Photoinduced Magnetization in the Organic-Based Magnet Mn(TCNE)$_x$ · y(CH$_2$Cl$_2$)

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Photoinduced magnetization in a magnet based on organic species is reported for the first time. Upon optical excitation in the blue region of spectrum, Mn(tetracyanoethylene)$_x$ · y(CH$_2$Cl$_2$) ($x \approx 2$, $y \sim 0.8$) exhibits increased magnetic susceptibility at temperatures as high as 75 K, accompanied with photo-induced absorption in the visible and infrared spectral regions. These effects are partially reversible by lower energy visible light and fully reversible by thermal treatment. The results suggest trapping of the photoexcited charge in a metastable state with enhanced exchange interaction.

Recent years have witnessed a growing interest in the optical control of magnetic properties. Photoinduced magnetic effects have been extensively studied in a variety of systems, including cyanometalate-based magnets [1–6], spin crossover complexes [7], diluted magnetic semiconductors [8], doped manganites [9], and spinel ferrite films [10]. One of the challenges in this area of research is design of materials that exhibit both photoinduced magnetization and long-range magnetic order at relatively high temperatures.

We report here reversible photoinduced magnetization (PIM) in molecule-based magnet Mn(TCNE)$_x$ · y(CH$_2$Cl$_2$). The magnetic susceptibility of the material can be controlled by excitation with visible light. Strikingly, at low temperatures PIM is preserved for several days after illumination. This is, to the best of our knowledge, the first example of reversible PIM in a magnetically ordered material with spins on organic species, i.e., with spins supplied by electrons in p orbitals. We probe the PIM by both static and dynamic magnetic measurements and correlate their results with absorption studies in the ultraviolet–visible–near infrared (UV-Vis-NIR) and infrared (IR) regions of spectrum. We propose that the origin of PIM is in formation of a metastable state, stabilized by lattice distortion, in which the exchange interaction is enhanced.

The molecule-based magnet [11,12] Mn(TCNE)$_x$ · y(CH$_2$Cl$_2$) is a member of the family M(TCNE)$_x$ · y(solvent) (M = V, Fe, Mn, Co, Ni; TCNE = tetracyanoethylene) [13,14]. This class of magnets is characterized by relatively high magnetic ordering temperatures, the material with M = V being one of only a few room-temperature molecule-based magnets [14]. For M = Mn the unpaired electrons are on both the manganese ion and the bridging organic ligand [TCNE]$^-$. Based on the stoichiometry, infrared absorption data, studies of the precursor Mn^{II}[C$_4$(CN)$_8$](CH$_3$CN$_2$)$_2$(CH$_2$Cl$_2$) [15], and similarity with the analog, isostructural, material Fe^{II}(TCNE)$_2$ · x(CH$_2$Cl$_2$), it was proposed that manganese in this compound is present as Mn^{II} with spin S = 5/2, while [TCNE]$^-$ has one unpaired electron

(S = 1/2) in a π^* molecular orbital [13]. Elaborate magnetic studies and critical analyses revealed reentrant spin glass behavior, with a high-temperature (T) transition to a three-dimensional Heisenberg ferrimagnet at T_c = 75 K, and a low-T transition into a spin-glass–like state. It was proposed that the unusual low-T behavior is a result of the random exchange in the system [16].

Polycrystalline samples of Mn(TCNE)$_x$ · y(CH$_2$Cl$_2$) were synthesized by the literature method [13]. Elemental analysis gives values of $x \approx 2$, and $y \sim 0.8$. Samples for the studies of PIM were prepared by applying a small amount of the material ($\sim$0.05 mg) in a thin layer on an adhesive tape (for ac susceptibility measurements) or by dispersing the material in transparent mineral oil and sealing it in a quartz capsule (for dc magnetization measurements).

The magnetization was recorded on a Quantum Design MPMS-5 SQUID magnetometer. The alternating current (ac) magnetic susceptibility was measured with a Lake Shore 7225 ac susceptometer/dc magnetometer. Phase-sensitive detection allowed both the in-phase (χ') and out-of-phase (χ'') components of the susceptibility ($\chi_{ac} = \chi' - i\chi''$) to be extracted. Subtraction of diamagnetic backgrounds was done for all magnetic measurements. Both the magnetometer and susceptometer were equipped with fiber optics illumination systems.

