# Magnetism in materials

Solutions - Week 03

1. Let's assume that we have a 3d metal in a thetrahedral crystal.

   (a) Between the $e_g$ orbitals and the $t_{2g}$ orbitals, which one would have the highest energy due to the crystal field effect ?

   (b) Find the spin number $S$ for all the 3d metal ($3d^0$ to $3d^{10}$) in the high spin and low spin case.

**Solutions**

(a) The $t_{2g}$ orbits are closer to ligand, so their energy are higher then the orbitals $e_g$.

(b) The spin distribution is as followed :

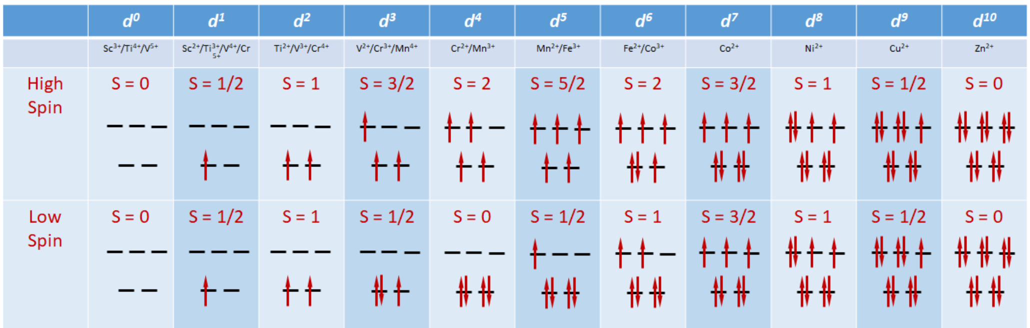


Figure 1: Spin repartition for 3d metal in an thetrahedral crystal

2. Using the spin distribution for a octahedral crystal discussed in course (for a 3d metal), determine in which situation the geometry will change due to the Jahn-Teller effect.

**Solutions** The configuration with Jahn-Teller effect are mark with 'J-T' in Fig.2

3. A $Sc^{2+}$ ion has one electron in the 3d shell. It is in an anisotropic crystal and the crystal field can be written as a potential acting on the 3d electron as $E = AL_z^2$. What are the lowest orbital states of the SC ion if $A > 0$ and $A < 0$ ?
   The spin-orbit coupling $\lambda$IS is much smaller than the crystal field. When this is included, what are the approximate ground states of the ion, for $A > 0$ and $A < 0$ ?

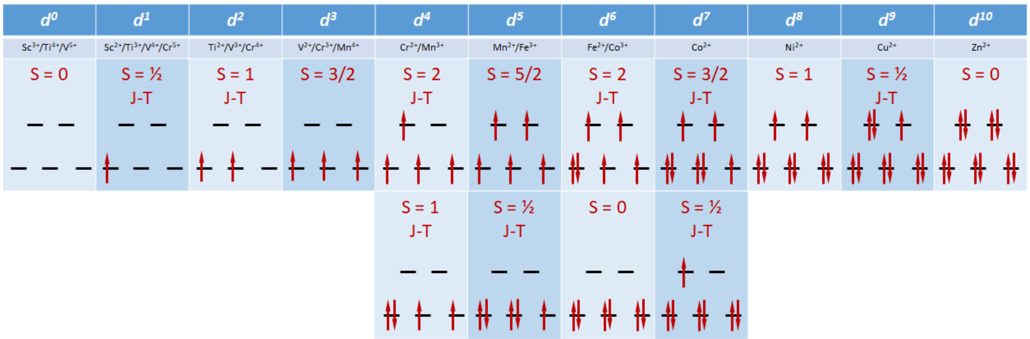


Figure 2: Spin repartition for 3d metal in an octahedral crystal

**Solution** $Sc^{2+}$ has one 3d electron(L=2,S = 1/2) and has 5 orbital states characterized by $L_z = -2, -1, 0, 1, 2$. The corresponding energy level are then $E(L_z) = 4A, A, 0, A, 4A$. We will write a state with $|L_z, S_z\rangle$.
If $A > 0$ the lowest orbital states are $|0, \pm\frac{1}{2}\rangle$.
If $A < 0$ the lowest orbital states are $|2, \pm\frac{1}{2}\rangle$ and $|-2, \pm\frac{1}{2}\rangle$.
Now the spin-orbit energy is taken in account.
If $A > 0$ the ground states are $|0, \pm\frac{1}{2}\rangle$ since $\lambda L_z S_z = 0$ for both states.
If $A < 0$ the ground states are $|2, -\frac{1}{2}\rangle$ and $|-2, \frac{1}{2}\rangle$.

