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Electron Spin Resonance Study of the Disorder in the $V(TCNE)_x \cdot_y(MeCN)$ High-T_c Molecule-Based Magnet

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ELECTRON SPIN RESONANCE STUDY OF THE DISORDER IN THE $V(TCNE)_x \cdot y(MeCN)$ HIGH-T_c MOLECULE-BASED MAGNET

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Abstract $V(TCNE)_x \cdot y(MeCN)$ is a molecule-based magnet with T_c varying from ~80 to ~150 K depending on the preparation. The electron spin resonance properties are reported for a preparation with $T_c \approx 82$ K. The temperature dependence of the ESR integrated intensities, linewidths and resonance field have been measured over the range from 3 to 300 K. Above ~ 150 K the linewidth increases linearly consistent with thermal broadening. Near T_c an anomalous minimum in the linewidth is observed which we attribute to critical behavior associated with the dipolar interaction as described by Huber and the presence of disorder. At low temperatures a resonance field shift and excess linewidth are observed to be consistent with the theory of Becker for spin glasses with anisotropy and zero remnant magnetization.

INTRODUCTION

High-T_c molecule-based magnets based on the $V(TCNE)_x \cdot y(solvent)$ (TCNE = tetracyanoethylene) system have attracted much interest since the discovery of cooperative magnetic behavior in $V(TCNE)_x \cdot y(CH_2Cl_2)$ at up to its 350 K decomposition temperature.[1] Recently this class of magnets also has been studied for their potential technological use as lightweight materials for magnetic shielding and inductive applications.[2] The related compound $V(TCNE)_x \cdot y(MeCN)$ has an experimentally accessible T_c in the range ~80 to ~150 K. Zhou *et al.* have reported[3,4] the static magnetization of this material and analyzed the critical behavior in the framework of random magnetic anisotropy.[5,6,7] AC susceptibility measurements[8] identify a spin glass phase with a freezing temperature $T_f \sim 10$ K which is attributed to disorder caused by the coordination of the spinless MeCN molecule. Charge transport measurements[9] show the system to be a semiconductor (insulator at low temperatures) with room temperature conductivities of $\sigma \sim 10^{-5}$ S/cm. Here we report results of the temperature dependent electron spin resonance of a $V(TCNE)_x \cdot y(MeCN)$ composition with $T_c \approx 82$ K. The

origins of the spin resonance behaviors over the measured range 3 to 300 K are discussed.

The $V(TCNE)_x \cdot y(MeCN)$ samples were prepared in a similar manner to the previously reported procedure[1] for $V(TCNE)_x \cdot y(CH_2Cl_2)$, with the MeCN substituted for the CH_2Cl_2. Due to the extreme insolubility of the precipitate, reactivity of the solvent, and high sensitivities to air and water, it is difficult to precisely control the composition of the samples and T_c's differing on the order of tens of Kelvin were observed. The stoichiometry of the material discussed here is usually $x \sim 1.5$ and $y \sim 2$. The structure of this compound is not known due to its disorder, however X-ray diffraction studies have established structural short range order on the scale of 10 Å.[10] The material is proposed to be composed of V^{II} with three unpaired electrons in 3d orbitals ($S = 3/2$) and $[TCNE]^-$ with one unpaired electron in a π^* orbital ($S = 1/2$).[1,3] The vanadium can coordinate with the N atoms of the $[TCNE]^-$ coupling antiferromagnetically to form a three-dimensional exchange coupled network.[1]

EXPERIMENTAL

The electron spin resonance spectra were obtained utilizing a Bruker Instruments ESP300 (X-Band) electron spin resonance spectrometer using a TE_{102} resonant cavity. Temperature control over the range 3 to 300 K was achieved using an Oxford 900 continuous flow Helium cryostat. The $V(TCNE)_x \cdot y(MeCN)$ samples studied were sealed under vacuum in 3 mm I.D. quartz EPR tubes. Due to the sensitivity of the experiment and the large magnetic susceptibility of the samples several precautions were taken to avoid significant loading of the resonant cavity causing distortion of the resonance lineshape. First, the sample mass was kept small, less than 0.5 mg. Second, in the cavity the sample was positioned in a region of low sensitivity near the bottom of the cavity. The linewidth measurements reported throughout the paper are the half width at half maximum (HWHM) linewidth. The resonance field is taken to be the position of maximum absorption.

