X-ray Magnetic Circular Dichroism Study of Molecule-based Magnetic Thin Film V[TCNE]$_{x\sim 2}$

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Introduction

The organic-molecule-based magnet vanadium tetracyanoethylene or V[TCNE]$_x$ (where x ~ 2), which has a very low density of magnetic vanadium ions, is remarkable in that it shows spontaneous ordering of moments at temperatures that are much higher than room temperature (T_c of ~400K) [1, 2]. What is even more surprising about the V[TCNE]$_x$ compound is that despite the fact that it has significantly shorter structural correlation lengths than those of its Fe- and Mn-based brethren [3], its T_c value is four times larger. It appears that the magnetic interactions underpinning the high value of T_c are critically tied to the local environment of the moment-bearing V ions. Recent x-ray absorption fine structure (XAFS) work [4] determined this local structure to be a slightly distorted octahedron of N atoms with one V^{2+} ion located at the center. Bulk magnetization measurements suggest that V[TCNE] is a ferrimagnet, with every localized V^{2+} moment (S = 3/2) aligned antiparallel to two diffuse moments (S = 1/2) on neighboring [TCNE]$^-$ molecules. The feasibility study discussed here focuses on determining how useful the x-ray magnetic circular dichroism (XMCD) technique could be for obtaining information on element-specific magnetization and magnetic interactions.

Methods and Materials

Recently, V[TCNE] was successfully grown as thin films by using a solvent-free, low-temperature analog of a high-temperature chemical vapor deposition (CVD) technique prevalent in the semiconductor industry. While the T_c value remained as high as it was for the bulk amorphous materials grown by using solvents, the degree of structural disorder associated with the solvent inclusions was essentially eliminated in these films, which provided us with a high-quality sample. Thin films of this compound were grown on glass substrates. Because of the low rate of deposition (~1 to 5 μm in 12 hours), a number of films were required in order to obtain sufficient material for the x-ray absorption measurements through the V K edge (5.462 keV). These films were then pulverized and mixed with Apiezon$^{\circledR}$ grease to fill the hole of a small, 1-mm-thick Al washer to make a disk-shaped sample. Because of the extreme air sensitivity of V[TCNE], the sample was prepared in a He atmosphere.

The effective thickness of the sample $\Delta\mu x$ was ~0.6. For the XMCD measurements, the washer was mounted between the pole pieces of a permanent magnet providing ~3 kG of magnetic field parallel to the washer surface. The washer (sample) surface was placed at an angle of 30° with respect to the incident beam.

Although the V K-edge dichroism is expected to be much weaker than its L-edge counterpart, it provides much better bulk sensitivity, which is necessary since V[TCNE] samples are prone to surface contamination. XMCD measurements were performed in the transmission channel, with the incident and transmitted flux monitored by ion chambers. A diamond (111) phase retarder was used to provide circularly polarized x-rays. The sample and magnet were cooled by using a closed-cycle displex. All the measurements were done at a sample temperature of ~20K.

Results

A summary of our main observations is provided in Fig. 1. The bottom panel shows the absorption spectra, and the top panel shows the dichroic spectra. Data were collected with two relative orientations (shown in blue and red) of the projected magnetization and incident beam direction. Since we used a permanent magnet, this collection was achieved by rotating the sample-magnet system by 180° in order to orient the projected magnetization anti-parallel to the beam. There are two features (peaks) in the near-edge region; they are centered on 5.471 and 5.483 keV. These peaks correspond to dipole-allowed transitions from the V atomic 1s state to unoccupied states above the Fermi level. Whereas the second feature is due to a $1s \rightarrow 4p$ transition, the lower-energy feature is associated with a $1s \rightarrow 3d$ transition, where the 3d level is strongly hybridized with states with p-character [5].

