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Soft X-ray magnetic circular dichroism in molecular based magnets

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Abstract

The molecular based magnet $\text{Cs}[\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ is a ferromagnet with a Curie temperature $T_C = 90$ K. Its structure consists of face centered cubic lattice of Ni^{II} ions connected by $\text{Cr}(\text{CN})_6$ entities. We have recorded X-ray Magnetic Circular Dichroism (XMCD) at the $L_{2,3}$ edges of Ni^{II} . It clearly evidences that nickel II is in a high spin configuration and ferromagnetically coupled to the surrounding Cr^{III} . Through Crystal Field Multiplet calculation we have determined the total magnetic moment carried by the Ni^{II} . By using sum rules derived for XMCD, it has been possible to extract the orbital and spin contributions to the total magnetic moment. A somewhat too small magnetic moment is found on nickel. A complete calculation taking into account the multiplet coupling effect and the covalent hybridization allowed to determine the precise ground state of nickel and showed that hybridization with surrounding nitrogen atoms is not responsible for the experimental low nickel magnetic moment.

1. Introduction

Conventional techniques in magnetism measure total magnetic moment (susceptibility measurements by SQUID, Faraday balance). Other more sophisticated techniques such as polarized neutron diffraction can give information on specific groups of atoms but measurements are only possible on large single crystals. X-ray magnetic circular dichroism (XMCD) is a new technique that has recently received a strong interest by the community of magnetism. Magnetic Circular Dichroism has long been known in the energy range of visible light but was not investigated till recently in the X-ray range due to the lack of sources of circular polarized X-rays. The development of Synchrotron Radiation in the last decade impulsed the field of X-ray spectroscopies and XMCD was first observed in 1987 [1].

In the first section we present the molecular magnets. The second section present XMCD principles and measurements. And the third one outlines the results concerning the magnetic properties of the magnet that have been obtained from the comparison between experiments and calculations.

2. Molecular based magnets

We have studied a new type of magnets that belongs to inorganic chemistry. The magnets are bimetallic cyanides whose general formulae are $\text{Cs}[\text{A}^{\text{II}}\text{B}^{\text{III}}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ where A and B are 3d transition metal ions. They are synthesized through soft chemistry engineering at room temperature [2,3].

$\text{Cs}[\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ compound is a bimetallic cyanide whose structure consists of a three-dimensional assembly of structural motifs $-\text{N} \equiv \text{C}-\text{Cr}-\text{C} \equiv \text{N}-\text{Ni}-$ where the metallic cations are arranged in a rock salt structure [3,4]. The Ni^{II} ions are surrounded by six nitrogen atoms and the Cr^{III} ions by six carbon atoms. Both have an octahedral symmetry. Cesium ions are present in half of the tetrahedral sites of the structure. In $\text{Cs}[\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, an orbital interpretation based on the model of Kahn et al. [5] allows to foresee a short-range ferromagnetic interaction between the two ions. Field cooled magnetization measurements at 10 G clearly evidence that the Curie temperature is 90 K [3].

3. Experimental measurements at nickel $L_{2,3}$ edges

XMCD consists of a X-Ray absorption measurement performed when the cross section of a magnetic sample is

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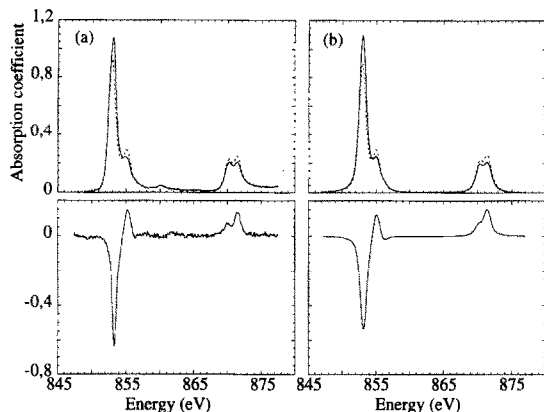


Fig. 1. (a) Top: experimental σ_L (line) and σ_R (dash) at nickel $L_{2,3}$ edges in $\text{Cs}[\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$. Bottom: XMCD signal renormalized to fully circular polarization. (b) Top: theoretical σ_L (line) and σ_R (dash) at nickel $L_{2,3}$ edges in $\text{Cs}[\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$. Bottom: XMCD signal renormalized to fully circular polarization.

recorded for circularly polarized light. The XMCD signal is the difference ($\sigma_R - \sigma_L$) between the two cross sections σ_L, σ_R for left and right circularly polarized light. It can be shown that an effect exists when there is a net magnetization parallel to the propagation vector.