4. Vesta is a software used to visualized crystal structure. We will in this exercise use it to analyse Ca3Co2O6 crystal. Download link, file and articles are all on moodle :

    (a) Download and install Vesta.

    (b) Load the structure of Ca3Co2O6.

    (c) Determine the environment of Co ions and discuss possible arrangements of d-orbital.

    (d) Compare the results obtained by measurements of susceptibility, magnetization and neutron diffraction.[1][2]

5. Let us consider a compound $ML_6$ where six ligands (L) occupy the vertices of an octahedron, and the metal ion (M) resides at the center. We establish a global right-handed coordinate system aligned with the diagonals of the tetrahedron.

    One of the normal modes of vibration associated with $ML_6$ is the *symmetric stretching*, depicted in (a) where ligands move along the green arrows. The normal coordinate for this mode is given by:

$$Q_1 = \frac{1}{\sqrt{6}}(X_2 - X_5 + Y_3 - Y_6 + Z_1 - Z_4)$$

    where $(X_i, Y_i, Z_i)$ represent deviations of the ligands from their equilibrium positions. $Q_1$ equals zero when all ligands are in equilibrium, $Q_1$ is positive when ligands move outward, and negative when ligands move inward.

    In (b) and (c), two additional normal modes termed *asymmetric stretching* are depicted. The green arrows illustrate ligand motion for these modes. Find the normal coordinates for them.

**Solution** For (b), the normal coordinate is given by

$$Q_2 = \frac{1}{2\sqrt{3}}(-X_2 + X_5 - Y_3 + Y_6 + 2Z_1 - 2Z_4).$$

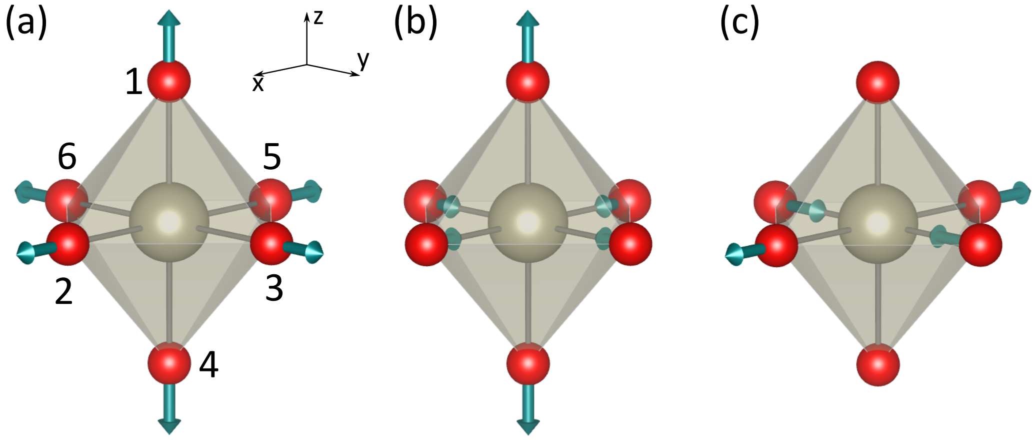


Figure 3: Normal modes of atoms in an octahedral complex $ML_6$.

When ligands $2, 5, 3, 6$ move inward (outward), and $1, 4$ move outward (inward), $Q_2 > 0$ ($Q_2 < 0$).

The normal coordinate for (c) is given by

$$Q_3 = \frac{1}{\sqrt{6}}(X_2 - X_5 - Y_3 + Y_6).$$

In this case, ligands $1, 4$ do not move. When ligands $3, 6$ move inward (outward), and $2, 5$ move outward (inward), $Q_3 > 0$ ($Q_3 < 0$).

*Note:* Generally, electronic states can couple to multiple normal modes or their linear combinations. To visualize this phenomenon, we can utilize the data and simulations provided in the file `Jahn_Teller.ipynb`. Specifically, we aim to depict the Mexican hat energy surface depicting the coupling between electronic states and the vibrational modes $Q_2$ and $Q_3$, as introduced in the previous exercise, in the case of linear Jahn–Teller effect within the harmonic approximation.

# References

[1] A. Maignan, C. Michel, A. C. Masset, C. Martin, and B. Raveau. Single crystal study of the one dimensional $ca_3co_2o_6$ compound: five stable configurations for the ising triangular lattice. *The European Physical Journal B - Condensed Matter and Complex Systems*, 15(4):657–663, Jun 2000.

[2] B. Haubackb S. Aasland, H. Fjellvag. Magnetic properties of the one-dimensional $ca_3co_2o_6$. *Solid State Communications*, 101(3):187–192, 1997.