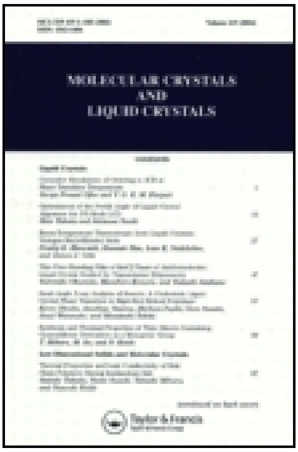

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Control of Magnetic Order by Light in Molecule-Based Magnets

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Control of Magnetic Order by Light in Molecule-Based Magnets

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An overview of recent progress in the optical control of magnetic properties of molecule-based magnets is given. In particular, we focus on the properties of cobalt iron Prussian blue magnets, in which we experimentally demonstrated coexistence of photoinduced magnetism and cluster glass-type magnetic order. These results will be contrasted with the recently discovered reversible photoinduced magnetic effects in the high-T_c molecule-based magnet Mn(TCNE)$_x$·y(CH$_2$Cl$_2$).

1. INTRODUCTION

Molecule-based magnets [1] have drawn increasing interest over the past fifteen years, due to a possibility for tailoring of their magnetic properties by flexible organic chemistry methods. In addition, they exhibit a variety non-conventional magnetic responses and novel phenomena. One of the most interesting such phenomena is recently discovered photoinduced magnetization (PIM) in Co-Fe Prussian blue-based magnets [2]. While photoinduced low-spin to high-spin transition in paramagnetic spin crossover complexes (LIESST effect) has been known since 1984 [3], the fundamentally novel aspect of the effects observed in the Prussian blue magnets is the presence of magnetic ordering and the possibility for optical control of this ordering. The materials have face-centered cubic lattice, with metal ions interconnected by CN bridges, Fig. 1. In general, significant structural disorder may be present, due to randomly distributed vacancies in the metal (Fe) sites. The general formula for Co-Fe Prussian blue magnets is $A_xCo_y[Fe(CN)_6]\cdot zH_2O$ (A = alkali metal). The alkali metal cations occupy interstitial positions in the lattice, while water molecules substitute for the missing CN groups of the $Fe(CN)_6$ vacancies (Fig. 1) [4].

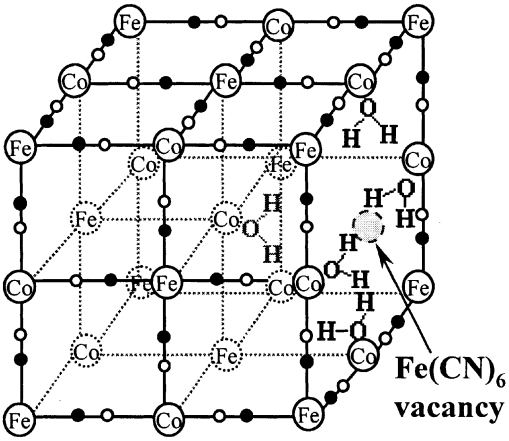

FIGURE 1. Schematic structure of cobalt-iron Prussian blue analogs. Solid (open) circles represent carbon (nitrogen) atoms. Alkali metal ions are interstitial.

Depending on the chemical composition and preparation method, the materials are dia- or paramagnetic, or exhibit magnetic ordering at temperatures below 25 K [2,4-8]. Predominantly antiferromagnetic coupling between spins in the lattice was proposed [2,4]. Upon optical excitation in the spectral region 500-750 nm dramatic changes in the magnetic state of the materials are observed, including increased magnetic ordering temperature, magnetization, remanence and coercivity [2]. At low temperatures these effects are preserved for several days after illumination. The materials can be brought to the ground state by blue or infrared light excitation, or by warming to ~150 K [2].

The mechanism for PIM in Prussian blue magnets has been the subject of a number of experimental and theoretical studies [4-25]. Infrared [4], Mössbauer [9] and X-ray absorption spectroscopy (EXAFS and XANES) [12-14] studies determined that the microscopic origin of PIM is in the light-induced electron transfer, followed by a spin (S) flip, within the Fe-CN-Co moieties. While in the initial state $\mathrm{Fe^{II}}(t_{2g}{}^6$, S=0)–CN–$\mathrm{Co^{III}}(t_{2g}{}^6$, S=0) the metal ions have no unpaired electrons, in the photoexcited state $\mathrm{Fe^{III}}(t_{2g}{}^5$, S=1/2)–CN–$\mathrm{Co^{II}}(t_{2g}{}^5e_g{}^2$, S=3/2) both ions carry nonzero spin. The increased number of spins is thus responsible for PIM. These studies also determined that in the photoexcited state Co-N/O bond lengths are significantly increased. This lattice distortion is viewed as the key for the extraordinary metastability of PIM, introducing a local energy minimum for the photoexcited state, in which the system is trapped at low temperatures [4,21].

