

# A review of basic spectroscopic properties of the ions with $d^3$ electronic configurations, such as $\text{Cr}^{3+}$ and $\text{Mn}^{4+}$ , for solid state lighting applications

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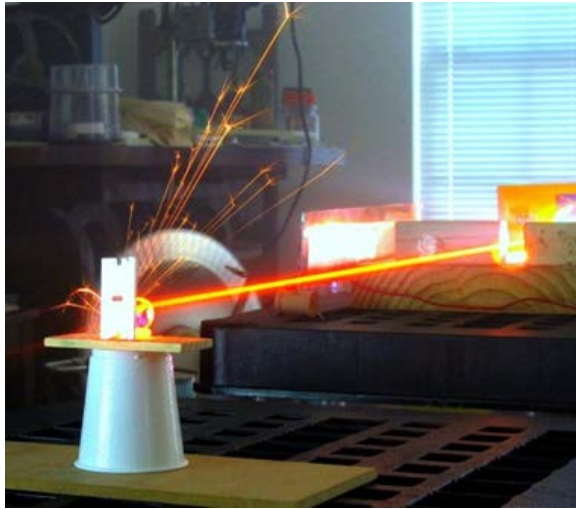
# Outline

- **Introduction: white LEDs for solid state lighting**
- **Mn<sup>4+</sup> and Cr<sup>3+</sup> as suitable red emitters for white LED**
  - Basic properties of the d<sup>3</sup> electron configuration: electronic terms, their energies
  - Properties of the Mn<sup>4+</sup> and Cr<sup>3+</sup> ions in solids: Tanabe-Sugano diagrams
  - Properties of the Mn<sup>4+</sup> and Cr<sup>3+</sup> ions in solids: calculations of the energy levels splitting in low symmetry hosts and analysis of the experimental results
- **Main misconceptions related to the spectra of Cr<sup>3+</sup> and Mn<sup>4+</sup> ions in solids**
  - Origin of the  ${}^2E \rightarrow {}^4A_2$  emission, zero-phonon lines and vibronics
- **Conclusions**

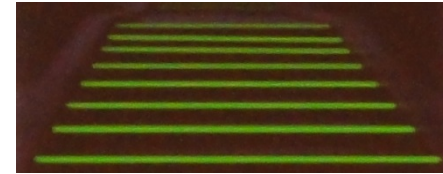
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# Applications of optical materials



**Lasers**



**Lighting**



**Mobile phones and TV displays**

**How to understand this and where does the color come from...**



**Traffic and street lights**



# Lighting – it has always been VERY important...



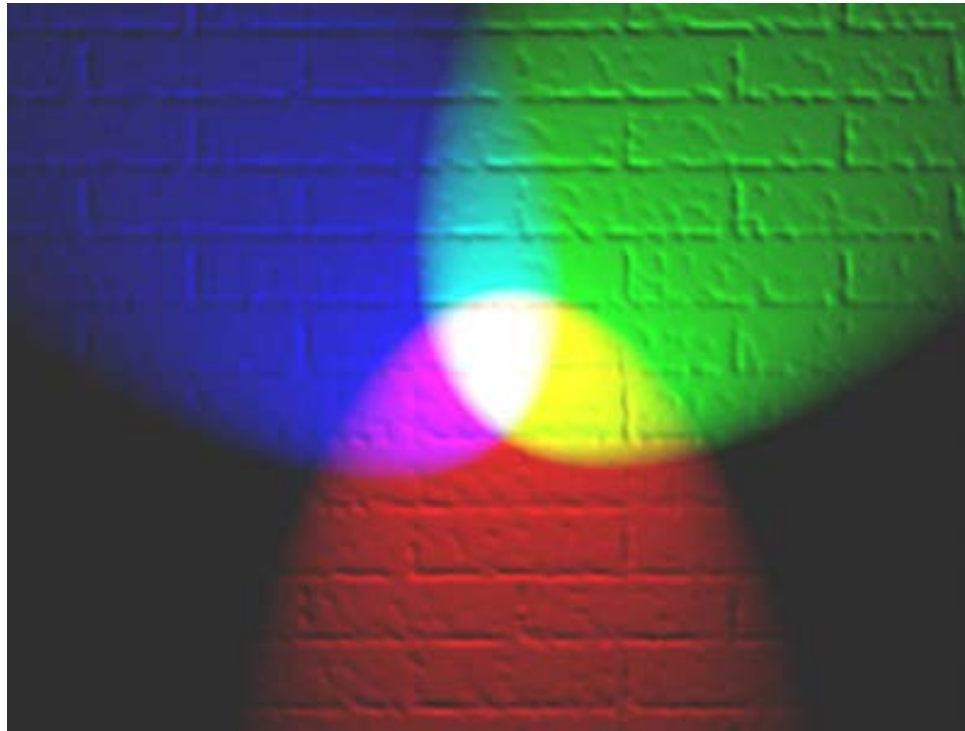
Lighting accounts for about 20% of global building electricity consumption (approximately 7 EJ (exajoule,  $10^{18}$ ) in 2013.

<https://videohive.net/item/world-map-night-lighting/19197777>

■ **Lighting – it has always been VERY important...**

**How to make white light?**

**Mix three colors: red, green, blue**

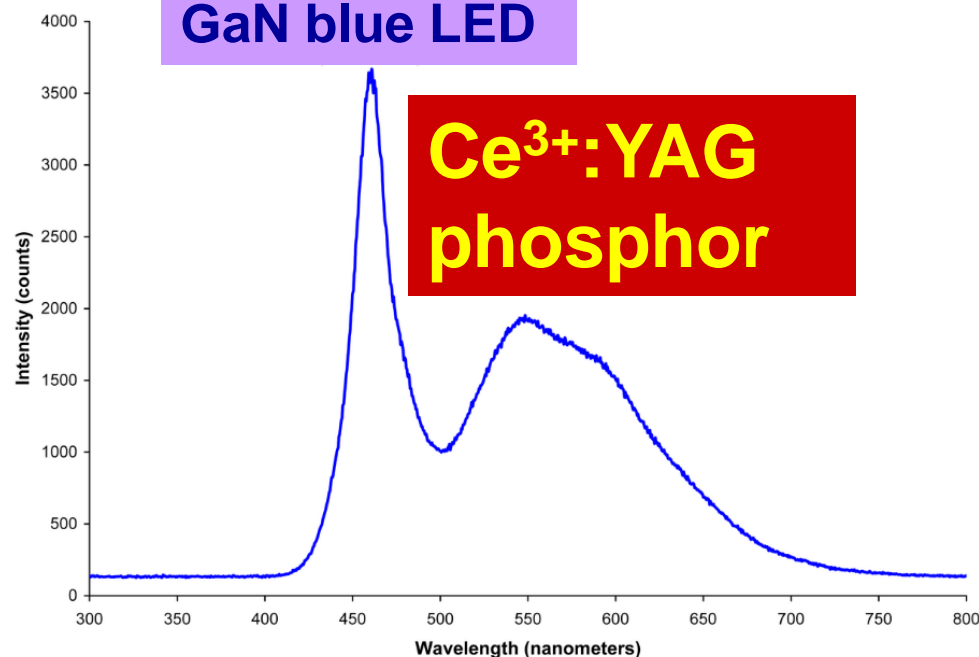
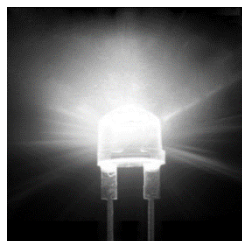
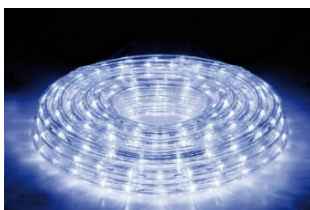
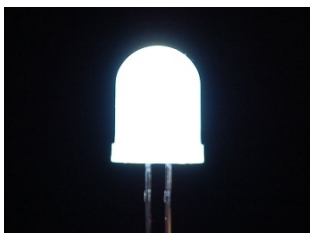


**White light is of paramount importance for indoor lighting, since it resembles the Sun light**



# White light emitting diodes (LEDs)

First white LEDs used the blue LED and yellow  $\text{Ce}^{3+}:\text{YAG}$  phosphor.



Absence of the red component significantly deteriorates the emitted white light characteristics, leading to a rather high correlated color temperature ( $\sim 6283$  K) (the light appears to be “cold”) and poor color rendering index ( $\sim 76$ ) [J. Mater. Chem. C, 2016, 4, 8611].

In view of this, great efforts are put into a search for efficient narrow band red phosphors to be used in white LEDs.

$\text{Mn}^{4+}$  is an excellent candidate for this purpose!

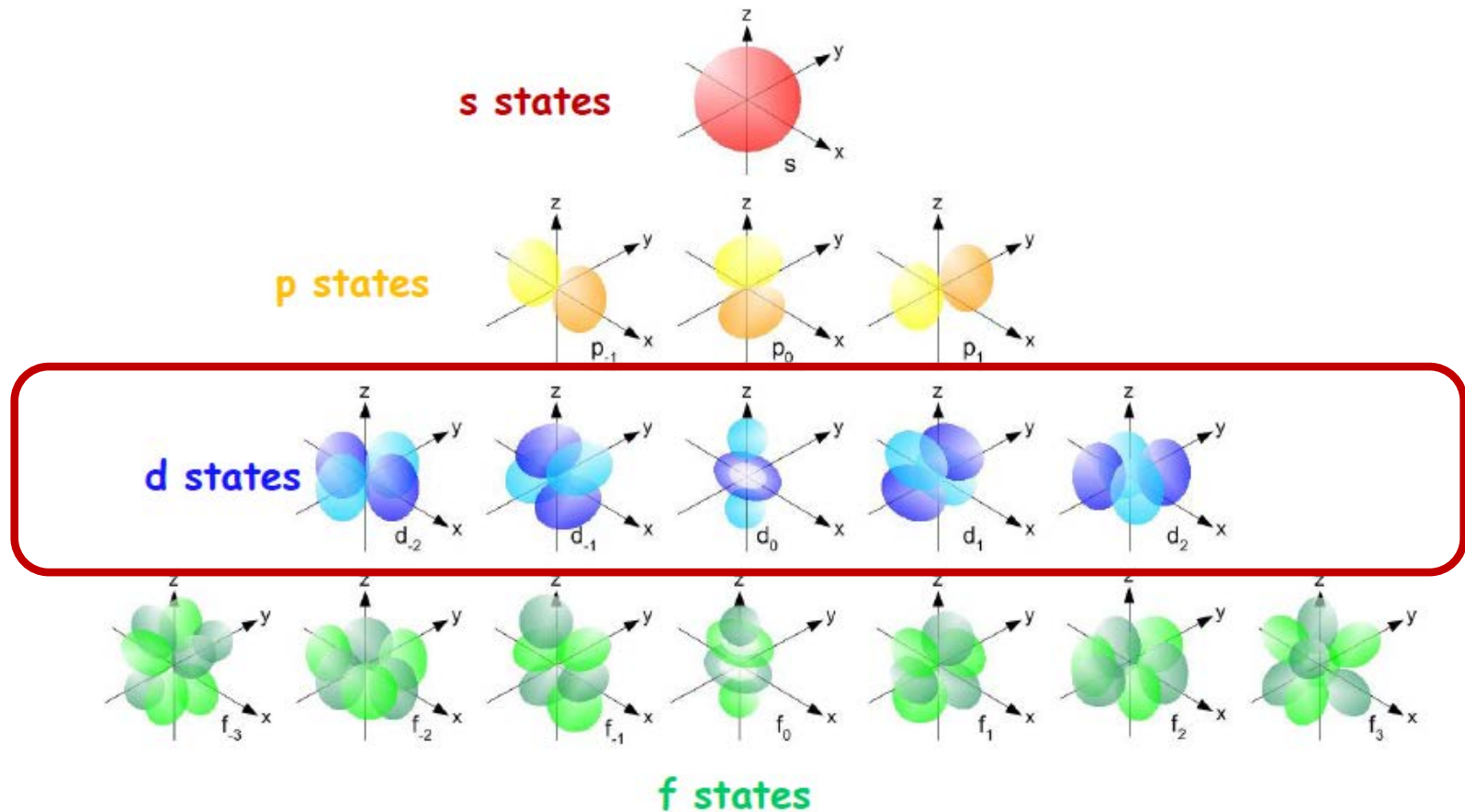
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# Electron configurations