RESULTS AND DISCUSSION

The ESR lineshape of $V(TCNE)_x.y(MeCN)$ is Lorentzian at all but very low temperatures, as expected for a system of 3D strongly coupled spins in the exchange narrowed limit. We attribute the distortion at low temperature to a small suppression of the absorption intensity in the center region of the resonance due to increased loading of the cavity caused by the large susceptibility of the sample at low temperatures near the resonance field. The deviation was small and did not significantly effect the determination of linewidths and resonance fields. The ESR lineshape indicated strong exchange coupling at all observed temperatures.

The ESR integrated intensity (double integral of the EPR derivative curve) versus

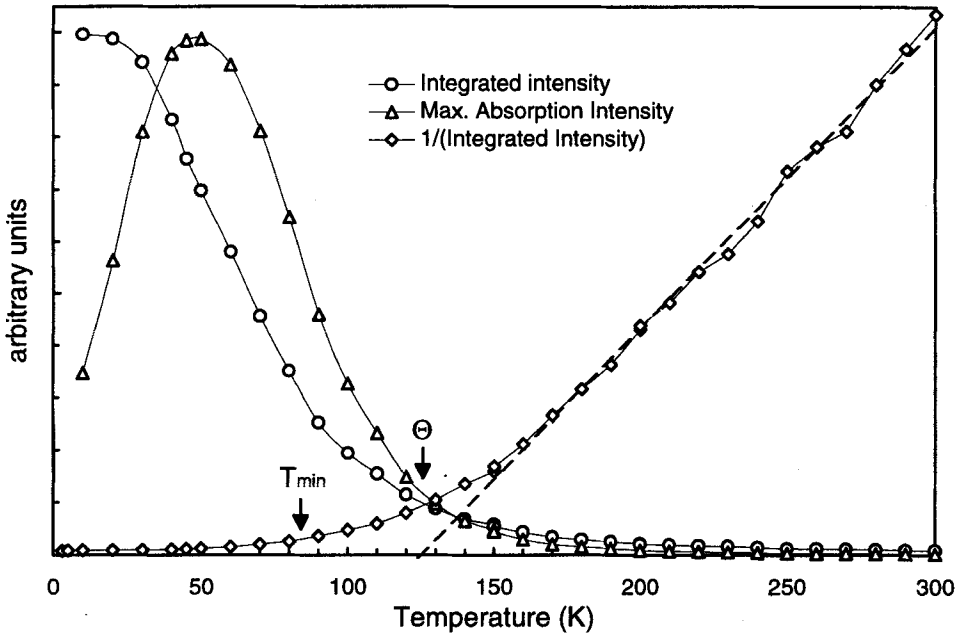

Figure 1: Scaled plots of integrated-intensity, inverse of integrated-intensity, and integrated-intensity/linewidth versus temperature for V(TCNE)$_x$.y(MeCN). The arrows denote the temperature for the minimum in the linewidth (T_{min}) and the Curie-Weiss temperature (Θ). The dashed line is a scaled plot of $(T-\Theta)/C$ where C is the Curie constant.

temperature for V(TCNE)$_x$.y(MeCN), Figure 1, scales with that of the static magnetization (M) where the linear decrease in M with increasing T was attributed to the effects of weak random magnetic anisotropy.[3] It is noted that the temperature dependence of the maximum absorption intensity (Y_{max}) taken as the integrated intensity divided by the linewidth, Figure 1, is similar to the AC susceptibility measured at low fields.[2,8]

The linewidth temperature dependence, Figure 2, shows a remarkable similarity to the temperature dependence reported for RKKY spin glass alloys, for example $AgMn_xSb_y$ and $(La_{1-x}Gd_x)Al_2$.[11,12] This similarity is unexpected as the microscopic interactions in theses alloys are very different from those proposed[3] for V(TCNE)$_x$·y(MeCN). Common to both material classes is the presence of disorder which results in frustration and therefore spin glass behavior. The RKKY exchange interaction introduces disorder through random exchange. In the V/TCNE systems it is unlikely that strong fluctuations in the exchange exist since the vanadium ions are coordinated directly to the $[TCNE]^-$. Instead it has been proposed[3] that disorder arises from random magnetic anisotropy. Becker has calculated the ESR linewidth and resonance field shift as a function of temperature and frequency near T_f for these spin glasses alloys based on RKKY exchange coupling and a smaller anisotropic interaction.[13,14] To fit our low temperature behavior

we adopt Beckers theory despite the obvious differences. As in the spin glass alloys, the linewidth of $V(TCNE)_x \cdot y(MeCN)$ in the high temperature regime, $T > T_c$, is dominated by thermal broadening.

