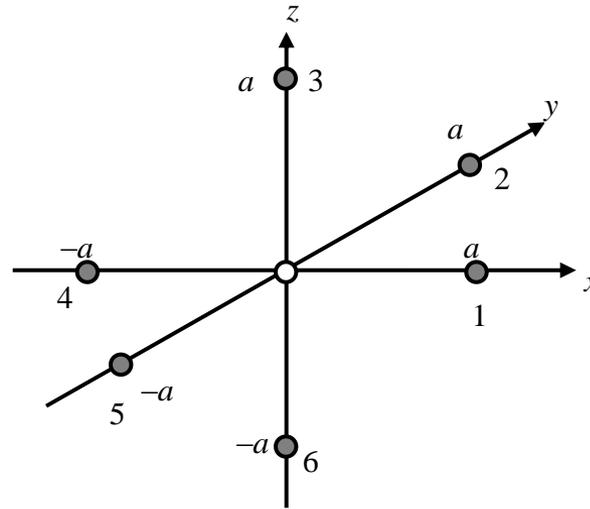
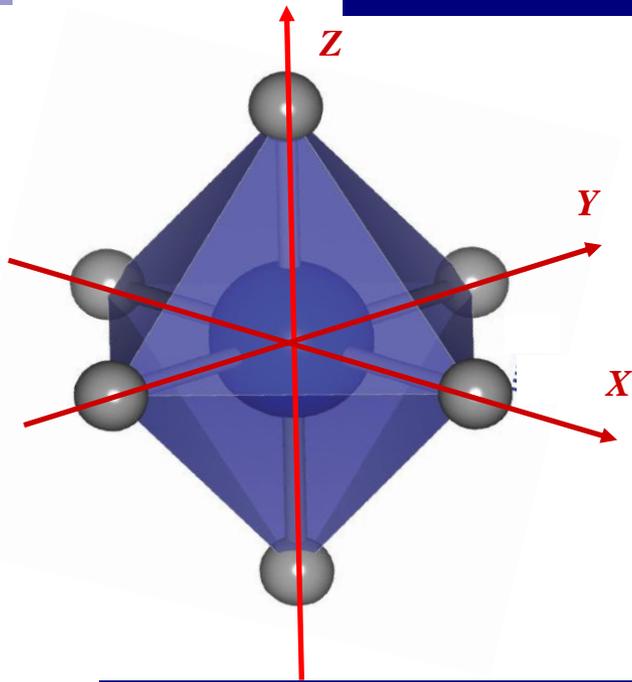
Corundum Al_2O_3 crystal
lattice (one unit cell)

Some Al ions are replaced by Cr: imperfections (defects) of crystal lattice

Spherical symmetry of a free ion is broken. As a result, degeneracy of some energy levels is removed (they are split).

The splitting can be calculated using the crystal field theory.

Octahedral impurity centers



Six surrounding ions (called ligands) have an electrical charge $-Ze$.

	Cartesian coordinates			Spherical coordinates		
	x	y	z	R	θ	φ
Central ion	0	0	0	0	0	0
1	a	0	0	a	$\pi/2$	0
2	0	a	0	a	$\pi/2$	$\pi/2$
3	0	0	a	a	0	0
4	$-a$	0	0	a	$\pi/2$	π
5	0	$-a$	0	a	$\pi/2$	$3\pi/2$
6	0	0	$-a$	a	π	0

Single d -electron in an octahedral crystal field (Ti^{3+} , V^{4+} , Cr^{5+} , ...)

The energetic states of a single d -electron (2D term) in a free ion are described by the following FIVE wave functions:

$$R_{32}(r)Y_{22}(\theta, \varphi), \quad R_{32}(r)Y_{21}(\theta, \varphi), \quad R_{32}(r)Y_{20}(\theta, \varphi), \quad R_{32}(r)Y_{2-1}(\theta, \varphi), \quad R_{32}(r)Y_{2-2}(\theta, \varphi)$$

$$\left(-\frac{\hbar^2}{2m} \Delta + U(\vec{r}) + V(\vec{r}) \right) \Psi = E\Psi$$

$$-\frac{\hbar^2}{2m} \Delta + U(\vec{r}) \text{ a free ion Hamiltonian}$$

$$V(\vec{r}) = \sum_{i=1}^6 \frac{Ze^2}{|\vec{R}_i - \vec{r}|}$$

potential energy V of the single d -electron of the central ion

Perturbation theory: $V(r)$ much smaller than the free ion Hamiltonian. Since the 2D term is 5-fold degenerated, the effects of the small perturbation will be revealed after diagonalizing the following 5 by 5 matrix, which can be built using the above-mentioned wave functions:

Values of M
(from -2 to +2)

	2	1	0	-1	-2
2	V_{22}	V_{21}	V_{20}	V_{2-1}	V_{2-2}
1	V_{12}	V_{11}	V_{10}	V_{1-1}	V_{1-2}
0	V_{02}	V_{01}	V_{00}	V_{0-1}	V_{0-2}
-1	V_{-12}	V_{-11}	V_{-10}	V_{-1-1}	V_{-1-2}
-2	V_{-22}	V_{-21}	V_{-20}	V_{-2-1}	V_{-2-2}

$$V_{n,n'} = \int R_{32}(\vec{r})Y_{2n}^*(\theta, \varphi)V(\vec{r})R_{32}(\vec{r})Y_{2n'}(\theta, \varphi)r^2 \sin \theta dr d\theta d\varphi$$

Single d -electron (Ti^{3+} , V^{4+} , Cr^{5+} , ...) in an octahedral crystal field – calculation of the matrix elements

$$V_{n,n'} = \int R_{32}(\vec{r}) Y_{2n}^*(\theta, \varphi) \sum_{i=1}^6 \frac{Ze^2}{|\vec{\mathbf{R}}_i - \vec{r}|} R_{32}(\vec{r}) Y_{2n'}(\theta, \varphi) r^2 \sin \theta dr d\theta d\varphi$$

How to manage this integral?..