The UV-Vis-NIR optical absorption was measured with a Perkin-Elmer Lambda-19 spectrometer. Infrared spectra in the region 1300–7000 cm^{-1} were recorded on a Bruker IFS 66v/s FTIR spectrometer. Samples for optical measurements were prepared as nujol (for UV-Vis-NIR) or fluorolube (for IR) mulls. The UV-Vis-NIR and IR photoinduced absorption spectra were determined from the difference in absorption *before* and *after* light excitation. Instrumental drifts during the illumination period of 10 min were insignificant.

Illumination of samples was performed using an argon-ion laser or a halogen lamp and interference filters.

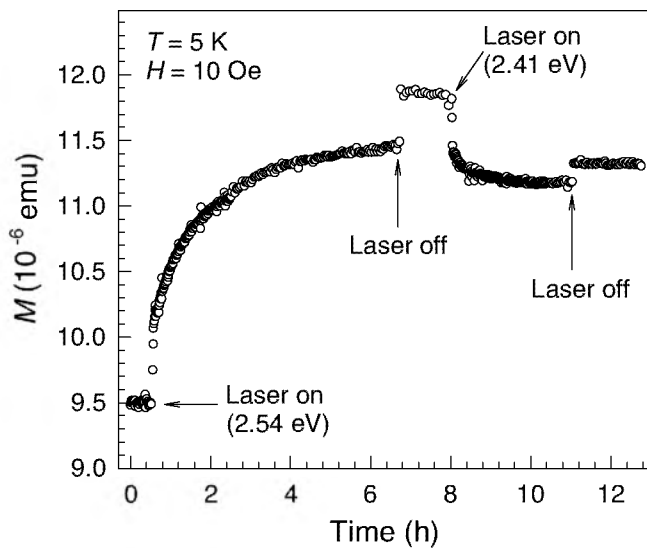Figure 1 shows the effect of illumination on the field-cooled magnetization (M), measured at T = 5 K, in static

FIG. 1. Effects of argon laser excitation on the field-cooled magnetization (light intensity ~ 10 mW/cm^2 for both laser lines).
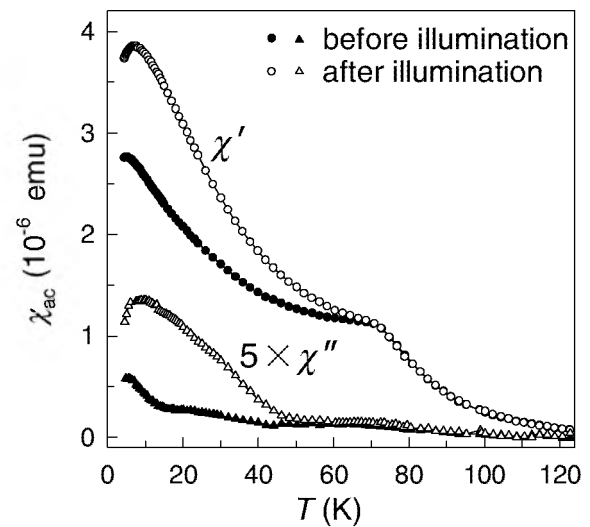

FIG. 2. In-phase and out-of-phase ac susceptibilities, measured at frequency of 333 Hz and ac magnetic field of 15 Oe, before and after illumination with argon laser (2.7 eV line, ~ 50 mW/cm^2, illuminated for 60 h at 90 K).

