

# Optical control of magnetic order in molecule-based magnet $\text{Mn}(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$

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Studies of photoinduced magnetization and photoinduced absorption in molecule-based magnet  $\text{Mn}(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$  ( $x \approx 2$ ,  $y \sim 0.8$ , TCNE=tetracyanoethylene) are reported. Optical excitation in the blue region of spectrum leads to increased magnetization, accompanied by changes in the electronic spectrum. These effects are preserved long after illumination, indicating formation of a highly metastable electronic state. Partial reversal of the photoinduced effects is obtained by excitation with lower energy visible light. The results suggest that the photoinduced effects are controlled by two distinct electronic transitions. © 2002 American Institute of Physics.

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## I. INTRODUCTION

Magnetically ordered materials with optically tunable magnetic properties are attractive systems for potential applications in the future information technology. One of the important directions of study is the search for materials in which magnetic order and photoinduced magnetic effects coexist at relatively high temperatures, which would greatly extend potential applicability.

The molecule-based magnets<sup>1,2</sup> from the family  $\text{M}(\text{TCNE})_x \cdot y(\text{solvent})$  ( $\text{M}=\text{V}, \text{Fe}, \text{Mn}, \text{Co}$ , and  $\text{Ni}$ ; TCNE=tetracyanoethylene) have recently been the subjects of extensive studies, due to their unusual magnetic properties and high magnetic ordering temperatures.<sup>3-9</sup> The  $\text{M}=\text{Mn}$  compound has unpaired spins ( $S$ ) on both the manganese (II) ion ( $S=5/2$ ) and the bridging organic ligand  $[\text{TCNE}]^-$  ( $S=1/2$ ).<sup>4</sup> Detailed magnetic studies revealed ferrimagnetic ordering below  $T_C=75$  K, and a low- $T$  re-entrant transition to a spin glass-like state.<sup>6</sup>

We have recently reported photoinduced magnetization (PIM) in  $\text{Mn}(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$  ( $x \approx 2$ ,  $y \sim 0.8$ ).<sup>10,11</sup> Upon excitation with light in the blue region of spectrum, the material exhibits a substantial increase in the magnetic susceptibility at temperatures below  $T_C$ . At low temperatures, the PIM is preserved for several days after light excitation. The material relaxes to the state before illumination upon warming to temperatures  $\sim 250$  K.

Here, we present magnetic and optical absorption studies of the photoinduced effects in  $\text{Mn}(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$  ( $x \approx 2$ ,  $y \sim 0.8$ ). These effects show strong dependence on the pumping energy. The PIM and the concomitant photoinduced absorption can be partially reversed by lower energy visible light. The studies indicate that the photoinduced effects are controlled by two distinct electronic transitions.

## II. EXPERIMENT

The material was synthesized by the literature method.<sup>4</sup> Elemental analysis gives values of  $x \approx 2$ , and  $y \sim 0.8$ . While the  $T_C$  value and energies of electronic and vibrational transitions were found to be nearly sample independent, the re-entrant transition temperature and magnitude of the photoinduced effects varied somewhat from sample to sample (probably due to a variation of the solvent content), although we did not notice a systematic trend. For the studies of PIM, polycrystalline samples were dispersed in transparent mineral oil and sealed in a quartz capsule. The magnetization was measured with a Quantum Design MPMS-5 superconducting quantum interference device magnetometer, equipped with a fiber optics illumination system.

The ultraviolet-visible-near infrared (UV/Vis/NIR) optical absorption was measured with a Perkin-Elmer Lambda-19 spectrometer, equipped with an optical cryostat. Samples were prepared as nujol mulls. The photoinduced absorption (PA) spectrum was determined from the difference in absorption before and after laser excitation. Instrumental drift during the illumination period was insignificant. Illumination of samples was performed using an argon-ion laser or a halogen lamp with interference filters.

## III. RESULTS AND DISCUSSION

Figure 1 shows the effect of illumination on the field-cooled magnetization ( $M$ ), measured at temperature  $T=5$  K, in applied magnetic field  $H=10$  Oe. Upon excitation with 488 nm (2.54 eV) argon laser line, the magnetization rapidly increases, and in about 6 h reaches a stationary value (saturation).<sup>12</sup> After discontinuing illumination, an additional increase in  $M$  occurs, due to cooling of the sample. From the  $M(T)$  dependence measured after illumination, it is estimated that the sample warms up by less than 2 K during illumination.<sup>13</sup> The photoexcited state is maintained for at