A solution is to expand the Coulomb potential in terms of the spherical harmonics:

$$V(\vec{r}) = \sum_{i=1}^6 \frac{Ze^2}{|\vec{\mathbf{R}}_i - \vec{r}|} = Ze^2 \sum_{i=1}^6 \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} \frac{4\pi}{2k+1} \sum_{m=-k}^k Y_{km}(\theta, \varphi) Y_{km}^*(\theta_i, \varphi_i)$$

Here $r_{<}$ and $r_{>}$ are the smallest and the greatest of r (an electron coordinate) and a (a distance between the central ion and surrounding point charges), (θ, φ) and (θ_i, φ_i) are the spherical angular coordinates corresponding to the electron and ligands, respectively. Since $r < a$ (an electron is between the central ion and ligands), we have:

$$V(\vec{r}) = \frac{Ze^2}{a} \sum_{i=1}^6 \sum_{k=0}^{\infty} \left(\frac{r}{a}\right)^k \frac{4\pi}{2k+1} \sum_{m=-k}^k Y_{km}(\theta, \varphi) Y_{km}^*(\theta_i, \varphi_i)$$

Will it help?..

Oh yes! A use will be made of some remarkable properties of the spherical functions!!



Calculation of the matrix elements of a crystal field potential

– a further simplification

From the sum (formally an infinite one!) over index k many terms vanish. The reason is that the matrix elements of $V(r)$ are proportional to the following integrals from the product of three spherical functions:

$$V_{n,n'} \sim \int_0^{2\pi} \int_0^\pi Y_{l_1 m_1}(\theta, \varphi)^* Y_{km}(\theta, \varphi) Y_{l_2 m_2}(\theta, \varphi) \sin \theta d\theta d\varphi$$

(in our case $l_1 = l_2 = 2$)

This integral is expressed in terms of the Wigner 3j-symbols:

$$\int_0^{2\pi} \int_0^\pi Y_{l_1 m_1}^* Y_{km} Y_{l_2 m_2} \sin \theta d\varphi d\theta = (-1)^{m_1} \sqrt{\frac{(2l_1+1)(2k+1)(2l_2+1)}{4\pi}} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & k & l_2 \\ -m_1 & m & m_2 \end{pmatrix}$$

$$\begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \neq 0 \Rightarrow \begin{array}{l} 1) l_1 + k + l_2 \text{ is even;} \\ 2) 0 \leq k \leq (l_1 + l_2) \end{array}$$

If $l_1 = l_2 = 2$ (d electrons) then $k = 0, 2, 4$.

If $l_1 = l_2 = 3$ (f electrons) then $k = 0, 2, 4, 6$.

Calculations of the matrix elements of the crystal field potential

$$V(\vec{r}) = \frac{6Ze^2}{a} + \frac{Ze^2}{2a^5} r^4 \left\{ C_0^4(\theta, \varphi) + \sqrt{\frac{5}{14}} (C_4^4(\theta, \varphi) + C_{-4}^4(\theta, \varphi)) \right\}$$

$$V_{n,n'} = \int R_{32}(\vec{r}) Y_{2n}^*(\theta, \varphi) V(\vec{r}) R_{32}(\vec{r}) Y_{2n'}(\theta, \varphi) r^2 \sin \theta dr d\theta d\varphi$$

	2	1	0	-1	-2
2	V_{22}	V_{21}	V_{20}	V_{2-1}	V_{2-2}
1	V_{12}	V_{11}	V_{10}	V_{1-1}	V_{1-2}
0	V_{02}	V_{01}	V_{00}	V_{0-1}	V_{0-2}
-1	V_{-12}	V_{-11}	V_{-10}	V_{-1-1}	V_{-1-2}
-2	V_{-22}	V_{-21}	V_{-20}	V_{-2-1}	V_{-2-2}

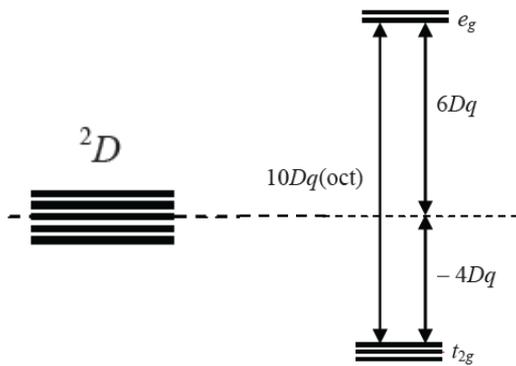
	2	1	0	-1	-2
2	Dq	0	0	0	$5Dq$
1	0	$-4Dq$	0	0	0
0	0	0	$6Dq$	0	0
-1	0	0	0	$-4Dq$	0
-2	$5Dq$	0	0	0	Dq

$$D = \frac{35Ze^2}{4a^5}, \quad q = \frac{2}{105} \langle r^4 \rangle_{32}, \quad \langle r^k \rangle_{32} = \int |R_{32}(r)|^2 r^{k+2} dr.$$

$$\begin{vmatrix} Dq - E & 5Dq & 0 & 0 & 0 \\ 5Dq & Dq - E & 0 & 0 & 0 \\ 0 & 0 & -4Dq - E & 0 & 0 \\ 0 & 0 & 0 & -4Dq - E & 0 \\ 0 & 0 & 0 & 0 & 6Dq - E \end{vmatrix} = 0$$

The calculated eigenvalues are:
 $-4Dq$ (three roots) and $6Dq$ (two roots).