$V(TCNE)_x \cdot y(MeCN)$ is a semiconducting (insulating at low temperatures) ferrimagnet and therefore on the microscopic level is analogous with insulating antiferromagnets that have been extensively studied. In these antiferromagnets near the critical temperature both a narrowed and divergent linewidth temperature dependence have been observed, $RbMnF_3$ and MnF_2 are examples respectively.[15,16] Huber has explained this difference in terms of the interplay of the dipolar interaction and the symmetry of the magnetic lattice.[17,18,19] In light of the microscopic similarities we analyze the line narrowing near T_c using Huber's theory. In the next three subsections we examine the linewidth and resonance field in the high, critical and low temperature regimes.

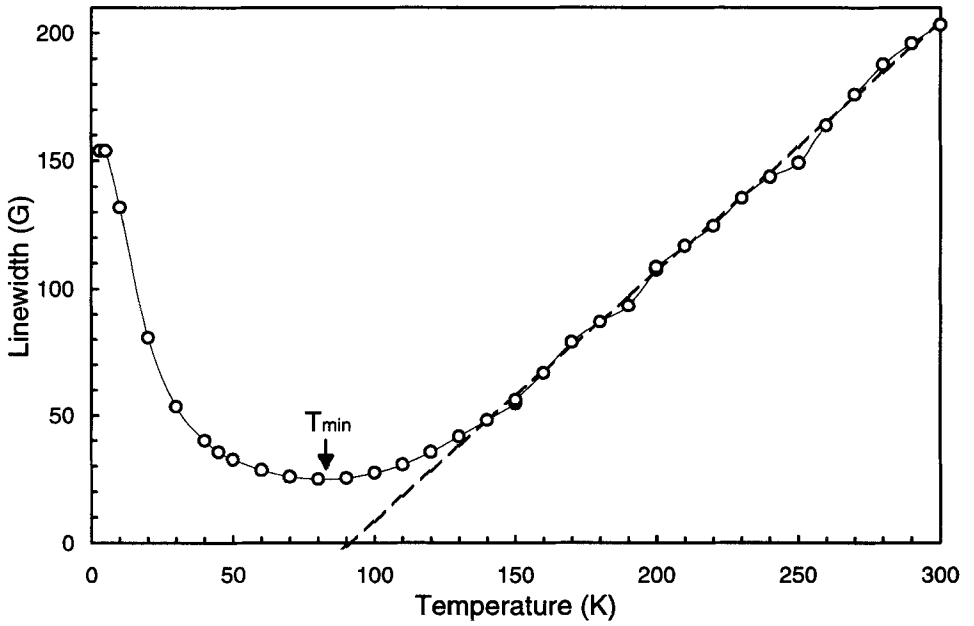

Figure 2: The half-width at half-maximum linewidth versus temperature for $V(TCNE)_x \cdot y(MeCN)$. The dash line a fit to the high temperature thermal broadening given by Equation (1).

Thermal Broadening, $T \gg T_c$

In this section we compare the linewidth behavior in the high temperature region, $T \gg T_c$, in terms of linear thermal broadening. For spin glass alloys thermal broadening is proportional to 1/M(T) where M(T) is the temperature-dependent magnetization.[11,20] Stewart showed that if M(T) follows a Curie-Weiss law the thermally broadened

linewidth, ΔH, will be given by[20]

$$\Delta H = (a_0 - b\Theta) + bT \tag{1}$$

where a_0 is the residual linewidth, Θ is the Curie-Weiss temperature and b is the thermal broadening constant. In addition Stewart also showed that the *g*-shift or resonance field shift should be independent of temperature in the region of thermal broadening.[20] The resonance field above T_c is independent of temperature (see below) consistent with a temperature independent g-value. The fit of (1) to the high temperature region is shown in Figure 2 as a dash line where $(a_0 - b\Theta) = -89.4$ G and $b = 0.977$ G/K. The Curie-Weiss temperature is estimated to be $\Theta = 125$ K as the x-intercept of $(T - \Theta)/C$ fit to the inverse integrated-intensity versus temperature curve in the high temperature regime (see Figure 1). The residual linewidth is calculated to be $a_0 = (b\Theta - 89.4) = 32.7$ G in very good agreement with the value $a_0 = 25$ G estimated in the following section based on equation (2).