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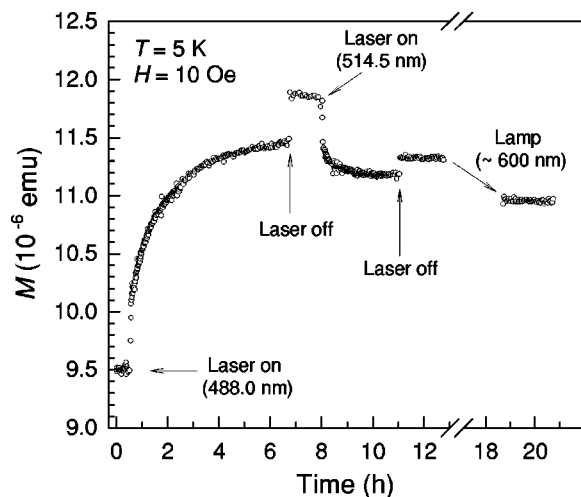


FIG. 1. Effects of illumination on the field-cooled magnetization. Light intensity was  $I \sim 10$  mW/cm<sup>2</sup> for both argon laser lines. Broad-band source used was a halogen lamp with an interference filter (peak transmission at 600 nm, bandwidth=80 nm, and  $I \sim 10$  mW/cm<sup>2</sup>).

least 100 h at 5 K. Subsequent excitation with 514.5 nm (2.41 eV) laser line leads to a partial reversal of the PIM (Fig. 1).

A detailed study shows that PIM nearly identical to the one obtained by the 2.54 eV line can be induced by excitation in the entire region  $\sim 2.54$ – $3.00$  eV, with both monochromatic and broad-band light, while lower values of PIM are obtained by excitation in the region  $\sim 2.35$ – $2.50$  eV. Partial reversal of the PIM from its maximum value is obtained upon excitation in the region  $\sim 1.8$ – $2.5$  eV. The reversal is the most effective for excitation at  $\sim 2$  eV, which reduces PIM to about 60% of its maximum (Fig. 1).

The UV/Vis/NIR absorption spectrum, measured at  $T = 13$  K, is shown in Fig. 2(a). The band in the region  $\sim 2.5$ – $3.5$  eV, with conspicuous vibrational structure, is very similar to the absorption band of [TCNE]<sup>-</sup> reported earlier,<sup>14,15</sup> and assigned to the  $\pi \rightarrow \pi^*$  transition of this ion,<sup>15</sup> thus we adopt this assignment. The [TCNE]<sup>-</sup> band partially overlaps with a weaker band that extends down to  $\sim 1.5$  eV. As [TCNE]<sup>-</sup> does not absorb at energies less than about 2.3 eV,<sup>14</sup> and as  $d-d$  transitions of Mn<sup>II</sup> are spin forbidden, and thus expected to produce very weak absorption bands, the lower-energy band may be assigned to a charge-transfer transition between [TCNE]<sup>-</sup> and Mn<sup>II</sup>.<sup>10</sup> The spectrum indicates that PIM is obtained by excitation at the  $\pi \rightarrow \pi^*$  band, while reversal of PIM is obtained by excitation in energy region overlapping with the charge-transfer band.

The spectrum of photoinduced absorption after 10 min of excitation with 488 nm laser line, Fig. 2(b), shows increased absorption in the regions 1.5–2.4 eV and 3.1–3.8 eV, and small bleaching in the region 2.4–3.0 eV. Assuming the assignment of the optical transitions given herein, the PA peak at  $\sim 2$  eV indicates enhanced charge transfer in the metastable state. The origin of the PA peak at  $\sim 3.4$  eV is ambiguous. It possibly results from the enhanced absorption at a weak band unresolved due to its partial overlap with the stronger  $\pi \rightarrow \pi^*$  band. The photoinduced effect is preserved long after illumination, and can be partially re-

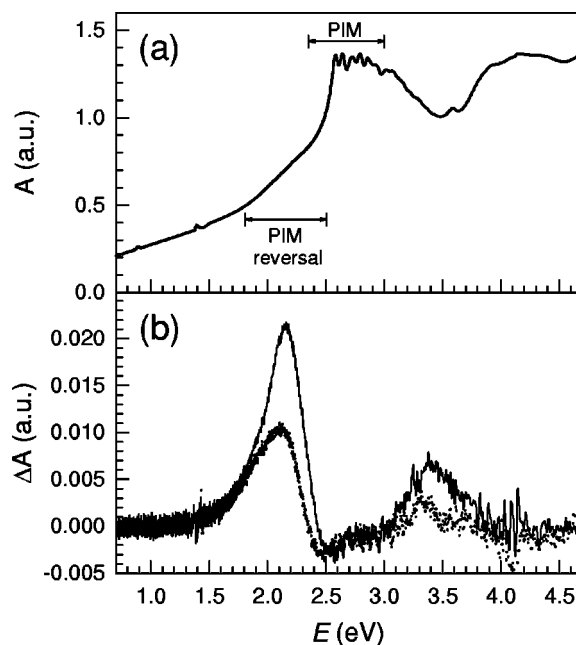


FIG. 2. (a) Absorption spectrum at 13 K. Intervals indicate excitation regions for photoinduced magnetization and its partial reversal. (b) Photoinduced absorption spectrum measured at 13 K, after 488 nm (2.54 eV) excitation (solid line), and after subsequent 514.5 nm (2.41 eV) excitation (dots). Light intensity  $\sim 10$  mW/cm<sup>2</sup>, 10 min illumination for both laser lines.

versed by 514.5 nm line excitation, in correlation with the PIM effects.

