

Local Structure of Amorphous V[TCNE]_x Molecular Magnet

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Introduction

The discovery of vanadium tetracyanoethylene, V[TCNE]_x ($x \sim 2$), a molecular-based magnet with a remarkably high magnetic ordering temperature ($\sim 400\text{K}$), has reinforced the idea that organic-based magnets will likely play a major role in the race for developing future magnetic devices [1]. Recent progress in the optical manipulation of the magnetic state has further expanded this view [2]. V[TCNE]₂ belongs to the class of organic magnets that carry magnetic moment on both the metal site and the organic molecule. However, a detailed understanding of its magnetic ordering mechanism is still lacking, partly because the chemical structure of this compound is unknown. Samples grown as thin films are amorphous [3], and conventional techniques for structural determination, such as diffraction, are therefore not suitable. The x-ray absorption fine structure (XAFS) technique does not require crystallinity since it only probes the short-range order in the atomic arrangement about selected atoms.

Methods and Materials

XAFS measurements at the V *K*-edge were done at beamline 4-ID-D of sector 4 in transmission geometry. A Si(111) double-crystal monochromator was used with a harmonic rejection mirror. Samples were sealed in an airtight Be can filled with He gas for thermal exchange and mounted in the cold finger of a displax refrigerator for temperature-dependent measurements (10-300K). Two V[TCNE]₂ samples, 5- and 20- μm thick, respectively, were measured, as were several reference compounds, for valence and amplitude reduction factor (S_0^2) determination.

Results

Figure 1 shows x-ray absorption near-edge structure (XANES) spectra for V[TCNE]₂ and a series of reference compounds with known valence states. By measuring the energy shifts in absorption features in the reference compounds with an increased valence state, we can determine the valence state of vanadium in V[TCNE]₂. The energies of the absorption edge and the $1s \rightarrow 4p$ peak were obtained from line shape fits to the absorption

spectra and their derivatives. These two absorption features are the most sensitive to changes in valence state [4]. As seen in Fig. 1, the valence state of V in V[TCNE]₂ is in the [2-2.4] range. Figure 2 shows the x-ray absorption coefficient $\mu(E)$ across the V *K*-edge, the derived XAFS oscillations after background removal at $\chi(k) = [\mu(E) - \mu_0(E)]/\mu_0(E)$ where $k = \sqrt{2m(E - E_0)}$ is the photoelectron wave number, and the Fourier transform of the XAFS, $\chi(R)$, together with fit results at $T = 300\text{K}$. The $\chi(R)$ is related to the radial distribution function about V atoms. It shows a well-defined first coordination shell. Structural parameters, such as average interatomic distance (R) and its rms disorder (σ) and coordination number (N), were derived by fitting the data in real space by using FEFF6 theoretical standards [5]. The coordination number can be determined only if the amplitude-reduction factor S_0^2 is known, and vice-versa. Since the latter only depends on the V absorbing atom and not on its environment, we determined its value from XAFS measurements and fits to V-metal and VO standards that have known coordinations. Values of $S_0^2 = 0.77 \pm 0.05$ and 0.81 ± 0.06 were obtained, respectively, from these fits, and $S_0^2 = 0.79$ was set for the V[TCNE]₂ fits.

It was assumed that V atoms are coordinated by nitrogen atoms, whose number, distances, and rms disorder were varied in the fits. Best fits yielded $R = 2.09 \pm 0.01 \text{ \AA}$, $N = 4.06 \pm 0.37$, and $\sigma = 0.04 \pm 0.02 \text{ \AA}$, independent of temperature. These results were obtained by following two independent venues to break the existing correlation between fitting parameters N and σ in order to avoid false local minima. One approach was to simultaneously fit data sets for various temperatures in the 10-300K interval and constrain $\sigma(T)$ to follow a 1-D Einstein model for the mean-squared relative displacement in the V-N bond. This yielded an Einstein temperature of $\theta_E = 1400 \pm 200\text{K}$, corresponding to a zero-point motion $\sigma(0) = 0.04 \pm 0.02 \text{ \AA}$, a vibrational frequency of about $1023 \pm 200 \text{ cm}^{-1}$, and the coordination number given above. The second approach was to weight the $T = 300\text{K}$ data set by different k -weights $k^w \chi(k)$ ($w = 1, 2, 3$) and simultaneously fit these "identical" sets with a single parameter set. Different k -weights emphasize different