magnetic field $H = 10$ Oe. Upon excitation with 2.54 eV argon laser line, the magnetization increases, and reaches saturation in about 6 h [17]. After turning the laser off, M exhibits an additional increase, Fig. 1, due to cooling of the sample (M decreases with the increase of T). From the measured $M(T)$ dependence it is estimated that the sample warms up by less than 2 K during laser excitation. The photoexcited state is preserved even in the dark after illumination. At $T = 5$ K, the magnetization decreases by only about 0.5% within 60 h after illumination. Assuming that relaxation of PIM is exponential, this gives a lifetime of the photoexcited state greater than 10^6 s. Illumination with 2.41 eV laser line leads to a partial reduction of the PIM (Fig. 1). Detailed study shows that PIM nearly identical to the one obtained by the 2.54 eV line can be induced by excitation anywhere in the region $\sim 2.54 - 3.00$ eV, with both monochromatic and broadband light, while a weaker PIM effect is obtained by laser excitation in the region $\sim 2.35 - 2.50$ eV. Partial reduction of the maximum value of PIM is obtained by excitation in the region $\sim 1.8 - 2.5$ eV; the energies around 2 eV are the most effective and reduce PIM to about 60% of its maximum value.

The ac susceptibility, for both the ground and photoexcited states, is displayed in Fig. 2. The susceptibility shows a shoulder near $T_c = 75$ K, and a low-temperature peak (at ~ 5 K in the ground state) attributed to the reentrant transition, similar to the previous report [16]. After illumination (argon laser, 2.7 eV line, light intensity $I \sim 50$ mW/cm^2, illuminated at $T = 90$ K for 60 h [17]), χ_{ac} exhibits a substantial increase in the entire temperature region below T_c. The low-temperature peak is shifted to ~ 7 K, indicating increased reentrant transition temperature. The increase in χ' is more than 50% in the region

13–18 K, while the increase in χ'' is more than fourfold in the same temperature region. While the PIM detected below T_c was obtained by excitation at $T = 90$ K $> T_c$, no PIM was detected in the paramagnetic region ($T > T_c$). Sensitivity and noise level of our apparatus put the upper limit for the photoinduced increase in χ' at temperatures just above T_c to about 2%.

Stability of the photoexcited state was studied by warming the illuminated material to temperatures above T_c, cooling it back to the lowest temperatures, and repeating the measurement of χ_{ac}. This study showed that even after warming to 200 K the photoexcited state is not fully erased (about 5% of increase in χ' is maintained at 5 K). After warming above 250 K the material fully relaxes to the state before illumination. Thus, while photoinduced effects on the magnetic state were not detected in direct measurement of χ_{ac} above T_c, the photoexcited state is preserved at temperatures high above the magnetic ordering temperature.