Thermal broadening occurs in a two sublattice system as a result of a bottleneck in the relaxation process. V(TCNE)$_x$·y(MeCN) differs from earlier studied spin glass alloys in very fundamental ways. Spin glass alloys consists of two spin subsystems, magnetic ions contributing localized spins and conduction electrons. The V(TCNE)$_x$·y(MeCN) system has two strong antiferromagnetically coupled sublattices. We speculate that the $[TCNE]^-$ spins can rapidly relax to the lattice (due to their internal vibrational degrees of freedom and also torsional motion as a unit) in analogy to conduction electrons, with the $V^{++\cdots}$ relaxation to the $[TCNE]^-$ system being the origin of the bottleneck.

Critical Regime, $T \sim T_c$

In V(TCNE)$_x$·y(MeCN) we observe an anomalous narrowing of the resonance linewidth with a minimum at or near the critical temperature, Figure 3. We have fit the linewidth about the minimum to the function

$$\Delta H = a_0 + b' \left| \frac{T - T_{min}}{T_{min}} \right|^n \tag{2}$$

where a_0 is the residual linewidth, and T_{min} corresponds to the temperature for minimum linewidth. The best fit is show in Figure 3 as the dashed line where $a_0 = 25$ G, $b' = 47$ G, $T_{min} = 82$ K, and $n = 2.0$. This power law is in good agreement with the experimental data from 50 to 170 K, a surprisingly large temperature range. The origin of the residual component of the linewidth in the spin glass alloys has been attributed to crystal-field effects and local moment imperfections through a demagnetization mechanism.[12] The value of $a_0 = 25$ G suggests that demagnetization and crystal field effects in V(TCNE)$_x$·y(MeCN) are small.

Huber's theory for linewidths in insulating ferromagnets[17] and antiferromagnets[18,19] in the immediate region above the critical temperature is used to interpret this power law

behavior. Huber calculated the spin-spin relaxation time, T_2, taking into account both dipolar and exchange induced spin diffusion. For an insulating Heisenberg antiferromagnet[18,19] with only dipolar anisotropy Huber showed that the critical contribution to the linewidth comes from fluctuations in the vicinity of $q = 0$ and K_0, where K_0 is the reciprocal lattice vector of the ordered state. Fluctuations in the total magnetization, $q = 0$, contribute to a narrowing of the linewidth where as the K_0 contributions result in divergence of the linewidth. For systems with high symmetry it is only the $q = 0$ contribution are important and Hubers theory gives[18]

$$\Delta H = A + B\xi^{-3/2} \tag{3a}$$

where

$$\xi \propto \left|\frac{T - T_c}{T_c}\right|^{-\nu} \tag{3b}$$

is the correlation length associated with the staggered magnetization. Comparing equations (2) and (3), $n = 3\nu/2 = 2.0$, gives the critical exponent ν=1.33. For the mean field 3D Heisenberg model $\nu = 0.71$.[21] The large value of ν we obtain is consistent with the presence of strong disorder which is expected to increase the rate at which the correlation length decreases as the temperature moves away from the critical temperature.

The presence of the narrowing of the linewidth, as opposed to a divergence, at the critical temperature may give insight into the structure of $V(TCNE)_x \cdot y(MeCN)$. Huber's

