An energy competition of Co$^{3+}$ and Co$^{4+}$ ions during spin state transition in Ca$_3$Co$_4$O$_9$ complex

N Karaman$^1$, A Bayṛ$^2$, S Ekmekçi$^3$

$^1$ Adiyaman University, Science and Art Faculty, Physics Department, 02040, Adiyaman, Turkey
$^2$ Inonu University, Science and Arts Faculty, Physics Department, 44280, Malatya, Turkey
$^3$ Adiyaman University, Education Faculty, Science Education Department, 02040, Adiyaman, Turkey

E-mail: nkaraman@adiyaman.edu.tr

Abstract. The magnetic behavior of Ca$_3$Co$_4$O$_9$ complex shows a very interesting phase transition at high temperature. It is probably that this ordering is due to the spin states of Co$^{3+}$ and Co$^{4+}$ ions. It is quite obvious that spin states of Co ions generally change as a function of temperature. We have shown that there is a strong correlation between oxidation states and ligand field parameters during spin state transitions.

1. Introduction

Magnetic molecular materials should have a key role to improve systems such as switches, optical displays, data storage devices and etc. Especially, switchable magnetic materials gained considerable interest in view of the potential technological applications after the spin crossover phenomenon (SCO) which was first discovered by Cambi et al [1]. Spin Crossover (SCO) is a phenomena on that occurs in some metal complexes where in the spin state of the complex changes due to external conditions such as, variation of temperature, pressure, light irradiation or even an influence of a field. Spin crossover behavior may be observed in compounds with transition metals of the first series with 3d$^4$ to 3d$^7$ electron configurations and can be explained qualitatively by ligand-field theory [2].

In order to explain the effect of surroundings, there are two fundamental approaches namely Crystal Field Theory (CFT) and Ligand Field Theory (LFT). CFT is based upon a completely ionic picture of bonding. On the other hand LFT is based on covalent bonding. Figure 1 is a simple picture of how the degeneracy of d-orbitals are removed by the crystal field. When examining a single transition metal ion, the five d orbitals have the same energy. When we substituted it in a spherically symmetric field, the five d orbitals energies will be increased but the degeneracy will not change. When ligands approach the metal ion from different directions, all the energies of d electrons will be altered. For example, consider a molecule with octahedral geometry. Ligands approach the metal ion along the $x$, $y$ and $z$ axes. Therefore, $d_{x^2}$ and $d_{x^2-y^2}$ orbitals (which lie along these axes) are more effected compare with $d_{xy}$, $d_{xz}$, $d_{yz}$ orbitals (which are oriented between $x$, $y$ and $z$ axes). This causes a splitting in the energy levels of the d-orbitals. This is known as crystal field splitting.
The five d orbitals lose their degeneracy by an octahedral arrangement of ligands.

For octahedral complexes, crystal field splitting energy (CFSE) is denoted by $\Delta_0$. In an $O_h$ point group, $d_{z^2}$ and $d_{x^2−y^2}$ orbitals are called $e_g$ orbitals and they belong to the $E_g$ irreducible representation. Also in an $O_h$ point group, $d_{xy}, d_{xz}, d_{yz}$ orbitals are called $t_{2g}$ orbitals and they belong to $T_{2g}$ representation. The effects of ligand and crystal field are generally occurred in $d^{4}−d^{7}$ electrons. Up to three electrons, the configuration is same with atomic orbitals. On the other hand between $d^{4}−d^{7}$ electrons, configuration is generally different from atomic case. For example, as seen in Fig. 2, in $d^{3}$ configuration there would be 3 unpaired electrons. If we insert an extra electron in this configuration, there would be 2 possibilities because of strength of crystal field splitting energy. One of them is High Spin (HS) which has four unpaired electrons and the other is Low Spin (LS) configuration which has two unpaired electrons. The SCO phenomenon has uses in many applications due to the inherent bistability which leads to changes in the color of the material and major magnetic changes [3]. Molecular switches, like electrical switches, have the requirement for a mechanism that will turn the switch on and off. Figure 3 shows a schematic of the two different output signals that can be obtained from an Fe$^{II}$ compound upon an external stimuli. In this study we have investigated magnetic properties of Ca$_3$Co$_4$O$_9$ complex which may be a candidate to be magnetic switch.
2. Magnetic behavior of Ca$_3$Co$_4$O$_9$

Crystal structure of Ca$_3$Co$_4$O$_9$ consists of two subsystems and all Co ions in this structure have octahedral environment[4]. The magnetic moment of the sample obviously comes from Co ions. Co ions have three oxidation states in the complex; divalent (Co$^{2+}$), trivalent (Co$^{3+}$) and tetravalent (Co$^{4+}$)[5]. All possible electronic configurations and symmetry term of Co ions are given in Figure 3.

![Figure 3](image)

Figure 3. All possible electronic configurations and symmetry of Co ions.

Figure 4 shows temperature dependence of the magnetic susceptibility, in the temperature range of 2–1000 K. It is quite clear that there are two different spin state transition in the sample. First spin state transition is at about 380 K and second spin state transition intervals of 680 – 920 K and there is a sudden anomaly between 680 and 920 K [6]. We did two modeling in order to explain this anomaly and which Co ion will promote HS state earlier than other.