Figure 3 shows the time dependence of the PA measured at a fixed wavelength of 560 nm ( $\sim 2.2$  eV). Excitation with 488 nm laser line leads to a rapid increase in the absorbance ( $A$ ), which reaches a stationary value in several minutes.<sup>12</sup> The reversal process induced by 514.5 nm excitation occurs on nearly equal time scale. Turning the laser off causes negligible changes in  $A$ , indicating that heating of sample by radiation has insignificant effect on the optical response.

Figure 4 shows the PA response in the case in which the sequence of excitation with these two laser lines is reversed. Excitation of the sample in the ground state with 514.5 nm laser line leads to an increase in  $A$ , which in several minutes reaches a stationary value  $A_1$ . Subsequent excitation at 488

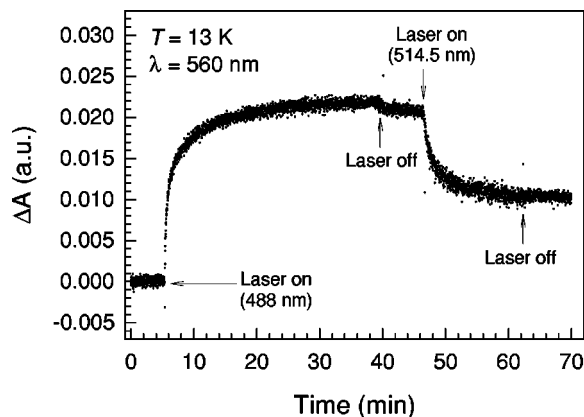


FIG. 3. Effects of argon laser excitation on the absorbance, measured at a fixed wavelength of 560 nm and at temperature of 13 K. Light intensity was  $\sim 10$  mW/cm<sup>2</sup> for both laser lines.

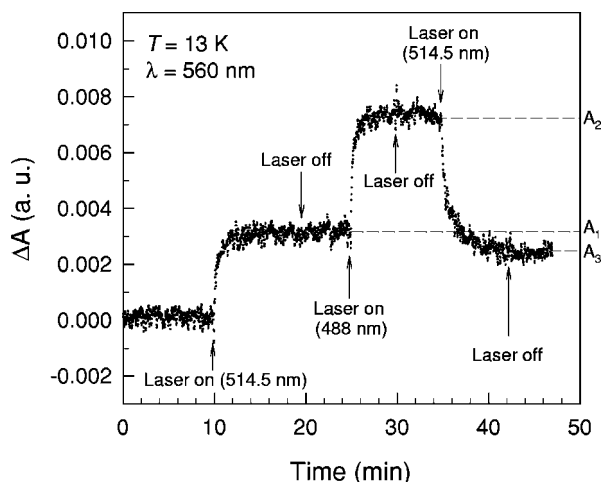


FIG. 4. Dependence of the photoinduced absorption on the pumping energy. The absorbance was measured at wavelengths of 560 nm and temperature of 13 K. Light intensity  $\sim 10$  mW/cm<sup>2</sup> for both laser lines.

nm leads to further increase in  $A$ , up to the stationary value  $A_2$ . From this state, repeated excitation at 514.5 nm leads to a decrease in PA, with final stationary value  $A_3$  close to  $A_1$ . Excitation with 496.5 nm (2.50 eV) and 501.7 nm (2.47 eV) laser lines produces behavior similar to the one induced by excitation at 514.5 nm: a PA lower than the maximum PA (obtained with 488 nm line), and a partial reversal of the maximum PA. The PA values obtained for the four laser lines used decrease with increasing wavelength. This behavior is consistent with the behavior of PIM in the region  $\sim 2.35$ – $2.54$  eV, in which the values of PIM also decrease with increasing wavelength, as mentioned.

