

Complex ac susceptibility studies of the disordered molecular based magnets $V(\text{TCNE})_x \cdot y$: Role of spinless solvent

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The effect of different spinless solvents on the magnetism of $V(\text{TCNE})_x \cdot y(\text{solvent})$ (TCNE=tetracyanoethylene) is studied by temperature (T) dependent ac susceptibility above 2.3 K. Though $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$ has a critical temperature $T_c \sim 400$ K, for $V(\text{TCNE})_x \cdot y(\text{C}_4\text{H}_8\text{O})$, $T_c \sim 205$ K and the coercive field is reduced, while for $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$, $T_c \sim 140$ K or below and a spin glass phase exists below a spin freezing temperature of $T_f \sim 7-15$ K. The variations with solvent are suggested to be due to spin dilution and random anisotropy introduced by the spinless solvents.

INTRODUCTION

There has been increasing interest in the magnets formed from molecular systems,^{1,2} which was heightened with the report of magnetism at room temperature in $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$, where TCNE is tetracyanoethylene.³ Some properties of $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$ have been reported previously.³ The material shows hysteresis at room temperature with a coercive field of 60 G. The saturation magnetization, chemical analysis, and infrared spectrum are consistent with a ferrimagnet with spin of 3/2 at the vanadium site and a spin of 1/2 at the TCNE sites with $x \sim 2$. The powder x-ray diffraction pattern⁴ shows broad peaks, indicating a distorted crystalline structure with the degree of disorder varying with the specific solvent.

Three $V(\text{TCNE})_x \cdot y(\text{solvent})$ complexes were selected for study: solvent=dichloromethane (CH_2Cl_2), tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$), and acetonitrile (CH_3CN). In this paper we present the ac susceptibility and dc magnetization of $V(\text{TCNE})_x \cdot y(\text{solvent})$. While $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$ is magnetic at room temperature, T_c is reduced below room temperature for materials containing the other solvents. A mechanism is proposed to explain the large impact of spinless solvent on the magnetic state through the effects of solvent introduced disorder.

EXPERIMENT

The insoluble materials were prepared as described in the literature.³ The composition, including solvent content, varies from preparation to preparation. In these materials, it is difficult to accurately measure the solvent content y , especially for $\text{C}_4\text{H}_8\text{O}$ and CH_3CN solvents because of the composition similarity to TCNE. (Caution: samples on some occasions are pyrophoric upon exposure to air.)

ac susceptibility studies were performed using the mutual inductance technique.⁵ Static magnetization was measured using Faraday techniques.^{3,6} Low-field magnetization was acquired using a Quantum Design MPMS 2 SQUID Magnetometer. Separate sample preparations were used for dc and ac susceptibility studies.

The samples were sealed in quartz tubes. Samples prepared from the same solvent showed the same general behavior though T_c , susceptibility, and magnetization varied. Data presented here were taken for samples which had a T_c higher than the average value for a given solvent, because it is less likely that these samples were degraded.

RESULTS

The field cooled (FC) dc magnetization, Fig. 1(a), is at a field of 2000 G for $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$ ³ and 1000 G for $V(\text{TCNE})_x \cdot y(\text{C}_4\text{H}_8\text{O})$ and $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$. Saturation moment studies at higher fields show a moment in each material which is consistent with an ferrimagnetic phase below T_c , with T_c depending strongly on the solvent used. All preparations of $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$ studied have a spontaneous magnetization at room temperature, while T_c for $V(\text{TCNE})_x \cdot y(\text{C}_4\text{H}_8\text{O})$ was ~ 205 and T_c for $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$ was in the range of 60–150 K. The coercive field is reported to be ~ 60 G at room temperature and at 4.2 K in $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$,³ is measured to be less than 20 G in $V(\text{TCNE})_x \cdot y(\text{C}_4\text{H}_8\text{O})$ at all temperatures, and is 0.2–0.5 G at 35 K in samples of $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$.

The susceptibility measured in an ac field of 220 mG at a frequency of 400 Hz is in Fig. 1(b). The samples were cooled to the lowest temperature used (2.3 K) and held at that temperature for at least one hour to equilibrate before the temperature was scanned. This was necessary because the susceptibility of $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$ was observed to decay with time at the lowest temperatures. The susceptibility for each sample was normalized assuming constant equal density. The phase of the susceptibility was zero within the resolution of the experiment (0.05 rad) for all three materials at all temperatures, with the exception of $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$ below 10 K.