The UV-Vis-NIR absorption spectrum, measured at $T = 13$ K, is shown in Fig. 3. The band in the region 2.5–3.5 eV, with pronounced vibrational structure, is very similar to the absorption band of $[TCNE]^-$ reported earlier [18–20], and assigned to the $\pi \rightarrow \pi^*$ internal transition of this ion [19]. Thus, we assign this band to the $\pi \rightarrow \pi^*$ transition of $[TCNE]^-$, which is further supported by the fact that we observed nearly identical band in the spectrum of the analog compound $Fe^{II}(TCNE)_2 \cdot x(CH_2Cl_2)$. We note that $[TCNE]^-$ does not absorb at energies less than about 2.3 eV [18]; furthermore, as $d - d$ transitions of Mn^{II} are spin forbidden, they are expected to give very weak absorption (at least 2 orders of magnitude weaker than for symmetry allowed transitions [21]). Thus, the absorption band in the region 1.5–2.5 eV may be assigned
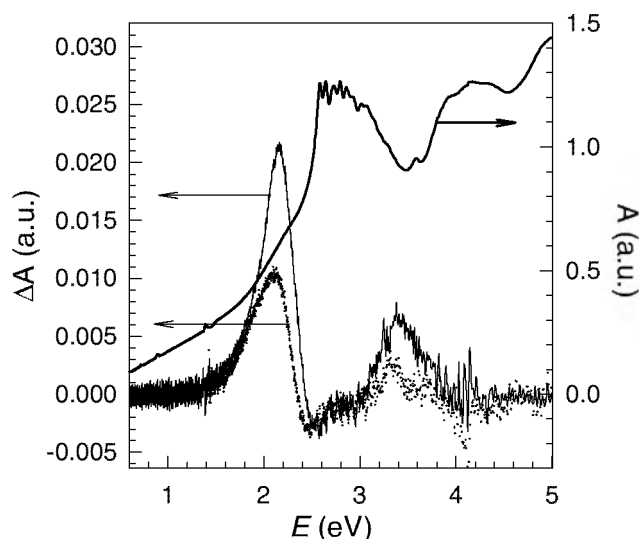
FIG. 3. UV-Vis-NIR spectra of absorbance (A) and photo-induced absorption (ΔA) at 13 K. ΔA was measured after excitation with 2.54 eV argon laser line (solid line), and after subsequent illumination with 2.41 eV line (dots). Light intensity ~ 10 mW/cm^2, 10 min illumination for both laser lines. The vertical axes show correct relative intensities of A and ΔA.
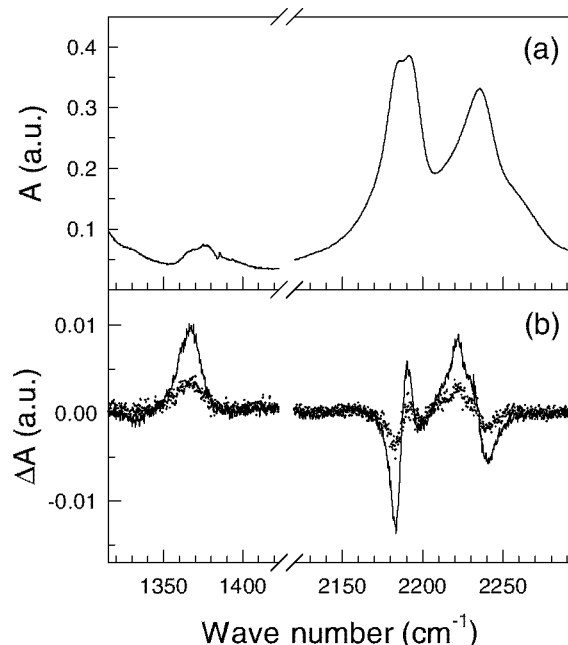

FIG. 4. (a) IR spectrum measured at 13 K. (b) IR photoin-duced absorption after illumination with 2.54 eV argon laser line (solid line), and after subsequent illumination with 2.41 eV line (dots). Light intensity ~ 10 mW/cm^2, 10 min illumination for both laser lines. The vertical axes show correct relative intensities of A and ΔA.

to a charge transfer transition between metal and ligand. The spectrum indicates that PIM is obtained by excitation at the $\pi \rightarrow \pi^*$ band, while reduction of PIM is obtained by excitation in energy region overlapping with the charge transfer band.

The photoinduced absorption spectrum, Fig. 3, was measured after 10 min illumination with 2.54 eV line [17]. Photoinduced absorption is detected in the regions 1.5–2.4 eV and 3.1–3.8 eV, while in the region 2.4–3 eV bleaching is observed. These photoinduced effects are also maintained long after illumination, and can be partially reduced with 2.41 eV line excitation (Fig. 3).

The room-temperature IR absorption spectrum shows several features in the region 2150–2300 cm^{-1}, very close in energies to the ones previously assigned [13] to the CN stretching vibrations of [TCNE]$^-$: peaks at 2174, 2185, and 2226 cm^{-1}, and a shoulder at ~ 2255 cm^{-1}. At $T = 13$ K the peak positions are shifted to higher energies: 2185, 2191, 2236, and ~ 2260 cm^{-1}, respec-tively [Fig. 4(a)]. The spectrum of photoinduced absorp-tion at 13 K after 10 min excitation with 2.54 eV line is shown in Fig. 4(b). The shown effects correspond to a decrease in magnitude of the 2185 cm^{-1} peak, while the 2191 cm^{-1} peak increases. Furthermore, the peak at 2236 cm^{-1} is slightly shifted to lower energies. Substan-tial photoinduced absorption is also detected in the region of a weak mode at 1367 cm^{-1}. We note that earlier stud-ies of [TCNE]$^-$ reported a mode at ~ 1370 cm^{-1}, which has been assigned to the infrared-active stretching vibra-tion of the central [TCNE]$^-$ carbon atoms [22]. Metasta-bility of the photoexcited state and partial reduction of the

photoinduced effect by the 2.41 eV line also are observed, Fig. 4(b), in full correlation with the effects observed in the magnetic and UV-Vis-NIR photoinduced absorption experiments.