Energy levels of a single d electron in an octahedral field



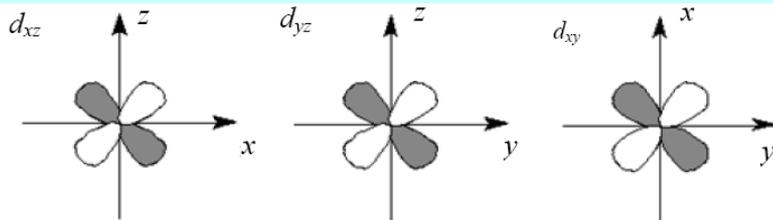
The group theoretical analysis: $D \rightarrow E + T_2$

Crystal field theory allows for quantitative estimation of the energy interval between the split states

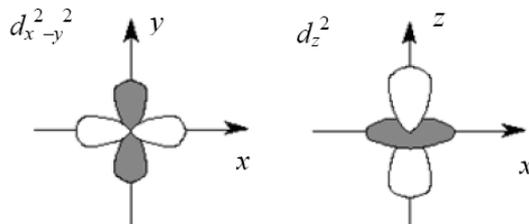
$$10Dq = \frac{5Ze^2 \langle r^4 \rangle}{3a^5}$$

The crystal field strength

The character of this splitting can be understood from the spatial distribution of the electron density



Directed into the space BETWEEN the ligands – smaller energy of the Coulomb repulsion – minimum of total energy



Directed into the space TOWARDS the ligands – higher energy of the Coulomb repulsion – maximum of total energy

Outline

- **Introduction: impurities in crystals and glasses**
- **Transition metal and rare earth ions**
 - Energy level schemes of free ions
 - Correlation between the Racah parameters, spin-orbit constant and atomic number for isovalent ions
- **Basic foundations of crystal field theory**
 - Splitting of free ion energy levels in crystal field
 - Tanabe-Sugano diagrams for d ions
- **Conclusions**

Tanabe-Sugano matrices for energy levels of impurity ions in a cubic crystal field

Three papers by Y. Tanabe and S. Sugano:

1. "On the absorption spectra of complex ions I". *Journal of the Physical Society of Japan* 9 (5), 1954, 753–766.
2. "On the absorption spectra of complex ions II". *Journal of the Physical Society of Japan* 9 (5), 1954, 766–779.
3. "On the absorption spectra of complex ions III". *Journal of the Physical Society of Japan* 11 (8), 1956, 864–877.

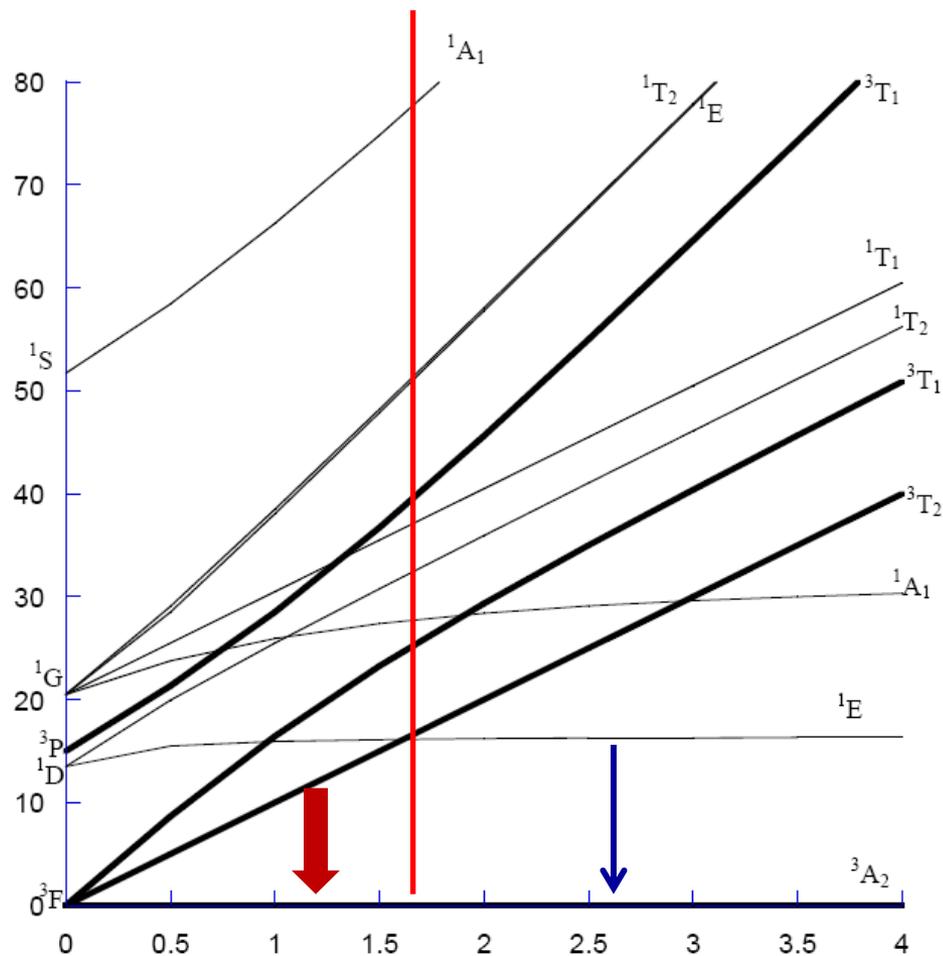
Famous book:

S. Sugano, Y. Tanabe, H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals*, Acad. Press, New York, 1970

Splitting of all LS terms of the d-electron configurations in the cubic crystal field as a function of the Dq , B , C parameters

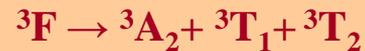
Energy levels of two *d*-electrons in a tetrahedral field

The ground state configuration $(e)^2(t_2)^0$, two excited configurations $(e)^1(t_2)^1$ and $(e)^0(t_2)^2$.