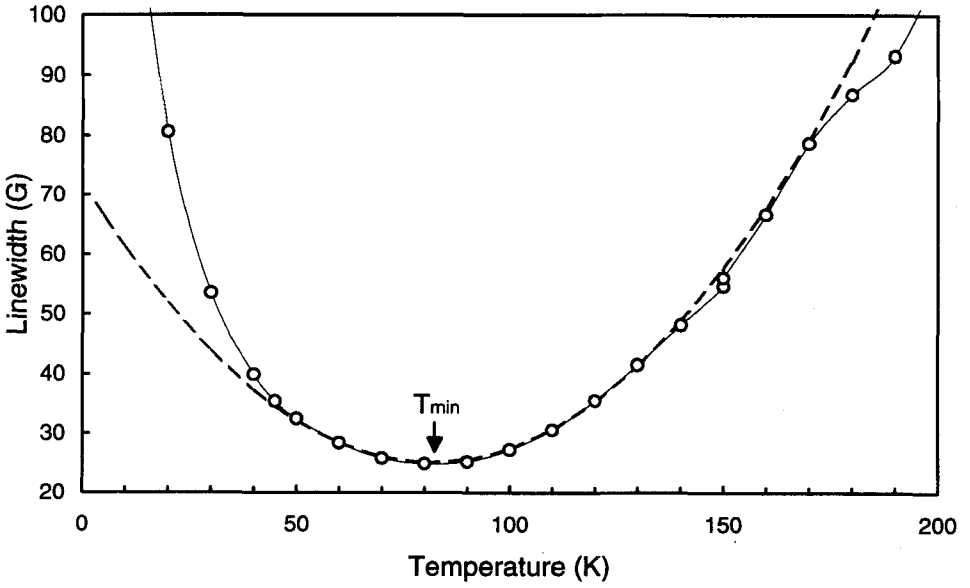

Figure 3: Plot of linewidth versus temperature near the ~ 82 K critical temperature for $V(TCNE)_x \cdot y(MeCN)$ [open circles connected by solid line] and fit to power law, Equation (2) [dashed line].

work was originally prompted by linewidth measurements in the antiferromagnets, MnF_2 and $RbMnF_3$ for which a divergence and minimum in the linewidth at the critical point were reported, respectively.[15,16] The MnF_2 system has local tetrahedral symmetry resulting in broadening of the linewidth near the critical temperature where as $RbMnF_3$ has a cubic lattice and a minimum linewidth at the critical temperature. In our system if vanadium were coordinated with four TCNEs in tetrahedral symmetry Huber's theory would predict a divergence in the linewidth. However if $V(TCNE)_x \cdot y(MeCN)$ has an octahedral lattice, consistent with vanadium coordinating with six $[TCNE]^-$, Huber's theory could account for the minimum in the linewidth. Thus the critical linewidth behavior points towards a magnetic lattice with local high symmetry and at the same time the presence of strong disorder.

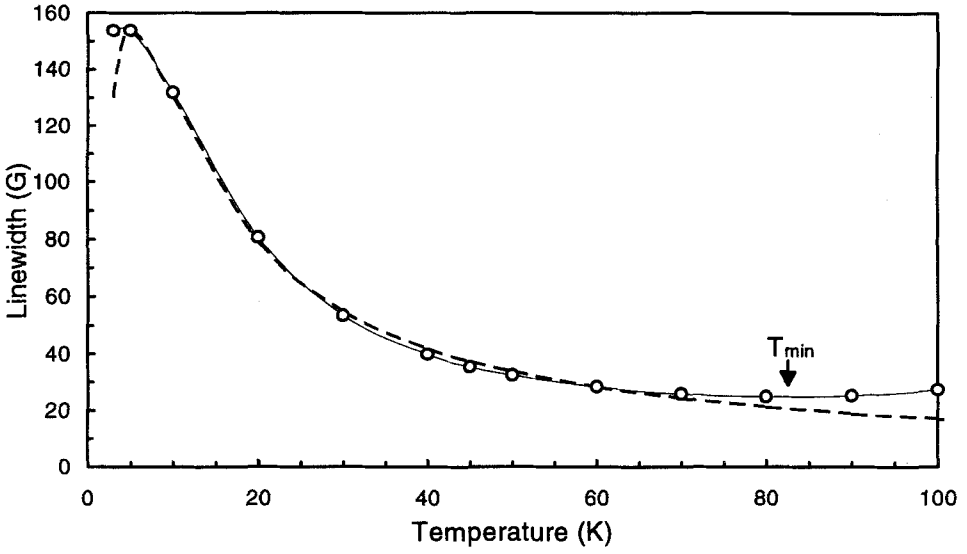

Figure 4: Plot of linewidth versus temperature and fit to Equation (4), dashed line, for $V(TCNE)_x \cdot y(MeCN)$.