Chemical composition of the materials is critical for the occurrence and magnitude of the photoinduced effects. The experiments show that PIM occurs only in a limited region of concentrations of the $\mathrm{Fe(CN)_6}$ vacancies (e.g., for A = K, PIM is observed only for the Co/Fe ratios between 1.2 and 1.4) [11,15]. This has been explained by the variation of the ligand field at the Co sites [4]. In the vicinity of a vacancy substitution of CN by H_2O lowers the ligand field. Low ligand field favors the high-spin state $\mathrm{Co^{II}}(t_{2g}{}^5e_g{}^2)$, therefore materials with more vacancies are expected to have higher concentration of the $\mathrm{Fe^{III}}$–CN–$\mathrm{Co^{II}}$ moieties and, consequently, higher overall spin concentration, which was experimentally confirmed [4,8,15]. However, materials with very high vacancy concentration do not exhibit PIM [4,15], presumably because of an insufficient number of diamagnetic moieties $\mathrm{Fe^{II}}$–CN–$\mathrm{Co^{III}}$. In the opposite case of a very low concentration of vacancies (and low initial spin concentration) PIM is also suppressed, which was attributed to the rigidity of lattice in these materials that does not allow the bond dilatation that accompanies PIM [15]. At optimum vacancy concentrations photoinduced transition from dia- or paramagnetic state to a magnetically ordered state can be obtained [5,6,15].

Even more profound role of the structural disorder was indicated by the quantum chemical cluster calculations [21]. They suggest a cooperative nature of PIM, which is probably caused by the lattice relaxation following the Co-N bond length change that accompanies photoinduced charge transfer. It is noted that cooperative nature of PIM was also suggested by earlier experimental observations [4]. The calculations indicate that the photoinduced forward and backward transitions (induced by red and infrared light, respectively) are initiated by excitations of different local regions in the lattice [21]. The forward transition (responsible for PIM) is initiated by the photoinduced charge transfer occurring in the regions with relatively large number of vacancies (and, consequently, low ligand field at Co sites), and spreading to the neighboring regions through the lattice relaxation. In contrast, the backward transition (reversal of PIM) is triggered by the regions with lower vacancy concentration and expanding to neighboring regions in a similar way.

The presence of structural disorder is thus a necessary condition for PIM in Prussian blue. For determination of whether disorder also has effect on the dynamics of magnetic ordering, we performed detailed magnetic studies of Prussian blue analogs $K_xCo_y[Fe(CN)_6]\cdot zH_2O$ [7,8,18,19]. The studies determined that the magnetic state of the materials is highly non-conventional and that, contrary to the earlier assumption [4], true long-range colinear magnetic order does not occur. Instead, materials show coexistence of short-range colinear order and correlated spin glass properties. We proposed a cluster glass model for the magnetic state of the materials which qualitatively explains all the observed magnetic and PIM phenomena. A summary of this work is given in this article.

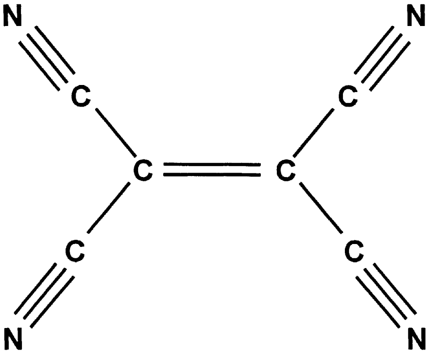

FIGURE 2. Schematic structure of tetracyanoethylene (TCNE).

Continued search for new materials with PIM properties brought about the discovery of photoinduced magnetic pole inversion in mixed ferro-ferrimagnetic Prussian blue analogs $(Fe^{II}{}_xMn^{II}{}_{1-x})_{1.5}[Cr^{III}(CN)_6]$ [26], as well as the PIM in other cyanometalate-based magnets, including $CoFe(CN)_5NH_3{\cdot}6H_2O$ [27] and $Cu^{II}{}_2[Mo^{IV}(CN)_8]{\cdot}7.6H_2O$ [28].

