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Soft X-ray magnetic circular dichroism in molecular based magnet

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Abstract

The molecular based magnet $Cs^{I}[Ni^{II}Cr^{III}(CN)_6]\cdot 2H_2O$ 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 $Cr(CN)_6$ entities. We have recorded X-ray Magnetic Circular Dichroism (XMCD) at the $L_{2,3}$ edges of Ni^{II}. 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 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

The molecular based magnet $Cs^{I}[Ni^{II}Cr^{III}(CN)_6]\cdot 2H_2O$ is a bimetallic cyanide where the metallic cations are arranged in a rock salt structure and coupled through cyano bridges [1]. The Ni^{II} ions are surrounded octahedrally by six nitrogen atoms. $Cs^{I}[Ni^{II}Cr^{III}(CN)_6]\cdot 2H_2O$ is ferromagnetic with a Curie temperature of 90 K.

We measured XMCD at $L_{2,3}$ edges of Ni^{II} in $Cs^{I}[Ni^{II}Cr^{III}(CN)_6]\cdot 2H_2O$ [2] on the soft X-ray SU22 beam line of the storage-ring Super-ACO at LURE (Orsay) [3].

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2. XMCD at Ni $L_{2,3}$ edges

The spectra σ_L, σ_R for left and right polarization and the dichroic signal $\sigma_R - \sigma_L$ at Ni^{II} $L_{2,3}$ edges are plotted in Fig. 1(a). The experimental XMCD signal has been renormalized to 100% of circular polarization rate. We performed multiplet calculations in the crystal field multiplet theory developed by B.T. Thole. The calculation has been performed at 20 K and the best agreement is obtained for a crystal field parameter $10Dq = 1.4$ eV and an exchange field of 30 T (0.0016 eV) [2]. The crystal field parameter is similar to the one obtained by optical spectroscopy. All the features of the experimental spectra have been reproduced except for a satellite at 860 eV. This satellite is interpreted as due to hybridization with

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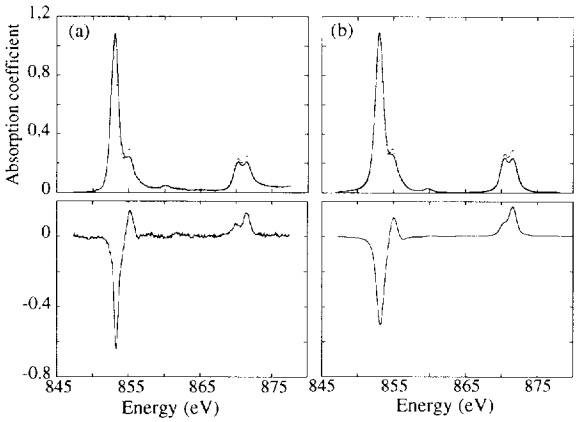

Fig. 1. (a) Top: experimental σ_L (line) and σ_R (dots) at nickel $L_{2,3}$ edges in $Cs^I[Ni^{II}Cr^{III}(CN)_6]\cdot 2H_2O$; bottom: XMCD signal renormalized to fully circular polarization. (b) Top: theoretical σ_L (line) and σ_R (dots) at nickel $L_{2,3}$ edges in $Cs^I[Ni^{II}Cr^{III}(CN)_6]\cdot 2H_2O$; bottom: XMCD signal renormalized to fully circular polarization.

the surrounding ligands [4]. To take into account this effect, we performed multiplet calculations with electronic configuration interactions [4]. In that model it has been possible to reproduce the satellite at 860 eV with the correct intensity and the correct energy position [2]. In Fig. 1(b), we have plotted the theoretical spectra calculated with hybridization. The spectra σ_L and σ_R are calculated with the experimental polarization rate (37% at L_3 and 30% at L_2). The XMCD spectra is plotted with 100% of circular polarization rate.

To extract the orbital and spin magnetic moment of Ni^{II}, we used sum rules developed by Thole et al. [5]. From the application of the sum rules to the experimental spectra, we obtained a total magnetic moment of 0.90 μ_B carried by Ni^{II} and we found $\langle L_z\rangle/\langle S_z\rangle = 0.25$. On the other hand, we also performed EPR measurement on $Cs^I[Ni^{II}Cr^{III}(CN)_6]\cdot 2H_2O$ and we found a value of $\langle L_z\rangle/\langle S_z\rangle$ close to the one obtained from XMCD. From the application of the sum rules to the theoretical spectra, we found that 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).

3. Conclusion

We have been able to evidence a strong XMCD signal on the Ni^{II} in the bimetallic cyanide $Cs^I[Ni^{II}Cr^{III}(CN)_6]\cdot 2H_2O$. 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. We have shown that hybridization has to be introduced for a complete simulation of the experimental spectra. The $3d^9\underline{L}$ configuration weights for 11% in Ni^{II} ground state and tends to decrease the magnetic moment.

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