The frequency dependence of the linear ac susceptibility was measured between 200 Hz and 100 kHz in all three materials at 3 and 30 K. The susceptibility was independent of frequency for $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$, and $V(\text{TCNE})_x \cdot y(\text{C}_4\text{H}_8\text{O})$. For $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$,

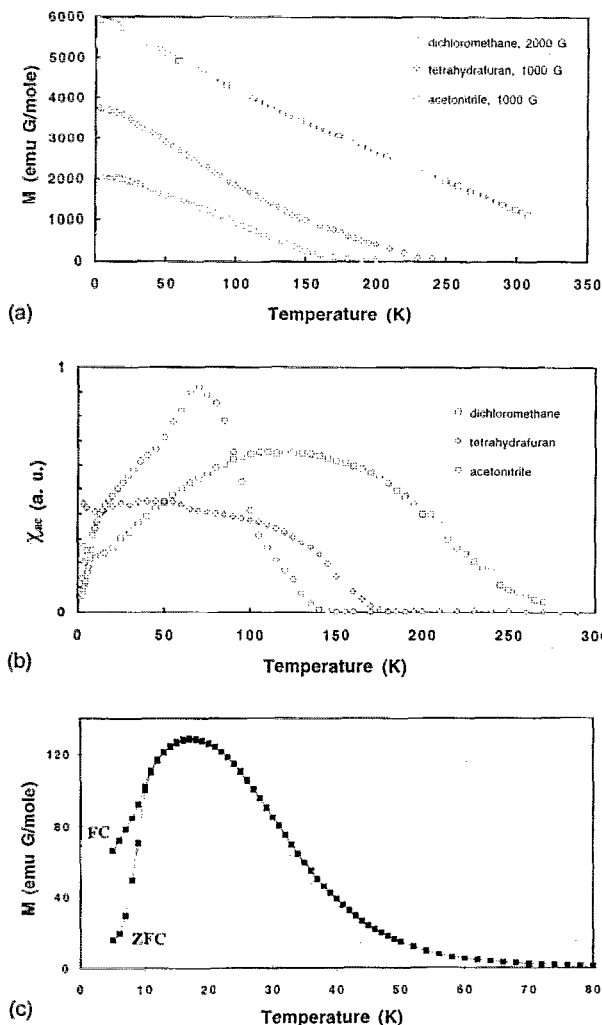


FIG. 1. (a) Field cooled magnetization of $V(TCNE)_x \cdot y(\text{solvent})$ at 2000 G for dichloromethane solvent (from Ref. 4), and for tetrahydrofuran and acetonitrile at 1000 G. (b) ac susceptibility of $V(TCNE)_x \cdot y(\text{solvent})$, H_{ac} is 220 mG, $f=400$ Hz. (c) Field cooled (FC) and zero field cooled (ZFC) magnetization of $V(TCNE)_x \cdot y(\text{CH}_2\text{Cl}_2)$. Note that T_c for this sample is different from that of the sample utilized in (b). The irreversibility below $T_f=10$ K is due to the onset of a spin glass phase.

there is no frequency dependence at 30 K, but below 7 K there are complex relaxation effects, discussed below. To study nonlinear magnetic field effects, the susceptibility of $V(TCNE)_x \cdot y(\text{CH}_2\text{Cl}_2)$ was measured at 15 Hz at H_{ac} between 1.4 and 16.2 G. The curves are shown in Fig. 2(a) as $M=\chi H_{ac}$. The susceptibility is linear below 1 G.

DISCUSSION

Though the field cooled static magnetization of the materials prepared in each of the three solvents show the same qualitative features, with differences characteristic of nonmagnetic dilution, the low field ac susceptibility reveals striking differences which cannot be explained by simple dilution alone. $V(TCNE)_x \cdot y(\text{CH}_2\text{Cl}_2)$ has the highest T_c and the largest coercive field H_c . General features of the data include a broad increase in χ_{ac} below T_c , then a slow decrease, as the temperature is lowered.

