Solutions: Jahn Teller and charge transfer Mott insulator

Exercise 1: Jahn-Teller Effect

Once the TM ions are placed in a crystal, the crystal field of the surrounding atoms splits the energy levels of the TM ion. The structure of these energy levels and their filling is determined by the crystal field, the Hund's, and Jahn Teller distortion. This exercise looks at some critical consequences of putting TM ion in an octahedral environment.

Consider an octahedral crystal field splitting given by Δ_{CF} and a Hund's coupling provided by J_H.

(a) For a d^4 electron configuration, what is the energy gained for an $S = 1$ as compared to an $S = 2$ configuration?

Solution: The five states of the d orbital splits into three t2g states, d_{xy}, d_{xz}, d_{yz} and two eg states, $d_{x^2-y^2}$ and d_{z^2}. The high spin $S = 2$ configuration is shown below. Following the method from Exercises Sheet 4, we find that the mean field

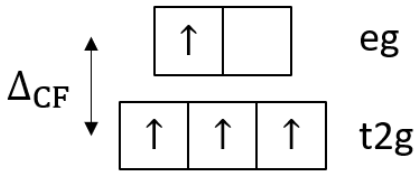


Figure 1: High spin state for d^4 configuration.

Hunds energy is $\mathcal{H}_H^{MF} = -6J_H$.

The $S = 1$ low spin configuration is shown below.

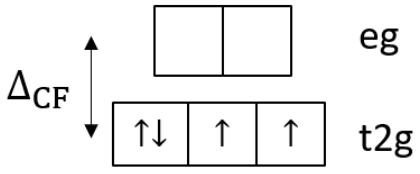


Figure 2: Low spin state for d^4 configuration.

The low spin state has $\mathcal{H}_H^{MF} = -3J_H$.

In addition to the difference in the Hunds energy, the high spin state has an extra Δ_{CF} of energy due to one electron being in the higher lying state. This leads to an energy difference of $\Delta_{CF} - 6J_H - (-3J_H) = \Delta_{CF} - 3J_H$.

(b) What condition determines if the compound would have a high spin or a low spin state?

Solution: Whether the ground state is the high or low spin state depends on which one has lower energy. This is determined by the value of Δ_{CF}. If $\Delta_{CF} < 3J_H$, then the high spin state is the ground state. If $\Delta_{CF} > 3J_H$, then the low spin state is the ground state.

(c) What is the condition for a d^5 configuration?

Solution: The high spin (HS) state is:

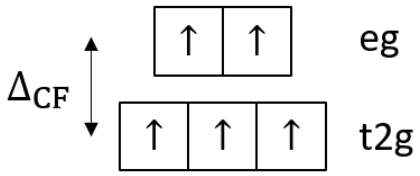


Figure 3: High spin state for d^5 configuration.

with a Hunds energy of $-10J_H$, with $S = 5/2$. The low spin (LS) state is given by:

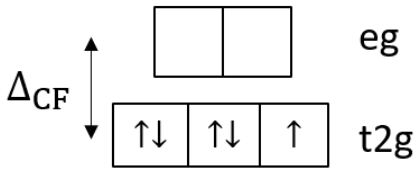


Figure 4: Low spin state for d^5 configuration.

with a Hunds energy of $-4J_H$. In the HS state there are two electrons in the upper states, so the additional energy is $2\Delta_{CF}$ plus the difference in Hunds energy, giving $E_{HS} - E_{LS} = 2\Delta_{CF} - 6J_H$. The ground state is the LS state so long as $\Delta_{CF} > 3J_H$.

(d) For a d^6 configuration, what is the energy difference between a high spin, low spin, and intermediate spin configuration?

Solution: The spins states of d^6 are shown below.

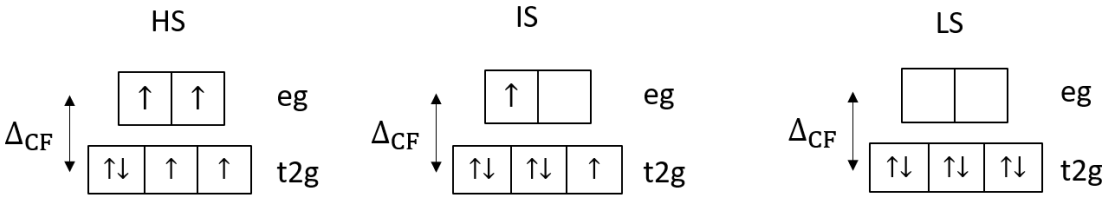


Figure 5: High, intermediate and low spin states for d^6

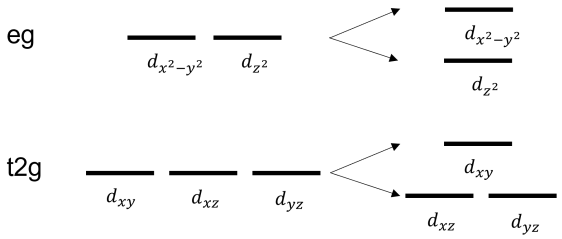
The energy of these three states (minus an arbitrary constant) is given in the table.