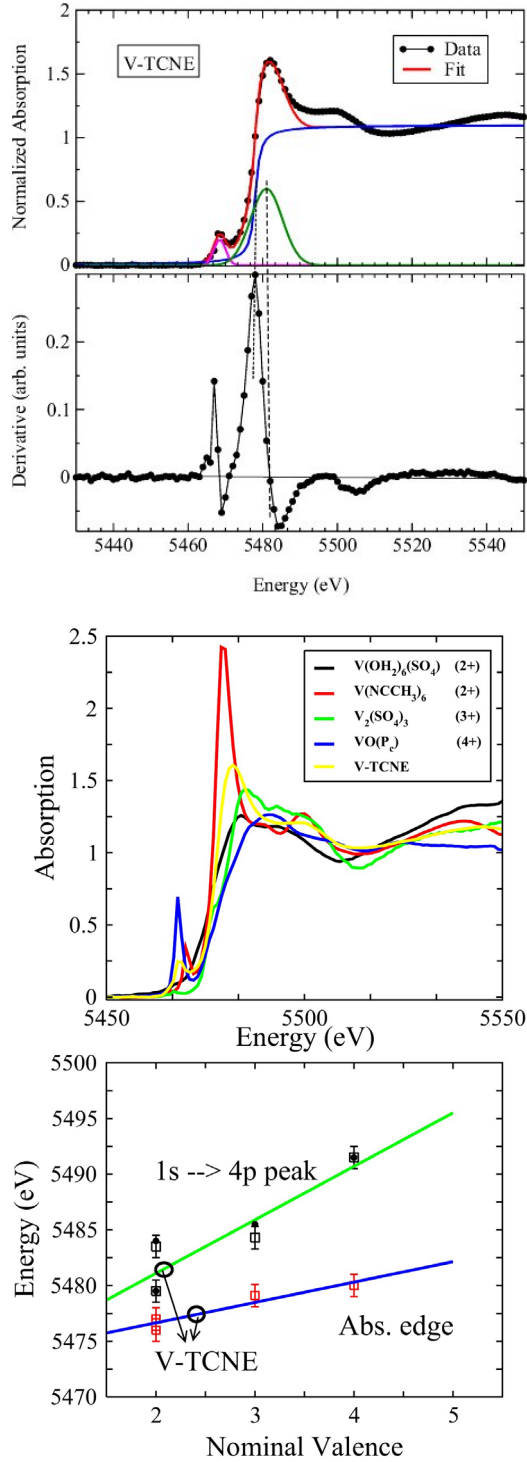


FIG. 1. Top: V K-edge XANES spectrum and its derivative for $V[TCNE]_2$ at $T = 300K$ indicating the energy position of the absorption edge and $1s \rightarrow 4p$ features. Bottom: XANES spectra of reference compounds with known valence state and derived energy position of the above features as function of valence state. The unknown valence of V in $V[TCNE]_2$ is obtained by interpolation.

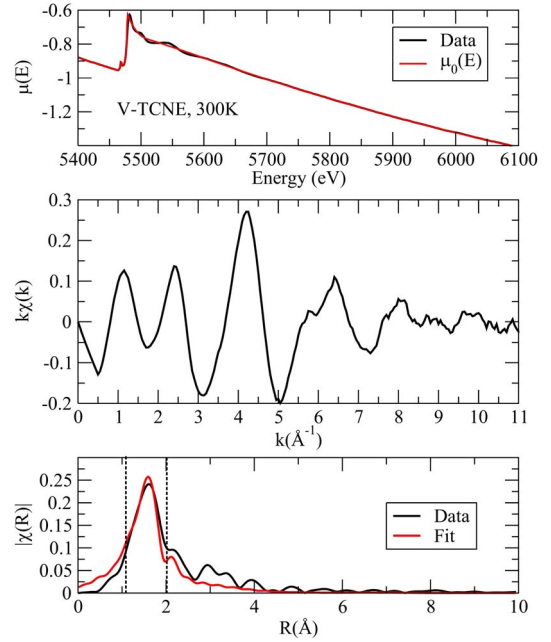


FIG. 2. Top: V K-edge absorption spectrum for $V[TCNE]_2$ at 300K. The atomic background used to isolate the XAFS oscillations is also shown. Middle: XAFS signal. Bottom: Magnitude of the complex Fourier transform of $k\chi(k)$, together with a first shell fit. Vertical dashed lines indicate fitting range. The “peak” positions appear shifted from the actual interatomic distances because of scattering phase shifts.

