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Photo-induced magnetic effects in [MnR₄TPP][TCNE]*2PhMe molecular magnet

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Abstract. The photo-induced magnetic effects (PME) have been observed during the investigation into magnetic properties of [MnR₄TPP][TCNE]*2PhMe (R=OC₁₂H₂₅, TPP tetraphenylporphyrin, TCNE tetracyanoethylene) charge transfer salt molecular magnet. The study of magnetic properties of [MnR₄TPP][TCNE]*2PhMe and PME were performed in both static (DC) and dynamic (AC) modes with Lake Shore 7225 equipment using a sample probe with optical fiber. The Xe lamp with optical cut-off filters or the He-Ne laser was used. Results of DC magnetization relaxation measurements obtained for different magnetic fields in He bath temperature (4.2 K) during illumination differ significantly from those obtained before illumination. Both the value and the time dependence of magnetization changed during illumination. Hysteresis loop measured before and during illumination was also found to undergo considerable change. On the other hand the AC measurements revealed only slight alteration in the real and imaginary components of the susceptibility. Simple theoretical description of the magnetization process recorded at 4.2 K, was performed and the relaxation data were found to be consistent with the model.

1. Introduction

Electron-transfer salts of Mn-porphyrin and TCNE belong to a family of molecular ferrimagnets, receiving marked attention for over a decade [1-4]. In this paper we focus on [MnIII₄TPP][TCNE]*2PhMe, a member of that family and an excellent system for studying several interesting magnetic phenomena (spin flop, re-entrant spin glass phase).

According to the detailed study of [MnIII₄TPP][TCNE]*solvent made by Miller et al. [1] the compound is composed of 1D chains of alternating ions: D=[MnTPP]+ (D-donor) and A=[TCNE]*− (A-acceptor) (Figure 1; Figure 2). Magnetic moments originating from cation’s d-orbitals (S=2) and those from anion’s (s=½) were found to be coupled antiferromagnetically in the chain. The magnetic ordering of the [MnR₄TPP][TCNE]*solvent salt substituted with R=OC₁₂H₂₄ functional group was investigated for the polycrystalline sample by Bałanda et al. [4]. At Tc=22 K the transition between the short range ferrimagnetic coupling and the low temperature 3D ordered state was registered. Between Tc and ~8 K the substance shows properties characteristic of mixed spin glass and ferromagnetic phase. At T₀ ~ 8 K re-entrance to spin-glass was observed. The field induced magnetization jump observed for a critical value of the external magnetic field H_{cr}=4 kOe at T=4.2 K was identified as the spin flop being the transition from the longitudinal to transverse spin glass [5].
In this paper we report the observation of photo-induced changes in magnitude and relaxation rate of isothermal magnetization, a significant change of the hysteresis loop and a small modification of the real and imaginary components of the AC susceptibility. Similar research were performed by Hashimoto et al. [7] for another Mn-porphyrin based molecular magnet. Data analysis of the magnetization relaxation recorded at 4.2 K was carried out assuming the stretched-exponential character of the process and satisfactory agreement was found.

2. Experimental
The research into magnetic properties of [MnR₄TPP][TCNE]*2PhMe and PME were performed in both the static (DC) and dynamic (AC) modes with Lake Shore 7225 equipment using a sample probe with an optical fiber. The optical system consisted of a Xe lamp with optical cut-off filters (λ_max=436 nm and λ max=579 nm) or the He-Ne laser was used. The sample was placed in the sample holder at the end of the fiber. Measurements of magnetic quantities were performed before and during illumination. DC measurements were performed at helium bath temperature. After cooling the sample in zero magnetic field to 4.2 K, the time dependence of the magnetization for several fixed values of external magnetic field was registered. After each measurement the sample was heated up to 60 K and cooled to helium temperature again. The intensity of light at the sample was constant during measurements and was estimated to be between 60 and 155 µW/cm² (depending on the wavelength).

3. Results and discussion
We present the hysteresis loop as well as the time dependence of magnetization for several fixed values of magnetic field, both measured before and during illumination at T=4.2 K. AC measurements of both components of the susceptibility were performed between 4.2 K and 32 K.

3.1. DC measurements
Figure 3 shows hysteresis loops obtained for the sample before and during illumination with the Xe lamp. Characteristic shape of the virgin magnetization curve was observed for the sample before illumination.
Changes of the hysteresis loop induced with light comprise a substantial reduction of the coercive field $H_c$ from 3 kOe before illumination to 0.36 kOe during illumination as well as an increase of the magnetization reached for a fixed value of applied magnetic field. In our opinion the observed behavior may be explained as follows. Incident light generates additional defects in the chain-like structure of the charge transfer compound. A photon absorbed by donor-acceptor pair (effective spin $\frac{3}{2}$) force electron back to the donor creating an excited pair $A^0D^2$ (effective spin $\frac{5}{2}$) introducing a gap in the intrachain magnetic interactions path. Due to that magnetic clusters present in the chain before illumination are disunited by the light. Such a process causes enhancement of magnetization value due to increase of the number of defects having higher effective spin. On the other hand, disuniting of chains leads to the decrease of the dipolar interchain interactions, responsible for the 3D ferromagnetism in the compound. That may be the reason why the magnetization reached at 12 kOe during illumination decreases compared to that registered before illumination.