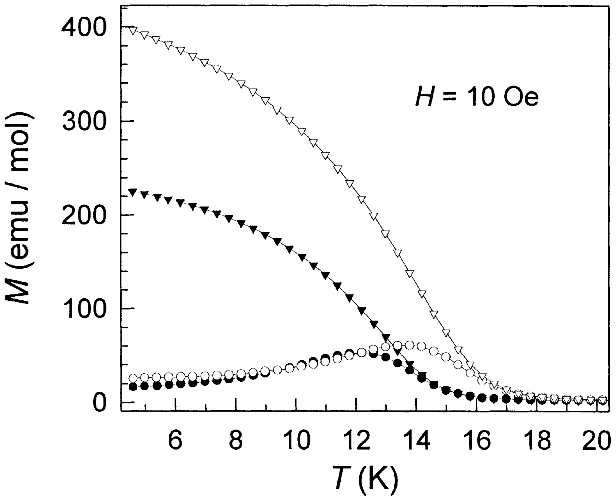

FIGURE 3. Field-cooled (triangles) and zero-field-cooled (circles) magnetization of $K_{1-2x}Co_{1+x}[Fe(CN)_6]{\cdot}yH_2O$ ($x \approx 0.3, y \approx 4.6$) at $H = 10$ Oe. Solid symbols: ground state. Open symbols: photoexcited state. (After Ref. [8].)

Our efforts to find magnets with coexisting magnetic order and PIM beyond the cyanometalate family led to the discovery of PIM in $Mn(TCNE)_x{\cdot}y(CH_2Cl_2)$ (TCNE = tetracyanoethylene, Fig. 2) [29,30]. This magnet has unpaired electrons on both the Mn^{II} ion (S= 5/2), and the organic molecular ion $[TCNE]^-$ (S = 1/2) [31]. The proposed coupling between spins is antiferromagnetic, leading to a ferrimagnetic long-range ordering below $T_C = 75$ K [32], a temperature several times higher than ordering temperatures in Co-Fe Prussian blue analogs. This is the first example of PIM in a long-range magnetically ordered material containing spins on organic species. Here we give an overview of basic photoinduced effects observed in this material and contrast them with the PIM of Prussian blue analogs.

2. EXPERIMENTAL

The polycrystalline sample of $K_{1-2x}Co_{1+x}[Fe(CN)_6]\cdot yH_2O$ ($x \approx 0.4$, $y \approx 4.6$) and $Mn(TCNE)_x\cdot y(CH_2Cl_2)$ ($x \approx 2$, $y \sim 0.8$) were synthesized by literature methods, Refs. [2] and [31], respectively. The samples for the studies of PIM were prepared by encapsulating the powder in transparent nonmagnetic resin (for Prussian blue analog) or by applying the material in a thin layer on an adhesive tape (for $Mn(TCNE)_x\cdot y(CH_2Cl_2)$). The ac susceptibility data were collected on a Lake Shore 7225 ac susceptometer/dc magnetometer. The dc magnetization was recorded on a Quantum Design MPMS-5 SQUID magnetometer. Prussian blue analog samples were illuminated using a halogen lamp and an interference filter ($\lambda_{peak} = 650$ nm, bandwidth = 80 nm, light intensity ~50 mW/cm^2). Illumination was done at $T = 5$ K for one hour, after which the sample was warmed to 30 K, which erased the magnetic ordering, while preserving the photoinduced effect [7,8]. Illumination of $Mn(TCNE)_x\cdot y(CH_2Cl_2)$ was performed by an argon ion laser at $T = 85\ \mathrm{K} > T_C$. Long illumination of 67 h was needed in this case because of very small penetration depth of light in this material.

3. RESULTS AND DISCUSSION

3.1. Prussian blue analog

The temperature dependence of the dc magnetization (M) of $K_{1-2x}Co_{1+x}[Fe(CN)_6]\cdot yH_2O$ ($x \approx 0.4$, $y \approx 4.6$), measured at applied magnetic field $H = 10$ Oe, is displayed in Fig. 3. Below $T_C \approx 15$ K (for the ground state), M starts to rapidly increase. At a temperature T_b just below T_C a deviation between the field-cooled (M_{fc}) and zero-field-cooled (M_{zfc}) magnetization curves arises, indicating irreversible magnetic behavior. While M_{fc} increases monotonically as temperature is lowered, M_{zfc} exhibits a maximum at temperature $T_{max} \approx 12$ K (in the ground state), below which temperature the irreversibility becomes much more pronounced.