k-regions of the data set. Since the effect of rms disorder σ is predominant at high k-values, different k-weights change the degree of correlation between N- and σ -fitting variables as well as their derived uncertainties. The physical answer should be independent of k-weighting of the data, and this procedure gives a set of parameters that satisfy this requirement. We obtained $\sigma = 0.034 \pm 0.02 \text{ \AA}$ and $N = 4.0 \pm 0.4$, in good agreement with the results from the other constrained fits.

Discussion

Because of the amorphous nature of the $V[TCNE]_2$ films, XAFS can only determine the radial component of the distribution function of atoms around vanadium. A coordination of four likely indicates a tetrahedral environment. This is a significant new result, since in the absence of this information, the coordination of vanadium was typically, until now, assumed to be octahedral [6]. We note that forcing a coordination of six nitrogens around V decreased the fit quality by a factor of 3. The presence of the otherwise dipole-forbidden $1s \rightarrow 3d$ pre-edge peak in the absorption spectrum (Fig. 1) indicates lack of centro-symmetry about the V site. The

strength of this peak is consistent with the measured tetrahedral “cage” size [4]. The small zero-point disorder σ ($T = 0$) in the V-N interatomic distance indicates very strong interatomic bonding with a characteristic vibrational frequency of about 1000 cm^{-1} . This is indicative of a strong hybridization between V and N orbitals, which for a tetrahedral environment, involves mostly $4sp$ orbitals on the V site but could also include $3d-t_{2g}$ orbitals as well. The very sharp distribution of V-N distances measured by XAFS, together with the absence of significant line broadening in the absorption edge, indicates a single valence state for V in this compound and not a mixed valence state. The question remains whether a tetrahedral environment for V is consistent with the high-spin $S = 3/2$ state derived from the magnetization measurements. The tetrahedral crystal field splitting of the V $3d$ orbitals results in e_g and t_{2g} levels, which are reversed relative to those in octahedral splitting; i.e., e_g below and t_{2g} above. Since the V-N distance is relatively large ($R = 2.09 \text{ \AA}$), this crystal field splitting is small. For a V^{2+} ion with a $3d^3$ electronic configuration, two electrons occupy x^2y^2 and z^2 orbitals in the e_g manifold in a high-spin $S = 1$ state. The third electron could enter an e_g orbital, resulting in an $S = 1/2$ state with significant on-site Coulomb repulsion, or it could enter the t_{2g} manifold, resulting in an $S = 3/2$ state. The small crystal field splitting associated with the large V-N distance makes the

latter a more likely scenario. Theoretical calculations of the electronic structure of this compound in the newly suggested tetrahedral environment are needed to verify this hypothesis.

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References

- [1] J. M. Manriquez, G. T. Yee, R. S. McLean, A. J. Epstein, and J. S. Miller, *Science* **252**, 1415-1417 (1991).
- [2] D. A. Pejakovic, C. Kitamura, J. S. Miller, and A. J. Epstein, *Phys. Rev. Lett.* **88**, 57202 (2002).
- [3] K. Pokhodnya, A. J. Epstein, and J. S. Miller, *Advanced Materials* **12**, 410 (2000).
- [4] J. Wong, F. W. Lytle, R. P. Messmer, and D. H. Maylotte, *Phys. Rev. B* **30**, 5596 (1984).
- [5] S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, and M. J. Eller, *Phys. Rev. B* **52**, 2995 (1995).
- [6] A. L. Tchougreff and R. Hoffmann, *J. Phys. Chem.* **97**, 350 (1993).