Weak field – broad emission corresponding to the spin-allowed transitions

Strong field – narrow emission corresponding to the spin-forbidden transitions

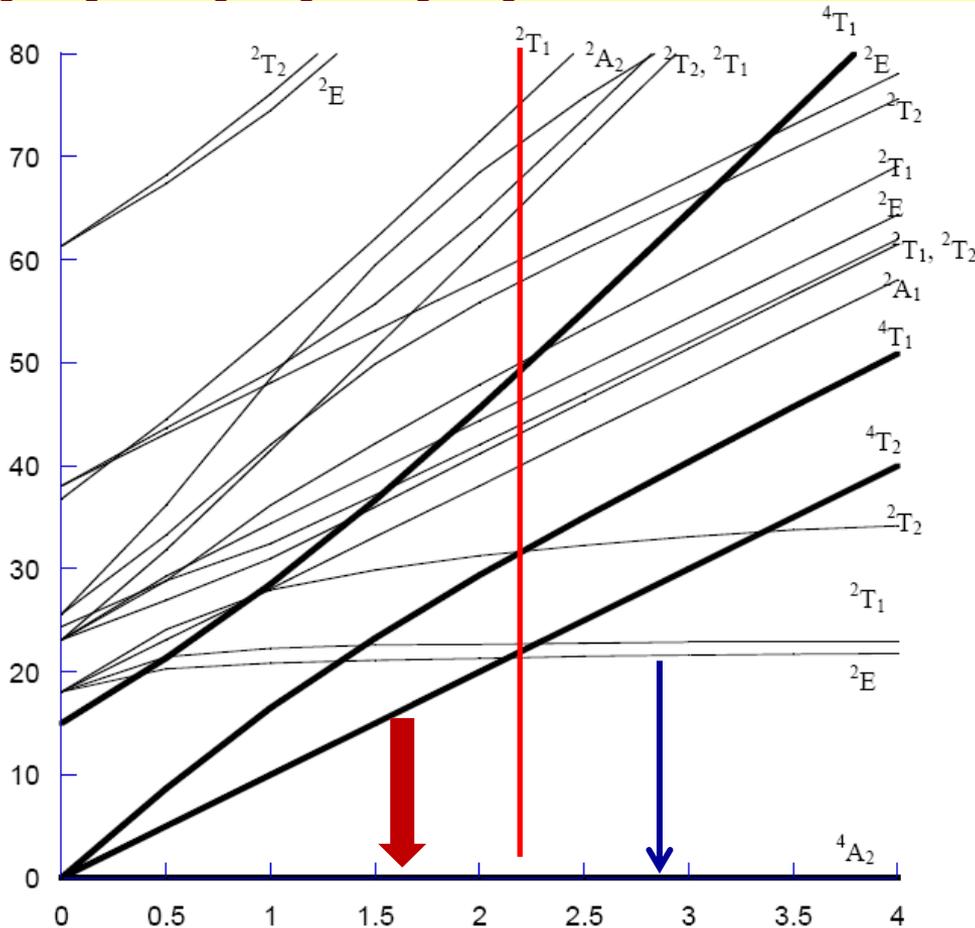


Tanabe-Sugano diagram for the d^2 configuration in a tetrahedral field. The horizontal axis – Dq/B ; the vertical axis – energy in (E/B) .

$C/B=4.25$

Energy levels of three d -electrons in an octahedral field

The ground state configuration $(t_{2g})^3(e_g)^0$ (the energy is 0), and three excited configurations $(t_{2g})^2(e_g)^1$, $(t_{2g})^1(e_g)^2$, $(t_{2g})^0(e_g)^3$ with the energies $10Dq$, $20Dq$, and $30 Dq$, respectively.



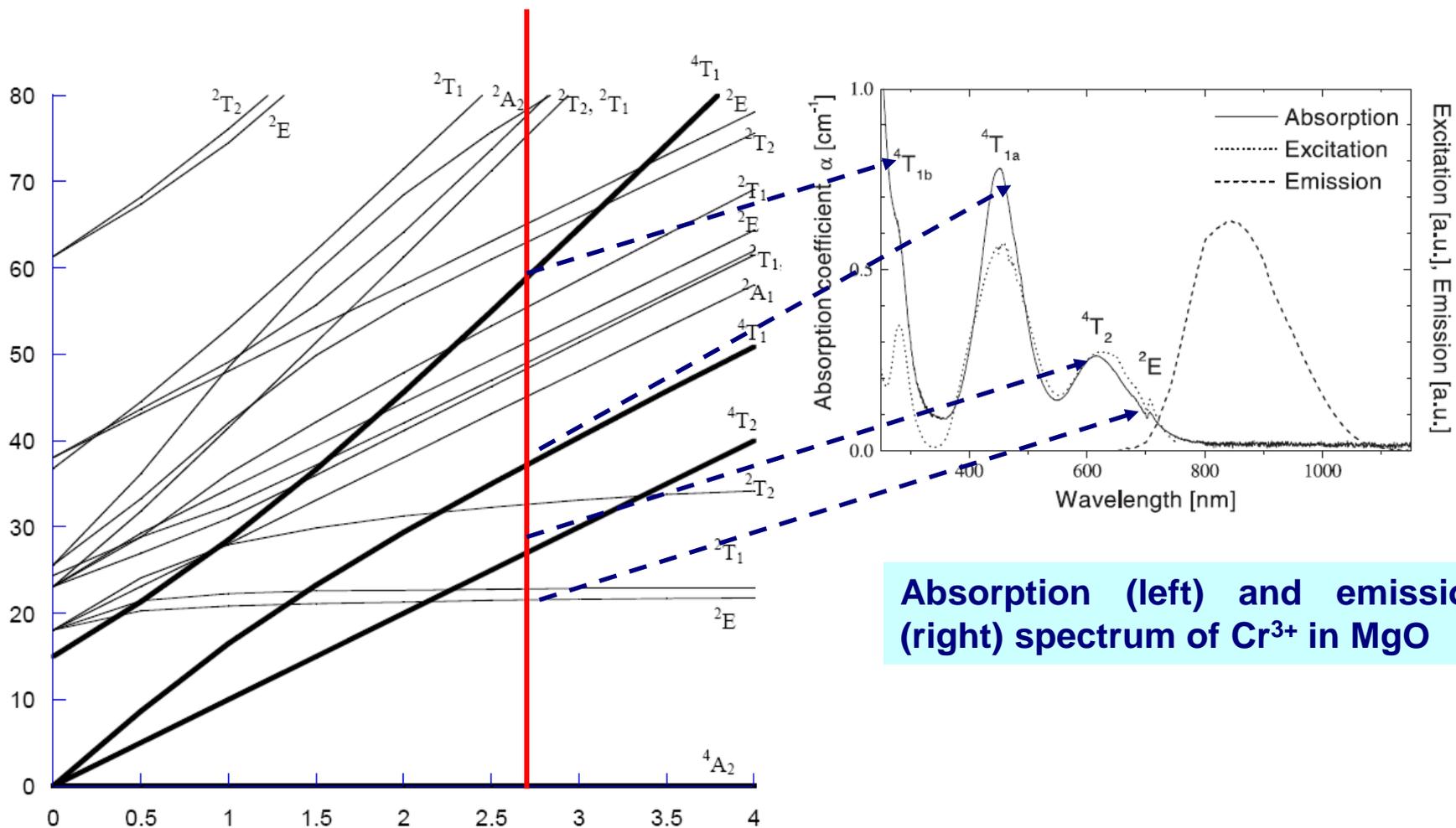
Tanabe-Sugano diagram for the d^3 configuration in an octahedral field. The horizontal axis - Dq/B ; the vertical axis - energy in (E/B) .