Impurities used for the solid state lighting (3d, 4f ions) – MULTI-ELECTRON systems



# 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:

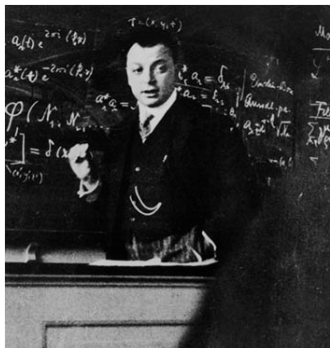
Principal quantum number  $n=4$ , or 5

Orbital quantum number  $l=3$

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

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

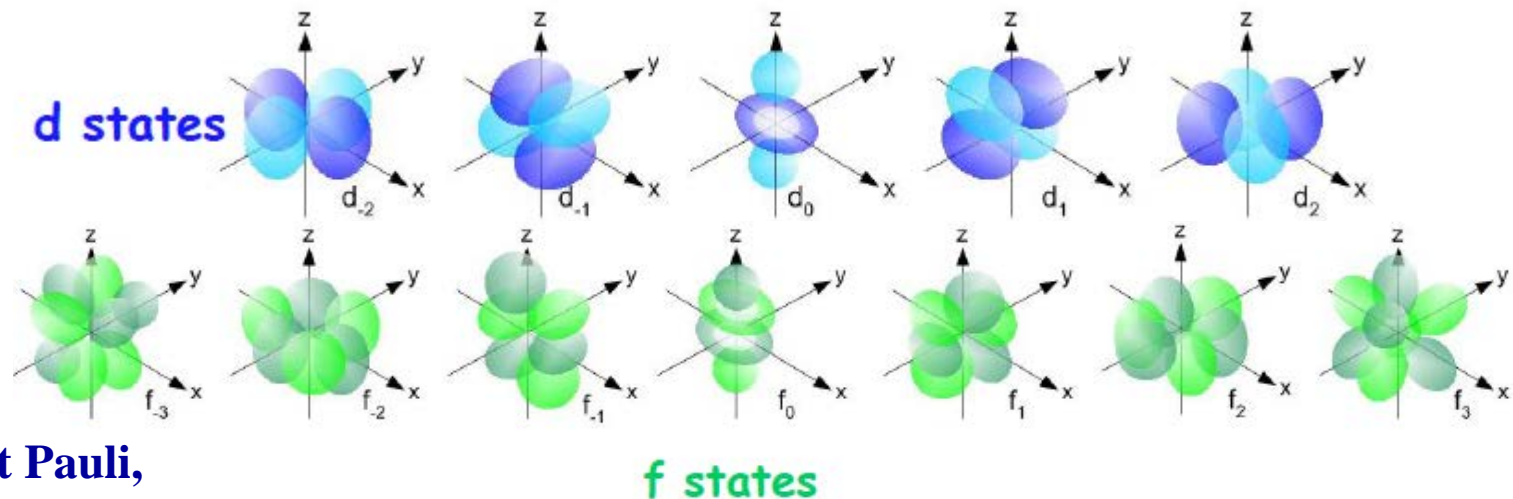
14 states in total



Wolfgang Ernst Pauli,  
25.04.1900-15.12.1958

Nobel prize in physics 1945

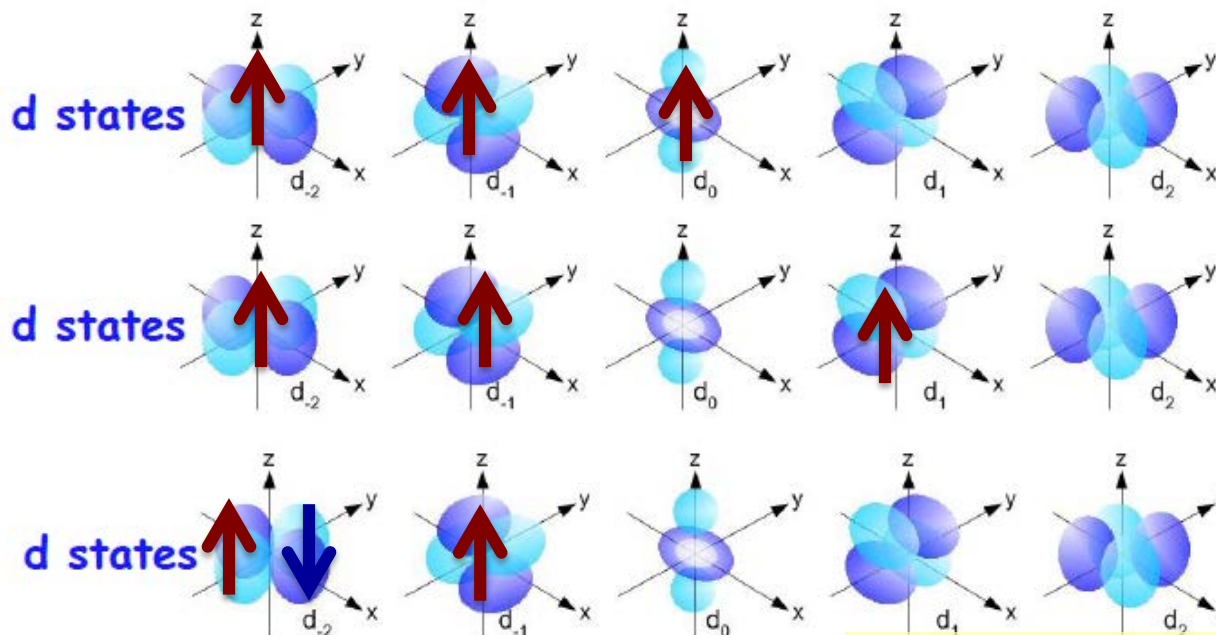
Pauli exclusion principle: no electrons with identical quantum numbers!



# $d^3$ electron configuration (3d transition metals)

The  $[\text{Ar}]3d^3$  electron configuration is characteristic of the following ions:  $\text{V}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Fe}^{5+}$  ( $[\text{Ar}] = 1s^2 2s^2 2p^6 3s^2 3p^6$ ).

Different ways to arrange three d electrons in five d orbitals  
(Coulomb repulsion + Pauli exclusion principle)



OR:

OR:

OR...

$d^3$  configuration:  $q=10$ ,  $k=3$

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

Number of permutations of  $k$  electrons through  $q$  orbitals

$$N = \frac{10!}{3!(10-3)!} = 120$$

Number of allowed states

# 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?..

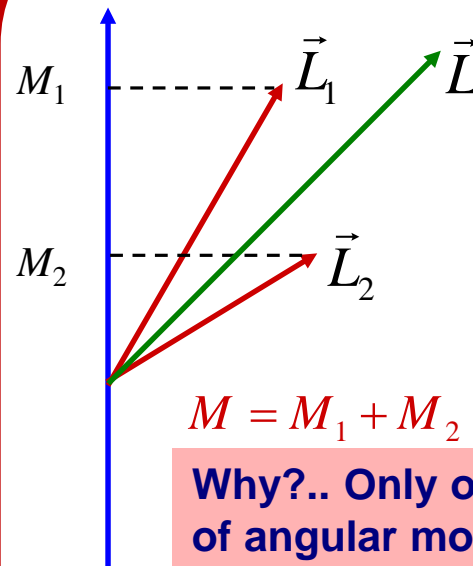
??

# 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.



$$M = M_1 + M_2$$

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

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

# Spectral terms of free ions

Addition of angular momenta of individual electrons allows to introduce a convenient notation for the multielectron states.

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 with $d$ electrons in the unfilled electron shell

## Equivalent configurations of $d$ -electrons:

$d^1$ and $d^9 - {}^2D$	1 energy level
$d^2$ and $d^8 - {}^1SDG, {}^3PF$	5 energy levels
$d^3$ and $d^7 - {}^2PD_{(2)}FGH, {}^4PF$	8 energy levels
$d^4$ and $d^6 - {}^1S_{(2)}D_{(2)}FG_{(2)}I, {}^3P_{(2)}DF_{(2)}GH, {}^5D$	16 energy levels
$d^5 - {}^2SPD_{(3)}F_{(2)}G_{(2)}HI, {}^4PDFG, {}^6S$	16 energy levels

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  $L$

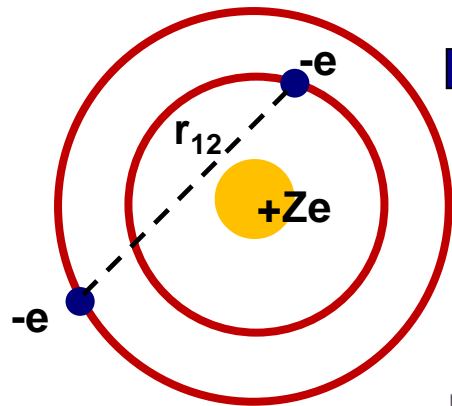
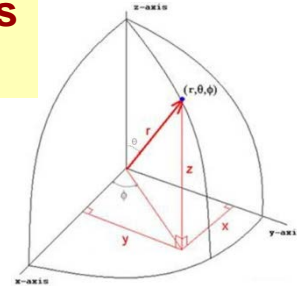
Friedrich Hund, 04.02.1896 – 31.03.1997

