Eur. Phys. J. B **38**, 43–48 (2004)
DOI: 10.1140/epjb/e2004-00097-9

**THE EUROPEAN
PHYSICAL JOURNAL B**

X-Ray magnetic circular dichroism on vanadium molecular derivatives

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Received 26 September 2003 / Received in final form 19 November 2003

Abstract. X-Ray Magnetic Circular Dichroism experiments have been conducted on a vanadium inorganic salt and a vanadium enamino-ketone complex. Measurements at the K edge of oxygen and nitrogen reveal the amount of magnetic moment transferred in the $2p$ orbitals of the ligand atoms from the magnetic V ion. Measurements at the L edge of vanadium show that the orbital moment is small and that $J = L + S$, contrary to the expected $J = L - S$ coupling for a $3d$ metal with less than five d-electrons. This surprising inobservance of Hund's third rule emphasizes the need for more detailed studies and calculations on such hybrid molecules.

PACS. 75.20.-g Diamagnetism, paramagnetism, and superparamagnetism – 75.70.Ak Magnetic properties of monolayers and thin films – 78.70.Dm X-ray absorption spectra

1 Introduction

Molecular magnetism deals with the magnetism of molecules or, more generally, the magnetism of open shell molecular compounds. Contrary to the vast majority of molecules, these possess one or more unpaired electrons and have therefore a net magnetic moment. Research is essentially focused on the synthesis of new magnetic systems, since organic chemistry allows for the creation of novel molecules, usually with applications in mind. As an example, this research field being very active, it is possible to devise chimeric materials in which two or more functions coexist, like magnetic and photosensitive [1,2], magnetic and chiral [3] etc. Historically, the first magnetic molecules were metal-based (copper acetate, Prussian blue) but it soon became clear that metal-free compounds could also exhibit magnetism, even though the problem has originally been debated [4]. When dealing with magnetic molecules, the main difficulties are the fact that the magnetic moment they bear is delocalized, sometimes all over the molecule, and that the magnetic intermolecular coupling can either be ferro- or antiferromagnetic, depending on the interacting atoms and their relative orientation. One must admit that little is known about i) how exactly the spin is spread over a given molecule and ii) how to proceed so that neighboring molecules predictably interact ferromagnetically to give a magnetically ordered phase. This is illustrated by the fact that today, the highest Curie temperature for a ferromagnetic organic is only 1.5 K [5], the compound has been found by pure chance 10 years ago and no progress has been made so far [6]. The interactions between a magnetic center and its neighbors are almost never simple, be it in molecules or in alloys. Many surprising effects can arise, often counter intuitively, like the strong magnetic moment appearing on vanadium atoms when dispersed in a sodium film, because of a strong induced polarization of the alkali host [7]. One of the motivations of this study was to try getting some information on the magnetic state of a $3d$ magnetic ion and of its nearest neighbors. Probing the magnetic interactions at the atomic or molecular level is indeed a challenging task, only a limited number of techniques are available (polarized neutrons scattering, NMR, ESR, muon spin rotation), single crystals are very often required, and most of the time the results are obtained indirectly through modelling [8,9].

In the present paper, we discuss measurements of the magnetic circular dichroism taken on two vanadium

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derivatives, namely vanadyl sulphate and a vanadyl-*bis*-enaminoketone. These measurements enabled us to estimate the amount of magnetization on the V and the magnetic polarization of the O and N atoms. To the best of our knowing these are the first vanadium $L_{2,3}$ edges experiments having been performed on a molecular system and the first observation, on a paramagnetic system, of the magnetic polarization of the $2p$ orbitals of the oxygen and nitrogen atoms. Furthermore, our unexpected finding of the violation of Hund's third rule in these two vanadium derivatives sheds a new light on the behavior of such organic and inorganic magnetic materials and questions our understanding of these vanadium systems.