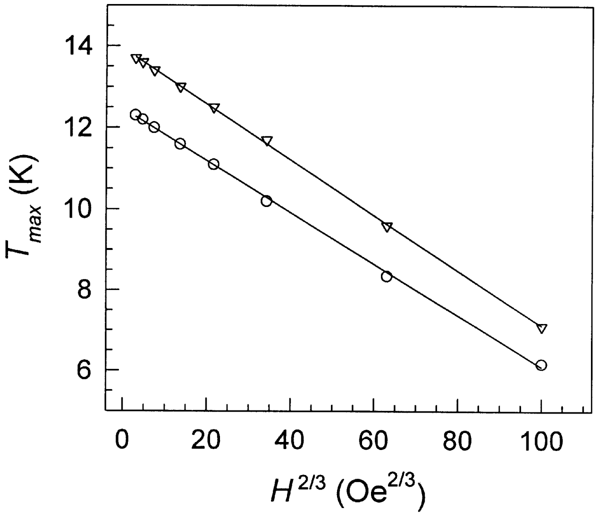

FIGURE 4. Dependence of the zero-field-cooled magnetization peak temperature T_{max} on the applied magnetic field for $K_{1-2x}Co_{1+x}[Fe(CN)_6]\cdot yH_2O$ ($x \approx 0.3$, $y \approx 4.6$), for the ground and photoexcited states (circles and triangles, respectively). Lines represent linear fits to the data ($T_{max} \propto H^{2/3}$). (After Ref. [8].)

While at low applied magnetic fields the temperature of the M_{fc}/M_{zfc} bifurcation T_b approaches T_c, as H is increased T_b shifts to lower temperatures [7,8]. Furthermore, T_{max} also decreases with increased H, and the M_{zfc} peak becomes more rounded [7]. The presence of irreversibility, with a field-dependent bifurcation, is characteristic for spin glasses and spin glass-like materials [33]. The magnetic field dependence of T_{max} (Fig. 4) is reminiscent of the Almeida-Thouless irreversibility line ($T_{max} \propto H^{2/3}$) predicted by the mean-field theory of spin glasses [33], suggesting that in the zero-field limit T_{max} corresponds to the spin glass freezing temperature. We also detected [8,19] very slow relaxation of M_{zfc} and of the thermoremanent magnetization (TRM) at $T < T_c$, which indicates long relaxation times in the material, characteristic for a system that undergoes freezing of magnetic moments.

The ac susceptibility ($\chi_{ac} = \chi' - i\chi''$) of $K_{1-2x}Co_{1+x}[Fe(CN)_6]\cdot yH_2O$ ($x \approx 0.4$, $y \approx 4.6$) for frequencies (f) between 11 and 1100 Hz is displayed in Fig. 5. Below ~15 K (in the ground state) the in-phase component χ' becomes f-dependent, which is accompanied by occurrence of a nonzero out-of-phase component χ''. At lower temperatures χ' and χ'' exhibit f-dependent peaks. Frequency dependence of χ_{ac} is additional evidence for long relaxation times in the system. The χ' peak temperature T_p has a small relative shift per decade of frequency: $\delta T_p \equiv (\Delta T_p/T_p)/\Delta(\log f) \sim 0.01$ [7,8]. This fact, together with the observed divergent-like behavior of the nonlinear susceptibility [8] indicates that magnetic moments in the system undergo cooperative (spin glass-like) freezing, not progressive blocking of individual moments (superparamagnet-like) [8].

In the photoinduced state both the magnetization (Fig. 3) and the ac susceptibilities (Fig. 5) are substantially increased. Furthermore, all characteristic temperatures (T_c, T_p, T_{max}, T_b) are increased by 1.5-2 K.

We studied several other Prussian blue analogs $K_{1-2x}Co_{1+x}[Fe(CN)_6]\cdot yH_2O$, with x in the range 0.2-0.4, and detected cluster glass behavior in all these materials [7,8,18,19].