$d^3$  and  $d^7 - {}^2PD_{(2)}FGH, {}^4PF$  - the ground term is  ${}^4F$



# 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

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

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

$r_2 > r_1$   
 $r_1 > r_2$

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

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

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

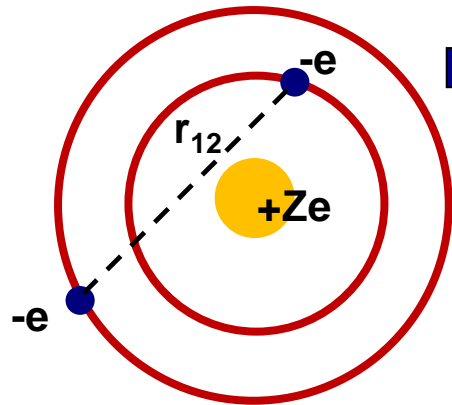
This integral is expressed in terms of the Wigner 3j-symbols:

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

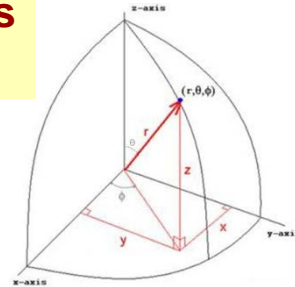
Not zero, if  $l_1 + k + l_2$  is an even number.  $k=0, 2, 4$  for d-electrons  
 $k=0, 2, 4, 6$  for f-electrons

# 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

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

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

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

Giulio Racah (1909 - 1965),  
 Italian-Israeli physicist

# Energy of spectral terms of $d^3$ electron configuration

8 LS terms:  $^4F$ ,  $^4P$ ,  $^2P$ ,  $^2D_{(1)}$ ,  $^2D_{(2)}$ ,  $^2F$ ,  $^2G$ ,  $^2H$

Their energies as expressed in terms of the Racah parameters are as follows:

$^4F$	0
$^4P$	$15B$
$^2G$	$4B + 3C$
$^2P$	$9B + 3C$
$^2H$	$9B + 3C$
$^2D_{(1)}$	$20B + 5C - \sqrt{193B^2 + 8BC + 4C^2}$
$^2F$	$24B + 3C$
$^2D_{(2)}$	$20B + 5C + \sqrt{193B^2 + 8BC + 4C^2}$

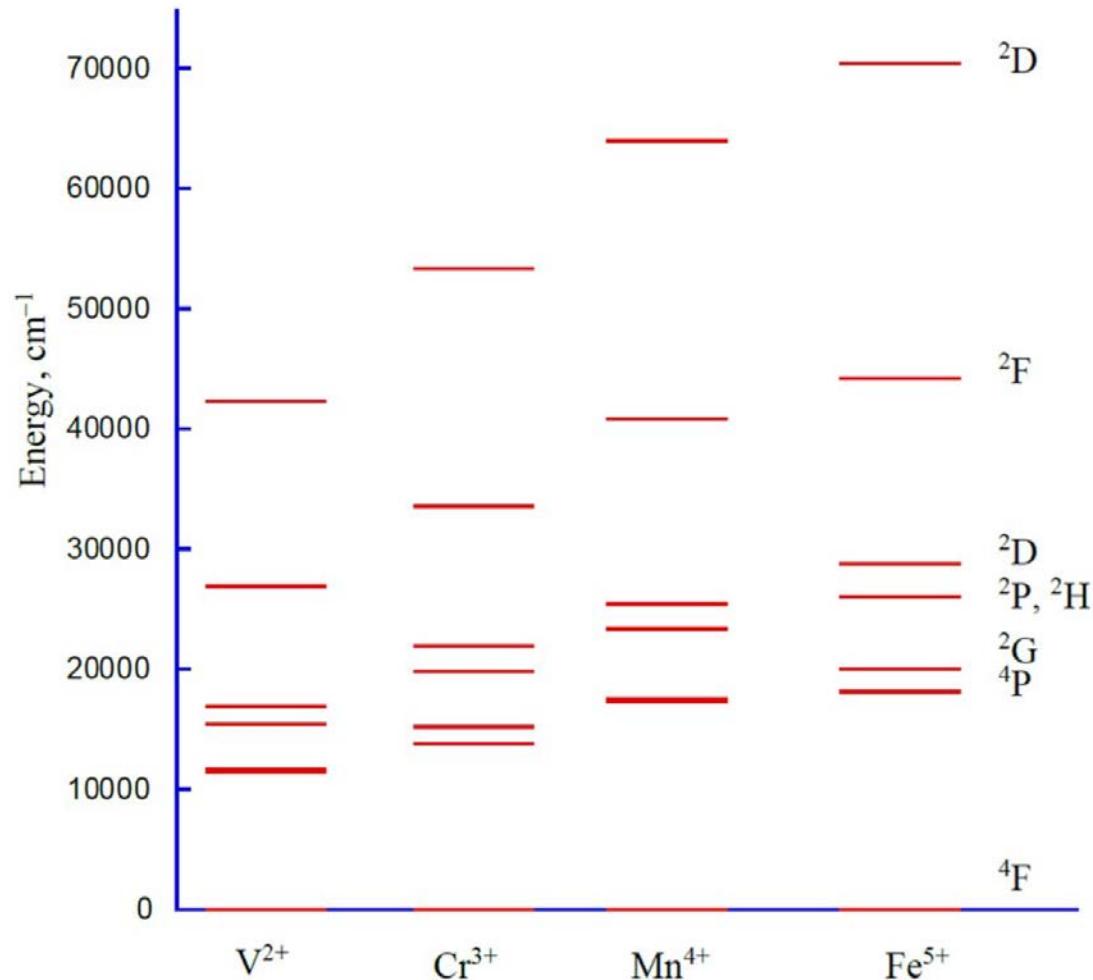
Typical values (in  $\text{cm}^{-1}$ ) of the Racah parameters  $B$ ,  $C$  for some  $d^3$  ions

Ion	$B$	$C$
$\text{V}^{2+}$	766	2855
$\text{Cr}^{3+}$	918	3850
$\text{Mn}^{4+}$	1160	4303
$\text{Fe}^{5+}$	1210	5066

Increase of the atomic number and electric charge  $\rightarrow$  increase of the Racah parameters

# Energy of spectral terms of $d^3$ electron configuration

8 LS terms:  $^4F$ ,  $^4P$ ,  $^2P$ ,  $^2D_{(1)}$ ,  $^2D_{(2)}$ ,  $^2F$ ,  $^2G$ ,  $^2H$



**B and C – the Racah parameters,  $B_0=1160 \text{ cm}^{-1}$ ,  $C_0=4303 \text{ cm}^{-1}$  for a free  $\text{Mn}^{4+}$  ion and  $B_0=918 \text{ cm}^{-1}$ ,  $C_0=3850 \text{ cm}^{-1}$  for a free  $\text{Cr}^{3+}$  ion**

# Energy levels of free $\text{Mn}^{4+}$ or $\text{Cr}^{3+}$ ions

120 electronic states give rise to 8 energy levels (so called LS-terms) in a free state:

$^4\text{F}$  (ground term),  $^4\text{P}$  (spin-quartets)  $^2\text{G}$ ,  $^2\text{P}$ ,  $^2\text{H}$ ,  $^2\text{D}$ ,  $^2\text{F}$ ,  $^2\text{D}$  (spin-doublets)

$^{2S+1}\text{L}$  notation is used (S – total spin, L – orbital momentum).

These energy levels are split if these ions are incorporated into a solid. The reason for such splitting is the symmetry lowering – from the spherical symmetry of a free ion to the point symmetry of the crystal lattice site occupied by an impurity ion.

The splitting pattern depends on the crystal structure and charges of surrounding ions.

A photograph of a man with dark hair, wearing a green and black striped shirt, sleeping with his head resting on a wooden desk in a lecture hall. To his left, a woman with dark hair is partially visible, also at the desk. In the background, rows of blue plastic chairs are visible, indicating a classroom or lecture hall setting. The image has a blue and white pixelated graphic in the top left corner.

**that day when**

**you fall asleep in the middle of a lecture**

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# Energy levels of three *d*-electrons in an octahedral field

Due to the symmetry lowering, the free ion terms are split according to the following table (group theory is used to get these splittings):

Application of  
group theory

Splitting of LS terms of the  $d^3$  ( $d^7$ ) configuration in the  
 $O$  or  $T_d$  group.

$T_d$  or  $O$  groups irreducible representations\*

P-term ( $L = 1$ )	$T_1$
D-term ( $L = 2$ )	$T_2 + E$
F-term ( $L = 3$ )	$A_2 + T_1 + T_2$
G-term ( $L = 4$ )	$A_1 + E + T_1 + T_2$
H-term ( $L = 5$ )	$E + 2T_1 + T_2$

\*Subscript “g” denoting the even irreducible representations should be added to all states if the local symmetry is  $O_h$ .

# 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.

## A famous book:

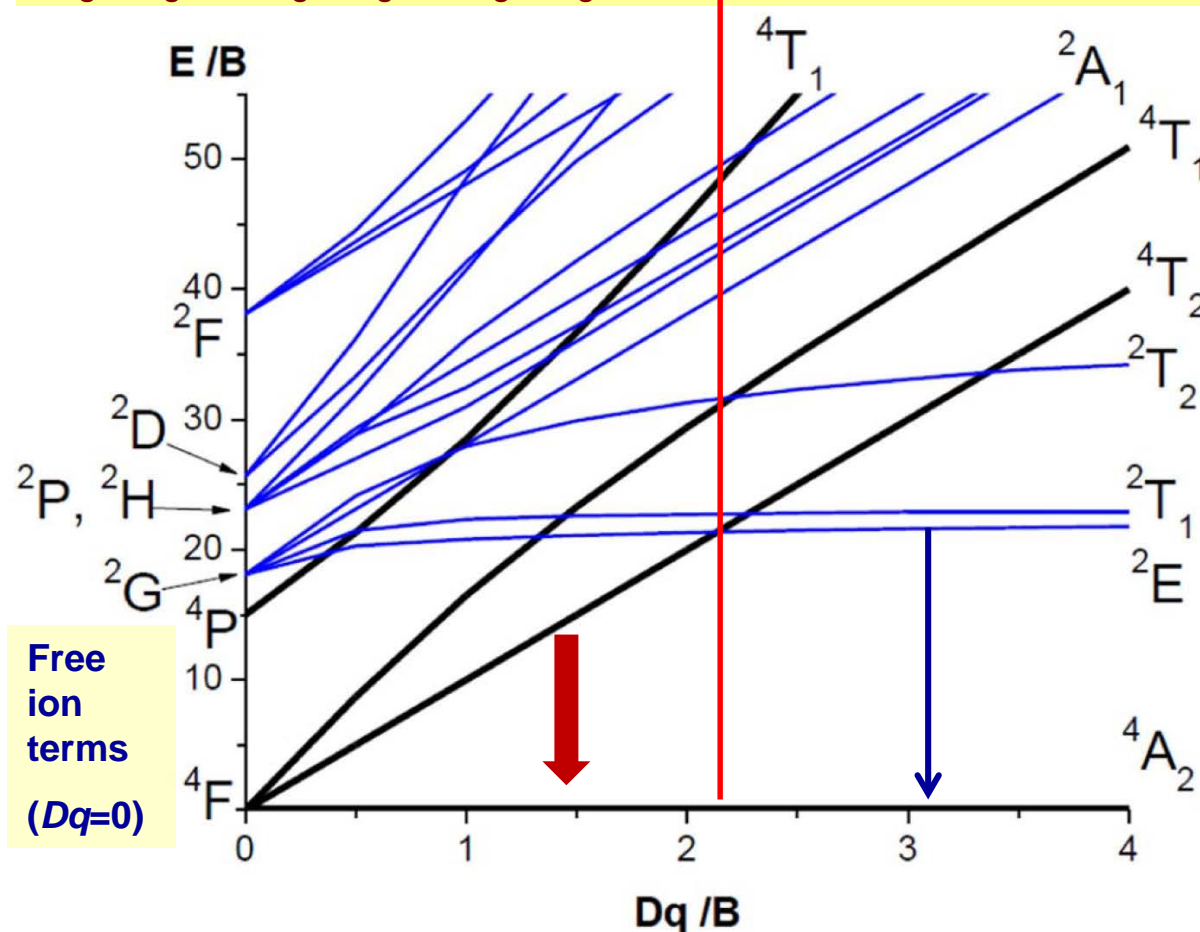
S. Sugano, Y. Tanabe, H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals*, Acad. Press, New York, 1970

