

Novel mechanism of photoinduced magnetism in organic-based magnetic semiconductor $V(\text{TCNE})_x$, $x \sim 2$

Jung-Woo Yoo,¹ R. Shima Edelstein,¹ N. P. Raju,¹ D. M. Lincoln,² and A. J. Epstein^{3,a)}

¹Department of Physics, The Ohio State University, Columbus, Ohio 43210-1117, USA

²Department of Chemistry, The Ohio State University, Columbus, Ohio 43210-1173, USA

³Department of Physics and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210-1117, USA

(Presented on 9 November 2007; received 13 September 2007; accepted 16 October 2007; published online 26 February 2008)

The organic-based magnet $V(\text{TCNE})_x$, $x \sim 2$ ($T_c \sim 400$ K), is a room temperature magnetic semiconductor with spin polarized valence and conduction bands. It was reported that this material exhibits persistent photoinduced change in both magnetization and conductivity. The simultaneous change in IR spectra by illumination shows photoinduced activation to the metastable state with a small structural change. Here, we employed photoinduced ferrimagnetic resonance (FMR) study to investigate photoinduced magnetization in $V(\text{TCNE})_x$ film. The FMR spectra display substantial changes in their linewidth and line shift by the illumination indicating substantial increase in random magnetic anisotropy. The results demonstrate optical control of magnetism by changing magnetic anisotropy of the system. © 2008 American Institute of Physics. [DOI: 10.1063/1.2830960]

I. INTRODUCTION

Recently, organic- and/or molecule-based magnets have received growing attention for their new science and phenomena.¹ Particularly, interesting phenomenon in this class of magnets is “magnetic bistability.” Notable examples are spin-crossover complexes, which exhibits high-spin and low spin thermal transition,² high-spin complexes, which exhibit macroscopic quantum tunneling of magnetization,³ and mixed metal ion ferro-ferrimagnetic Prussian blue analogs, which exhibit multiple compensation temperatures.⁴ In addition, their magnetic bistabilities often allow light control. $V(\text{TCNE})_x$ ($x \sim 2$) is one of the few room temperature organic-based magnets. It is a ferrimagnet of uncompensated antiparallel $(\text{TCNE})^-$ ($S=1/2$) and V^{2+} ($S=3/2$) spins with a $T_c \sim 400$ K.⁵ Transport studies indicate exotic electronic structure of semiconductor with an energy gap of ~ 0.5 eV between spin polarized valence and conduction bands.^{6–8} It was reported that $V(\text{TCNE})_x$ exhibits concomitant photoinduced magnetic and electrical phenomena upon optical stimulus.⁹ Both the magnetization and conductivity show persistent and thermally reversible change induced by the $\pi \rightarrow \pi^*$ excitation in $(\text{TCNE})^-$ anions.⁹ At low field, the magnetization of $V(\text{TCNE})_x$ decreases substantially by the illumination, whereas the saturation magnetization remains the same as that of the ground state.⁹ The light-induced magnetization and conductivity have long lifetime at low T , and the effects are erased when the illuminated sample is warmed up to 250 K.⁹ The optical investigation suggested light-induced activation to a metastable state associated with small structural changes.^{9,10}

In this study, we employed photoinduced ferrimagnetic resonance (PIFMR) to investigate the mechanism of photoinduced magnetization (PIM) in $V(\text{TCNE})_x$ films prepared

by chemical vapor deposition (CVD). The local structure of CVD deposited $V(\text{TCNE})_x$ film has octahedral coordination of N around V with a homogeneous V-N length (2.084(5) Å).¹¹ However, the absence of crystalline x-ray diffraction peak indicates disordered structure leading to random magnetic anisotropy (RMA).^{11,12} The PIFMR study shows that RMA plays a central role in photoinduced magnetic phenomena in $V(\text{TCNE})_x$.