$$C/B=4.25$$

Weak field - broad emission corresponding to the spin-allowed transitions

Strong field - narrow emission corresponding to the spin-forbidden transitions

Tanabe-Sugano diagram and absorption spectrum of Cr^{3+}

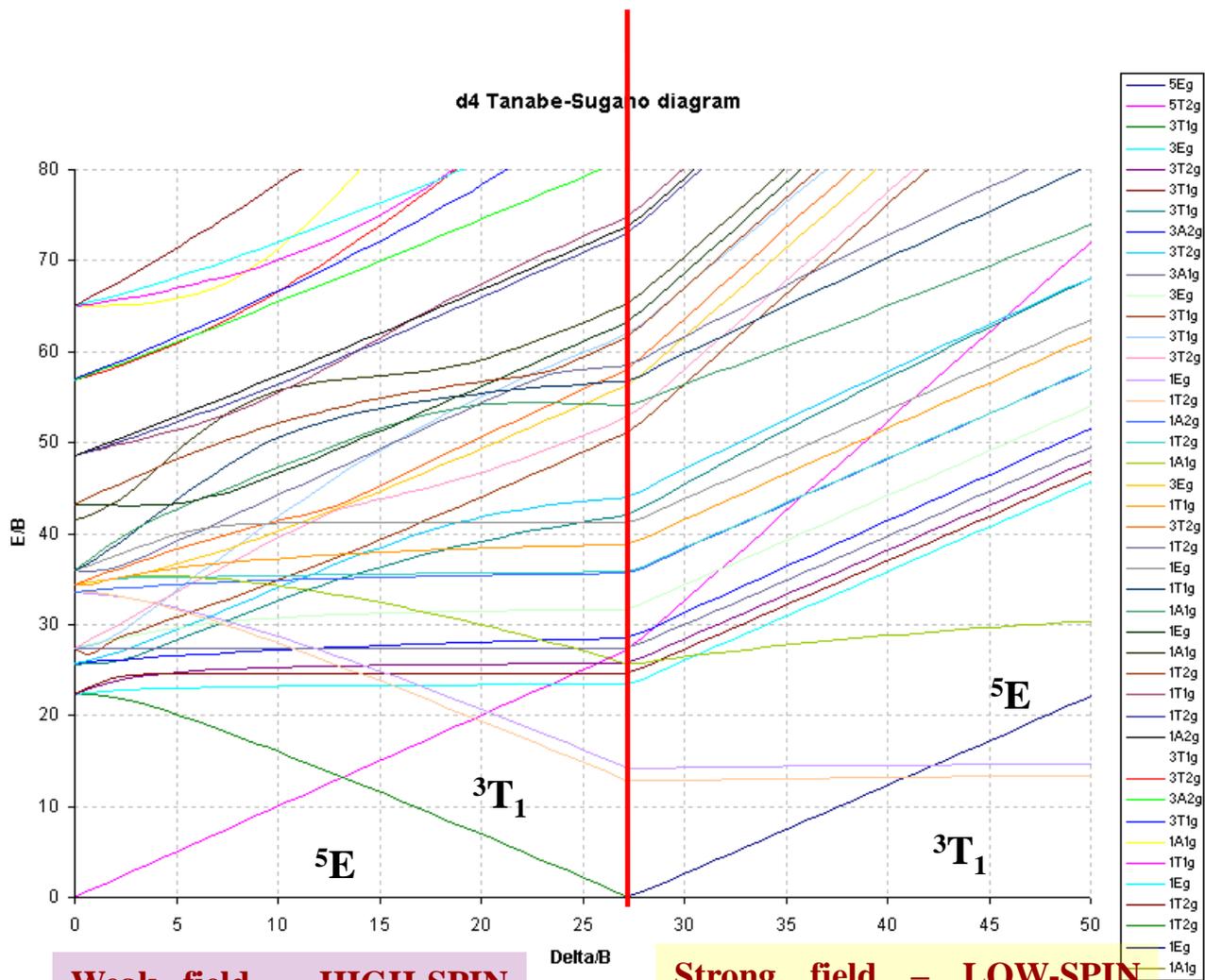


Absorption (left) and emission (right) spectrum of Cr^{3+} in MgO

Energy levels of four *d*-electrons in an octahedral field

The ground state configuration $(t_{2g})^3(e_g)^1$ (**High spin**), and excited configurations $(t_{2g})^2(e_g)^2$, $(t_{2g})^1(e_g)^3$, $(t_{2g})^0(e_g)^4$, with the energies $10Dq$, $20Dq$, $30Dq$, respectively.