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

How to visualize (we have three variables...)? Fix the  $C/B$  ratio and plot the energy  $E/B$  as a function of  $Dq/B$

# 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  $(E/B)$ .

$C/B=4.25$

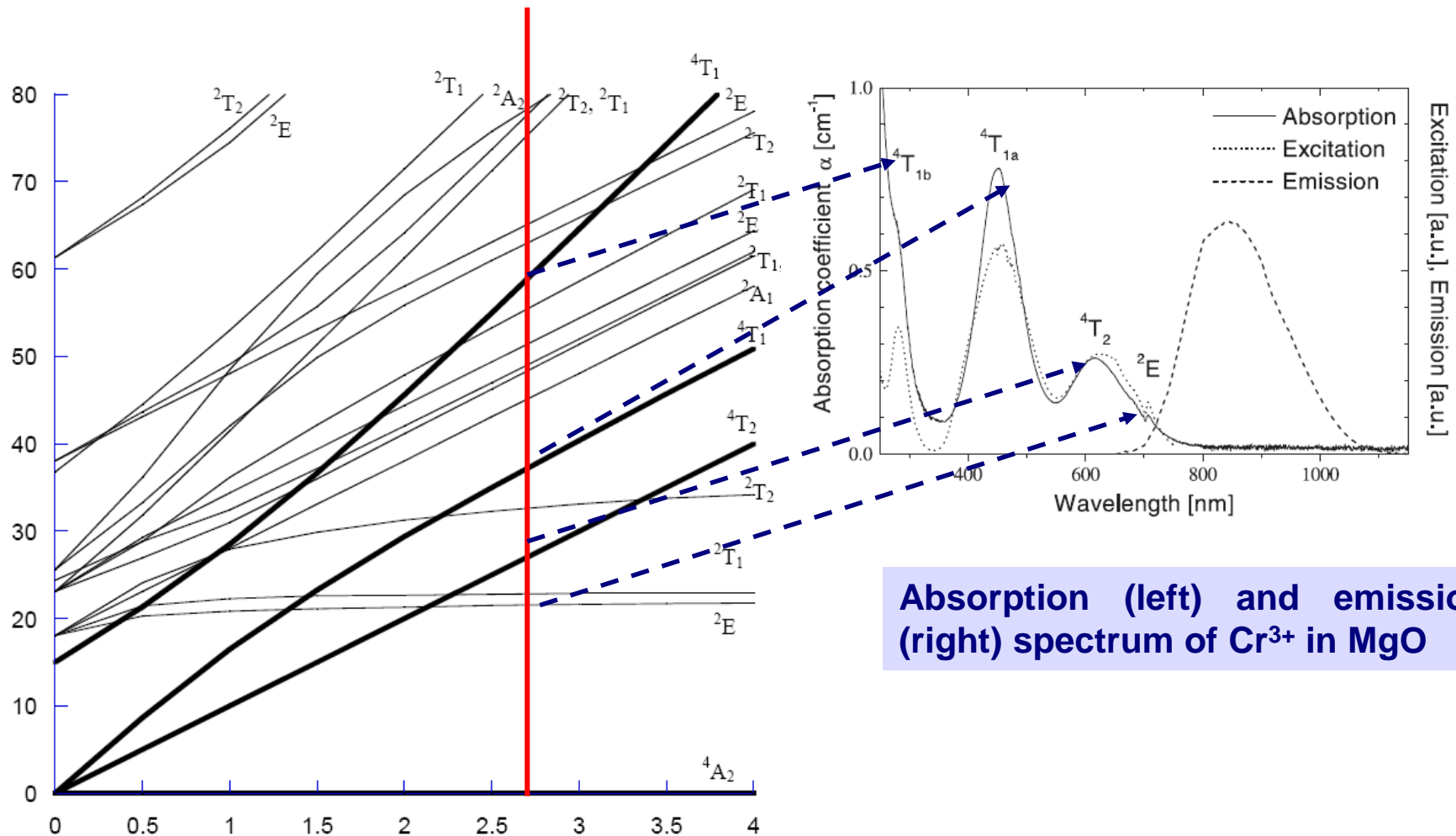
$Mn^{4+}$  - is always a strong field case


$Cr^{3+}$  – can be found in both strong and weak crystal fields

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 $\text{Cr}^{3+}$



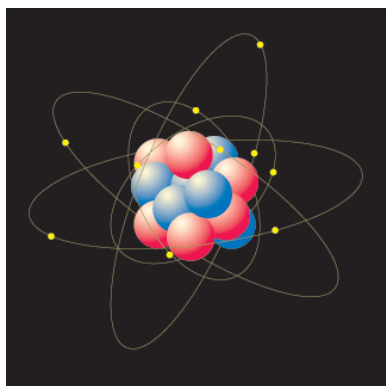


# **A general scheme of the energy levels splitting of 3d-ions in solids**

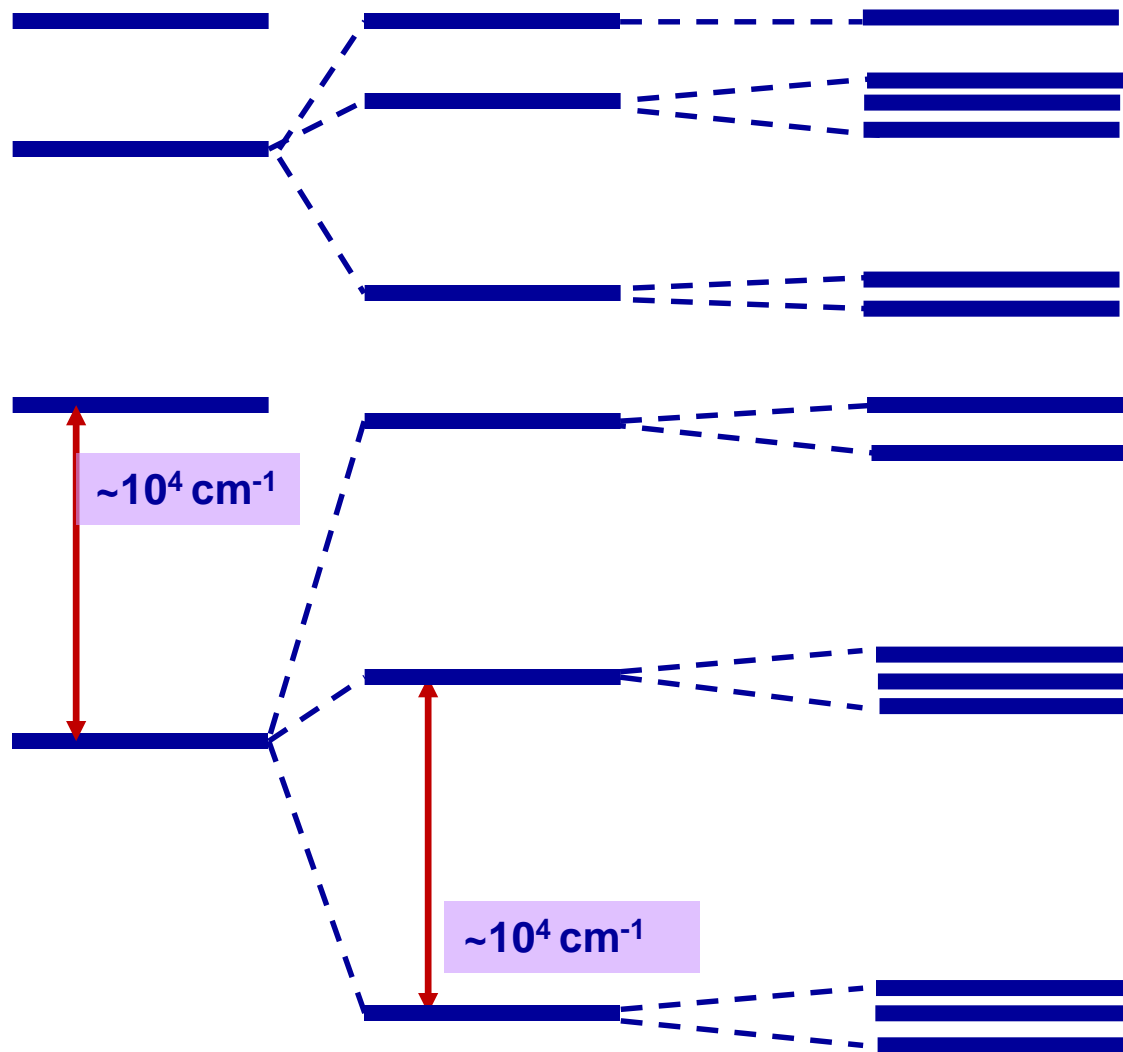
# 3d ions: what are they?