Amongst all the existing techniques for characterizing electronic structure and magnetic interactions, L-edge X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) are receiving an increasing interest [10] motivated by several reasons: i) the elemental and orbital selectivity of XAS and its sensitivity to the oxidation state, ii) the strong interaction of soft X-ray with matter which provides sensitivity down to one monolayer and iii) the fact that XMCD enables investigation of previously inaccessible magnetic properties such as orbital and spin contributions to the magnetic moment on a specific shell and site, especially in the case of $3d$ systems, since $2p_{1/2,3/2} \rightarrow 3d$ transitions ($L_{2,3}$ edges) give direct information on the $3d$ band responsible for magnetism.

XMCD is defined as the difference between the absorption of right- and left-handed circularly polarized light when the applied magnetic field (which determines the direction of the magnetization M_z) is parallel to the incident X-ray wave-vector. The so-called Thole's sum rules allow-under certain conditions-to estimate the value of the orbital and spin moments [10–12]. The sole condition for observing a dichroic effect is a nonzero M_z projection. This technique can therefore also be used for studying isolated paramagnetic ions or atoms and complex molecules. By lowering the sample temperature it is possible to obtain an almost complete magnetization of the paramagnetic ion or atom with an external magnetic field of a few teslas. For a given J state, it is worth pointing that the shape of the XMCD spectrum is independent of the temperature and applied magnetic field. By simulations of the experimental spectra with Ligand Field Multiplet (LFM) calculations the crystal field, spin orbit coupling parameters and magnetic exchange energy can be extracted, giving a precise description of the ground state of the absorbing atoms [13].

Vanadium lends itself to a very rich chemistry as it can be found in oxidation numbers between −1 and +5, the +4 state being the most frequent, with the oxovanadium ion VO^{2+} (or vanadyl) dominating the vanadium (IV) chemistry [14]. In most cases the geometry is square pyramidal, with four ligands forming the base and the V=O at the top, O extending outwards. The pyramid can be distorted if the four atoms at the base are not identical like in our compound (see below). The V=O bond is very strong, possibly having a triple bond character and in many oxovanadium complexes the V=O units are stacked to form V=O· · ·V=O chains giving rise to original properties such as ferroelectricity. Coordination of VO with different ligands leads to numerous compounds displaying various magnetic properties like ferromagnetism in dinuclear complexes bridged with pyrimidine [15], spin frustration and antisymmetric exchange in giant clusters embedding vanadium (IV) and Mo [16], redox switching between ferro and antiferro states in a di-vanadium complex [17]. Our study has been performed on a vanadyl *bis*-enaminoketone complex in which the V(IV) atom is a chiral center [18] contrary to other vanadium (IV) complexes whose structure is symmetrical, like in vanadyl sulphate. The molecular formula of the molecule under study is given in Figure 1. This particular compound only has weak antiferromagnetic interactions in the bulk (powder) and the molecules do not seem to form the aforementioned chains.

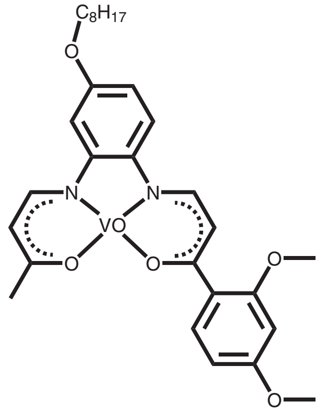

Fig. 1. Formula of the vanadyl-bis-enaminoketone complex.

2 Experimental details

The XAS data have been acquired on the the BACH beam line of ELETTRA and on the ID08 beam line of ESRF. The sample is in a cryostat allowing temperatures down to *ca.* 2 K to be reached, that is equipped with a superconducting magnet (magnetic field up to 7 teslas). The spectra are recorded in the Total Electron Yield (TEY) mode. The value of the $L_{2,3}$ edge has been fixed to 517 eV, the reproducibility of the energy scans is about ±50 meV. More experimental details on this low temperature cryostat can be found in reference [19].