Or: the ground state configuration $(t_{2g})^4(e_g)^0$ (**Low spin**), and excited configurations $(t_{2g})^3(e_g)^1$, $(t_{2g})^2(e_g)^2$, $(t_{2g})^1(e_g)^3$, and $(t_{2g})^0(e_g)^4$, with the energies $10Dq$, $20Dq$, $30Dq$, and $40Dq$ respectively.



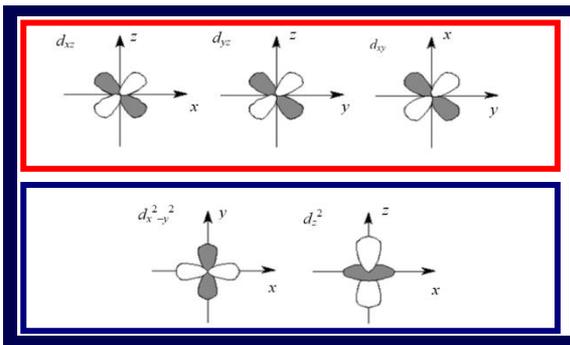
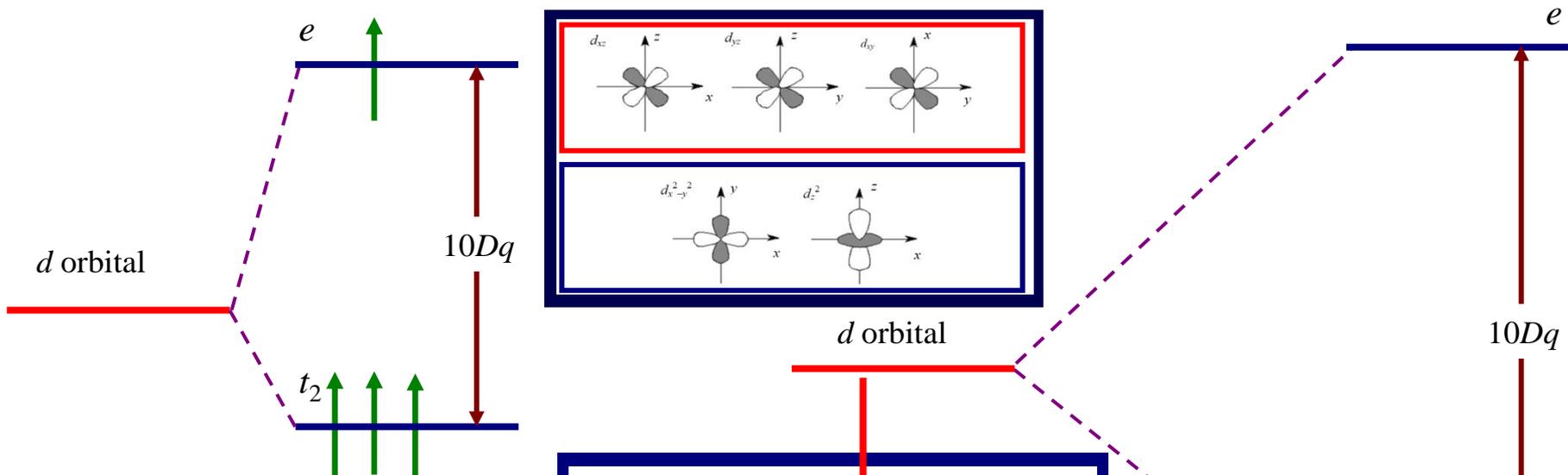
Weak field – HIGH-SPIN state

Strong field – LOW-SPIN state

Tanabe-Sugano diagram for the d^4 configuration in an octahedral field. The horizontal axis – Dq/B ; the vertical axis – energy in (E/B) .

$C/B=4.25$

Difference between the high and low spin states of a d^4 configuration in an

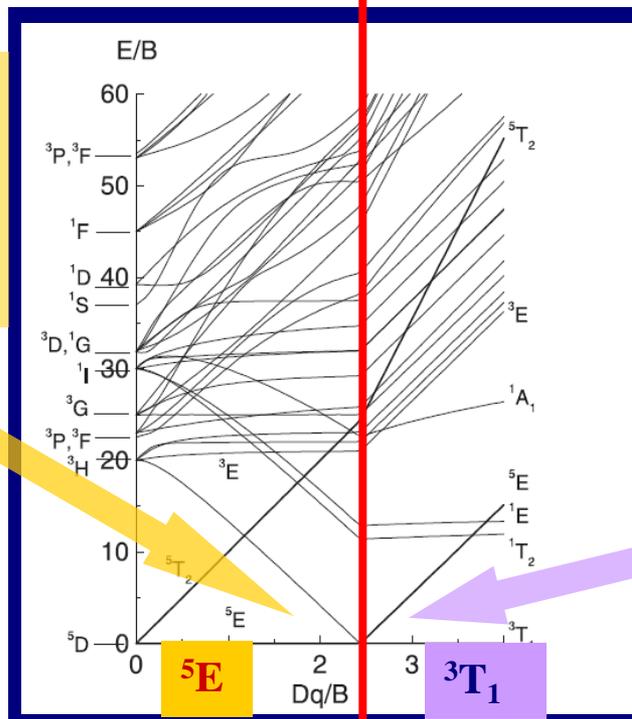


High spin (energy of spin-pairing is greater than the crystal field strength $10Dq$)