Group Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	1 H																	2 He	
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			*		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			**		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

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



A multi-electron ion



**Coulomb  
Interaction**  
 $2S+1L$  terms

**Crystal  
field**

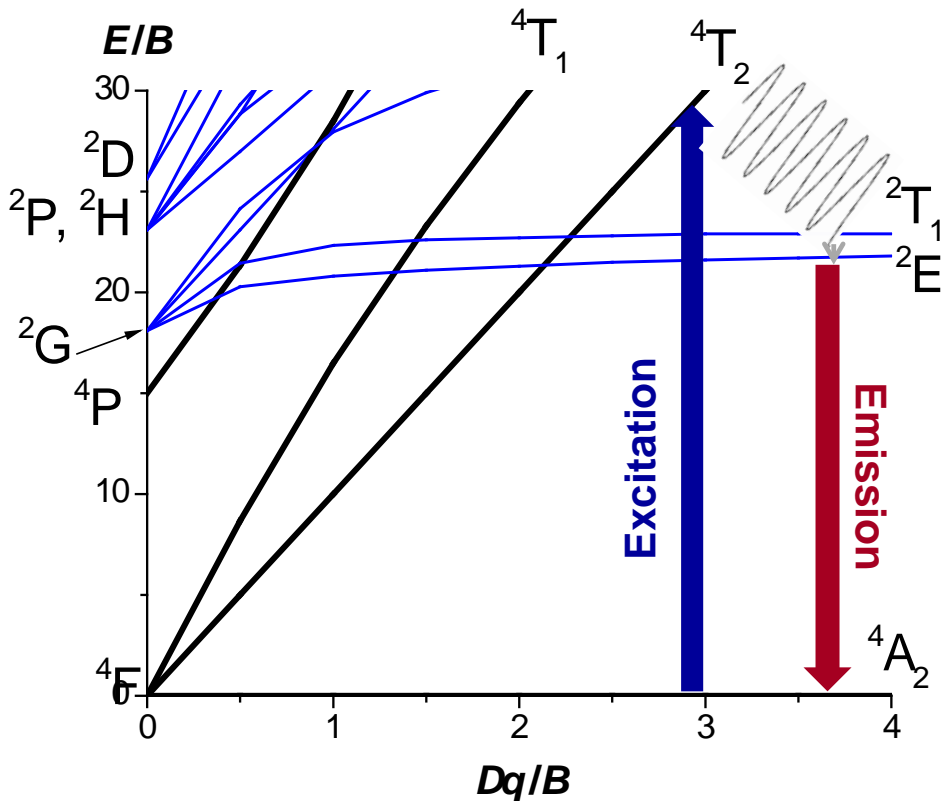
**Spin-orbit  
interaction**



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  - Properties of the Mn<sup>4+</sup> and Cr<sup>3+</sup> ions in solids: Tanabe-Sugano diagrams
  - Properties of the Mn<sup>4+</sup> and Cr<sup>3+</sup> ions in solids: calculations of the energy levels splitting in low symmetry hosts and analysis of the experimental results
- **Main misconceptions related to the spectra of Cr<sup>3+</sup> and Mn<sup>4+</sup> ions in solids**
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# Advantages of $\text{Mn}^{4+}$ ions over other red-light-emitting ions



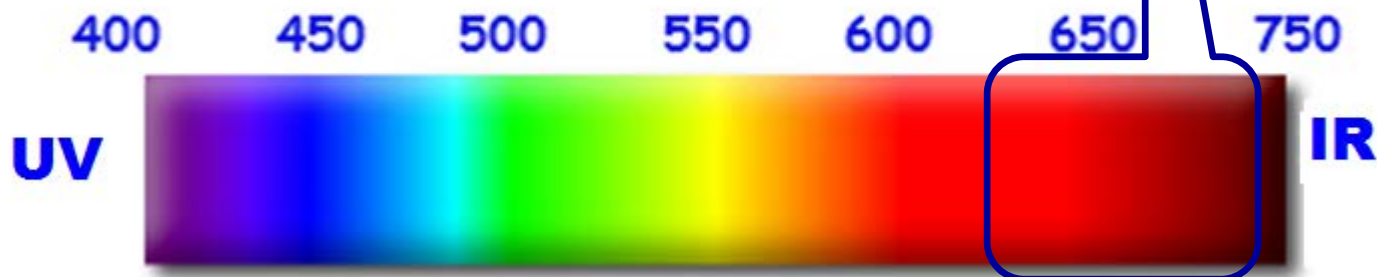
1. Efficient absorption at  $\sim 450$  nm ( ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$  spin-allowed transition).  
Can be excited with blue LED.

(Not the case with  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$ )

2. Possibility to tune the wavelength of the  ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$  emission from host to host (from  $\sim 617$  nm to  $\sim 720$  nm)

(Not the case with  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$ )

Visible spectrum (nm)



# Exchange charge model of crystal field

$$\hat{H} = \sum_{p=2,4,\dots}^{2l} \sum_{k=-p}^p B_p^k O_p^k$$

Calculation of CFP

$$B_p^k = B_{pq}^k + B_{ps}^k$$

$$B_{pq}^k = -K_p^k (1 - \sigma_p) e^2 \langle r^p \rangle \sum_L \frac{Q_L V_p^k(\Theta_L, \Phi_L)}{R_L^{p+1}}$$

**Point charge contribution**

$$B_{ps}^k = \frac{2(2p+1)}{(2l+1)} K_p^k e^2 \sum_L \frac{S_p V_p^k(\Theta_L, \Phi_L)}{R_L}$$

**Exchange charge contribution**

B.Z. Malkin

*Spherical coordinates of ligands are needed*

$$S_p = G \left( S_s^2 + S_\sigma^2 + \gamma_p S_\pi^2 \right)$$

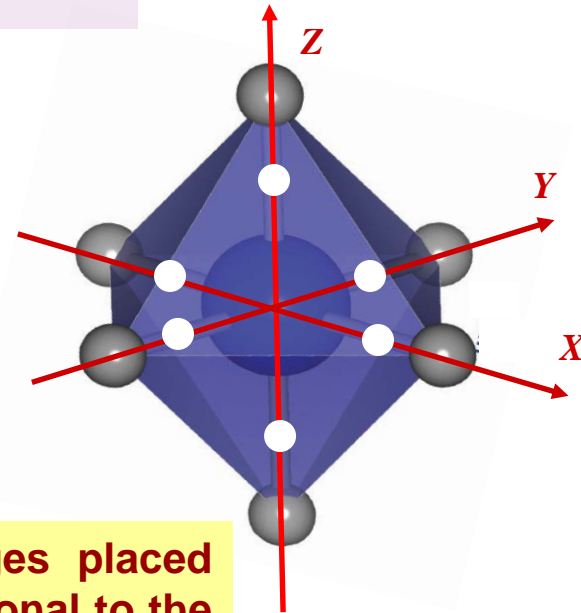
**Overlap integrals**

**G** is a fitting parameter determined from the first absorption band in the exp. spectrum

$$S_s = \langle d0 | s0 \rangle; S_\sigma = \langle d0 | p0 \rangle; S_\pi = \langle d1 | p1 \rangle$$

**d-functions of the central ion and p- and s- functions of ligands**

Exchange effects can be modeled by the imaginary charges placed between an impurity ion and ligands. The charges are proportional to the overlap integrals.



## Site Occupancy Preference, Enhancement Mechanism, and Thermal Resistance of Mn<sup>4+</sup> Red Luminescence in Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>: Mn<sup>4+</sup> for Warm WLEDs

Mingying Peng,<sup>\*,†</sup> Xuewen Yin,<sup>†</sup> Peter A. Tanner,<sup>\*,‡</sup> M. G. Brik,<sup>§,||,⊥,±</sup> and Pengfei Li<sup>†</sup>

<sup>†</sup>The China-Germany Research Center for Photonic Materials and Device, The State Key Laboratory of Luminescent Materials and Devices, School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, P.R. China

<sup>‡</sup>Department of Science and Environmental Studies, The Hong Kong Institute of Education, 10 Lo Ping Road, Tai Po, New Territories, Hong Kong S.A.R. P.R. China

<sup>§</sup>College of Sciences, Chongqing University of Posts and Telecommunications, Chongqing 400065, P.R. China

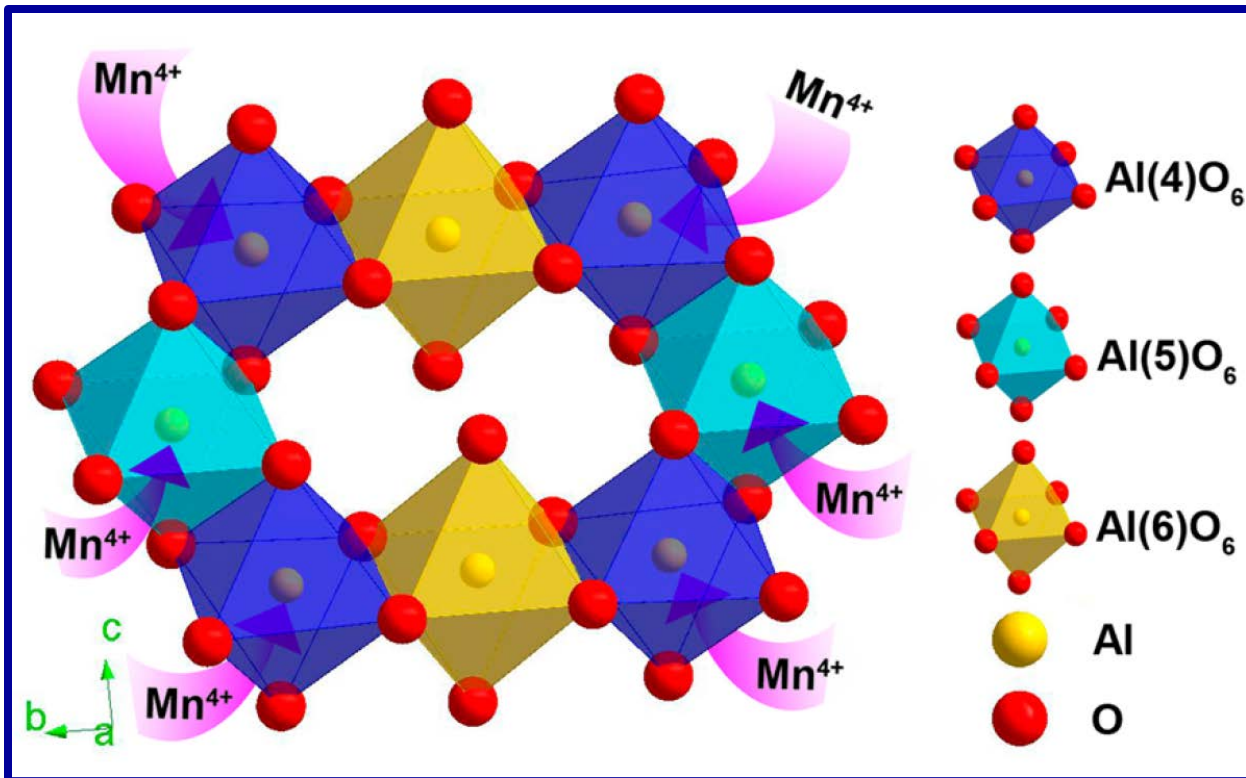
<sup>||</sup>Institute of Physics, University of Tartu, Ravila 14C, Tartu 50411, Estonia