The XMCD measurements have been taken on samples prepared with the Langmuir-Blodgett (LB) technique [20] and consisted of *ca.* 100 monomolecular layers deposited on crystalline silicon plates. Each layer is 30 Å thick, with a molecule, i.e. one vanadium atom, every 50 $Å^2$. In the case of $L_{2,3}$ absorption edges of $3d$ transition metals, the TEY detection has a probing depth of *ca.* 50 Å and the number of electrons reaching the surface decays exponentially as a function of the depth of the photon absorption [21]. Hence, more than 90% of the total absorption occurs within the first and second monolayers which contain less than 10^{11} V atoms only. For comparison, a standard

Table 1. Values of the Landé factor, total, orbital and spin moments for a free V^{4+} ion without and with orbital quenching.

No orbital quenching			
g_J	$M_T = -g_J J$	$\langle L_z \rangle = (g_J - 2)$ J	$\langle S_z \rangle = (1 - g_J)$J
4/5	6/5	−9/5	3/10
Full orbital quenching			
g_J	$M_T = -2\langle S_z \rangle$	$\langle L_z \rangle$	$\langle S_z \rangle$
2	1	0	−1

SQUID equipment needs about 10^{14} atoms to perform a moment measurement. Note that the samples are without any upper protection (capping) layer. For $VOSO_4$•$5H_2O$, a microcrystalline powder sample (commercial, Fluka) was used both in SQUID and XMCD experiments.

3 Experimental results

Vanadium (IV) has [Ar]$3d^1$ electronic configuration and therefore has the following quantum numbers: $S = 1/2$, $L = 2$ and $J = L - S = 3/2$, according to Hund's rules. The magnetic properties of the isolated ion, associated quantum numbers and moments are summarized in Table 1, with the two limiting cases $\langle L_z \rangle \neq 0$ and $\langle L_z \rangle = 0$ for the orbital moment (all magnetic moments being given in μ_B).

The following usual conventions must also be kept in mind: $M_{spin} = -2\langle S_z \rangle \mu_B$ and $M_{orb} = -\langle L_z \rangle \mu_B$. In the presence of an external magnetic field, the total magnetic moment $\mathbf{M}_T = M_z \hat{z}$ is always in the direction of the field.

3.1 SQUID magnetometer experiments

The magnetic moments of the two compounds (vanadyl sulphate and complex) have been measured on microcrystalline powders with a SQUID magnetometer (it has proven impossible to grow single crystals of the vanadyl complex) [22]. SQUID magnetometry results are given in Figure 2, data having been corrected for diamagnetism of sample holder. The magnetic susceptibility of the complex follows a Curie-Weiss law, with weak antiferromagnetic interaction, the Weiss constant being $\theta = (0.3 \pm 0.1)$ K.

Magnetization measurements performed at 2 K and 4 K have been fitted with a Brillouin function (with a Weiss constant of −0.3 K), yielding a saturation moment of $M_{sat} = (0.9 \pm 0.1)\,\mu_B$, slightly below the minimal value of $1\,\mu_B$ expected in case of full orbital quenching. This borderline discrepancy could originate from antiferromagnetic interactions. The magnetization curve of the inorganic vanadyl sulphate could also be fitted with a Brillouin function, yielding a saturation moment of $M_{sat} = (1.0 \pm 0.1)\,\mu_B$, in perfect agreement with the expected value.

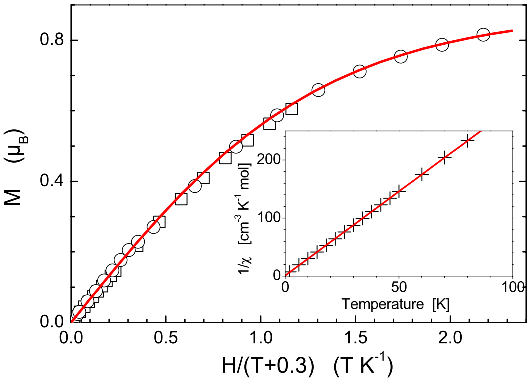

Fig. 2. SQUID magnetometry on the vanadyl complex in powder form. The main graph is a plot of the magnetic moment as a function of field over temperature ($T = 2$ K (○), 4 K (□)). Temperatures have been shifted by 0.3 K to account for the Weiss constant. Inset is a Curie-Weiss plot of the magnetic sucseptibility, for $T < 100$ K.