The time dependence of magnetization registered before and during illumination with white light at $T=4.2$ K for $H=$2 kOe and 3 kOe respectively is shown in Figure 4. The two-stage magnetization process [5] visible in Figure 4 during illumination at 3 kOe, may be explained in terms of the spin-flop transition consisting of the step-like reorientation of the magnetization axis followed by the rotation of magnetic moments towards the direction of the applied field. Both of them proceed at their own rates. A significant increase of the relaxation rate was observed during illumination. The enhancement of the relaxation is consistent with the proposed mechanism of influence of light on the magnetic structure of chains hence interchain interactions in the system. Creation of defects and thus decoupling of the chain caused by the light leads to enhancement of magnetization process. Due to decrease of the size of locally ordered magnetic segments of the chain, the spin-flop reorientation proceeds faster. Influence of light on magnetization rate is more pronounced for values of the applied fields more close to $H_{cr}$. Dependence of magnetization process on strength of the applied field was also registered.

Immediate increase of the magnetization (Figure 5) tending to higher saturation value may be explained in terms of the above mentioned increase of the number of excited $A^0D^2$ pairs\(s=\frac{3}{2} \rightarrow \frac{5}{2}\). Though the magnetization shown in Figure 5 is far from the saturation value, one should expect further increase of saturation magnetization according to the strength of the applied field.
Figure 5. The influence of light on the magnetization process for $H = 3 \, \text{kOe}$, $T = 4.2 \, \text{K}$

Figure 6. Dependence of magnetization process on wavelength of applied light for $H = 0.5 \, \text{kOe}$, $T = 4.2 \, \text{K}$

Figure 6 shows results of measurements performed for different wavelengths of the applied light. Resting on the absorption spectra registered for some metalloprotoporphyrin derivatives [6] we conclude that magnetization significantly depends on the wavelength of the incident light. The strongest effect was observed during illumination with red light.

3.2. AC measurements
AC mode measurements revealed only slight alteration of the real and imaginary components of the magnetic susceptibility. Results of the measurements performed for different frequencies of applied field $H_{AC} = 10 \, \text{Oe}$ are shown in Figure 7 and Figure 8.

Figure 7. $\chi'$ measured at $H_{AC} = 10 \, \text{Oe}$ AC field before (open symbols) and during (full symbols) illumination.

Figure 8. $\chi''$ measured at $H_{AC} = 10 \, \text{Oe}$ AC field before (open symbols) and during (full symbols) illumination.

Small increase (of the order of $\sim 5\%$) of magnitude of the $\chi'$ and $\chi''$ components of AC susceptibility was observed. This effect is consistent with the increase of the number of magnetic domains in the sample due to generation of additional $A^0 D^5_2$ defects. There was no change in $T_C$ value ($T_C = 22 \, \text{K}$) due to illumination with light. Dependence of $\chi'$ and $\chi''$ on frequency of AC field, characteristic of the spin glass was observed, confirming results obtained by Balanda et al [4].
4. Possible mechanism of magnetizing process

The key concept is that there are 3 thinkable types of defects (Figure 9) and they propagate along the chain due to thermal fluctuations.

![Figure 9. Three types of defects considered in the chain structure:](image)

- (i) $A^0$ - single, neutral acceptor, $s=0$
- (ii) $D^\frac{5}{2}$ - single excited donor, $S = \frac{5}{2}$
- (iii) $A^0D^\frac{5}{2}$ - "excited" pair, $S = \frac{5}{2}$

In the initial pre-transfer state the electrons can move to the left-hand-side or the right-hand-side nearest neighbour in the chain with equal probability. One may expect fragments of the chain with electrons transferred to the left as well as segments with charge transferred to the right. The defects separate these two kinds of clusters each possessing its own magnetization axis. If there is a $A^0$ or $D^\frac{5}{2}$ in the chain then the superexchange interactions between the spin centers on both sides of the defect become negligible or vanish. As mentioned earlier, illumination of the sample cause generation of additional defects in the chain. Presence of excited $A^0D^\frac{5}{2}$ pair next to $A^0$ or $D^\frac{5}{2}$ leads to displacement of that defect (Figure 10). The $A^0D^\frac{5}{2}$ pair is a metastable object hence the electron from $D^\frac{5}{2}$ should be transferred to one of his neighbours ($A^0$ - in this case) to assure the minimal energy of the system. In external magnetic field such a process can lead to the growth of the clusters with direction of the magnetization axis nearest to that of the applied field (Figure 11). For $H=H_{cr}$ the spin flop occurs and rapid magnetization jump is observed. Due to the decoupling in the chains with light the spin flop reorientation proceeds at a higher rate and hence the relaxation rate increases too.

5. Data analysis

Resting on the model of hierarchically constrained dynamics proposed by Palmer et al. [8] we have carried out fits of the stretched exponential $q(t) = q_0 + \exp[-(t/\tau)^{\beta}]$ (where $0 < \beta < 1$; $\tau$-mean relaxation time scale) to the experimental data obtained for $H=3$ kOe and $H=4$ kOe.
Both data sets were found to be consistent with that type of relaxation pattern (Figure 12, Figure 13). The best-fit parameters are listed in Table 1.

![Figure 12. Fit of the q(t) to experimental data measured at H=3 kOe](image1)

![Figure 13. Fit of the q(t) to experimental data measured at H=4 kOe](image2)

Table 1. The best-fit parameters of the stretched exponential curve.

<table>
<thead>
<tr>
<th>H [kOe]</th>
<th>before illumination</th>
<th>during illumination</th>
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<td></td>
<td>τ [s]</td>
<td>β</td>
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6. Conclusions
Illumination of the sample with light strongly influenced the magnetization process. In principle mentioned effect significantly depends on the value of applied field. Dependence of the magnetization relaxation on wavelength of the incident light was observed. Proposed mechanism of the magnetization process seems to be consistent with result registered for the sample below 8 K.

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References