<sup>⊥</sup>Institute of Physics, Jan Długosz University, Armii Krajowej 13/15, PL-42200 Częstochowa, Poland

<sup>±</sup>Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warsaw, Poland

*Chem. Mater.* 2015, 27, 2938–2945

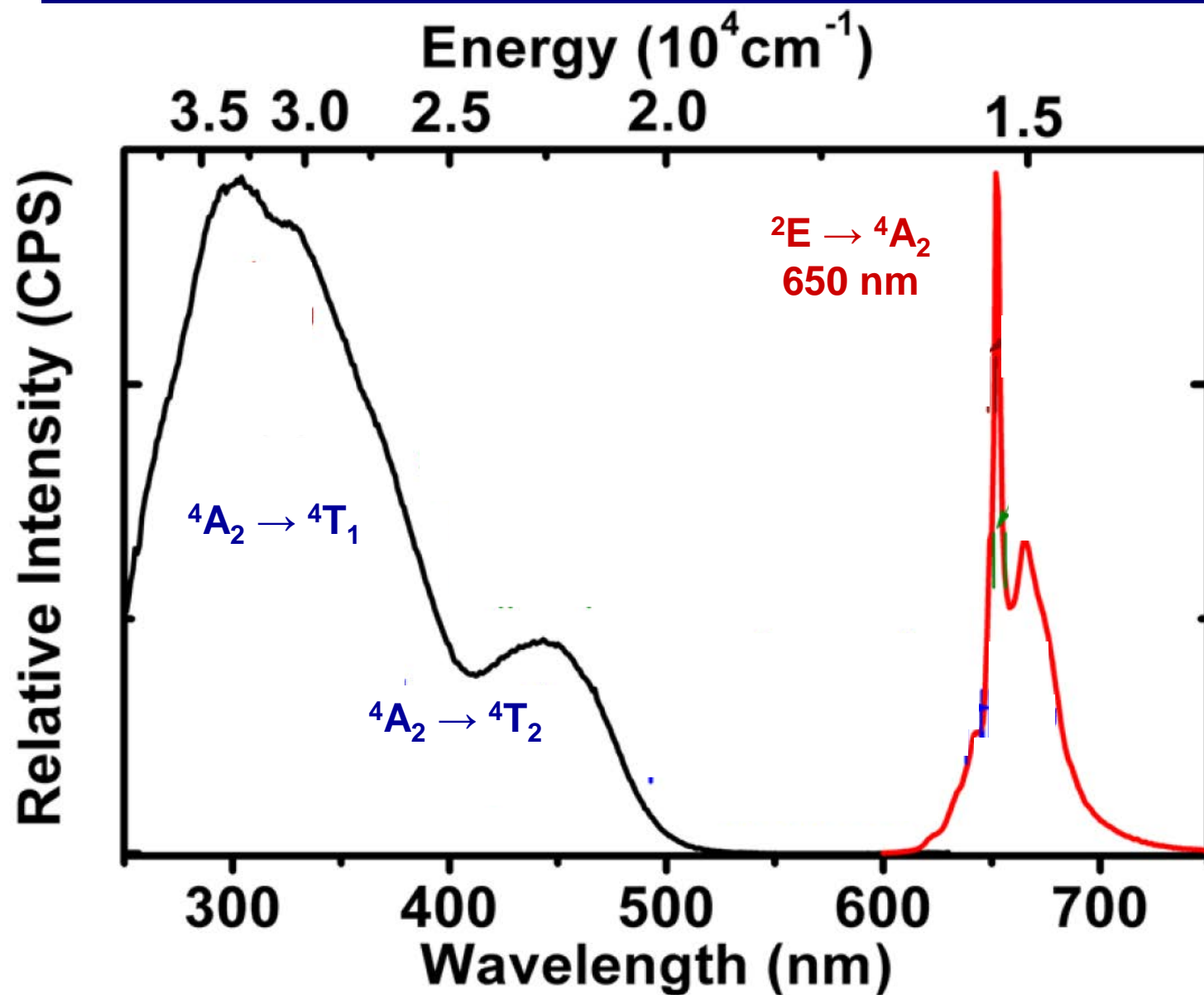
# $\text{Mn}^{4+}$ in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phosphor



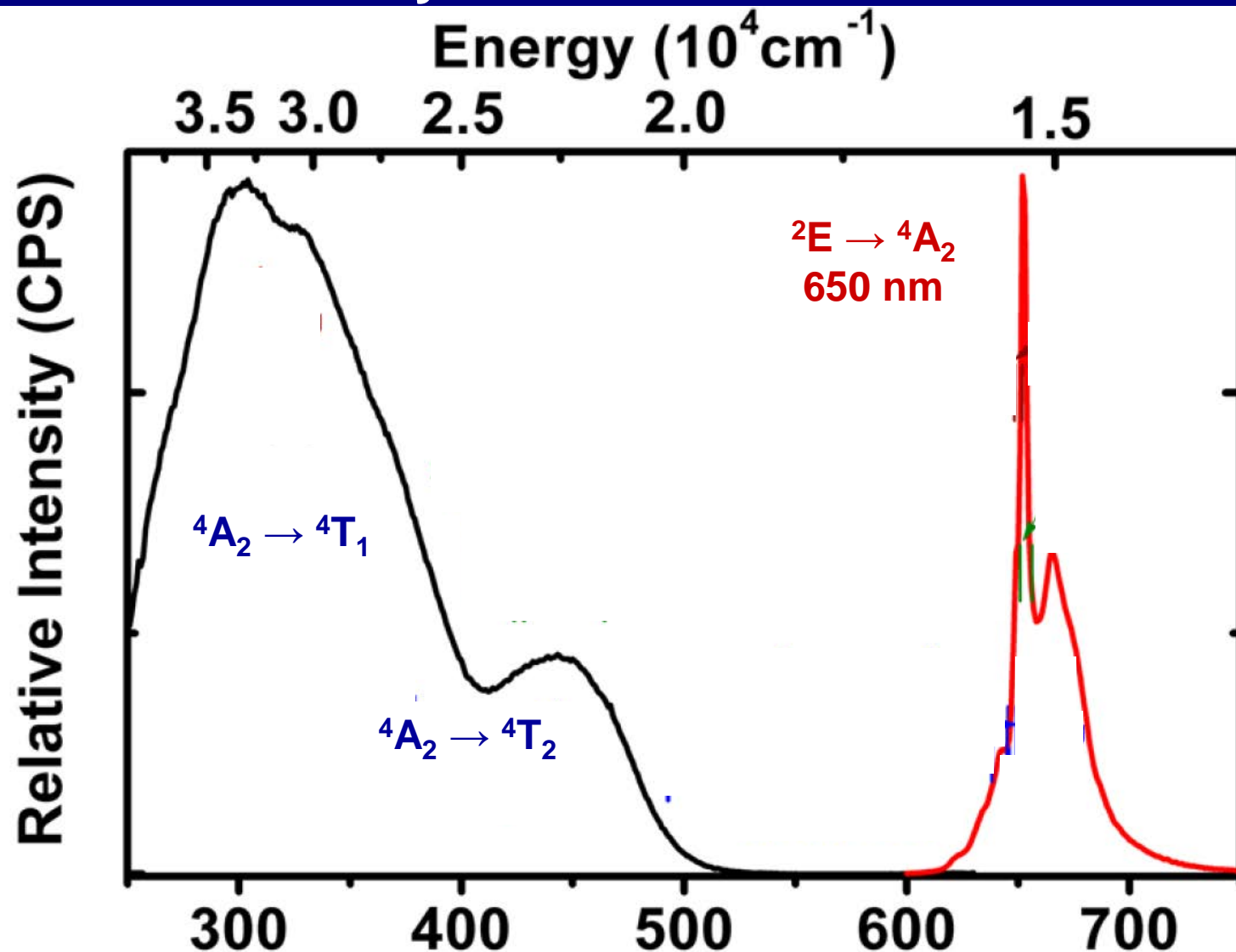
Complicated structure – three octahedral Al sites suitable for the  $\text{Mn}^{4+}$  doping.

Is it possible to understand which site is preferably occupied?

# Mn<sup>4+</sup> in Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> phosphor: optical spectra



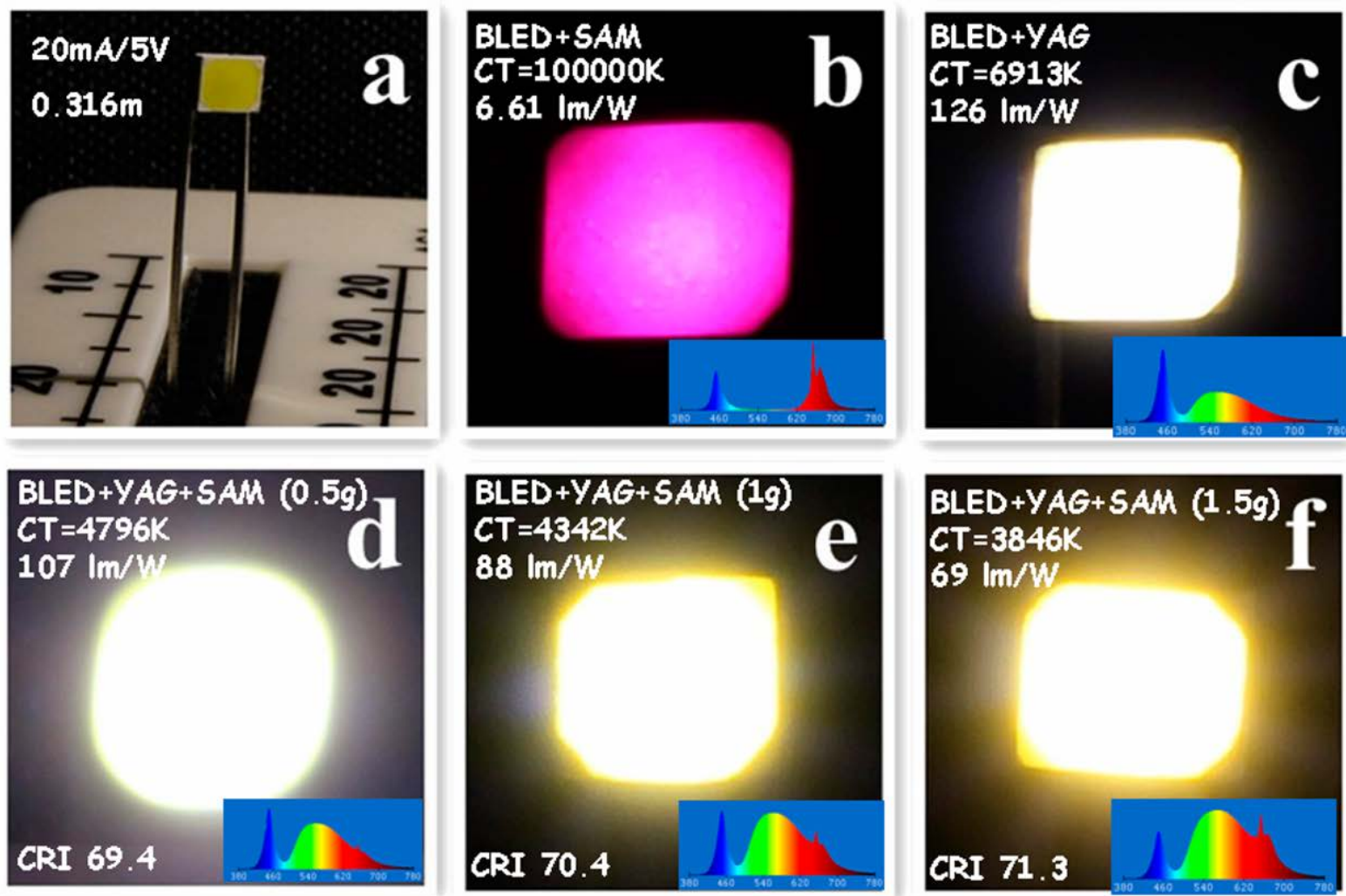
# Mn<sup>4+</sup> in Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> phosphor: optical spectra and crystal field calculations



Possible to identify preferred sites (Al4, Al5) for the impurity!