The detected PA, which is maintained after illumination and concomitant with PIM, indicates that PIM results from formation of a metastable electronic state. As noted, the intervals of excitation energies for which PIM and partial reversal of PIM are observed suggest that these two processes are controlled by two distinct electronic transitions, corresponding to the absorption bands in the regions  $\sim 2.5$ – $3.5$  eV and  $\sim 1.5$ – $2.5$  eV, respectively. The fact that excitation energies in the region  $\sim 2.41$ – $2.50$  eV can produce both an increase and decrease in absorption, depending on the excitation sequence (consistent with behavior of PIM in the region  $\sim 2.35$ – $2.50$  eV), can be understood as a consequence of the overlap of the  $[\text{TCNE}]^-$  and charge-transfer bands in this region. In the overlap region, a competition between the direct process (responsible for PIM) and the reversal process (responsible for the reversal of PIM) is expected. Thus, the population of the metastable state and, consequently, stationary values of PIM and PA reached upon illumination, depend on the relative probabilities of these two processes.

The increased oscillator strength for the charge-transfer transition, Fig. 2(b), indicates an increased overlap between

the metal and ligand orbitals. We propose<sup>10</sup> that PIM in the material results from enhanced exchange at a fraction of sites in the lattice, caused by enhanced overlap between the metal and ligand spin-carrying orbitals. Our studies showed no photoinduced change in the magnetic ordering temperature,<sup>10,11</sup> thus, the concentration of sites with enhanced exchange is expected to be below the percolation threshold for the lattice.

In conclusion, photoinduced absorption studies demonstrate that PIM in  $\text{Mn}(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$  ( $x \approx 2$ ,  $y \sim 0.8$ ) is accompanied by changes in the electronic spectrum, indicative of formation of a metastable state with enhanced metal–ligand interaction. The dependence of the PIM and PA responses on the excitation energy indicates that two electronic transitions are operative in the processes of population and depopulation of the metastable state.

## ACKNOWLEDGMENTS

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- <sup>1</sup> *Proceedings of the Seventh International Conference on Molecule-Based Magnets*, San Antonio, TX, edited by K. R. Dunbar, Polyhedron **20** (11) (2001).
- <sup>2</sup> J. S. Miller and A. J. Epstein, *Angew. Chem.* **33**, 385 (1994); J. S. Miller and A. J. Epstein, *MRS Bull.* **25**, 21 (2000).
- <sup>3</sup> J. M. Manriquez, G. T. Yee, R. S. Mclean, A. J. Epstein, and J. S. Miller, *Science* **252**, 1415 (1991).
- <sup>4</sup> J. Zhang, J. Ensling, V. Ksenofontov, P. Gütlich, A. J. Epstein, and J. S. Miller, *Angew. Chem. Int. Ed. Engl.* **37**, 657 (1998).
- <sup>5</sup> J. Zhang, L. M. Liable-Sands, A. L. Rheingold, R. E. Del Sesto, D. G. Gordon, B. M. Burkhardt, and J. S. Miller, *J. Chem. Soc. Chem. Commun.* **1998**, 1385.
- <sup>6</sup> C. M. Wynn, M. A. Girtu, J. Zhang, J. S. Miller, and A. J. Epstein, *Phys. Rev. B* **58**, 8508 (1998).
- <sup>7</sup> M. A. Girtu, C. M. Wynn, J. Zhang, J. S. Miller, and A. J. Epstein, *Phys. Rev. B* **61**, 492 (2000).
- <sup>8</sup> K. I. Pokhodnya, A. J. Epstein, and J. S. Miller, *Adv. Mater.* **12**, 410 (2000).
- <sup>9</sup> K. I. Pokhodnya, D. A. Pejaković, A. J. Epstein, and J. S. Miller, *Phys. Rev. B* **63**, 174408 (2001).
- <sup>10</sup> D. A. Pejaković, C. Kitamura, J. S. Miller, and A. J. Epstein, *Phys. Rev. Lett.* **88**, 057202 (2002).
- <sup>11</sup> D. A. Pejaković, J. L. Manson, C. Kitamura, J. S. Miller, and A. J. Epstein, *Polyhedron* **20**, 1435 (2001).
- <sup>12</sup> The time needed for saturation of the photoinduced effect depends on the thickness of the sample. In the magnetic measurements, long illumination was necessary because a thicker sample had to be used in order to obtain good sensitivity. In contrast, in the optical experiments saturation of PA is reached within a few minutes.
- <sup>13</sup> For excitation at wavelengths greater than 488 nm, an increase in the sample temperature is even lower than in the case of 488 nm excitation (at equal light intensities), since the absorption of light in the material drops monotonically as wavelength is increased above 488 nm [see Fig. 2(a)].
- <sup>14</sup> D. L. Jeanmaire, M. R. Suchanski, and R. P. Van Duyne, *J. Am. Chem. Soc.* **97**, 1699 (1975).
- <sup>15</sup> D. A. Dixon and J. S. Miller, *J. Am. Chem. Soc.* **109**, 3656 (1987).