



Supporting Information

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Co Ligand Field : a Key Parameter in Photomagnetic CoFe Prussian blue Derivatives.**

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• Ligand Field Multiplet Calculations.

In order to extract quantitative information from $L_{2,3}$ edges absorption spectra, we simulated experimental data performing calculations using the so-called Ligand Field Multiplet Theory. This approach takes into account all the electronic interactions, the spin-orbit coupling on any electronic open shell and treats the geometrical environment of the absorbing atom through crystal field potential. The parameters used are:

- (i) the atomic spin-orbit coupling constants, ζ_{3d} and ζ_{2p} calculated through the mono-electronic potential around the ion;
- (ii) the reduction factor of the Slater integrals κ depends on the electronic delocalisation and on the covalence of the chemical bond;
- (iii) the crystal field potential which strength is given by the crystal field parameter $10Dq$ for an octahedral symmetry.

Then, to take into account the resolution (intrinsic and instrumental), the calculated spectra are broadened by Lorentzian (0.15 eV) and Gaussian (0.20 eV) functions.

This approach has been used to reproduce the spectra of $[\text{Co}(\text{OH}_2)_6]^{2+}$ and compound **1**. The parameters used are given in the following table :

	ζ_{2p} /eV	ζ_{3d} /eV	κ	$10Dq$ /eV
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	9.75	0.022	0.8	1
1	9.75	0.022	0.68	0.55

The charge transfer introduced by covalence of the metal-ligand bond can be taken into account in the calculation by a new ground state, which is no more built from a pure configuration but is a mixture of two appropriate configurations (interaction configuration). The initial ground state is taken as a linear combination of two configurations: $|\phi_i\rangle = \alpha |2p^6 3d^n\rangle + \beta |2p^6 3d^{n+1} \underline{L}\rangle$, where $|3d^{n+1} \underline{L}\rangle$ stands for an electronic configuration with an extra d-electron (d^{n+1}) coming from the ligands L and with the corresponding hole in the ligand orbital (\underline{L}). In the same way the final state is $|\phi_f\rangle = \alpha' |2p^5 3d^{n+1}\rangle + \beta' |2p^5 3d^{n+2} \underline{L}\rangle$. The new calculation parameters which describe the interaction configurations are Δ , Δ' , $V_{t_{2g}}$ and V_{e_g} . Δ and Δ' are the energy differences between the pure 3d configuration and the $3d \underline{L}$ one in the initial and final state respectively. The strength of the covalency is represented in octahedral symmetry by $V_{t_{2g}}$ for the t_{2g} 3d orbitals levels and by V_{e_g} for the e_g symmetry 3d orbitals where $V = \langle 3d^n | H | 3d^{n+1} \underline{L} \rangle$ is the ligand-metal charge transfer integral between the $3d^n$ state and the charge transfer $d^{n+1} \underline{L}$ state, H being the interaction Hamiltonian. The classical value of the $V_{t_{2g}}/V_{e_g}$ ratio is fixed to -0.5.

For compound **2**, we simulated separately the contributions coming from $\text{Co}^{\text{II}}(\text{HS})$ and $\text{Co}^{\text{III}}(\text{LS})$. For $\text{Co}^{\text{II}}(\text{HS})$, the calculation was the same than for $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and for **1**. For

Co^{III}(LS), due to the high covalency of Co^{III}-ligands bonds, multiplet calculations with configuration interaction have been necessary to reproduce all the features. Finally, the simulation of the experimental data was obtained by linear combination of Co^{II}(HS) and Co^{III}(LS) simulated contributions. The parameters used are given in the following table :

	κ	ζ_{2p} /eV	ζ_{3d} /eV	Δ /eV	Δ' /eV	V_{t2g}/V_{eg}	10Dq /eV
Co ^{II} (HS)	0,68	9.75	0.022	-	-	-	0.7
Co ^{III} (LS)	0,60	9.75	0.022	4	3,25	-0,5	2.4

• f parameter evaluation.

In the model developed by Jorgensen, the crystal field parameter is treated as the product of two independent factors f and g ($10Dq = f.g$) where f describes the strength of a ligand relative to water, which is assigned a value of 1 and g is characteristic of the metal ion. Depending on the spectroscopic measurements (UV Visible or X-ray Absorption spectroscopy) and the formalisms used to calculate the crystal field parameters, the 10Dq absolute values can be a little bit different. So, they cannot be directly compared. However, the spectrochemical series and the f values should not depend neither on the spectroscopic techniques nor on the formalism used to obtain 10Dq. For a given metallic ion at a given oxidation state, the f parameter which directly reflects the spectrochemical series is given by the $(10Dq(ML_6)/10Dq(M(OH_2)_6))$ ratio if the 10Dq values have been obtained by the same technique and the same formalism :

$$\frac{10Dq(Co^{II}L_6)}{10Dq([Co^{II}(OH_2)_6](NO_3)_2)} = \frac{f(Co^{II}L_6)}{1}$$

When the metallic ions or the oxidation states are different, the $10Dq(M_1L_6)/10Dq(M_2(OH_2)_6)$ ratio obtained by a single technique and formalism has to be pondered by the $(g(M_2)/g(M_1))$ ratio.

The g parameter values reported in the literature were obtained by UV Visible spectroscopy. Whereas the absolute g value slightly depends on the measurement and the formalism, the $(g(M_2)/g(M_1))$ ratio should reflect the relative position of the metallic ion within the series. In order to calculate the f parameter associated to Co^{III} in **2**, we took $g(Co^{III})/g(Co^{II}) = (18600/9300) = 2$. In this ratio, both values, $g(Co^{III}) = 10Dq([Co^{III}(OH_2)]) = 18600 \text{ cm}^{-1}$ and $g(Co^{II}) = 10Dq([Co^{II}(OH_2)]) = 9300 \text{ cm}^{-1}$, are obtained by UV Visible spectroscopy^[17]. The f parameter is then given by :

$$\frac{10Dq(Co^{III}L_6)}{10Dq([Co^{II}(OH_2)_6](NO_3)_2)} = \left(\frac{f(Co^{III}L_6)}{1}\right) \times \left(\frac{g(Co^{III})}{g(Co^{II})}\right)$$