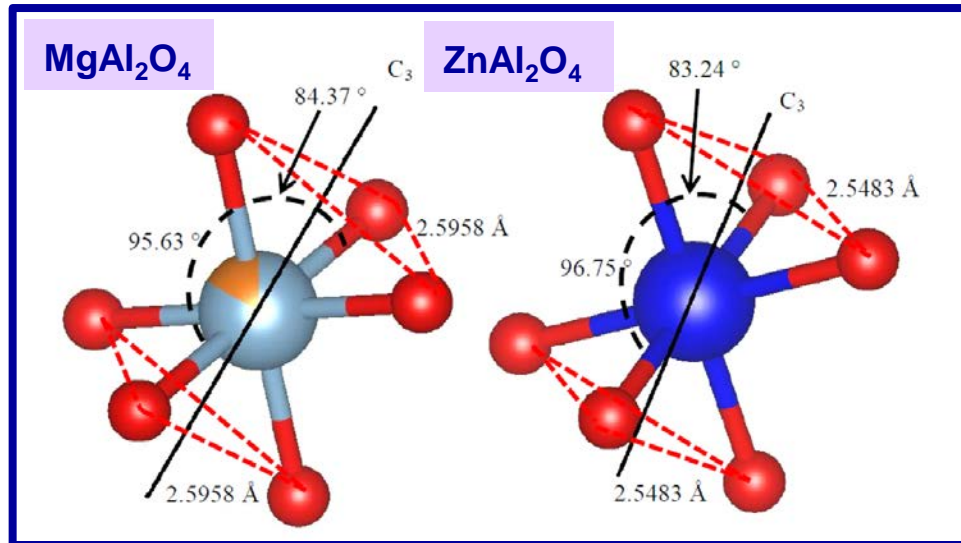
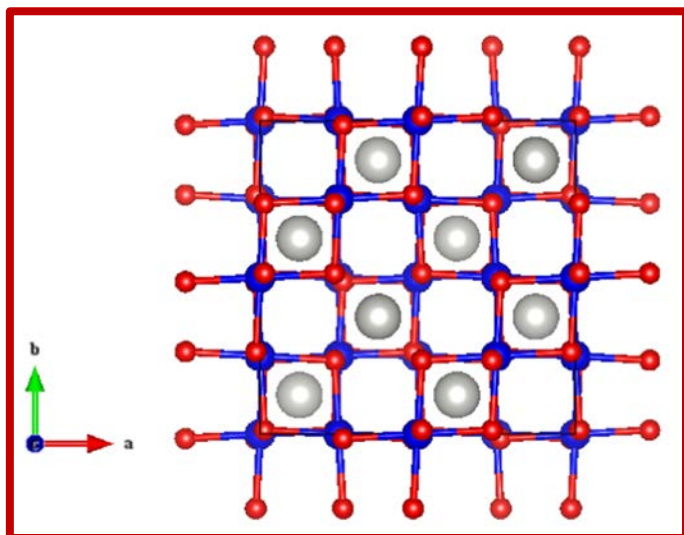


# Mn<sup>4+</sup> in Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> phosphor: white LED manufacturing



CCT can be tuned by the amount of the SAM phosphor:  
more SAM – lower CCT

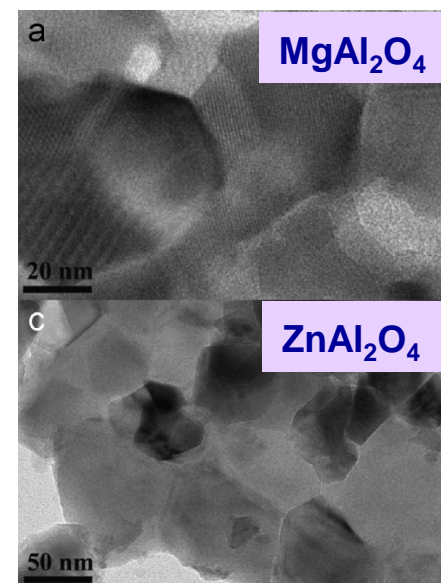
# Cr<sup>3+</sup> in ZnAl<sub>2</sub>O<sub>4</sub> and MgAl<sub>2</sub>O<sub>4</sub> spinels: structure



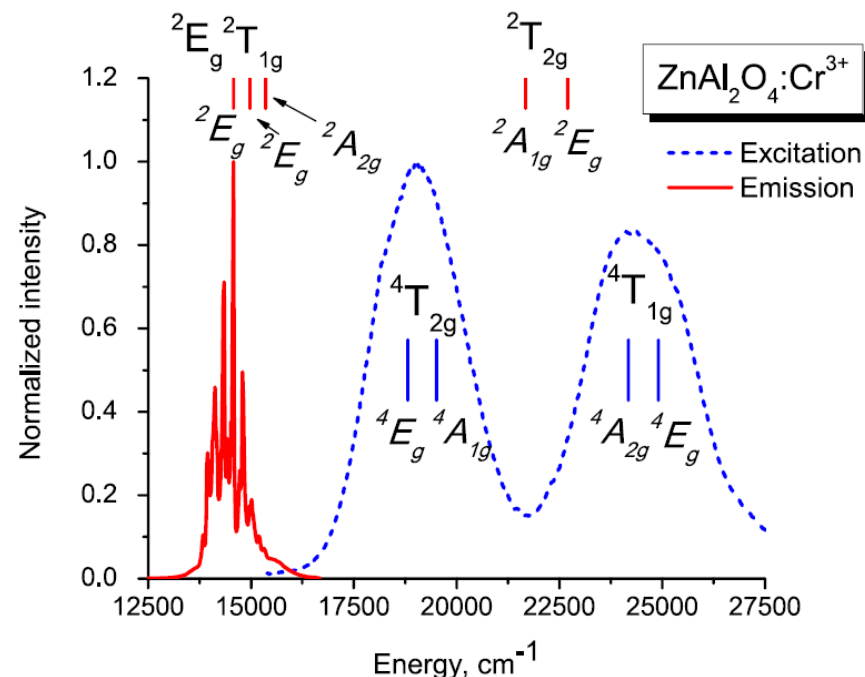
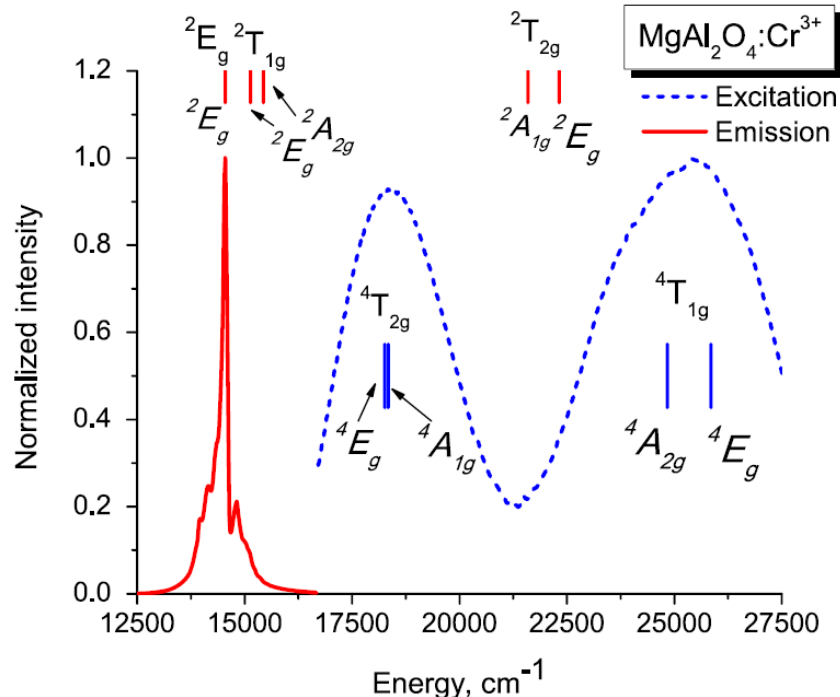
Trigonal symmetry of the Al site, which is suitable for the Cr<sup>3+</sup> doping.

Structure → crystal field parameters

CFP	MgAl <sub>2</sub> O <sub>4</sub>	ZnAl <sub>2</sub> O <sub>4</sub>
$B_2^0$	1299	2838
$B_4^0$	-3480	-3671
$B_4^3$	87471	90025



# Cr<sup>3+</sup> in ZnAl<sub>2</sub>O<sub>4</sub> and MgAl<sub>2</sub>O<sub>4</sub> spinels: optical spectra



Calculated energy levels (all in cm<sup>-1</sup>) for the Cr<sup>3+</sup> ions at the Al sites in MAl<sub>2</sub>O<sub>4</sub> (M=Mg, Zn) spinels. The orbital doublet states are denoted with an asterisk.