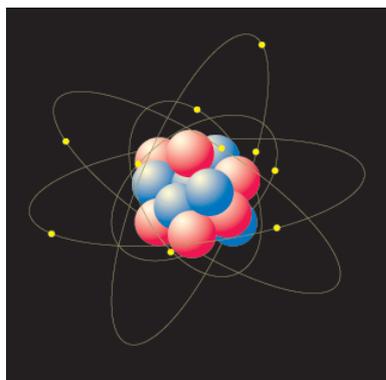
$S = 2$

Low spin (energy of spin-pairing is less than the crystal field strength $10Dq$)

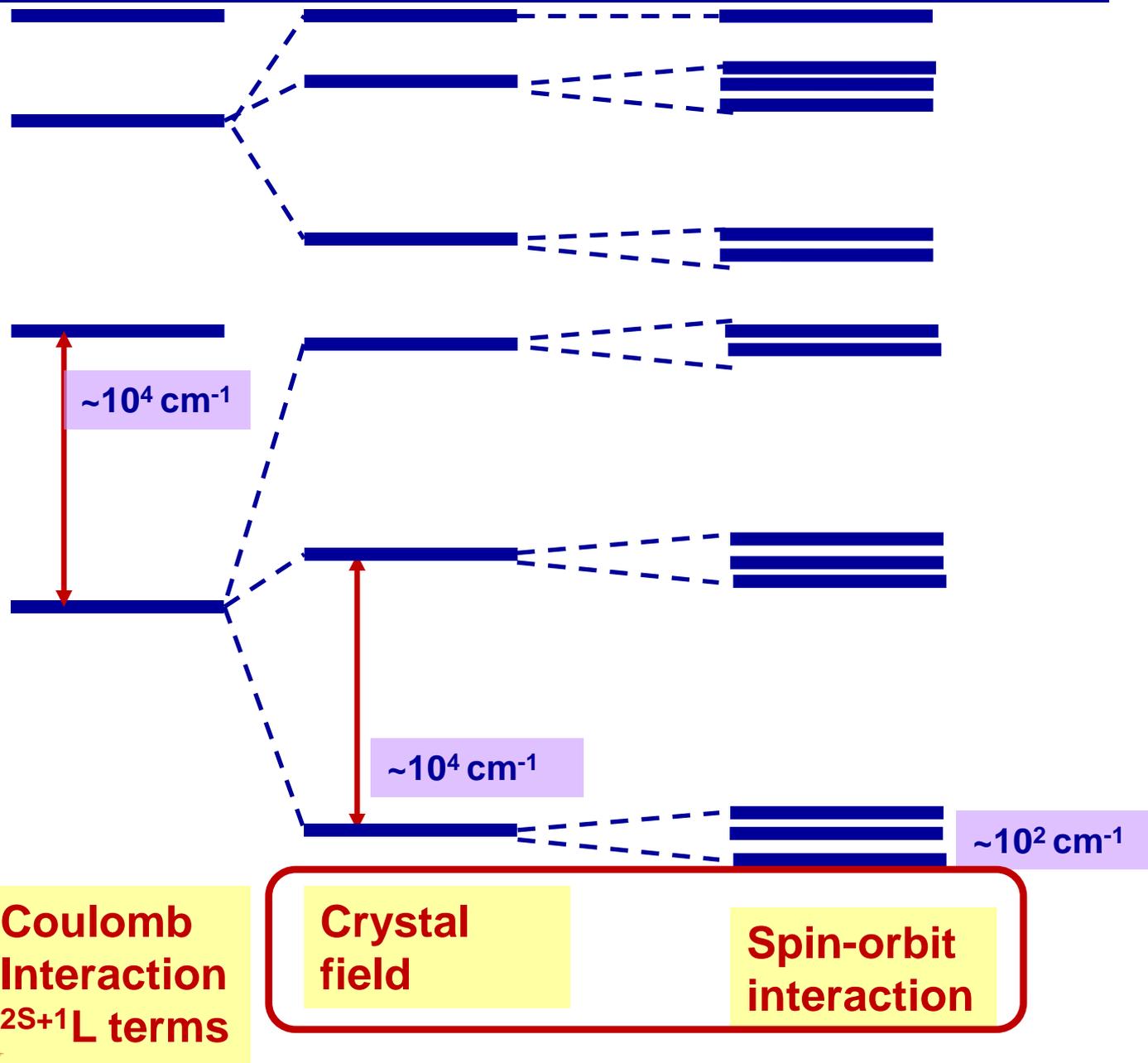
$S = 1$



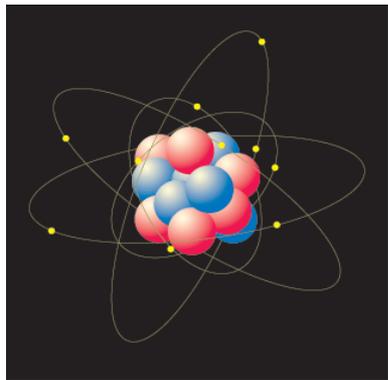
How the energy levels of the d ions are formed...



