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UMI
OPTICAL CONTROL OF MAGNETIC ORDER IN MOLECULE-BASED MAGNETS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the
Graduate School of The Ohio State University

By

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The Ohio State University

2001

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The control of magnetic properties by light (photoinduced magnetism, PIM) is a rapidly developing area of research, attractive both for novelty of the observed phenomena and for potential applications. Recently, a new impetus to this field has been given by the discoveries of materials in which PIM coexists with a cooperative magnetic behavior (magnetic order). This opened a possibility for optical control of magnetic ordering, bringing about a number of striking and easily detectable new effects.

This dissertation addresses PIM in two distinct classes of molecule-based magnets. These novel magnets, based on organic and organo-metallic compounds, have drawn increasing interest over the past fifteen years, due to a possibility for tailoring of their magnetic properties by flexible organic chemistry methods.

The first class of materials studied in the thesis are Co-Fe Prussian blue magnets: K₂Co₉[Fe(CN)₆]·zH₂O. While PIM in these materials and its microscopic mechanism have been subjects of extensive studies, the mechanism and dynamics of magnetic ordering have been disregarded. Based on extensive experimental magnetic studies, including the first dynamic susceptibility study of PIM, it is found that the materials exhibit a highly unconventional magnetic order. Long range ferrimagnetism is not present, contrary to the prevalent assumption. Instead, a coexistence of a short-range colinear order and cooperative spin glass-like freezing occurs, identifying the materials
as cluster glasses. A model is proposed that elucidates the observed macroscopic magnetic and PIM behavior.

As the second part of the project, PIM is demonstrated in Mn(TCNE)$_2$·$x$(CH$_2$Cl$_2$) (TCNE = tetracyanoethylene). This is structurally entirely novel optically controllable magnet, with considerably higher magnetic ordering temperature (75 K) than that of K$_2$Co$_4$[Fe(CN)$_6$]·$x$H$_2$O. Extensive magnetic and optical studies of this material were performed. It is determined that PIM is accompanied by changes in the electronic and vibrational spectra. The results suggest a novel mechanism for PIM, based on the formation of a metastable state with locally enhanced exchange interaction. This is the first example of PIM in a magnet with spins supplied by electrons from $p$ orbitals, and it opens a promising new pathway towards optical control of magnetic order at relatively high temperatures.
To my parents,

Bosiljka and Aleksandar
I wish to thank my adviser, Professor Arthur J. Epstein, for his support and guidance, and for the tremendous opportunities he has provided. His unceasing enthusiasm for science has always been encouraging and stimulating. Working under his supervision has given me a wealth of diverse experiences, invaluable for my future career.

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**FIELDS OF STUDY**

Major Field: Physics

Studies in:

- Experimental Condensed Matter Physics
  - Magnetism and Magnetic Materials

Professor Arthur J. Epstein
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CHAPTER 1

INTRODUCTION

During the past several years the control of magnetic properties by light has emerged as a rapidly growing area of research. While first reports on the effects of illumination on the macroscopic magnetic properties of materials date back to late 1960's [1, 2], interest in this field has been recently renewed due to the needs of modern technology, which searches for 'smart', adaptable materials, responsive to external stimuli. In particular, as the information technology's ever increasing need for faster information processing speeds and higher storage densities require new ways to write, erase, and read information, the possibility to manipulate information bits at microscopic (molecular) level by light beams is very attractive.

A new impetus to this field has been given by discoveries of materials in which photoinduced magnetic phenomena (photoinduced magnetism, or PIM in the text to follow) coexist with cooperative magnetic behavior, i.e., with magnetic order. This coexistence brought about a possibility for optical control of the magnetic order (OCMO), and a number of novel, spectacular and easily detectable effects, such as optical control of the magnetic ordering temperature, spin freezing temperature, coercivity, etc. These novel materials include Prussian blue analogs [3, 4, 5], diluted magnetic semiconductors [6], doped manganites [7, 8], and spinel ferrite films [9, 10].
When referring to the photoinduced magnetism, one in fact refers to a variety of distinct physical mechanisms, different for each of these materials.

In addition to the obvious scientific importance due to the novelty of the phenomena involved, OCMO has a significant technological potential. Possible applications include information technology, mentioned above, and magneto-optic devices [3, 11]. While technologically applicable OCMO has not been achieved to date, it is important to articulate some requirements that a functional OCMO material should meet. Having in mind primarily use in the information storage and processing, these requirements are:

(i) The photoinduced effects should be preserved for a considerable period of time after optical excitation has stopped (the memory effect).

(ii) The photoinduced magnetism should be reversible, i.e., it should be possible to erase the effects of light excitation (e.g., by thermal treatment, by application of external fields, by optical excitation at different energies, etc.), and subsequently repeat the excitation process. This contrasts some systems in which change in the magnetic response is induced through irreversible photochemical reactions [12].