II. EXPERIMENTAL DETAILS

The solvent-free $V(\text{TCNE})_x$ films were deposited on thin corning glass substrates via CVD method following the literature procedure.¹² The dc magnetization was recorded on a Quantum Design MPMS-5 superconducting quantum interference device (SQUID) magnetometer. The Bruker X-band (9.6 GHz) ESP300 spectrometer with a TE_{102} resonant cavity was employed for ferrimagnetic resonance (FMR) measurements. A 457.9 nm single line of an Ar-ion laser (Coherent I300) was used for illumination through a fiber optic coupling. Samples for the SQUID and FMR measurements were sealed in electron spin resonance quartz tubes under vacuum for protection from oxidation.

III. RESULTS AND DISCUSSIONS

The temperature dependence of magnetization, for both ground and photoexcited states, is displayed in Fig. 1. After illumination ($\lambda \sim 457.9$ nm and $I \sim 20$ mW/cm² at 10 K illuminated for 10 h), substantial decrease of magnetization can be observed below 90 K (black symbols and curve). The photoexcited state is preserved even in the dark after illumination with an extremely long lifetime $> 10^7$ s. While the photoinduced effects are present below the reentrance temperature, where the magnetization starts to decrease as T lowered, no PIM is detected above the reentrance temperature.⁹ The red curve in Fig. 1 was collected after

^{a)}Electronic mail: epstein@mps.ohio-state.edu

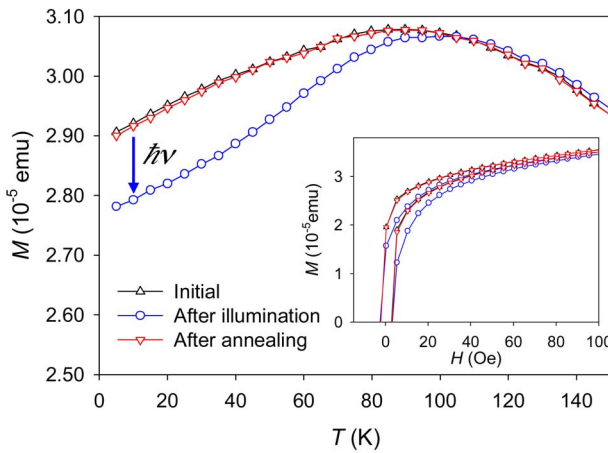


FIG. 1. (Color online) Temperature dependence of field-cooled magnetization [black: before illumination, blue: after illumination ($\lambda \sim 457.9$ nm and $I \sim 20$ mW/cm² at 10 K for 10 h), and red: after annealing sample (to 280 K and waiting for 10 min)]. The inset shows the hysteresis loop for both photoexcited and ground states. Solid lines are guides for the eyes.

annealing the irradiated sample up to 280 K, showing complete recovery of the ground state without any degradation of the sample. The inset of Fig. 1 shows hysteresis curves for both photoexcited and ground states. Substantial decrease of magnetization at low field can be found, whereas the high-field magnetization remains the same for both photoexcited and ground states. Therefore, there is no photoinduced change in the number of unpaired spins, and the mechanism of PIM is different from that of charge transfer induced PIM in cyanometalate-based magnets.^{13–15}