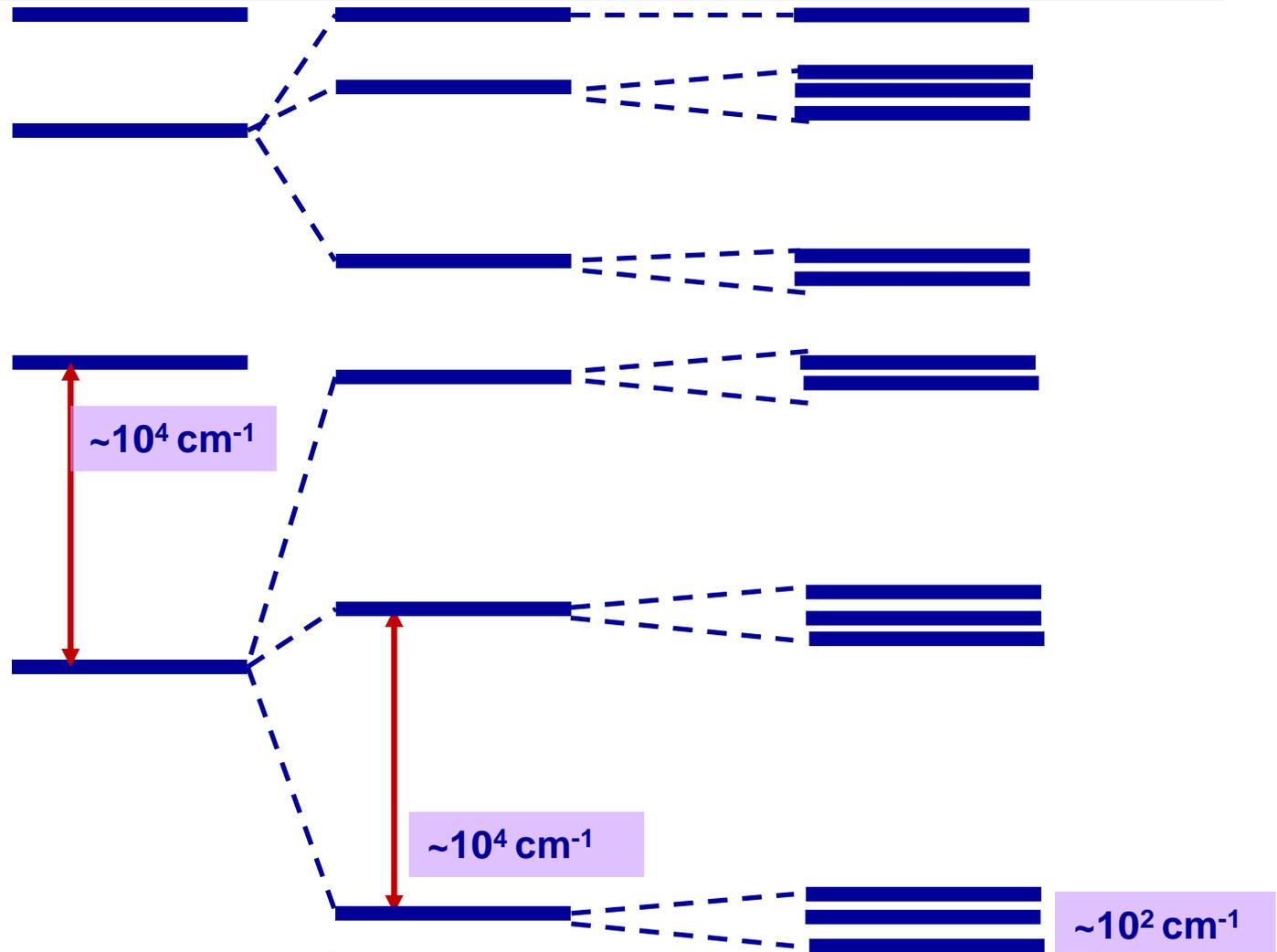
A multielectron ion



How the energy levels of the f ions are formed...



A multielectron ion



Coulomb Interaction
 $2S+1L$ terms

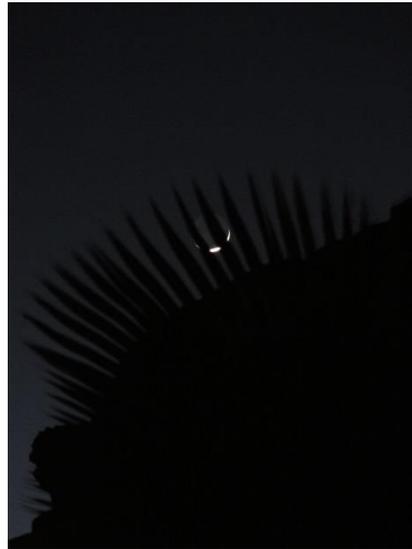
Spin-Orbit Interaction
 $2S+1L_J$

Crystal field splitting

Outline

- **Introduction: impurities in crystals and glasses**
- **Transition metal and rare earth ions**
 - Energy level schemes of free ions
 - Correlation between the Racah parameters, spin-orbit constant and atomic number for isovalent ions
- **Basic foundations of crystal field theory**
 - Splitting of free ion energy levels in crystal field
 - Tanabe-Sugano diagrams for d ions
- **Conclusions**

Multielectron ions energy levels: things to remember



Multielectron ions energy levels: things to remember

- **Multi-electron configurations**
- **Electrostatic (Coulomb) and spin-orbit interactions produce the (rich) energy level schemes**
- **Different terms are denoted by the ^{2S+1}L notation (spin S and orbital momentum L ; TM ions) OR $^{2S+1}L_J$ notation (total angular momentum J ; RE ions)**
- **These states are highly degenerated: $(2S+1)(2L+1)$ number of states**
- **The energies of different terms are expressed in terms of the Racah parameters (Slater integrals)**
- **Parameters of electrostatic interaction increase linearly with atomic number Z in the isovalent series**
- **The SO constant increase linearly with Z^4**
- **Crystal field removes degeneracy of free ion energy levels**

When I see a cow in the field, it is not a cow,
but ... a crazy dance of electrons.

S. Chase





Acknowledgement: financial support



Sir Winston Churchill about Christopher Columbus' voyage to "India", which eventually led to the discovery of the New World:

"He left without knowing where he was going, arrived where he did not think he would, and all of it at the expense of others."



The taxpayers should be always acknowledged!

Marie Curie Initial Training Network LUMINET, grant agreement no. 316906