(iii) The material should exhibit OCMO at, or near room temperature. This implies the magnetic ordering temperature near or above room temperature, as well as the photoexcited state that is sufficiently robust to withstand the vibrational excitations in the material at room temperature.

(iv) The material should be available in the form of thin films. This, on the one hand, allows their deposition on various substrates, necessary in device fabrication. On the other hand, thin film configuration allows light to induce photoinduced effects in the bulk of the material.
In order to develop materials that meet these requirements, detailed knowledge of the underlying physical mechanisms for OCMO is needed. In particular, aspects of the structure that control the occurrence and magnitude of OCMO need to be elucidated. The next challenge is to predict and design, based on the accumulated expertise, new materials with structure that supports the desired OCMO properties.

This dissertation attempts to meet some of the challenges specified above, concentrating on two structurally substantially different classes of molecule-based magnets, cobalt iron Prussian blue analogs \( \text{K}_2\text{Co}_y[\text{Fe}(\text{CN})_6]\cdot z\text{H}_2\text{O} \), and \( \text{Mn(TCNE)}_{z-y}(\text{CH}_2\text{Cl}_2) \) (TCNE = tetracyanoethylene).

The first goal of this project is to study, using experimental magnetic studies, macroscopic magnetic properties of Co-Fe Prussian blue magnets, and, based on these studies, determine the type of magnetic order in these materials and effects of photoexcitation on this order. Prussian blue analogs are the first system in which OCMO was reported, in 1996 [3]. In the years following this discovery considerable experimental and theoretical effort concentrated on the microscopic mechanisms responsible for OCMO. However, in those studies the mechanism of magnetic ordering itself was all but ignored. This project examines possible effects of the structural disorder, which has been found to play a crucial role in the OCMO of these materials, on the magnetic properties. Furthermore, the project includes elaborate experimental studies of the photoinduced magnetism in this class of magnets, including the first ac susceptibility study of photoinduced magnetism on any material. Based on these studies, a model for the observed photoinduced magnetic phenomena consistent with the determined type of magnetic ordering will be proposed.
While the first goal of this dissertation is a study of magnetic ordering and the effects of optical excitation on this ordering in a material that has been known to exhibit OCMO, its second goal is demonstration of OCMO and study of its origin in a material previously studied for its unusual magnetic behavior. The molecule-based magnet Mn(TCNE)$_2$·$y$(CH$_2$Cl$_2$) has been recently found to exhibit a relatively high ferrimagnetic ordering temperature of 75 K (compared to < 25 K in Co-Fe Prussian blue magnets) and a reentrant spin glass behavior at low temperatures (< 10 K) [13]. This project studies effects of visible light irradiation on the magnetic properties of this material, using both static and dynamic magnetic susceptibility measurements. Furthermore, the project employs photoinduced absorption experiments to determine changes in the electronic and vibrational transitions that are concomitant to the observed photoinduced magnetism. On the basis of these experimental investigations a mechanism for the photoinduced magnetism in the material will be proposed.

The photoinduced magnetic behaviors of these two distinct classes of materials studied will be contrasted. While the important similarities suggest that there are general requirements for a molecule-based magnet to exhibit OCMO, significant differences indicate that the OCMO in Mn(TCNE)$_2$·$y$(CH$_2$Cl$_2$) is enabled by an entirely novel mechanism.

1.1 Molecule-Based Magnets

The conventional ('atomic') magnets owe their magnetism to unpaired electronic spins in atomic $d$ or $f$ orbitals. In contrast, molecule-based magnets are organic and organometallic systems in which electrons in molecular orbitals, made by superposition of atomic $p$ or even $s$ orbitals, play a crucial role in the magnetic ordering
In many cases at least some of the unpaired spins are localized on molecular orbitals of organic species. Perhaps the most striking examples are materials that exhibit long-range magnetic order while not having any metal ions or any atoms with occupied \( d \) orbitals, such as 4-nitrophenyl nitronyl nitroxide [16, 17] and a complex or fullerene \( \text{C}_{60} \) with tetrakis(dimethylamino)ethylene \( [(\text{CH}_3)_2\text{C}_2] \) [18], which exhibit magnetic ordering at 0.6 K and 16.1 K, respectively.

The interest in molecule-based magnets stems primarily from the fact that these materials, and their magnetic properties, can be modulated by flexible methods of organic and organo-metallic synthetic chemistry. This opens almost endless possibilities for design of materials with desired magnetic properties ('magnets by design' [15]). By changing transition metal ions used one can obtain various spin values. By changing the ligands bridging the metal ions one can vary various orbital overlaps, causing variations in the exchange coupling between spins, and/or achieve various magnetic lattices, with different dimensionalities. By a proper choice of ligands the relative strengths of relevant magnetic interactions (direct exchange, superexchange, dipole-dipole interaction, Dzyaloshinskii-Moriya interaction, etc.) can be varied. In addition, by intercalating various solvents in the structure, one can induce structural disorder, which may bring about interesting magnetic properties, such as spin-glass behavior.