Figure 2 displays the temperature dependence of FMR linewidth (full width at half maximum) [Fig. 2(a)] and resonance field [Fig. 2(b)] for both photoexcited and ground states. The measurement for the photoexcited state was performed after illumination with $\lambda \sim 457.9$ nm and $I \sim 20$ mW/cm² at 30 K for 1 h. The angle between the normal to the film and the external field was set to $\theta \sim 54.7^\circ$, where the spectrum collapses to a single resonance as the effects of demagnetization and uniaxial anisotropy of films are essentially eliminated.^{16,17} The broadening of the linewidth as the temperature is lowered is similar to the characteristic of spin glass system, where a slowing down of spin fluctuations reduces the effectiveness of the exchange narrowing.¹⁸ A corresponding shift in resonance field upon lowering T is also related to spin relaxation rather than a pure g shift.¹⁸ The inset in Fig. 2(b) displays first derivative FMR absorption spectra for both ground and photoexcited states at 30 K. After irradiation ($\lambda \sim 457.9$ nm and $I \sim 20$ mW/cm² at 30 K for 2 h), substantial change of linewidth and resonance field can be observed over a wide range of temperature. Following Becker's model, the behavior of linewidth and line shift can be described as $\Delta H = ABT/(B^2 + T^2)$, $H_r = H_0 + AT^2/(B^2 + T^2)$,¹⁹ where ΔH is linewidth, H_r is resonance field, $A = g\mu_B K / \hbar\omega\chi_\perp$, $B = M_2 / Kk_B\omega$, and $H_0 = \hbar\omega / g\mu_B$. Here, χ_\perp is a static transverse susceptibility, M_2 is related to spin relaxation, and K is the anisotropy constant.¹⁹ Here, we adopt constant $K = K(0)$ to fit Fig. 2 since the change of line shift and linewidth due to K becomes negligible as tempera-

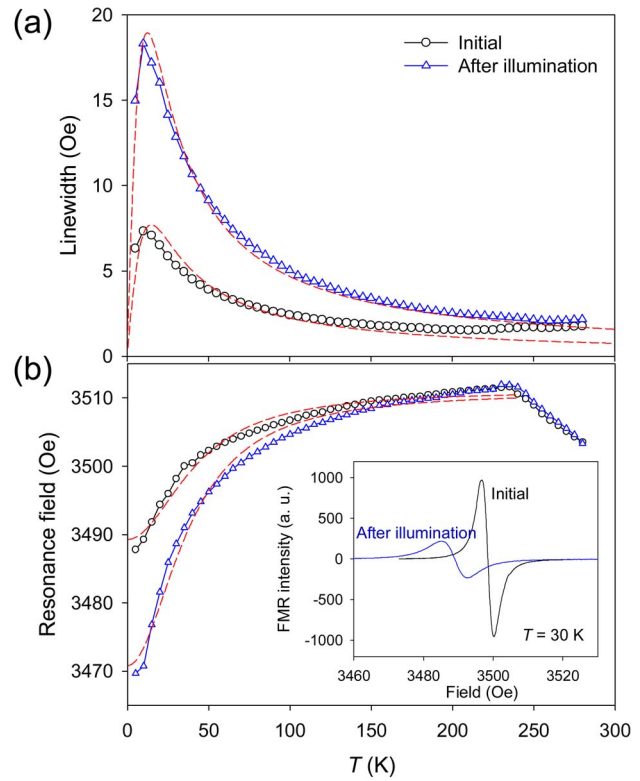


FIG. 2. (Color online) (a) Temperature dependence of linewidth of FMR spectra on V(TCNE)_x film [black: initial state, blue: after illumination ($\lambda \sim 457.9$ nm and $I \sim 20$ mW/cm² at 30 K for 1 h), and dashed red curve: best fit from $\Delta H = ABT/(B^2 + T^2)$ for both ground and photoexcited states, respectively]. (b) Temperature dependence of resonance field of FMR spectra on V(TCNE)_x film [black: initial state, blue: after illumination, and dashed red curve: best fit from $H_r = H_0 + AT^2/(B^2 + T^2)$ for both ground and photoexcited states, respectively].

ture increases. The best fits of linewidth and resonance field to the experimental data are shown in Figs. 2(a) and 2(b) with red dashed lines for ground and photoexcited states, respectively. For the ground state, an effective anisotropy constant $K = A\hbar\omega\chi_\perp / g\mu_B$ is estimated to be $K \sim 430$ G² by taking $\chi_\perp = 0.0056$ emu/(cm)³ from dc magnetic measurement and $\omega = 9.6$ GHz of X band. After illumination of light ($\lambda = 457.9$ nm and $I \sim 20$ mW/cm² for 2 h), the effective anisotropy constant is estimated to be ~ 810 G².