Thole et al. and Carra et al. [6,7] have developed several sum rules that can be applied to XMCD spectra [8]. From these sum rules, it is possible to extract the average values $\langle L_z \rangle$ and $\langle S_z \rangle$, hence also the magnetic moment $M = -\mu_B[\langle L_z \rangle + 2\langle S_z \rangle]$ carried by the absorbing atom.

We measured XMCD at $L_{2,3}$ edges of Ni in the molecular-based magnet $\text{Cs}[\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ [9] on the soft X-ray MTL beamline of the storage-ring Super-ACO at LURE (Orsay) [10]. The left polarization rate is 37% at L_3 edge (853 eV). The X-ray absorption spectra are recorded by measuring the photocurrent emitted by the sample.

4. Results and discussion

The spectra σ_L, σ_R and $\sigma_R - \sigma_L$ at $L_{2,3}$ edges are plotted in Fig. 1a. The experimental XMCD signal has been renormalized to 100% of circular polarization rate. The spectra are characteristic of Ni^{II} in the triplet state [11] as can be confirmed by the multiplet calculation that are presented in Fig. 1b.

We performed multiplet calculations in the crystal field multiplet theory developed by T. Thole. It takes exactly into account spin-orbit coupling and treats the environment of the absorbing atom through crystal field parameters. The calculation has been performed at 20 K and the best agreement is obtained for spin-orbit parameters $\zeta_{2p} = 11.42$ eV and $\zeta_{3d} = 0.1$ eV, a crystal field parameter

$10Dq = 1.4$ eV and an exchange field of 30 T (0.0016 eV). The crystal field parameter is in agreement with the one obtained by optical spectroscopy which is equal to ≈ 1.3 eV. The exchange field is somewhat lower than the one expected from high temperature magnetic susceptibility.

In Fig. 1b, we have plotted the theoretical spectra calculated with energy dependent polarization rates equal to those measured experimentally. The XMCD signal is plotted with 100% of circular polarization rate. Spectra of Figs. 1a and 1b are very much alike. The only difference is at 860 eV where a clearly visible feature is present on the experimental spectra and absent on the theoretical ones. This satellite is interpreted as due to hybridization with the surrounding ligands and will be evidenced by the hybridization calculation presented below [12,13]. Despite this resonance, the overall agreement between theory and calculation is good enough to allow us to rely on the description of the ground state made in the calculations: the irreducible representation of Ni^{II} ground state is Γ_5^+ . ${}^3A_{2g}$ represents the main part of the ground state Γ_5^+ [9].

The application of the orbital sum rule to the experimental spectra gives $M_L = -\langle L_z \rangle \mu_B = 0.10 \mu_B \pm 0.01 \mu_B$ where $\mu_B > 0$. We performed the same calculation with the theoretical spectra and we found $M_L = 0.15 \mu_B$. Experimental and calculated values of M_L agree well as expected from the agreement in shape and amplitude of XMCD spectra in Figs. 1a and 1b.

The computation of $\langle S_z \rangle$ through the spin sum rule requires the knowledge of the average value of the spherical tensor T_z . We calculated $\langle T_z \rangle$ for Ni^{II} ground state and we found $\langle T_z \rangle = 0.0017$. From the experimental spectra, we obtained $M_S = -2\langle S_z \rangle \mu_B = 0.80 \mu_B \pm 0.01 \mu_B$ and from the theoretical spectra we obtained $M_S = 1.02 \mu_B$.

From the application of the orbital and spin sum rules to the experimental spectra, the total magnetic moment on Ni^{II} is found equal to $M = -[\langle L_z \rangle + 2\langle S_z \rangle] \mu_B = 0.90 \mu_B$. And from the application of the orbital and spin sum rules to the theoretical spectra, we found $M = 1.17 \mu_B$. The magnetic moment is lower than the moment value $\approx 2 \mu_B$ expected for a fully magnetized Ni^{II} atom in ${}^3A_{2g}$ triplet state. The experimental XMCD ratio $\langle L_z \rangle / \langle S_z \rangle$ equals 0.25. On the other hand from EPR measurements we found $\langle L_z \rangle / \langle S_z \rangle = 0.18$ [9]. The value deduced from EPR is not as precise as the one obtained from XMCD, because EPR measurement is not chemically selective and it is more intricate to separate Ni and Cr contributions to the global signal. According to experimental errors, the XMCD $\langle L_z \rangle / \langle S_z \rangle$ ratio is comparable to the one obtained by EPR.