The absence of PIM in the paramagnetic regime sug-gests that no significant change in the number of spins oc-curs upon illumination, as an increased spin concentration is expected to affect both the susceptibility above T_c and the transition temperature itself. Thus, we suggest that the increased susceptibility in the photoexcited state has its ori-gin in altered spin organization and/or spin-spin coupling.

The fact that PIM is induced by the $\pi \rightarrow \pi^*$ transition of [TCNE]$^-$ strongly suggests that PIM in Mn(TCNE)$_x$ · y(CH$_2$Cl$_2$) is governed by a mechanism different from the ones previously reported. It contrasts the effects observed in cyanometalate-based magnets, in which excitation of charge transfer bands was responsible for PIM [1–6], as well as the PIM in spin crossover complexes, which is due to the photoinduced d-d transitions between the low-spin and high-spin states of metal ions [7]. Furthermore, in both these classes of materials PIM is a result of a significant increase in the number of spins, in contrast to Mn(TCNE)$_x$ · y(CH$_2$Cl$_2$).

The UV-Vis-NIR photoinduced absorption, maintained long after illumination, indicates that PIM is due to a photoinduced electronic transition into a metastable state. Assuming the assignment of optical transitions given above, the photoinduced absorption peak at ~ 2 eV, in

the region of charge transfer band, indicates that in the metastable state charge transfer is enhanced.

The changes in the IR spectrum, Fig. 4(b), suggest the presence of a lattice distortion, i.e., a change in the chemical bond lengths and/or in angles between bonds in the metastable state. Following the optically induced $\pi \rightarrow \pi^*$ transition, a fraction of electrons may relax from the π^* level into this state with altered geometry, occurring through the electron-phonon coupling. The altered geometry is expected to affect the overlap integrals between the metal and ligand orbitals, including the spin carrying orbitals (d orbitals of Mn^{II} and π^* orbitals of $[TCNE]^-$). As the overlap integrals control both the charge transfer between the metal and coordinating $[TCNE]^-$, and the kinetic exchange interaction, both the charge transfer and the exchange may be enhanced in the metastable state. This would lead to increased charge transfer absorption and increased magnetic susceptibility, consistent with our experiments. However, if the exchange interactions were enhanced throughout the material, it would lead to an increase in the magnetic ordering temperature T_c, in contrast to our data. Therefore, we propose that only a fraction of sites (below the percolation threshold) in the lattice reach the metastable state upon illumination, and that these sites are determined by local configurations that may favor the lattice distortion associated with the formation of the metastable state. This fraction of sites with enhanced exchange would lead to increased susceptibility, while not affecting T_c.

We speculate that the remarkable metastability of the photoexcited state also may have origin in the lattice distortion. Lattice relaxation may produce a local energy minimum for the excited state, separating it from the ground state by an energy barrier. At low temperatures vibrational excitations are insufficient to surmount the energy barrier, and the system is trapped in the excited state. We note that a lattice distortion was likewise proposed as a key for stabilization of PIM in the case of Prussian blue magnets [3,6].

In conclusion, we demonstrated optical control of magnetic order in $Mn(TCNE)_x \cdot y(CH_2Cl_2)$. Photoinduced magnetism is controlled by readily available light sources (e.g., argon laser), and it is detected at temperatures close to the N_2 boiling point. The demonstrated high-temperature PIM in an organic-based magnet opens a promising new pathway towards materials with desired PIM properties.

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[17] The time needed to reach saturation depends on the sample thickness. In the magnetic measurements thicker samples were used in order to achieve good sensitivity in the entire temperature region studied, which required very long illumination. In contrast, in optical studies saturation of the photoinduced effect is reached in several minutes.

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