3. Models

3.1. Symmetry modeling

Co$^{2+}$ ions have always the low spin state configuration. As seen in the figure 3, Co$^{3+}$ ions make an $^1A_{1g} \rightarrow ^5T_{2g}$ transition and Co$^{4+}$ ions make a $^2T_{2g} \rightarrow ^6A_{1g}$ transition when transitioned from LS to HS state. By the symmetry, A term is corresponding to spherically symmetric case. For this, A terms energy is smaller than the T term. Then, we have following suggestion; Co$^{3+}$ ion needs,

$$\varepsilon_1 = \Delta_{Co^{3+}} + E_1$$ (1)
energy and Co$^{4+}$ ion needs,

$$\varepsilon_2 = \Delta_{Co^{4+}} - E_2$$  \hspace{1cm} (2)

Energy to make a transition from LS to HS state. In order to determine which ion would promote HS state, we must determine energy difference between (1) and (2) which is $\varepsilon_1 - \varepsilon_2$.

3.2 Oxidation state modeling
In order to determine the CFSE which depends on oxidation states of Co ions, we must determine orbitals energies. If we examining the Co$^{2+}$ ion, it is a 3d$^7$ electrons. First, if we consider $d_{x^2-y^2}$ orbital and ligands (as seen in figure 5). Then coulomb interaction energy between electrons in orbital and ligands will be $\delta e/r$, where $r$ is distance between the electrons in orbital and ligands, $\delta$ is charge density of orbitals. Thus, $d_{x^2-y^2}$ orbitals energy, $E_{d_{x^2-y^2}}(Co^{2+})$ is,

$$E_{d_{x^2-y^2}}(Co^{2+}) = \text{atomic energy} + \frac{\delta e}{r}$$  \hspace{1cm} (3)
Second, if we consider $d_{xy}$ orbital and ligands (as seen in figure 6); then coulomb interaction energy between electrons in orbital and ligands will be $\delta e/r'$ where $r'$ is distance between the electrons in orbital and ligands, $\delta$ is charge density of orbitals. Thus, $d_{xy}$ orbitals energy $E_{d_{xy}}$ (Co$^{2+}$) is,

\[
E_{d_{xy}}(\text{Co}^{2+}) = \text{atomic energy} + \frac{\delta e}{r'}
\]

(4)

CFSE of Co$^{2+}$ion is energy differences between orbitals energies:

\[
\Delta_{\text{Co}^{2+}} = E_{d_{x^2-y^2}}(\text{Co}^{2+}) - E_{d_{xy}}(\text{Co}^{2+})
= \delta e \left( \frac{1}{r} - \frac{1}{r'} \right)
\]

(5)

We put a similar argument to determine the CFSE of Co$^{3+}$ ion where as we did Co$^{2+}$ ion.

\[
\Delta_{\text{Co}^{3+}} = E_{d_{x^2-y^2}}(\text{Co}^{3+}) - E_{d_{xy}}(\text{Co}^{3+})
= \delta' e \left( \frac{1}{r_1} - \frac{1}{r_1'} \right)
\]

(6)

Where $r_j$ is distance between the electrons in $d_{x^2-y^2}$ orbital and ligands, $r_1'$ is distance between the electrons in $d_{xy}$ orbital and ligands and $\delta'$ is charge density of orbitals for Co$^{3+}$ion. When a Co$^{3+}$ ion loses an electron, it oxidizes to Co$^{3+}$ ion and effective nuclear charge is increased. So ligands are closer to metal ion and repulsion between the d orbitals and ligands will be greater [7]. Namely; $r_1 < r$ and $\delta' > \delta$ then $E_{d_{x^2-y^2}}(\text{Co}^{3+}) > E_{d_{xy}}(\text{Co}^{3+})$ and also $r_1' < r'$ and $\delta' > \delta$ then $E_{d_{xy}}(\text{Co}^{3+}) > E_{d_{xy}}(\text{Co}^{2+})$. For these reasons $\Delta_{\text{Co}^{3+}}$ is greater than $\Delta_{\text{Co}^{2+}}$. For similar reasons, we can say $\Delta_{\text{Co}^{4+}} > \Delta_{\text{Co}^{3+}}$. In order to determine which ion would promote to HS state, we must determine CFSE difference between Co$^{3+}$ and Co$^{4+}$ ions; $\Delta_{\text{Co}^{4+}} - \Delta_{\text{Co}^{3+}}$. 

Figure 5. $d_{x^2-y^2}$ orbital and ligands.

Figure 6. $d_{xy}$ orbital and ligands.
4. Conclusion

We considered two different interaction models, namely the symmetry effect and oxidation state. It is obvious that symmetry prefers Co$^{4+}$ ions promote to HS state earlier than Co$^{3+}$ ions. On the other hand the oxidation state prefers earlier promotion of Co$^{3+}$ ions. It is certain that there is a competition between the set effects in Ca$_3$Co$_4$O$_9$ sample.

References

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