Spin Glass Regime, $T < T_c$

In the low temperature regime we observe a broadening of the linewidth and a shift in the resonance field. This temperature dependence is similar to that observed in spin-glass alloys such as $AgMn_xSb_y$ and $(La_{1-x}Gd_x)Al_2$.[11,12] In these alloys the excess linewidth has been attributed to an exchange narrowed anisotropic interaction. As the temperature is lowered a slowing down of spin fluctuations reduces the effectiveness of the exchange narrowing. In addition these alloys also show a corresponding shift in their resonance field which is neither a pure *g*-shift nor a frequency independent internal field. Becker calculated the ESR linewidth and line-shift effects for spin-glasses with anisotropy.[13,14]

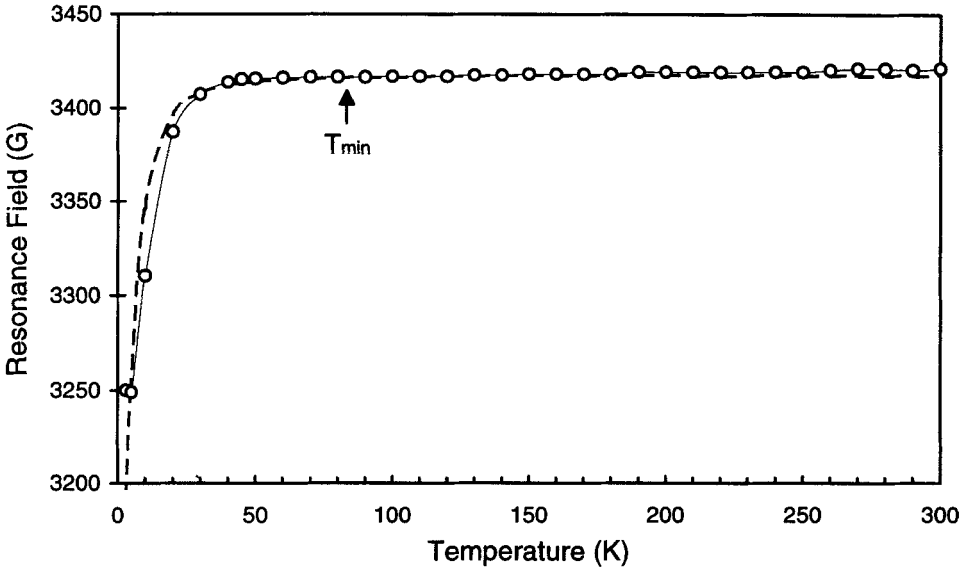

Figure 5: Plot of resonance field versus temperature and fit to Equation (5) for $V(TCNE)_x \cdot y(MeCN)$.

For systems with no remnant magnetization Becker showed that the linewidth and resonance field are given by

$$\Delta H = \frac{ABT}{B^2 + T^2} \tag{4}$$

and

$$H_{res} = H_0 + \frac{AT^2}{B^2 + T^2} \tag{5}$$

where $A = g\mu_B K/\hbar\omega\chi_\perp$, $B = M_2/Kk_B\omega$, $H_0 = \hbar\omega/g\mu_B$, and ω the resonance frequency. Here $\chi_\perp$ is the static transverse susceptibility, K is the anisotropy constant, and M_2 is related to spin relaxation. For simplicity we assume K, M_2, A, B, and H_0 are independent of temperature in $V(TCNE)_x \cdot y(MeCN)$. Also we assume that at low temperatures $\chi_\perp$ varies only weakly with temperature. The best fits of (4) and (5) to the experimental data, shown in Figures 4 and 5 as the dashed lines respectively, where $A = 309.4$ G, $B = 5.49$ K, and $H_0 = 3108$ G. Very good agreement is found. Given $\omega = 9.44$ GHz and assuming $\chi_\perp = 0.0017$ emu/g (roughly taken as M/H) an effective anisotropy constant $K = \hbar\omega\chi_\perp A/g\mu_B$ is estimated to be ~ 0.81 G^2·emu/g.

CONCLUSIONS

The electron spin resonance temperature dependence has been studied for

$V(TCNE)_x \cdot y(MeCN)$ a molecular magnet in the $V(TCNE)_x \cdot y(solvent)$ family with an experimentally accessible critical point. The linewidth and resonance field shift are consistent with a disordered ferrimagnet, above, in the vicinity of, and below its critical temperature.

ACKNOWLEDGMENT:

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