Based on our experiments, we proposed a model for the magnetic behavior of Co-Fe Prussian blue analogs, as well as for the photoinduced effects on this behavior [7,8]. The strong irreversibility, the f-dependent χ_{ac} with small values of δT_p, and the slow relaxation of TRM and M_{zfc} are evidences for long relaxation times in the material, in contrast to magnetic response of a long-range magnetically ordered system, and suggestive of a spin-glass like magnetic order. However, the monotonical increase in M_{fc} with decreased T indicates that short-range colinear order coexists with the spin glass-like order. These facts classify this material as a cluster glass - a system with short-range colinear (ferrimagnetic in this case) magnetic order within spin clusters,

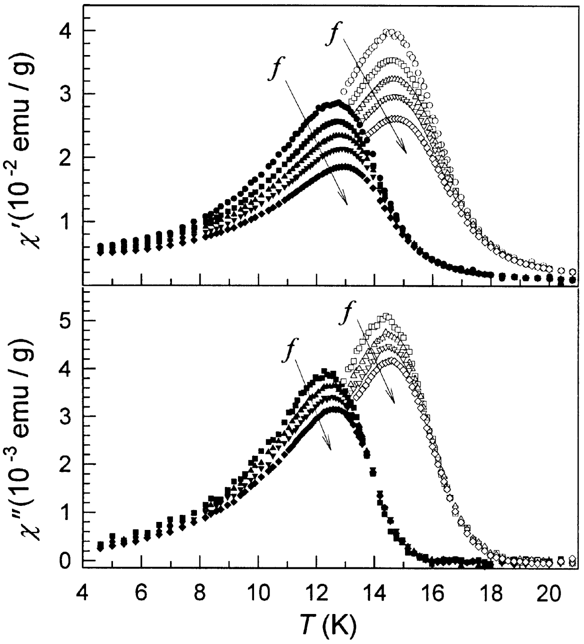

FIGURE 5. In-phase (top) and out-of-phase (bottom) ac susceptibilities for $K_{1-2x}Co_{1+x}[Fe(CN)_6]\cdot yH_2O$ ($x \approx 0.3$, $y \approx 4.6$), for the ground and photoexcited states (solid and open symbols, respectively). Measured at ac magnetic field of 1.4 Oe and at frequencies (*f*) of 11 Hz (O), 33 Hz (□), 110 Hz (☐), 333 Hz (☐), and 1100 Hz (☐).

and with spin glass-like order among clusters' magnetic moments [7,8]. The low-T magnetic response is characterized by two transitions:

(1) At $T = T_c$ (the 'quasicritical temperature') spin-spin interactions become significant enough to bring about short-range ferrimagnetic ordering of magnetic moments. The transition is characterized by: (*i*) rapid increase in M; (*ii*) onset of the weak M_{fc}/M_{zfc} irreversibility; (*iii*) occurrence of nonzero χ''; (*iv*) onset of the frequency dependence of χ'; (*v*) occurrence of the nonlinear susceptibility [8]. We proposed [7,8] that the ferrimagnetic order is limited to clusters of spins, the sizes of which increase as temperature is decreased, but always remain finite. At temperatures just below T_c individual clusters undergo progressive blocking due to energy barriers induced by crystalline and shape anisotropies, causing weak irreversibility and frequency-dependent behavior [8].

(2) At temperature defined as $T_f \equiv T_p(f \to 0) = T_{max}(H \to 0)$ (the freezing temperature) the cluster-cluster interactions produce cooperative freezing of their magnetic moments in random directions. The transition is characterized by: (*i*) peaks in χ', χ'' and the nonlinear susceptibility and (*ii*) onset of the strong M_{fc}/M_{zfc} irreversibility and a peak in the low-field M_{zfc}. This process is a real thermodynamic transition (with divergent spin glass correlation length [33]), as suggested by the size of δT_p and divergent-like behavior of the nonlinear susceptibility [8].

This qualitative model readily incorporates effects of light excitation on the low-T magnetic behavior [7,8]. Upon light irradiation new spins are introduced into the lattice, as discussed in the introduction. Higher spin concentration (n_s) in the photoexcited state enables formation of the spin clusters at a higher temperature $T_c^{illum.} > T_c$. Furthermore, at a given temperature, higher n_s leads to an increase in both the sizes of existing clusters and their magnetization. As larger clusters have longer relaxation times, the entire dynamics of the system is expected to shift to longer length and time scales in the photoexcited state, thus leading to freezing at a higher temperature $T_f^{\text{illum.}} > T_f$.