The flexible design of molecule-based magnets enables synthesis of the materials that are experimental realizations of various theoretical models. Notable recent examples are high-spin complexes, which exhibit macroscopic quantum tunneling of magnetization [19] and mixed ferro-ferrimagnetic Prussian blue analogs, which exhibit
multiple compensation temperatures [20]. In addition, these materials sometimes exhibit entirely new phenomena, some of which are the subjects of this dissertation. Besides scientific curiosity, importance of molecule-based magnets also comes from the range of potential applications. Applications in lightweight transformers, generators and motors, as well as in dc and low frequency shielding applications have already been proposed [21]. These magnets have advantage of low-temperature, low-cost organic or organometallic chemistry synthetic methods, in contrast to energy-consuming high-temperature metallurgical methods used for conventional metal-based magnets. In addition, their low density, biocompatibility and low environmental contamination, make them good candidates for replacing conventional magnets in a number of applications.

This project has been done in belief that the observed photoinduced magnetism in molecule-based magnets, in conjunction with possibilities for design of new molecule-based magnets with desired properties, may soon result in new, functional optically controllable magnets.

1.2 Co-Fe Prussian Blue Analogs

Prussian blue analogs are cyanometalate-based materials, with sodium chloride crystal lattice in which $d$ metal ions are interconnected via cyanide (CN) bridges. They are among the most extensively studied molecule-based magnets due to their versatility and high magnetic ordering temperatures achieved in some of their varieties [22, 23, 24, 25]. By changing the constituent metal ions not only their spin state can be controlled, but also the magnetic interaction can be switched from ferro- to ferrimagnetic. Furthermore, structural disorder, in the form of vacancies in metal
sites, can also be controlled, the importance of which in the context of OCMO will be discussed in this work.

Cobalt-iron Prussian blue analogs are the first system reported to exhibit OCMO [3]. These materials are paramagnets or exhibit magnetic ordering at low temperatures (< 25 K). Upon illumination with light in the red region of visible spectrum dramatic changes in the magnetic state of the materials are observed, including increased magnetic ordering temperature, magnetization, remanence and coercivity [3]. 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. It has been determined that the mechanism responsible for OCMO is photoinduced inter-ionic electron transfer accompanied by a spin flip, resulting in the increased number of unpaired spins on the metal sites.

It has also been determined that the structural disorder, noted above, plays the key role in stabilizing the photoexcited state. While the microscopic origin for the effects has been the subject of extensive studies, the mechanism of magnetic ordering and, particularly, the question whether structural disorder significantly affects the magnetic ordering, were disregarded. We performed the first systematic study of the magnetic state in this class of materials, employing both the static and dynamic magnetic susceptibility measurement. The study, presented in this thesis, includes detailed analysis of the effects of illumination on virtually every aspect of the magnetic ordering. It is determined that the materials exhibit a highly non-conventional type of magnetic ordering. True long-range ferrimagnetic order, assumed in previous studies, does not occur, probably due to a significant structural disorder. Instead, the
materials show a complex low-temperature magnetic behavior with coexisting short-
range colinear order and spin glass properties. A cluster glass model is proposed that
on a qualitative level accounts for all the observed magnetic and PIM behavior. In
this model increased spin concentration in the photoexcited state leads to a shift of
the entire dynamics of magnetic ordering towards longer length and time scales.

1.3 Mn(TCNE)$_x$·$y$(CH$_2$Cl$_2$)

The recently synthesized molecule-based magnets M(TCNE)$_x$·$y$(solvent) (M = V,
Fe, Mn, Co, Ni; TCNE = tetracyanoethylene) are of considerable interest because of
their unusual magnetic properties and high magnetic ordering temperatures [26, 27].
The M = V material is one of only a few room-temperature molecule-based magnets
[27]. For M = Mn the unpaired electrons are on both the manganese ion and the
bridging organic ligand [TCNE]$^-$. This material exhibits a paramagnet-ferrimagnet
transition at $T_c = 75$ K. The experimental studies presented in this dissertation
demonstrate OCMO in Mn(TCNE)$_x$·$y$(CH$_2$Cl$_2$). Upon excitation with blue light
the magnetic susceptibility is substantially increased in the entire temperature range
below $T_c$. The effect is reversible, and the material relaxes to the ground state by
thermal treatment, similar to the OCMO in Co-Fe Prussian blue magnets. Besides
the static and dynamic magnetic susceptibility studies of OCMO, the thesis presents
optical absorption and photoinduced absorption studies in a broad range of energies
(ultraviolet to mid-infrared). These experiments determine electronic transitions re-
sponsible for OCMO, as well as the changes in the electronic and vibrational spectra
that accompany the photoinduced magnetic effects. While positive interpretation of
all the experimental results is impeded by the facts that the structure of the material
is as yet unknown, and the electronic and vibrational transitions not yet assigned with certainty, a plausible model for the detected effects is proposed. The photoinduced magnetism is explained as a result of the formation of a metastable state, stabilized by a lattice distortion, in which exchange interaction is locally enhanced. The significance of this result is manifold. This is the first example of OCMO in a magnet containing spins on organic species, i.e., spins provided by electrons in \( p \) orbitals. There are strong indications that OCMO has different microscopic origin than in the OCMO materials known to date. In addition, the system exhibits a truly long-ranged magnetic ordering, in contrast to Co-Fe Prussian blue magnets, as well as a considerably higher ordering temperature than the latter.