3.2 Electron spin resonance experiments

A sample consisting of 513 layers of the vanadyl complex deposited on a 2.5 × 10 mm^2 plate made of fused silica has been investigated with electron spin resonance (ESR) performed at x-band. X-ray reflectivity measurements performed on a similar but larger sample brought evidence that the lamellar structure was well-defined, with a low roughness. Because of the nuclear spin $I = 7/2$ of ^{51}V, hyperfine splitting gives rise to an ESR line shape with several features which do not allow for a straightforward analysis to be performed [23]. The Landé factor g of vanadyl in ESR spectra is usually less than that of the free electron, usually *ca.* 1.95 [24]. We measure a value of 2.010 ± 0.001, significantly higher. Values of g as high as 2.18 have been reported for vanadyl ions trapped in conducting polymers [25], the large increase of g being ascribed to a high delocalization of the unpaired electrons on the ligands and to strong spin-orbit interactions in the ligands. These systems are very different from the one described here, in particular because of the electrical properties but in any case, the larger value of g that we observe with ESR supports our findings of an unusual magnetic behavior (see below). The doubly integrated ESR signal gives a measure of the number of spins within the sample and of its magnetic anisotropy. Measurements of the sample at liquid helium temperature indicate that *ca.* $(2.0 \pm 0.2 \times 10^{16})$ spins $S = 1/2$ are present within the ESR cavity, in excellent agreement with the number of molecules deposited on both sides of the silica plate, *ca.* $2.1 \pm 0.2 \times 10^{16}$, as deduced from the deposition conditions. Within experimental error, we can therefore assume that each molecule indeed bears a $S = 1/2$ spin. Rotation of the sample inside the ESR cavity while measuring the signal gives the anisotropy curve plotted in Figure 3. It is clearly seen that the sample is magnetically anisotropic, as the intensity of the ESR signal varies with the angle between the normal to the layers and the magnetic field. Given the bad signal-to-noise ratio, no further attempt

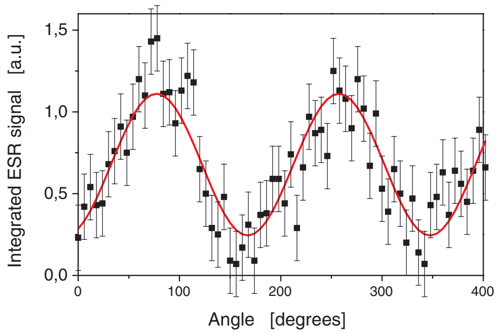

Fig. 3. Variation of the integrated ESR signal as a function of the angle between the normal to the layers and the magnetic field. Data taken at 5.0 K. Line is a fit to a cosine.

has been made to investigate more finely this anisotropy: we can only say that the in-plane magnetic interactions differ from the normal-to-plane ones.

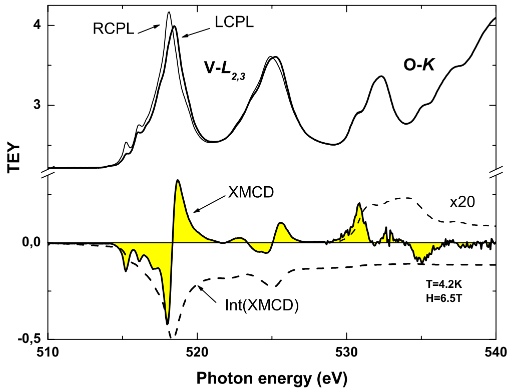

Fig. 4. XMCD spectra recorded at 4.2 K under a 6.5 T magnetic field on the vanadyl complex. The two upper curves are the X-ray absorption spectra for right- and left-handed circularly polarized light. The curves below are the XMCD spectrum and the integrated XMCD spectrum, with a zoom-in (×20) of the XMCD spectrum around oxygen K edge, evidencing transferred magnetic moment on the O atoms.