3.2. Mn(TCNE)$_x$·y(CH$_2$Cl$_2$)

Figure 6 shows the in-phase ac susceptibility of Mn(TCNE)$_x$·y(CH$_2$Cl$_2$) for the ground and photoexcited states. The susceptibility exhibits a shoulder around $T_c = 75$ K, similarly to

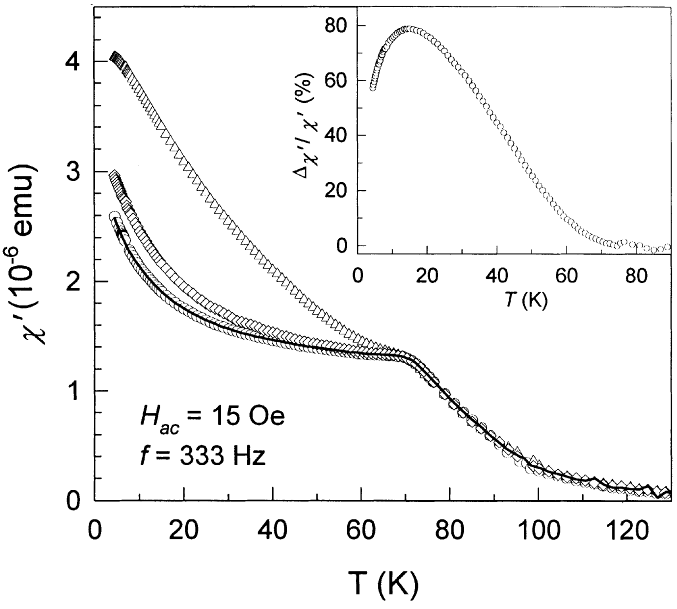

FIGURE 6 In-phase ac susceptibility for Mn(TCNE)$_x$·y(CH$_2$Cl$_2$), measured at frequency of 333 Hz and ac magnetic field of 15 Oe. Circles: before illumination (χ'_0); triangles: after illumination (χ'_{ill}) with argon laser (457.9 nm line, ~50 mW/cm^2, illuminated for 67 hours at T = 85 K); diamonds: illuminated, subsequently warmed to 200 K; line: illuminated, subsequently warmed to 250 K. Inset: relative photoinduced increase in χ' defined as (χ'_{ill} - χ'_0)/χ'_0×100%.

previously reported data [32]. After argon laser excitation, χ' in the region $T < T_C$ is substantially increased. While observed photoinduced effect is obtained by illumination at T = 85 K > T_C, no change in χ' is detected in the paramagnetic region $T > T_C$. This suggests that n_S is not significantly altered by illumination, in stark contrast with Prussian blue analogs, and suggests different mechanism for the PIM in Mn(TCNE)$_x$·y(CH$_2$Cl$_2$) [30]. Photoinduced effect is maintained for at least 100 h at temperatures < 50 K. After warming the illuminated material to 200 K the PIM below T_C is still not entirely annulled (Fig. 6). The material fully relaxes to the ground state only after warming to ~250 K, indicating that the photoexcited state is even more robust than in the case of Prussian blue analogs.

We determined that PIM in this material is accompanied by photoinduced absorption (PA) in both the uv-visible and infrared regions of spectrum [30]. These effects are also preserved long after illumination, at low temperatures. The uv-visible PA indicates electronic transition into a metastable state. The infrared PA was observed in the region of CN stretching vibrations of $[TCNE]^-$ as well as the stretching vibration of the central $[TCNE]^-$ carbon atoms, suggesting presence of a lattice distortion which includes altered configuration of $[TCNE]^-$ in the photoexcited state.

We proposed that the observed PIM is caused by a transition of a fraction of photoexcited electrons into a metastable state with locally enhanced exchange interactions [30]. The enhanced exchange is a result of a local distortion of the lattice, leading to an enhanced overlap between the spin-carrying orbitals. Furthermore, the lattice distortion was proposed as the source of the energy barrier between the ground and photoexcited states, i.e., of the metastability of PIM, similar to the mechanism proposed for Prussian blue analogs [4].

4. CONCLUSIONS

Optical control of magnetic order is a rapidly changing area of research that brings new prospect for functional molecule-based magnets. The presented studies of Co-Fe Prussian blue analogs reveal complex magnetic behavior and profound effects of disorder on both PIM and magnetic ordering. The discovery of PIM in $Mn(TCNE)_x \cdot y(CH_2Cl_2)$ opens a new pathway towards high-T_C optically-controllable magnets.

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