The resonance field shifts substantially according to the external magnetic field direction due to the demagnetization and anisotropy field. For $4\pi M \ll H$ (M is the magnetization and H is the applied magnetic field), small anisotropy field H_A , and $4\pi M - H_A \ll H_r$, the angular dependence of the resonance behavior for a planar sample can be expressed by $H \approx H_r + (2\pi M - H_A/2)(2 - 3 \sin^2 \theta)$,^{16,17,20} where θ is the angle from the normal to the plane of the film to the external magnetic field and H_r is the internal resonance field. H_A is a perpendicular uniaxial anisotropy field. Here, since the V(TCNE)_x has a disordered structure, crystalline anisotropy is negligible and RMA mainly accounts for H_A , which is constant to the angle. Figure 3 shows angular dependence of resonance field of specific FMR lines (three most pronounced resonance spectra) for both ground and photoexcited states and fits to the above equation for angle dependent line shift. Definitive reduction of angle dependent line

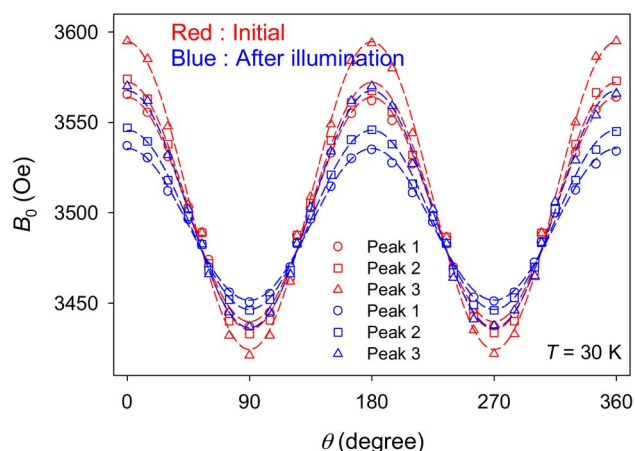


FIG. 3. (Color online) Effects of illumination on angular dependence of line shift for three most pronounced FMR line of $V(\text{TCNE})_x$ film for both ground (\circ) and photoexcited (\triangle) states. Solid lines are fits to equation in the text for angle dependent resonance field.

shifts after the light irradiation was observed. Such light-induced shifts of resonance field suggest substantial increase of H_A because the magnetization at $H \sim 3500$ Oe is almost identical for both ground and photoexcited states according to the SQUID measurements.⁹ Temperature dependence of $H_A(T)$ can be obtained from T dependences of the resonance fields for particular orientations, $\theta = 0^\circ$, 90° , and 54.7° , which reduce to $H(0^\circ, T) = H_\perp \approx H_r + 4\pi M - H_A$, $H(90^\circ, T) = H_\parallel \approx H_r - 2\pi M + H_A/2$, and $H(54.7^\circ, T) \approx H_r \approx 1/3(H_\perp + 2H_\parallel)$, respectively.¹⁶ The $H_A(T)$ were found to be linear to the temperature,¹⁶ which reflect role of RMA in this system.¹⁶ Definitive increase of $H_A(T)$ can be determined after the illumination over the wide range of temperature.¹⁶ This result is consistent with the increase of anisotropy constant by the illumination as predicted by Becker's model.

In conclusion, the PIM phenomena in $V(\text{TCNE})_x$ films were probed via PIFMR studies. The substantial increase of linewidth and the reduction of resonance field over a wide temperature range indicate light-induced increase of RMA resulting from increased structural disorder. The angular dependent line shift was also substantially affected by the increased magnetic anisotropy. Our results and conclusions contradict the theoretically proposed model for the mechanism of the PIM in related $\text{Mn}(\text{TCNE})_x$ magnets.²¹ The re-

sults provide an alternative mean for control of magnetism through optically changing magnetic anisotropy. The demonstrated light-induced phenomena introduce flexible applications of this family of organic-based magnets as an alternative to the dilute magnetic semiconductors for spin-related devices.