A possible origin for the loss of magnetic moment could be hybridization caused by the neighboring nitrogen atoms. To take into account the hybridization effects, we performed Multiplet calculations with electronic configurations' interactions [12,13]. In that model, the Ni^{II} state is a linear combination of the two electronic configurations $3d^8$

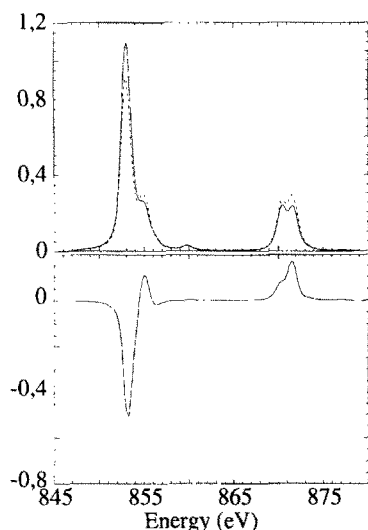


Fig. 2. Theoretical σ_L , σ_R and dichroic signals at nickel $L_{2,3}$ edges calculated with hybridization (relevant parameters are given in text).

and $3d^9\bar{L}$, where $d^9\bar{L}$ is a configuration where an extra electron coming from the ligand orbitals is added on the 3d shell; \bar{L} stands for ligand hole. Fig. 2 shows the theoretical σ_L and σ_R cross sections and theoretical XMCD signal. σ_L and σ_R are calculated for the experimental polarization rates and XMCD signal has been renormalized to a fully circular polarized light. In that model it has been possible to reproduce the satellite at 860 eV. We used $\Delta = 5$ eV, $U_{cd} - U_{dd} = 1$ eV, $V(e_g) = 2$ and $V(t_{2g}) = -1$ (these parameters have been described by Kotani and we kept his notations [14]). We find that the ground state of Ni^{II} is made up of 89% $3d^8$ and 11% $d^9\bar{L}$. This result shows that the nickel–nitrogen bond has a very ionic character compared to the values obtained by Kotani for a set of Ni^{II} compounds [14]. One finds by applying the sum rules to the theoretical cross sections that both M_L and M_S are not much affected by hybridization: we found $M_L = 0.12 \mu_B$ and $M_S = 0.88 \mu_B$. The covalency tends to decrease the magnetic moment by less than 15% ($M = 1.00 \mu_B$ with covalency and $M = 1.15 \mu_B$ without).

5. Conclusion

We have been able to evidence a strong XMCD signal on the Ni^{II} in the bimetallic cyanide $Cs[Ni^{II}Cr^{III}(CN)_6] \cdot 2H_2O$. The ratio $\langle L_z \rangle / \langle S_z \rangle$ obtained from the analysis of XMCD experiments compares well with previous results produced by EPR measurements. This partially confirms the validity of the sum rules.

We have shown that hybridization has to be introduced for a complete simulation of the experimental spectra: the small satellite at 860 eV is reproduced with correct inten-

sity and energy. The hybridization almost conserves the ratio $\langle L_z \rangle / \langle S_z \rangle$. The $3d^9\bar{L}$ configuration weights for 11% in Ni^{II} ground state and tends to decrease the spin and the orbital momentum. But this effect cannot explain completely the low value of the magnetic moment obtained from XMCD. Moreover the dichroic signal calculated at 0 K is much stronger than the experimental one. That means that the too low value of the total magnetic moment on Ni^{II} cannot receive other explanation than an incomplete magnetization that would originate from surface effects. The spectra have been recorded in drain current mode that is equivalent to total yield detection where only the about first 50 Å of the sample participate to the cross section. In these conditions, nickel ions belonging to the surface would not be saturated in agreement from the exchange field of 30 T that is found from the spectra. The surface non magnetic ions would contribute to the isotropic spectrum but not to the XMCD signal and this would lead to apparently reduced values of total, orbital and spin magnetic moments.

Acknowledgements

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