3.3 XMCD experiments

Vanadium $L_{2,3}$ edges

XMCD measurements recorded on LB films of the complex are given in Figure 4. The two upper curves, recorded at energies between 510 and 540 eV, show typical X-ray absorption spectra, for right-and left-handed circularly polarized light, at $T = 4.2$ K and $H = 6.5$ T. The characteristic features of the vanadium $L_{2,3}$ edges can clearly be seen on the left, and the K edge of oxygen on the right. The corresponding XMCD signal and its integral are given below (the XMCD magnetic field dependence is the same as the magnetization shown in Fig. 2). In spite of the insulating character of the samples and the TEY detection we observe a very high signal-to-noise ratio, even for only about 3×10^{10} absorbing V atoms (≈1 monolayer).

The resolution of the monochromator enables observation of the different structures in the V-$L_{2,3}$ edges characteristic of a V^{4+} state [26,27]. The dichroism signal is only due to the paramagnetic nature of the VO^{2+} state. Application of the sum rules generally allows for the spin and orbital moments to be extracted from XMCD measurements. If μ^+, μ^- and μ^0 are the absorption coefficients for RCPL, LCPL and linearly polarized light respectively, the orbital moment, $M_{orb} = -\langle L_z\rangle\mu_B$, is obtained from the L_z sum rule [10]:

$$\frac{\int\limits_{L_3+L_2}(\mu^+ - \mu^-)}{\int\limits_{L_3+L_2}(\mu^+ + \mu^- + \mu^0)} = \frac{\langle L_z\rangle\,\mu_B}{2(10-n)}$$

where n is the number of electron in the $3d$ valence shell ($n = 1$ in the present case). The question of the sum rules is often hotly debated, chiefly because of the approximations they are based on [28]. The spin sum rule is considered to be the most sensitive to failure, especially if there is intermixing between core split edges, as in the light $3d$ transition metals. The orbital sum rule is somewhat more robust, even if it can yield slightly erroneous values, in particular when two edges overlap. In this case the exact absolute value of $\langle L_z\rangle$ cannot be determined, due to the normalization by the isotropic edges, but its sign is always known for sure. For a free V^{4+} ion the atomic values $\langle L_z\rangle = -1.80\,\mu_B$ and $\langle S_z\rangle = +0.30\,\mu_B$ are expected, whereas in a C_{4v} symmetry the calculated [26] orbital and spin components are $\langle L_z\rangle = +0.06\,\mu_B$ (close to zero but positive) and $\langle S_z\rangle = -0.50\,\mu_B$ respectively, the strong reduction of the orbital moment being due to the electrical crystal field acting on the V^{4+} ions. As shown in Figure 4, the symmetric shape of the dichroic signal of the VO^{2+} complex leads to a very low integrated intensity, and consequently to a low $\langle L_z\rangle$ value: we observe that $\langle L_z\rangle$ ranges from -0.06 to $-0.11\,\mu_B$ when the incidence angle of the photons varies from 0 to 60° (the XAS spectrum itself is slightly anisotropic). Although somewhat larger, this anisotropy is reminiscent of the one observed in the ESR experiments. The incertitude on the $\langle L_z\rangle$ values is estimated to be of the order of 15%. As is usually observed in polyatomic structures [29,30], the orbital momentum is almost totally quenched, due to the strong axial ligand field. It is not possible to apply the $\langle S_z\rangle$ sum rule to the $3d^1$ configuration [31] however, if the orbital contribution is small, the spin component can be given by the measurement of the bulk magnetic moment. The total moment, obtained by SQUID measurements, $M_{sat} = (0.9 \pm 0.1)\,\mu_B$ implies therefore a $\langle S_z\rangle$ value of $(-0.4 \pm 0.1)\,\mu_B$, which must be compared with the expected value, $\langle S_z\rangle = -0.50\,\mu_B$. As suggested before, this small difference could be due to antiferromagnetic interactions. These results are in contradiction with the expected L-S coupling for a metal with a less than half-filled $3d$ band which should have $\langle L_z\rangle$ and $\langle S_z\rangle$ of opposite signs. This could be due to the idiosyncrasy of the V=O bonding, which produces huge charge transfers, or to the influence of the neighboring O and N atoms.