ACKNOWLEDGMENTS

This work was supported in part by the AFOSR under Grant Nos. F49620-03-1-0175 and FA9550-06-1-0175 and DOE under Grant Nos. DE-FG02-01ER45931 and DE-FG02-86ER45271.

- ¹A. J. Epstein, MRS Bull. **28**, 492 (2003).
- ²P. Gütlich and H. Goodwin, Top. Curr. Chem. **233**, 1 (2004).
- ³R. Sessoli, A. Caneschi, D. Gatteschi, L. Sorace, A. Cornia, and W. Wernsdorfer, J. Magn. Mater. **226**, 1954 (2001).
- ⁴S. Ohkoshi, Y. Abe, A. Fujishima, and K. Hashimoto, Phys. Rev. Lett. **82**, 1285 (1999).
- ⁵J. M. Manriquez, G. T. Yee, R. S. Mclean, A. J. Epstein, and J. S. Miller, Science **252**, 1415 (1991).
- ⁶V. N. Prigodin, N. P. Raju, K. I. Pokhodnya, J. S. Miller, and A. J. Epstein, Adv. Mater. (Weinheim, Ger.) **14**, 1230 (2002).
- ⁷N. P. Raju, T. Savrin, V. N. Prigodin, K. I. Pokhodnya, J. S. Miller, and A. J. Epstein, J. Appl. Phys. **93**, 6799 (2003).
- ⁸C. Tengstedt, M. P. de Jong, A. Kancirzewska, E. Carlegrim, and M. Fahlman, Phys. Rev. Lett. **96**, 057209 (2006).
- ⁹J. W. Yoo, R. S. Edelstein, D. M. Lincoln, N. P. Raju, C. Xia, K. I. Pokhodnya, J. S. Miller, and A. J. Epstein, Phys. Rev. Lett. **97**, 247205 (2006).
- ¹⁰D. A. Pejaković, C. Kitamura, J. S. Miller, and A. J. Epstein, Phys. Rev. Lett. **88**, 057202 (2002).
- ¹¹D. Haskel, Z. Islam, J. Lang, C. Kmety, G. Srajer, K. I. Pokhodnya, and A. J. Epstein, and J. S. Miller, Phys. Rev. B **70**, 054422 (2004).
- ¹²K. I. Pokhodnya, A. J. Epstein, and J. S. Miller, Adv. Mater. (Weinheim, Ger.) **12**, 410 (2000).
- ¹³O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, Science **272**, 704 (1996).
- ¹⁴D. A. Pejaković, J. L. Manson, J. S. Miller, and A. J. Epstein, Phys. Rev. Lett. **85**, 1994 (2000).
- ¹⁵S. Ohkoshi, S. Ikeda, T. Hozumi, T. Kashiwagi, and K. Hashimoto, J. Am. Chem. Soc. **128**, 5320 (2006).
- ¹⁶J. W. Yoo, R. S. Edelstein, D. M. Lincoln, N. P. Raju, and A. J. Epstein, Phys. Rev. Lett. **99**, 157205 (2007).
- ¹⁷R. Plachy, K. I. Pokhodnya, P. C. Taylor, J. Shi, J. S. Miller, and A. J. Epstein, Phys. Rev. B **70**, 064411 (2004).
- ¹⁸S. M. Long, P. Zhou, J. S. Miller, and A. J. Epstein, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **272**, 207 (1995).
- ¹⁹K. W. Becker, Phys. Rev. B **26**, 2409 (1982).
- ²⁰M. J. Pechan, M. B. Salamon, and I. K. Schuller, J. Appl. Phys. **57**, 3678 (1985).
- ²¹S. Erdin and M. van Veenendaal, Phys. Rev. Lett. **97**, 247202 (2006).