1.4 Outline

Magnetic ordering in a solid material is a complex effect, the understanding of which requires knowledge of the magnetic response of individual magnetic moments in the system, the ways these moments interact, and the cooperative behavior this interaction brings about. Chapter two gives an overview of some basic concepts of the solid state magnetism, with emphasis on the topics relevant for the materials studied. Different types of the magnetic response of a free ion will first be considered. The molecule-based magnets considered in this thesis are organometallic compounds, containing as structural units transition metal ions in the environment of coordinating organic molecular units (ligands). Electronic structure and magnetic properties of these metal-ligand complexes are described by the ligand field theory. The chapter summarizes main postulates and results of the ligand field theory, and discusses the effects of the ligand environment on the ionic magnetic response. In the next section of
the chapter interactions responsible for magnetic ordering are classified and discussed. The last section gives an overview of important types of magnetic ordering in solids, with focus on the spin glass ordering, which occurs in both systems studied in the thesis.

Chapter three is dedicated to the experimental techniques used. In the first section material synthesis procedures are given, as well as the methods used to prepare samples for the magnetic and optical measurements. The following section summarizes the methods used for illumination of samples. Magnetic properties and photoinduced magnetism were studied by two distinct and complementary methods. Magnetic behavior in static applied magnetic fields was investigated by a SQUID dc magnetometer, while response in alternating magnetic field was studied by an ac susceptometer. Optical absorption spectroscopy techniques were used to study electronic and vibrational transitions of the materials. Effects of illumination on these transitions were studied by the steady-state photoinduced absorption technique. In the ultraviolet-visible-near infrared (UV-Vis-NIR) region of spectrum (electronic transitions), measurements were done on a dispersive spectrophotometer, while in the mid-infrared (MIR) region (vibrational transitions) a Fourier transform infrared (FTIR) spectrometer was used. The chapter gives brief descriptions of the experimental equipment, together with the principles of their operation. Limitations, intrinsic pitfalls, and necessary precautions for obtaining trustworthy data, are emphasized for each of the experimental techniques. The data analysis methods used for each of the experimental methods are described in brief.

Chapter four presents extensive experimental studies of magnetic properties and photoinduced magnetism in Prussian blue analogs $K_xCo_y[Fe(CN)_6]zH_2O$, $0.2 \leq x \leq$
0.4, \( y \sim 5 \)). In the first section the family of Prussian blue analogs is introduced, followed by an overview of important earlier studies of PIM in this class of magnets. The following sections present dc magnetization and ac susceptibility studies of the magnetic state and PIM. The studies demonstrate cluster glass state in the materials, in which finite-range colinear ordering coexists with spin glass-like cooperative behavior. The photoinduced effects on the cluster glass state are discussed, including some effects that are direct consequences of the presence of glassiness. Finally, a cluster glass model is proposed, which qualitatively explains the observed magnetic and PIM behavior.

Experimental studies of PIM in \( \text{Mn(TCNE)}_{x-y}(\text{CH}_2\text{Cl}_2) \) are the subject of chapter five. An introduction into the metal-TCNE family of molecule-based magnets is given in the first section, including a summary of the previous magnetic studies of \( \text{Mn(TCNE)}_{x-y}(\text{CH}_2\text{Cl}_2) \). The following section presents static and dynamic magnetic susceptibility studies that demonstrate reversible photoinduced magnetism in the material. The chapter proceeds with presentation of UV-Vis-NIR and MIR absorption and photoinduced absorption studies. The closing section proposes a model for PIM in \( \text{Mn(TCNE)}_{x} \cdot y(\text{CH}_2\text{Cl}_2) \) consistent with the magnetic and optical experimental data.

The closing chapter summarizes the results of the dissertation and puts them in the context of the current status and trends in the field of OCMO. Finally, several possible directions for further research are proposed.
CHAPTER 2

MAGNETISM IN SOLIDS – BASIC THEORETICAL CONCEPTS

2.1 Magnetism of a Free Ion

The magnetic properties of solids are, to a very good approximation, due solely to the electronic magnetic moments, since the nuclear magnetic moments are typically about a thousand times smaller. The electronic magnetic dipole moment $\mu$ is the sum of the orbital and spin magnetic moments:

$$\mu = \mu_l + \mu_s = -\mu_B (1 + g_0 s).$$

(2.1)

Here $\mu_B = e\hbar/2mc$ is the Bohr magneton, $s$ and $l$ are the spin and orbital angular momenta, respectively, and the electronic $g_0$-factor is equal 2.0023 (assumed to be exactly 2 in the rest of the text).