State	Energy
HS	$2\Delta_{CF} - 10J_H$
IS	$\Delta_{CF} - 7J_H$
LS	$-6J_H$

Now consider an elongation of the octahedral along the z-axis (preserving the volume of the crystal to first order).

(e) What are the additional splitting in t_{2g} and e_g levels?

Solution: The elongation of the z-axis means that the z-orbitals are further away. The xy orbitals are closer in order to conserve volume. The xy orbital therefore now lie at a higher energy than the z orbitals due to increased orbital overlap along those axis. The new configuration is shown below:



(f) Consider a d^4 electronic configuration in its high spin state. A Jahn-Teller distortion would split the energy levels with energy $\pm gu$, where g is the electron-phonon coupling constant. The energy cost corresponding to the distortion is Bu^2, where B is the bulk modulus. What is the distortion u_0 corresponding to the minimum energy of the eg electron?

Solution: By inspecting the new configuration one can deduce that high spin state has one electron in each of the bottom four states. The total energy is

$$\begin{aligned} E_{yz} + E_{xz} + E_{xy} + E_{z^2} - 6J_H + Bu^2 &= -2gu + gu + \Delta_{CF} - gu - 6J_H + Bu^2 \\ &= -2gu + \Delta_{CF} - 6J_H + Bu^2 \end{aligned} \tag{0.1}$$

This is a parabola with a minumum at $2Bu - 2g = 0$, giving $u_0 = \frac{g}{B}$.

(g) What is the energy difference between the zero distortion and u_0 distortion state?

Solution: From (a) the energy of the zero distortion state is $\Delta_{CF} - 6J_H$. Substituting u_0 into the energy of the state in (f) gives $-\frac{g^2}{B} + \Delta_{CF} - 6J_H$. The energy difference is therefore $-\frac{g^2}{B}$.

Exercise 2: Charge transfer Mott insulator

The parent compound of the high T_c superconductor cuprates La_2CuO_2 is predicted to be metal from DFT calculations (see Figure 1). However, experiments demonstrated that it is an insulator with a gap width of 1 eV (see Figure 2). Which type of insulator is this system?

Solution: The system is a charge transfer insulator.

Note: Classical DFT is unable to capture the insulating behavior of the ground state (undoped) antiferromagnetic La_2CuO_2. Reason for this are that the AFM XC functionals are failing when trying to simulate the bands and magnetic properties. For that reason DFT+U etc have been developed. Additional progress is made in using density function approximations to correctly capture the band structure and metal-to-insulator transition under doping.
https://www.nature.com/articles/s41524-022-00711-z

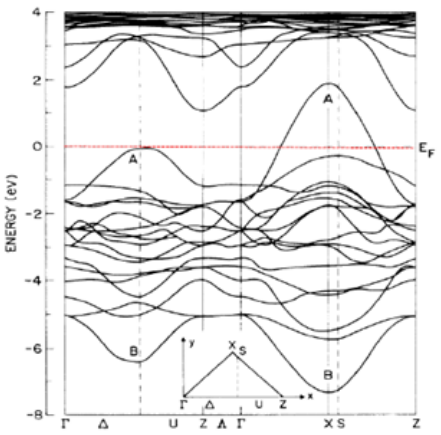


Figure 6: Electronic band structure of La_2CuO_2.

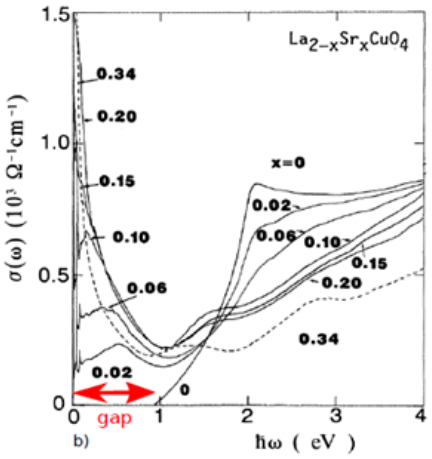


Figure 7: Optical conductivity of La_2CuO_2 for different doping, x.

How could you explain the gap of 1eV? Use the Hubbard model in your explanation.

Solution: The gap of 1eV results in the Oxygen bands being located between the Cu bands. Here the energy difference for transferring one electron from a Oxygen to a Cu site costs an energy of 1eV. In this case of insulator the energy difference resulting from the onsite Coulomb repulsion U is higher, than the charge transfer energy. This situation favors an exchange via ligand as opposed to direct Cu-Cu exchange.

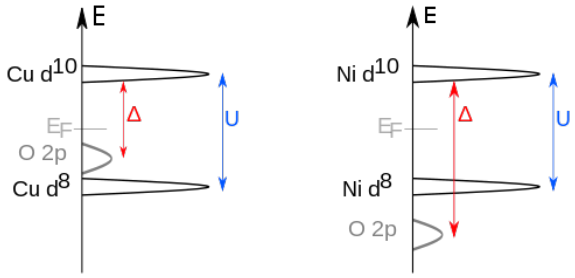


Figure 8: Sketch of CuO/NiO bands for the case of a CT and Mott-Insulator.
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