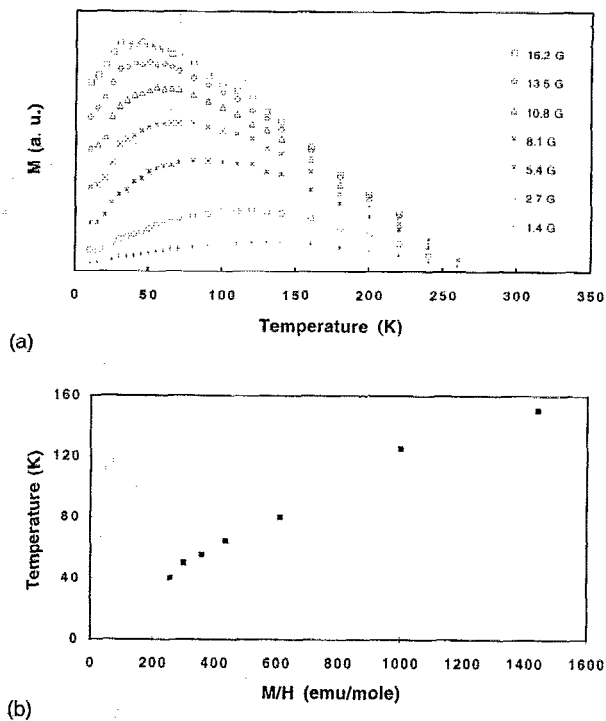


FIG. 2. (a) $M=\chi H_{ac}$ at field between 1.4 and 16.2 G for $V(TCNE)_x \cdot y(\text{CH}_2\text{Cl}_2)$. (b) The temperature T_p of the peak in the ac susceptibility (a) plotted vs M/H , where M is 2000 G magnetization taken from Fig. 1(a).

At fields below the coercive field of a material, ac susceptibility measures the motion of domain walls.⁷ Above 1 G, the ac susceptibility of $V(TCNE)_x \cdot y(\text{CH}_2\text{Cl}_2)$ is nonlinear in H_{ac} , [Fig. 2(a)]. At temperatures near to T_c , the ac susceptibility follows the magnetization curve; at lower temperatures it is suppressed from it. This suppression is due to the presence of potential barriers. Domain walls may be thermally activated over this potential barrier, or may tunnel through it. With thermal activation, the energy to nucleate motion of a domain wall is expected to follow the equation $E=16\langle S \rangle JH_c/nH_{ac}$,⁸ where $\langle S \rangle$ is the expectation value of the local spin component, J is the magnetic exchange, H_c is the coercive field, n is the width of the Bloch wall in lattice constants, and H_{ac} is the applied ac magnetic field. The temperature, T_p , for the maximum in the ac susceptibility is taken to be equal to the energy of the barrier at each applied ac field. $\langle S \rangle$ is taken to be the magnetization above the coercive field (2000 G Faraday balance data). The T_p is plotted vs M/H_{ac} in Fig. 2(b), and shows good agreement with the expected field dependent behavior for thermal activation of domain walls.

For $V(TCNE)_x \cdot y(\text{C}_4\text{H}_8\text{O})$ $T_c \sim 200$ K and $H_c < 20$ G are observed, less than those of $V(TCNE)_x \cdot y(\text{CH}_2\text{Cl}_2)$. There is a significantly higher solvent content, with $x \sim 2$ and $y \sim 1$ for $V(TCNE)_x \cdot y(\text{C}_4\text{H}_8\text{O})$. The ac susceptibility is similar to that of $V(TCNE)_x \cdot y(\text{CH}_2\text{Cl}_2)$, Fig. 1(b), though χ_{ac} does not decrease significantly at low temperatures. The reduction in T_c and H_c can be associated with nonmagnetic dilution by the $\text{C}_4\text{H}_8\text{O}$, i.e., the replacement of TCNE ($S=1/2$) with $\text{C}_4\text{H}_8\text{O}$ ($S=0$) at random sites, reducing the number of the 3-D magnetic interactions and

introducing a concomitant increase in the disorder. The variation of T_c ($\sim 190 \text{ K} < T_c < \sim 205 \text{ K}$) is in accord with variations in the solvent content.

In $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$, several other features are present. Like $V(\text{TCNE})_x \cdot y(\text{C}_4\text{H}_8\text{O})$, T_c and H_c are reduced. Again this is associated with nonmagnetic dilution by the solvent; similarly T_c varies with preparation ($\sim 60 \text{ K} < T_c < \sim 150 \text{ K}$). X-ray diffraction studies⁴ indicate even less order for the CH_3CN system, supporting the importance of increased randomness.