The magnetic response of a material is described by magnetization and magnetic susceptibility. Magnetization is defined as the total magnetic moment per unit volume. For a system of $N$ particles with magnetic moments $\mu_i$, located at sites $r_i$, the magnetization is given by

$$M = \frac{1}{V} \sum_i^N (\mu_i),$$

(2.2)
where \( \langle \rangle \) denotes the statistical mechanics average. In the absence of interactions among individual magnetic moments, the magnetization of a system is nonzero only in the presence of a magnetic field \( \mathbf{H} \). Expressed in terms of the (Helmholtz) free energy \( F \), the magnetization (in the direction of field) is given by

\[
M = -\frac{1}{V} \frac{\partial F}{\partial H} .
\] (2.3)

The susceptibility is defined as

\[
\chi = \frac{\partial M}{\partial H} = -\frac{1}{V} \frac{\partial^2 F}{\partial H^2} .
\] (2.4)

An isolated atom (or ion) in a magnetic field is described by the Hamiltonian [28, 14]:

\[
\mathcal{H} = \mathcal{H}_e + \mathcal{H}_{ee} + \mathcal{H}_{so} + \mathcal{H}_{para} + \mathcal{H}_{dia}
\] (2.5)

\[
= \sum_i \left( \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i<j} \frac{e^2}{r_{ij}} + \lambda \mathbf{L} \cdot \mathbf{S} + \mu_B (\mathbf{L} + g_0 \mathbf{S}) \cdot \mathbf{H} + \frac{e^2}{8mc^2} \sum_i (\mathbf{H} \times \mathbf{r}_i)^2 .
\] (2.6)

Here index \( i \) denotes the electrons in the ion, \( r_i \) and \( r_{ij} \) are the nucleus-electron and electron-electron displacements, and \( \mathbf{L} \) and \( \mathbf{S} \) denote the total spin and orbital angular momenta of the ion. The first two terms in (2.6) describe independent electrons moving in the spherical potential of the nucleus, and the Coulomb repulsion between electrons, respectively. The third term represents the spin-orbit coupling, which is a relativistic effect that can be understood as a magnetic interaction between the spin and orbital electronic magnetic moments. The last two terms describe the effects of the magnetic field, and they are responsible for paramagnetism and diamagnetism, respectively.

If an ion has all its electronic shells filled, the spin and orbital angular momenta are both zero in the ground state (\(|0\rangle\)). In this case only the term \( \mathcal{H}_{dia} \) contributes
to the magnetic response. This response is called \textit{Larmor diamagnetism}, and the diamagnetic susceptibility is given by [28]

$$\chi = -\frac{e^2}{6mc^2} \frac{N}{V} \langle 0 | \sum_i r_i^2 | 0 \rangle.$$ \hfill (2.7)

The negative sign indicates that the induced magnetic moment opposes the applied field. The diamagnetic susceptibility is thus temperature-independent, and its values are of the order of $1 - 100 \times 10^{-6}$ emu/mol. If the ion also exhibits paramagnetism (has partially filled shells), the diamagnetic susceptibility can often be neglected, especially at low temperatures.

If an ion has partially-filled shells, the term $\mathcal{H}_{\text{para}}$ also contributes to the magnetic response. Before we consider this response in detail, let us review \textit{the Hund's rules}, which are used to determine the ground states of ions with a partially-filled shell. The rules consider a free atom or ion in which all electronic shells are either filled or empty except one, the one-electron levels of which are characterized by orbital angular momentum $l$, and which contains $n$ electrons ($0 < n < 2(2l + 1)$). The degeneracy of this shell is $2(2l + 1)$, as there are $2l + 1$ different values of $l_z$ for a given $l$, and two spin directions for each $l_z$. This degeneracy is partially lifted by the Coulomb interactions between the electrons in the shell, as well as by the spin-orbit coupling. The ground state of the ion after the degeneracy is lifted is determined by the rules [28]:

- \textit{(Hund's first rule)} The ground state has the maximum total spin $S$ that is consistent with the Pauli exclusion principle. This means that for $n \leq 2l + 1$ we have $S = n/2$, while for $n > 2l + 1$ the total spin is reduced from its maximum value by $1/2$ for each electron after the $(2l + 1)^{\text{th}}$, i.e., $S = 2l + 1 - n/2$.  

14
Figure 2.1: Ground states of $d$ and $f$ ions as constructed from Hund’s rules. Arrows indicate the $s_z$ values of individual electronic spins ($\uparrow = \frac{1}{2}, \downarrow = -\frac{1}{2}$).

- **(Hund’s second rule)** The total angular momentum $L$ of the ground state has the largest value consistent with the Hund’s first rule and the exclusion principle. Thus for a shell less than half filled: $L = l + (l-1) + \cdots + [l-(n-1)]$. For a half-filled shell $L = 0$, and the second half of the shell is filled with electrons with opposite spin to those in the first half, thus the exclusion principle allows the same series of $L$ values as for the first half.