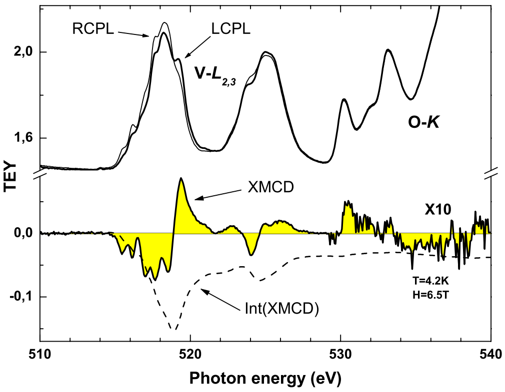

Fig. 5. XMCD spectra recorded at 4.2 K under a 6.5 T magnetic field on vanadyl sulphate. The two upper curves are the X-ray absorption spectra for right- and left-handed circularly polarized light. The curves below are the XMCD spectrum and the integrated XMCD spectrum, with a zoom-in (×10) of the XMCD spectrum around oxygen K edge.

Comparison with the reference V^{4+} compound $VOSO_4$•$5H_2O$ (Fig. 5) shows that almost the same shape of the dichroic signal is observed in both V compounds, but with more intense dichroic structures in the low energy side of the L_3 edge for the reference system. These differences will help us for LFM simulations. As in the case of the VO^{2+} complex, the XMCD spectrum leads to a very small negative value for the orbital angular momentum, $\langle L_z\rangle = (-0.10\pm0.02)\,\mu_B$. The SQUID measurements on $VOSO_4$•$5H_2O$ yield a total magnetic moment $M_{sat} = (1.0\pm0.1)\,\mu_B$, therefore $\langle S_z\rangle = (-0.5\pm0.1)\,\mu_B$ [32]. Here again, our data point to a violation of Hund's third rule in the sense that M_{spin} and M_{orb} are unexpectedly found to have the same orientation. The simulations of the XAS and XMCD spectra with the LFM method, based on the calculation of the atomic multiplets elements for atoms submitted to crystal field (effective symmetry of the absorbing atom) and configuration interaction (covalency or charge transfer), are in progress and will be published elsewhere.

Oxygen and nitrogen K edge

Due to the lack of suitable calculations of the density of states of these V systems we confine ourselves to a qualitative description of the oxygen and nitrogen K edge. Figure 4 shows the oxygen 1s edge in the VO^{2+} complex as the most right peaks. Above the threshold of K edge (540 eV) the spectrum presents a double structure which is the fingerprint of the oxygen 2p orbitals hybridized with the t_{2g} and e_g orbitals of the vanadium 3d. Because of the crystal symmetry these signatures are only due to the V=O bonding. We clearly observe the magnetic polarization of the O 2p orbitals, which illustrates the hybridization of the V and O orbitals. The magnetic signal, first positive and then negative, peaks at the energy of the two shoulders of the double-peaked structures with an absolute amplitude of a few % of the edge. The integrated magnetic signals lead to propose an antiferromagnetic coupling of the orbital components of V 3d and O 2p. We make the same conclusions (Fig. 5) for the vanadyl sulphate, even if the data are much more noisy than for the complex. This shape is equivalent to that already observed at the K edge in 3d metals. In other words, this signal should be the counterpart of what would be observed at the vanadium K edge. In the complex, a quantitative analysis of the relative intensity of the dichroic peaks, as proposed in the study of 3d metal oxides by de Groot [13], might be difficult because the threshold is distorted by the V L_2 edge. As pointed by Yokoyama et al. [33], K edge XMCD measurements are difficult to perform and to analyze. In their paper they investigate O K edge of molecular CO adsorbed on Ni films and apply the sum rule while pointing that it is not always clear whether it can be employed because of core-hole effects. All other XMCD studies have been done on metallic oxides, not molecules. A magnetic signal is also observed in the VO^{2+} complex at the nitrogen K edge, as seen in Figure 6. Here the shape does not resemble to the standard 3d K edge and indeed, to the two main peaks of the N K absorption correspond two sets of dichroic structures, as it has recently been observed in bimetallic cyanide complexes [34]. The dichroic signal we observe is very weak, and the experiment suffered from pollution by adsorbed molecular N_2 coming from the residual gases. Still, we believe that is can be taken as the qualitative proof of spin transfer on the nitrogen atoms of the ligands.