XMCD is the difference in absorption for x-rays with opposite helicities, and it is proportional to the magnetization of the absorbing atom. As the incident energy was scanned through the V K edge, the absorption spectra were collected for left and right circularly polarized x-rays. Despite the poor statistical quality of the data, the top panel in Fig. 1 shows that there is a small but unmistakable dichroic effect centered on 5.481 keV (dashed line). The effect is normalized to an edge jump
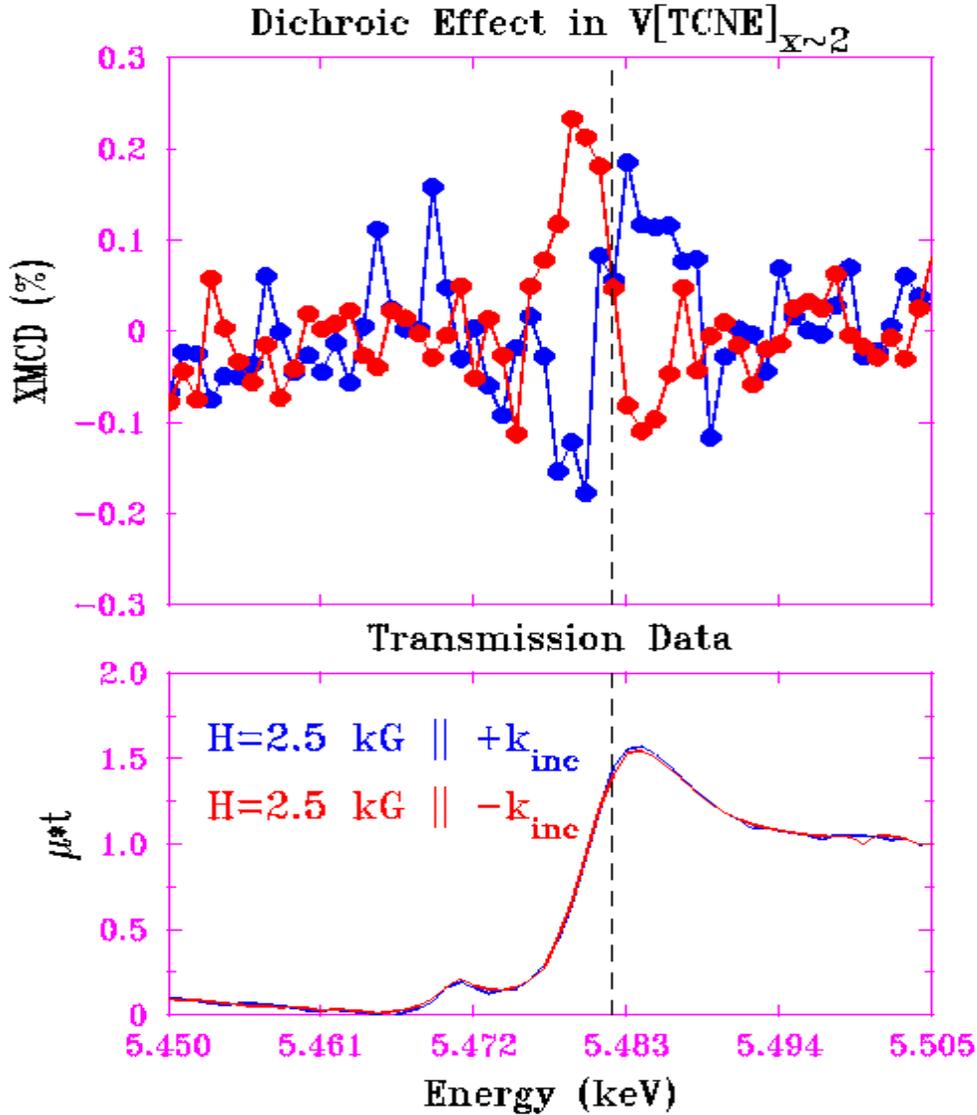
FIG. 1 Top panel: Dichroic spectra of V, with the projected magnetization parallel (blue) and anti-parallel (red) to the incident beam direction. Six sets of data were collected for each orientation in a total of ~20 hours. Bottom panel: Absorption spectra normalized to an edge jump of 1.

of 1, giving a maximum of ~0.2% of the edge jump. This dichroic signal is small, as is expected for signals at the K edge of transition metal atoms. For example, in elemental iron, the effect is ~0.6%.

Discussion

The observation of V dichroism at the K edge implies that there is spin polarization of the $4p$ states at the Fermi level. However, it is difficult to glean an absolute value for the moment. Because of the amorphous and semiconductive nature of this compound and the very local nature of the magnetic interactions, theoretical models based on V-centered clusters may be constructed to completely explain XMCD, both qualitatively and quantitatively. Current data sets lack the accuracy that would enable such modeling to provide meaningful information on magnetic interactions. Higher-quality XMCD data and data on magnetic-field dependence that would be obtained by employing lock-in techniques are necessary for such a theoretical endeavor to be successful.

Acknowledgments

References

[1] J.M. Manriquez, G.T. Yee, R.S. McLean, A.J. Epstein, and J.S. Miller, *Science* **252**, 1415 (1991).

[2] K.I. Pokhodnya, A.J. Epstein, and J.S. Miller, *Adv. Mater.* (Weinheim, Ger.) **12**, 410 (2000).

[3] M.A. Girtu, C.M. Wynn, J. Zhang, J.S. Miller, and A.J. Epstein, *Phys. Rev. B* **61**, 492 (2000).

[4] D. Haskel, Z. Islam, J.C. Lang, C. Kmety, G. Srajer, A.J. Epstein, K.I. Pokhodnya, and J.S. Miller (to be published, 2003).

[5] J. Wong, F.W. Lytle, R.P. Messmer, D.H. Maylotte, *Phys. Rev. B* **30**, 5596 (1984).