O <sub>h</sub> group notation and "parent" LS term	D <sub>3d</sub> group notation	MgAl <sub>2</sub> O <sub>4</sub>		ZnAl <sub>2</sub> O <sub>4</sub>	
		This work	[40]	This work	[40]
<sup>4</sup> A <sub>2g</sub> ( <sup>4</sup> F)	<sup>4</sup> A <sub>2g</sub>	0	0	0	0
<sup>2</sup> E <sub>g</sub> ( <sup>2</sup> G)	<sup>2</sup> E <sub>g</sub>	14555*	14564*	14576*	14558
<sup>2</sup> T <sub>1g</sub> ( <sup>2</sup> G)	<sup>2</sup> E <sub>g</sub> + <sup>2</sup> A <sub>2g</sub>	15135*	15108,	14978*	15100,
		15436	15823	15355	15836
<sup>4</sup> T <sub>2g</sub> ( <sup>4</sup> F)	<sup>4</sup> E <sub>g</sub> + <sup>4</sup> A <sub>1g</sub>	18263*,	18495,	18811*,	18720,
		18347	19957	19509	20230
<sup>2</sup> T <sub>2g</sub> ( <sup>2</sup> G)	<sup>2</sup> A <sub>1g</sub> + <sup>2</sup> E <sub>g</sub>	21592,	21555,	21680,	21572,
		22317*	23265	22703*	23334
<sup>4</sup> T <sub>1g</sub> ( <sup>4</sup> F)	<sup>4</sup> E <sub>g</sub> + <sup>4</sup> A <sub>2g</sub>	24838,	25742,	24184,	26011,
		25853*	26562	24904*	26835

Symmetry lowering: O<sub>h</sub> → D<sub>3</sub>

Triplet states splitting: singlet + doublet

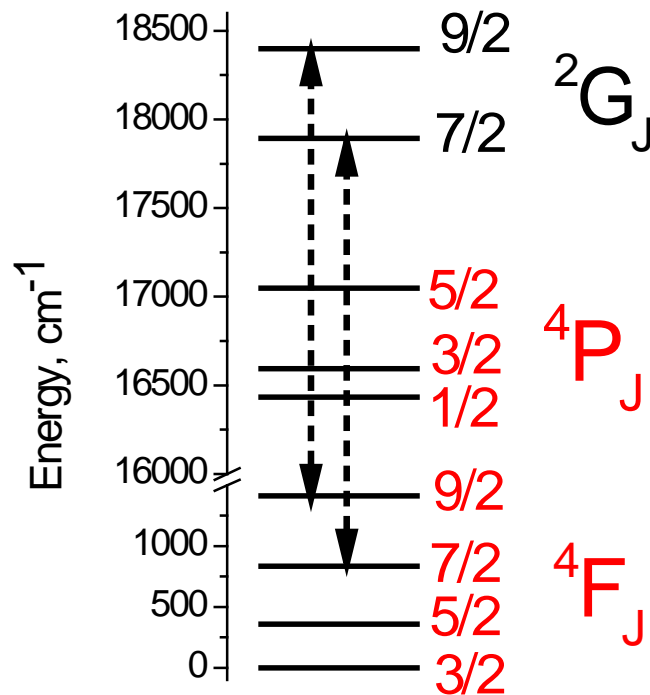
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# Main misconceptions about the ${}^2E_g \rightarrow {}^4A_{2g}$ transition

1. The  ${}^2E_g \rightarrow {}^4A_{2g}$  transition is allowed because of crystal lattice vibrations.

**WRONG!** Even in the free ion's spectra the spin-forbidden transitions are detected because of spin-orbit coupling (mixture of states with the same quantum number  $J$ ).



Total momentum  $J = L + S$   
 $|L - S| \leq J \leq |L + S|$

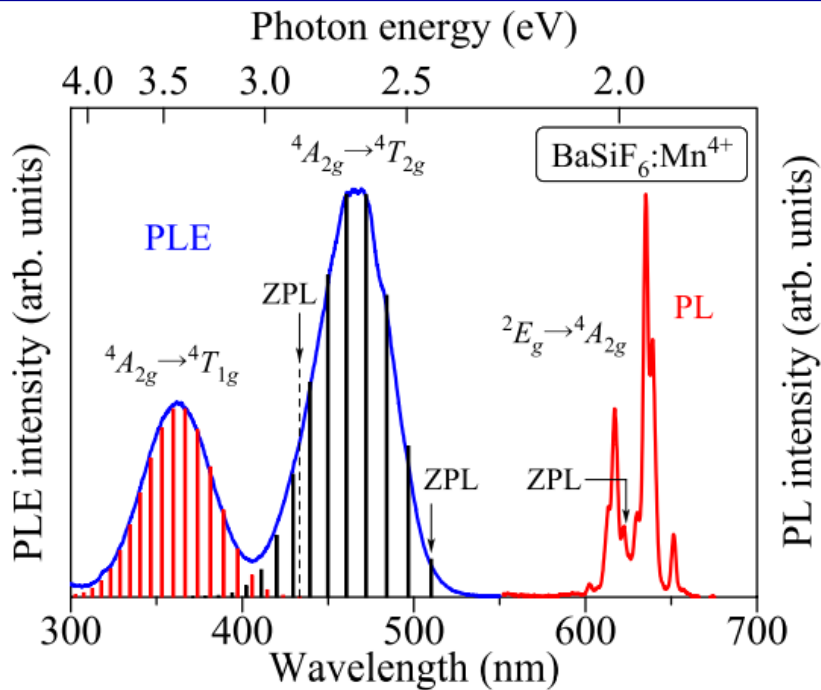
${}^4F$  term:  $L=3, S=3/2$   
 $J=3/2, 5/2, 7/2, 9/2$

${}^4P$  term:  $L=1, S=3/2$   
 $J=1/2, 3/2, 5/2$

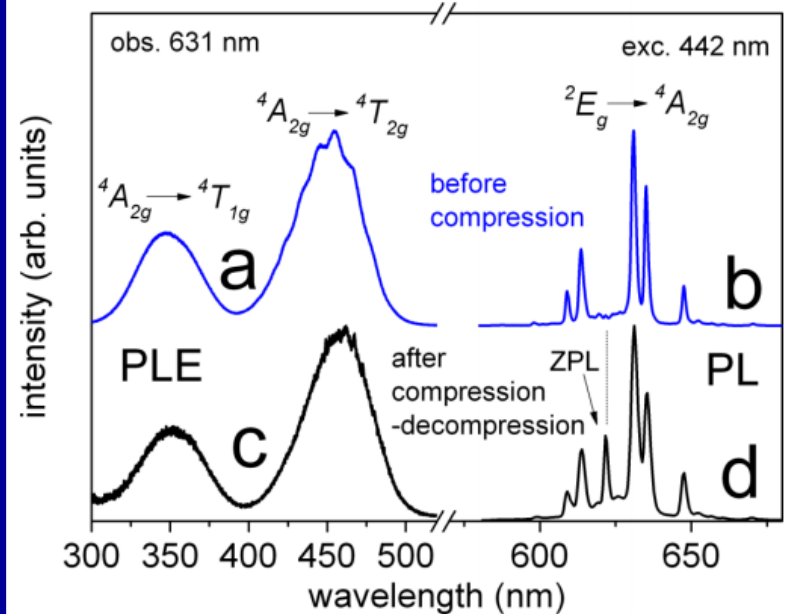
${}^2G$  term:  $L=4, S=1/2$   
 $J= 7/2, 9/2$

# Main misconceptions about the ${}^2E_g \rightarrow {}^4A_{2g}$ transition

## 2. Difficulties with identification of the zero-phonon line of the ${}^2E_g \rightarrow {}^4A_{2g}$ transition (hidden by vibronic progressions).



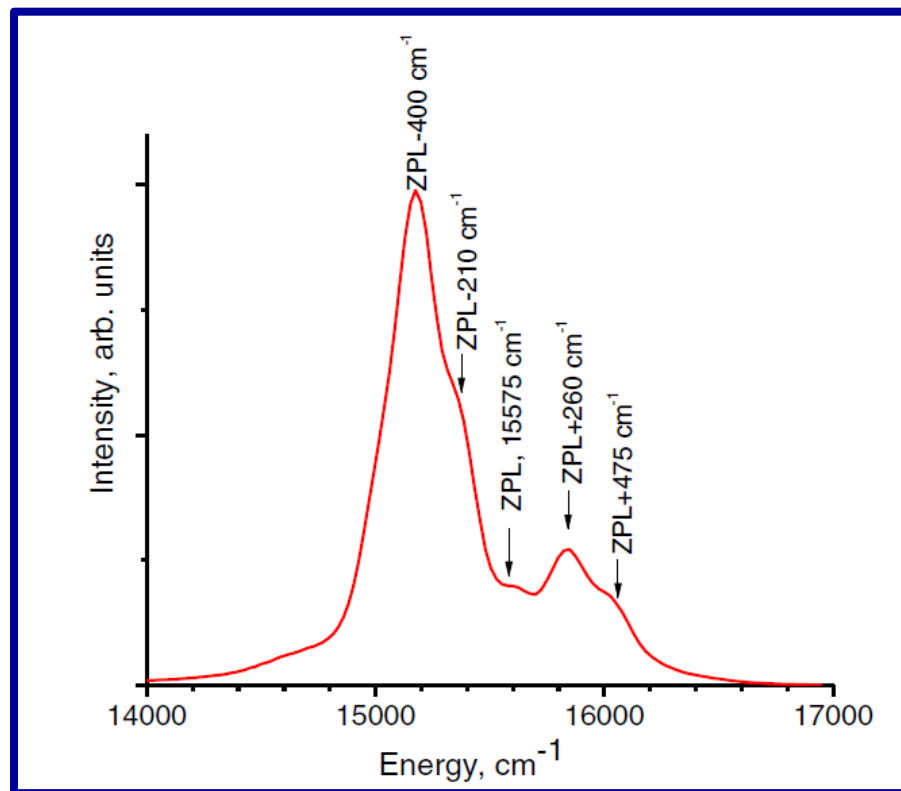
D. Sekiguchi, J. Nara, S. Adachi,  
J. Appl. Phys., 113 (2013) 183516.



A. Lazarowska et al,  
J. Chem. Phys., 143 (2015) 134704.

# Main misconceptions about the ${}^2E_g \rightarrow {}^4A_{2g}$ transition

## How to identify the zero-phonon line location?



Look at the emission spectrum, and find symmetric (about the ZPL position) peaks of the Stokes (longer wave lengths, lower energy and anti-Stokes (shorter wavelengths, higher energy) vibronic progressions.

# Main misconceptions about ${}^2E_g \rightarrow {}^4A_{2g}$ transition

## 3. Attempts to attribute structure of the ${}^2E_g \rightarrow {}^4A_{2g}$ emission lines to the crystal field splitting.

The  ${}^2E_g$  state is an orbital doublet; it can be split by crystal field into two states only (if and only if the symmetry is lower than trigonal or tetragonal).

A large number of peaks in the  ${}^2E_g \rightarrow {}^4A_{2g}$  emission line can be due either to:

i) vibronic progressions

or

ii) presence of several  $Mn^{4+}$  centers.



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## d<sup>3</sup> ions optical properties: things to remember

- This is a multi-electron configuration
- 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)
- 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
- Crystal field removes degeneracy of free ion energy levels
- Cr<sup>3+</sup> and – especially – Mn<sup>4+</sup> are very suitable for red phosphors in white LED applications



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***Thank you for your  
attention!***