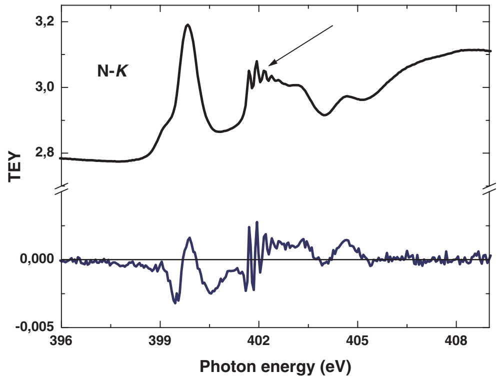

Fig. 6. Top curve: absorption spectrum at the K edge of nitrogen taken on the complex; bottom curve: XMCD signal. The arrow points to the multiplet absorption feature of adsorbed molecular N_2 resulting from a pollution of the cryostat.

4 Discussion

For lack of any calculations allowing a more quantitative analysis of the results to be made, we shall not discuss further our observation of induced magnetic moment on the light atoms N and O. We shall therefore restrict the discussion to the question of the relative orientation of M_{orb} and M_{spin}. Even though originally developed for atoms, so-called Hund's rules work remarkably well in solids. The third rule states that the total angular momentum equals

$J = L - S$ for less than half-filled bands, $J = L + S$ otherwise. In the case of V^{4+}, it is therefore expected that M_{orb} and M_{spin} be antiparallel. To the best of our knowledge, there is no report on the observation of a breaking of the third rule in a magnetic solid. There has been a report of such a violation for a 5d non-magnetic metal [35], but is has been argued that Hund's rules do not generally apply to induced moments. True, the question of third rule being violated is conceptual in most solids where the quenching of $\langle L_z \rangle$ is almost complete. Recently Galanakis et al. have addressed theoretically the question of the L-S coupling in the intermetallic VAu_4 compound [36,37]. In their papers they demonstrate the important role of the ligand field on the formation of the orbital moment and on its orientation. They show that the L-S coupling can not only be inverted but also possibly "tuned" by a suitable choice of the ligands, Cu versus Au in their case. Even though our system is molecular instead of metallic, we believe that a similar mechanism could be operating here. The covalent bonding between the metal and the ligand certainly enables hybridization between the V and O and N states, as required by the mechanism of Galanakis et al. We take as an additional indication the fact that an induced moment has been found on the latter atoms.

In conclusion, we have studied two vanadium derivatives, one organic and one inorganic. For both samples, the XMCD analysis reveals an almost quenched orbital momentum for the VO^{2+} ions, parallel to the spin moment. We also report the observation of the magnetic polarization of the 2p orbitals of the nitrogen and oxygen atoms in such paramagnetic Vanadium systems.

This work was financially supported by the CNRS-LURE-ELETTRA contract. We thank the staff of the ID08 beam line (ESRF), and Ph. Sainctavit and M. Drillon for fruitful discussions.

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