The $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$ differs further in a rapid decrease in the ac susceptibility below 7 K [Fig. 1(b)]. This is accompanied by a large increase in the χ_{ac} phase angle, which is indicative of a spin glass. Low field (3G) cooled (FC) and zero field cooled (ZFC) magnetizations [Fig. 1(c)] were measured by cooling in zero field to 5 K, applying 3 G field, and measuring the ZFC magnetization on warming. The FC magnetization was taken on cooling. A clear irreversibility is evident below $T_f = 10 \text{ K}$. This spin glass phase was seen in all samples of $V(\text{TCNE})_x \cdot y(\text{CH}_3\text{CN})$, with freezing temperature T_f varying $7 \text{ K} < T_f < 18 \text{ K}$. Samples with higher T_c in general had a lower T_f , as has been observed in other reentrant spin glasses.⁹

The existence of a spin glass phase implies that there is a frustration in the magnetic interaction. Possible causes include next nearest neighbor interactions, random exchange, and random anisotropy.¹⁰ While none of the possibilities can be excluded, studies of $M(H, T)$ suggest that the random anisotropy plays the largest role.¹¹

The variation of magnetic phenomena with specific spinless solvent used correlates with the ability of the solvent to bind to the vanadium ion. Dichloromethane is least likely to bind, and here the role of the weakly bound solvent is likely that of a spinless spacer among the $S = 1/2 [\text{TCNE}]^{-\bullet}$, as well as filling in vacant TCNE positions. In contrast, $\text{C}_4\text{H}_8\text{O}$ strongly coordinates with vanadium due to the lone pair electrons at the oxygen site. This coordination will replace some of the TCNE's (in agreement with the larger solvent to TCNE ratio as compared to that for CH_2Cl_2) and reduce the 3-D connectivity between V's. In addition, the $\text{C}_4\text{H}_8\text{O}$ will also act as a spinless spacer among the $S = 1/2 [\text{TCNE}]^{-\bullet}$ as is the case for the CH_2Cl_2 . The CH_3CN is likely to even more effectively compete with the TCNE for coordination with vanadium ions, coordinating with the CN's lone pair of electrons. Since CH_3CN is in great excess it is expected that even more of the CH_3CN is bound to the vanadium ions than is for the $\text{C}_4\text{H}_8\text{O}$ solvent case. In addition, the CH_3CN will be an effective spinless spacer among the $S = 1/2 [\text{TCNE}]^{-\bullet}$ as is the case for the CH_2Cl_2 and $\text{C}_4\text{H}_8\text{O}$. It is noted that while TCNE has four CN groups enabling an individual TCNE to coordinate with up to four vanadium ions, the $\text{C}_4\text{H}_8\text{O}$ and CH_3CN will coordinate with only one vanadium ion, blocking the formation of

even a superexchange pathway and reducing the 3-D connectivity between V's.

These solvents are suggested to effect the magnetic state through several mechanisms. These mechanisms include (1) reducing the number of nearest neighbor spins surrounding the vanadium ion, (2) reducing the connectiveness among the vanadium ions via the multicoordinating molecular unit, and (3) effecting the degree of crystalline order around each of the vanadium ion sites (thus introducing random anisotropy and also random exchange). Recent x-ray diffraction studies show that there is an increase in disorder as one progresses from CH_2Cl_2 to $\text{C}_4\text{H}_8\text{O}$ to CH_3CN , in accord with the progressive reduction in T_c and the presence of a spin glass phase at low temperatures for the CH_3CN system.

In conclusion the coordinating ability of the spinless solvent is shown to have a major role in the magnetism of $V(\text{TCNE})_x \cdot y(\text{solvent})$. It is suggested that reduction in the number of nearest neighbor spin sites, reduced connectiveness, and change in the structural order, and hence magnetic anisotropy, are the origins of these effects.

ACKNOWLEDGMENTS

We thank G. Yee and C. Vasquez for preparing samples, and R. S. McLean for his preliminary Faraday balance magnetization data. This work is supported in part by Department of Energy Division of Material Sciences Grant Number DE-FG-02-86BR456271.

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