- **(Hund’s third rule)** The value of the total angular momentum $J$ for the ground state is given by $J = |L - S|$ for $n \leq 2l + 1$, and by $J = L + S$ for $n > 2l + 1$.  

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The first two rules are results of minimization of the Coulomb repulsion energy. The third rule has its origin in the spin-orbit coupling, which favors parallel orbital and spin angular momenta for negative $\lambda$ (which is the case for more-than-half-filled shells), and antiparallel orbital and spin angular momenta for positive $\lambda$ (less-than-half-filled shells).

The ground states of ions with partially-filled $d$ and $f$ shells are given in Table 2.1. The states are labeled according to the spectroscopic notation: $^{2S+1}X_J$, where the orbital angular momentum is given by a letter: $X = S, P, D, F, G, H, I$ for $L = 0, 1, 2, 3, 4, 5, 6$, respectively.

For ions with zero total angular momentum $J$, but nonzero $L$ and $S$, the term $\mathcal{H}_{\text{para}}$ gives zero energy contribution in the first order of the perturbation theory, but nonzero contribution in the second-order. This results in the susceptibility given by

$$\chi = \frac{2N\mu_B^2}{V} \sum_n \frac{|\langle 0 | L_z + g_0 S_z | n \rangle|^2}{E_n - E_0}, \quad (2.8)$$

where the index $n$ denotes the excited states. The susceptibility is positive, thereby producing a moment parallel to the applied field. This response is called the Van Vleck paramagnetism, and it is typically even weaker than Langevin diamagnetism.

Finally, let us consider the most important case, when $J \neq 0$. The term $\mathcal{H}_{\text{para}}$ then gives the first-order contribution to the energy, $\mu_B \mathbf{H} \cdot \langle 0 | \mathbf{L} + g_0 \mathbf{S} | 0 \rangle$. In zero field the ground state is $(2J + 1)$-fold degenerate, and these $2J + 1$ states can be labeled as $|JLSJ_z\rangle$, $J_z = -J, \ldots, J$. It can be shown [28] that this degenerate state is split by the applied field into states with definite values of $J_z$, the energies of which are separated by $g \mu_B H$, where $g$ is the Landé factor, given by

$$g = \frac{3}{2} + \frac{1}{2} \left[ \frac{S(S+1) - L(L+1)}{J(J+1)} \right]. \quad (2.9)$$
Furthermore, using the Wigner-Eckart theorem [28], one obtains

\[ \langle JLSJ_z | L + g_0 S | JLSJ'_z \rangle = \langle JLSJ_z | gJ | JLSJ'_z \rangle. \] (2.10)

Thus, within the basis \( |JLSJ_z\rangle \), \( J_z = -J, \ldots, J \), one can write

\[ L + g_0 S = gJ. \] (2.11)

The total angular momentum of the ion can then be written as: \( \mu = -g\mu_B J \).

However, Eq. (2.11) is strictly speaking valid only if there is no significant mixing with the excited states, i.e., if the states from the multiplet \( |JLSJ_z\rangle \), \( J_z = -J, \ldots, J \) are the only states that contribute appreciably to the free energy. This is the case if the spin-orbit coupling is much larger than \( k_B T \), a condition often satisfied in practice.

Under the same assumption, we can calculate the magnetization and susceptibility, starting from the free energy:

\[ e^{-F/k_B T} = \sum_n e^{-E_n(H)/k_B T} = \sum_{J_z=-J}^J e^{-g_0 H J_z/k_B T}. \] (2.12)

Using (2.3), the magnetization is given by

\[ M = \frac{N}{V} g\mu_B J B_J \left( \frac{g\mu_B J H}{k_B T} \right), \] (2.13)

where \( B_J(x) \) is the Brillouin function, defined as

\[ B_J(x) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{1}{2J} x. \] (2.14)

In the high-temperature limit, \( k_B T \gg \mu_B H \), the Brillouin function can be approximated by

\[ B_J(x) \approx \frac{J+1}{3J} x, \] (2.15)
which gives for the high-temperature paramagnetic susceptibility

\[
\chi = \frac{N (g \mu_B)^2 J(J+1)}{\frac{3}{k_B T}} \quad (2.16)
\]

The expression (2.16) is the *Curie law*. At room temperature the Curie paramagnetic susceptibility is larger by a factor of the order 500 than the Larmor diamagnetic susceptibility [28].

In cases in which the spin-orbit coupling is comparable with \( k_B T \), the higher energy states become accessible by thermal excitations, and the susceptibility has contributions from all these states. The paramagnetic susceptibility can then be described by a more general formula. The energy of the \( n \)-th state can be expanded in powers of the applied field as:

\[
E_n = E_n^{(0)} + E_n^{(1)} H + E_n^{(2)} H^2 + \cdots
\]

The susceptibility is given by the expression [29, 30]

\[
\chi = \frac{N}{V} \sum_n \frac{(E_n^{(1)})^2 / k_B T - 2E_n^{(2)} \exp(-E_n^{(0)}/k_B T)}{\sum_n \exp(-E_n^{(0)}/k_B T)}, \quad (2.17)
\]

known as the Van Vleck equation.

