Tanabe-Sugano diagrams

So far in the course, we focused our attention on how the ground state of a transition metal is modified when adding perturbation like spin-orbit coupling, crystal-field splitting, Jahn-Teller effect, and so on. However, most interesting properties of transition metal compound rely on excited state, that are also modified by the aforementionned perturbations. Luckily, there exists a tool giving energy of the electronic structure as a function of the crystal field splitting energy : the Tanabe-Sugano diagramms

1 Brief overview of how to construct a Tanabe-Sugano diagram

1. Consider the Co^{3+} ion. What is its electronic configuration ? What is the associated degeneracy of electronic microstates ?
2. What is the spectroscopic term in the ground state if we don't include any crystal field ? Why is it called a high spin state ?
3. Suppose now that we have a very strong crystal field splitting energy Δ_0. What would be the ground state ? Why is it called a low spin state.
4. Write down the energy of the low and high spin state as a function of crystal field. Find out the critical cristal field splitting between these two states.
5. Between low and high spin, we could envision an intermediate state. Give its spectroscopic term and the associated energy. Is it achievable in practice ?
6. How would you study this high-spin/low-spin transition in practice [1] ?

2 Spectroscopy of Ruby and Emerald

The ruby cristal is made up with Cr^{3+} impurities trapped in a corundum (Al_2O_3) environment. This crystal has been used to develop the first laser in history. Using Tanabe-Sugano diagram, we can understand why Ruby is such a good candidate.

1. What is the electronic configuration of Cr^{3+} ?
2. In the case of ruby, $D_q/B = 2.2, B = 960\text{cm}^{-1}$. What states will be populated under visible light pumping ? Using this information, explain why ruby is red.
3. Stimulated emission in ruby occur between the ^2E and A_2 states. Why should ^2E state be metastable ? What is the color you will get ?
4. Emerald also consists in Cr^{3+} impurities, but trapped in a beryl crystal. How does the crystal-field splitting compare to ruby ? We give $a_{corundum} = 480pm$ and $a_{beryl} = 920pm$.
5. Why is emerald green ? In which color should it emit light ?

1. Have a look at : Lengsdorf et al, PHYSICAL REVIEW B 69, 140403 (R) (2004)

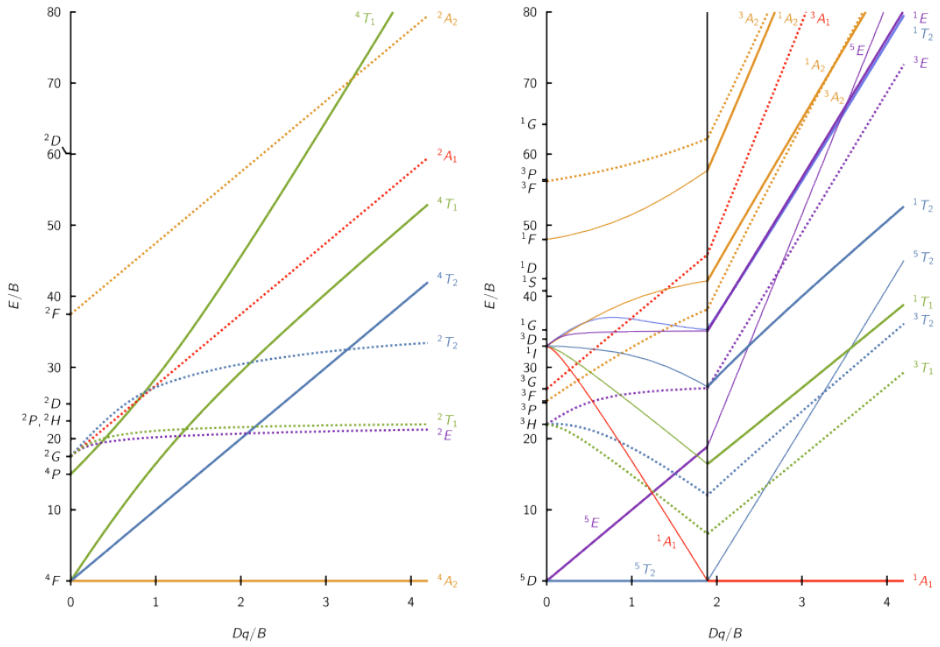

FIGURE 1 – Tanabe Sugano diagrams for the d^3 (left) and d^6 (right) electronic configuration in octahedric field

3 Quenching of Angular momentum

Quenching of orbital angular momentum is an important phenomenon with many experimentally observable effects. In systems with orbital angular momentum quenched, the net magnetism is purely due to spin degrees of freedom. All the spin orbit related effects like g-factor anisotropy are absent (or significantly reduced).
When a transition metal ion is placed in a octahedral environment the electron levels are split into t_{2g} and e_g orbitals, which are given by :

$$e_g : \begin{cases} |z^2\rangle & = |0\rangle \\ |x^2-y^2\rangle & = \frac{1}{\sqrt{2}}(|2\rangle + |-2\rangle \end{cases} \quad (1) \qquad t_{2g} : \begin{cases} |xy\rangle & = \frac{-i}{\sqrt{2}}(|2\rangle - |-2\rangle) \\ |xz\rangle & = \frac{-1}{\sqrt{2}}(|1\rangle - |-1\rangle) \\ |yz\rangle & = \frac{i}{\sqrt{2}}(|1\rangle + |-1\rangle) \end{cases} \quad (2)$$

Where $|n\rangle$ is the angular momentum eigenstate corresponding to $m_z = n$.

a) Show that the orbital angular momentum L is quenched in the e_g orbitals i.e. $\langle e_g|L|e_g\rangle = 0$.

b) Show that the linear combination of t_{2g} orbitals given by :

$$|t_{2g}^0\rangle = |xy\rangle, \qquad |t_{2g}^1\rangle = \frac{1}{\sqrt{2}}(|xz\rangle + i|yz\rangle \qquad |t_{2g}^{-1}\rangle = \frac{1}{\sqrt{2}}(|xz\rangle - i|yz\rangle)$$

form a triplet in their eigenstates of L_z.