### 2.2 Transition Metal Ion in a Crystal Field

When magnetic ions (ions with partially-filled shells) are situated in a crystal or an organometallic complex, their electronic and magnetic properties can be significantly affected by the environment. As a result of the electrostatic interaction between the magnetic ion and the surrounding ions (ligands), the spherical symmetry of a free ion is in general lowered. In the simplest approach to the problem, the *ligand field theory*, all the effects of this interaction are represented by an effective electrostatic field (‘crystal field’ or ‘ligand field’) acting on the magnetic ion, the field having the symmetry of the crystal lattice site occupied by the ion.
In the case of ions with partially-filled f-shells (rare-earth ions) the crystal field effects are relatively small (~ 0.01 eV), due to the screening effect of the outer 5s and 5p orbitals [31]. Typical spin-orbit coupling energies in these ions are of the order of 0.1 eV, an order of magnitude higher than the crystal field energies. In contrast, in ions with unpaired electrons in d-shells, the crystal field effects (> 1 eV) dominate the spin-orbit coupling (ranging from ~ 0.01 eV for 3d ions to ~ 0.1 eV for some 4d ions). Here the discussion will be limited to the iron-group (3d) ions, as the materials studied in this thesis contain metal ions from this group.

In most compounds containing iron-group ions, each (positive) metal ion is located at the centre of an octahedron of negative ions (or polar molecules, with their negative ends at the metal ion). In order to illustrate how the ligand field theory works, we consider an ion with 3d^1 configuration (e.g., Ti^{3+}) in a crystal field of octahedral symmetry, due to ligands with point charges $-Ze$. In a free ion there are five degenerate 3d orbital states, which can be written as products of radial $R$ and angular $Y_l^m$ factors as: $\psi_{3,2,m}(r, \theta, \phi) = R(r)Y_l^m(\theta, \phi), m = 0, \pm1, \pm2$. Here $Y_l^m$ are the spherical harmonics. For a free ion any linear combination of these functions gives a satisfactory description of a stationary state of the ion. In order to calculate the perturbation due to the crystal field, we must choose a basis, formed from linear combinations of functions $\psi_{3,2,m}$, that is adapted to the symmetry of the octahedral field. Such basis is given by

$$d_{xy} = \frac{R(r)}{r^2}xy, \quad (2.18)$$

$$d_{x^2-y^2} = \frac{R(r)}{r^2}(x^2 - y^2), \quad (2.19)$$

$$d_{yz} = \frac{R(r)}{r^2}yz, \quad (2.20)$$

$$d_{xz} = \frac{R(r)}{r^2}xz. \quad (2.21)$$
\[ d_{z^2} = \frac{R(r)}{r^2}(2z^2 - x^2 - y^2), \quad (2.22) \]

where \( x, y, z \) are Cartesian coordinates of the octahedron (i.e., the ligands are positioned at the axes). The leading term of the octahedral crystal field potential can be written as [32, 33]

\[ V_c(x, y, z) = \frac{35 Z e^2}{4 a^5} [x^4 + y^4 + z^4 - \frac{3}{5} r^4], \quad (2.23) \]

where \( a \) is the metal-ligand distance. The first-order correction to the energy of the orbitals 2.22 is now given simply by the matrix elements \( \langle d_{xy}|V_c|d_{xy} \rangle \), etc. As a result, the fivefold-degenerate \( d \)-level is split into a twofold-degenerate level (denoted as \( e_g \)), corresponding to the functions \( d_{z^2} \) and \( d_{x^2-y^2} \), and a threefold-degenerate level (denoted as \( t_{2g} \)), corresponding to \( d_{xy}, d_{yz}, \) and \( d_{dz} \). The douplet is higher in energy than the triplet by energy \( \Delta \), since these orbitals are oriented towards the ligands, and experience higher Coulomb repulsion. In the case of a tetrahedral crystal field, the analogous approach also gives splitting into a doublet and a triplet, however in this case the triplet is higher in energy than the doublet [34].

For configurations with more than one 3\( d \) electron, the occupations of the above determined one-electron levels \( e_g \) and \( t_{2g} \) depend on the relative strengths of the crystal field splitting \( \Delta \) and Coulomb repulsion \( U \) between electrons located on the same orbital. In the weak crystal field limit \( (\Delta < U) \) the electrons will be distributed one on each orbital with all spins parallel, before pairing up, resulting in the high-spin state (HS). In the strong crystal field limit \( (\Delta > U) \) the energy cost for electron pairing is smaller than the crystal field splitting, which results in the low-spin state (LS). The low-spin and high-spin cases are illustrated in Fig. 2.2(a) for the example.
Figure 2.2: (a) Scheme of high-spin (HS) and low-spin (LS) states for a $d^6$ ion. (b) Schematic LS and HS adiabatic potential curves for a spin crossover compound. $Q$ denotes the metal-ligand coordinate (after Ref. [30]).

of a $d^6$ ion (e.g., Fe$^{II}$) in octahedral environment, in which the LS state has zero total spin, while the HS state has a spin of 2.

If the difference between $\Delta$ and $U$ is small ($|\Delta - U| \sim k_BT$), in many organometallic complexes the spin crossover phenomenon is observed. At low temperatures, the population of the LS state in an assembly of $N$ molecules is higher than that of the HS state, but above some characteristic temperature, the HS state becomes more populated. This transition can be rather abrupt if the complex is in a solid state [30, 35]. The phenomenon has been explained as a consequence of the large entropy gain for the LS→HS transition. The increase in entropy is due to the higher degeneracy $\Omega$ of the HS state ($\Delta S = Nk \ln(\Omega_{HS}/\Omega_{LS})$), as well as a greater vibrational entropy contribution, as in the HS state the vibrational disorder is higher, owing to
the longer metal-ligand bonds [30, 35, 36]. The lengthening of the bonds arises due to the fact that the \( e_g \) orbitals, occupied in the HS state, are more antibonding than the \( t_{2g} \) orbitals [30]. The spin crossover transition is accompanied by a large enhancement of the Curie paramagnetic response of the complexes, due to increased number of unpaired spins.

The schematic adiabatic potentials for the LS and HS states are shown in Fig. 2.2(b), where \( Q \) represents the inter-nuclear metal-ligand coordinate. The existence of two potential minima, separated by an energy barrier, allows for a very interesting phenomenon, called light-induced excited spin state trapping (LIESST) [36, 37, 38]. The effect, first observed in the complex Fe(1-propyltetrazole)\(_6\)(BF\(_4\))\(_2\), consists of a LS→HS transition upon excitation with visible light at low temperatures (\( \sim 10 \) K). The photoexcited HS state decays very slowly (on the scale of hours or days) if temperature is maintained low, due to the energy barrier between the LS and HS potential minima. Above 50 K the metastable-HS state relaxes back to the LS state. As the LS and HS states have different spins, the direct photoexcitation from LS (spin singlet for Fe\(^{II}\)) to HS is forbidden by the spin selection rule. The proposed mechanism involves photoexcitation from LS to an intermediate singlet state, and subsequent multi-step decay to the HS state, during which the spin multiplicity is changed through the spin-orbit coupling (intersystem crossing) [35].

Besides the total spin, the total orbital angular momentum can also be affected by the environment. In most of the 3d transition metal ions the orbital angular momentum is 'quenched' by the crystal field, i.e., its effective value is reduced. Returning to the example of a 3d\(^1\) ion, it is obvious that the wavefunctions (2.22) are not eigenfunctions of the \( z \) component of the orbital angular momentum \( L_z \), except for \( d_{z^2} \).
which, being independent of \( \phi \), has the eigenvalue zero. Moreover, the expectation value of \( L_z \) for the other four states is readily shown to be zero. Thus, \( L_z \) is not a constant of motion, although the magnitude of \( L \) for the ion remains definite (with value \( \sqrt{2(2+1)}\hbar \)). The crystal field can reduce the orbital quantum number from \( L = 2 \) to \( L_{\text{eff}} = 1 \) (partial quenching) or \( L_{\text{eff}} = 0 \) (total quenching). In the case of partial quenching, the threefold degeneracy is often further removed by additional distortions of the original cubic symmetry (such as tetragonal or trigonal distortions.)

Let us consider a 3d ion, the lowest orbital state of which is a singlet as a result of quenching. The effects of the spin-orbit coupling and the applied field \( H \) can be described by treating them as a perturbation given by the Hamiltonian [39]

\[
\mathcal{H}_p = \lambda L \cdot S + \mu_B H \cdot (L + 2S).
\]  

(2.24)

The perturbation calculation is carried out by the method introduced by Pryce [40, 39, 33, 41]. As neither the intraionic Coulomb interaction nor the crystal field has mixed orbital and spin states, one can choose the basis of eigenfunctions that are products of the orbital and spin parts: \( \ket{n|S, M_S} \). Let \( E_n \) and \( n \) be the energy level and the corresponding orbital part of the eigenfunction due to the crystal field splitting. As the ground state is nondegenerate, first-order perturbation theory gives

\[
\langle 0|\mathcal{H}_p|0 \rangle = \langle 0|\mu_B H \cdot 2S|0 \rangle + \langle 0|\mu_B H \cdot L + \lambda L \cdot S|0 \rangle.
\]  

(2.25)

The first term on the right-hand side gives just \( \Delta E_0^{(1)} = 2\mu_B H \cdot S \), as no operation is made on the orbital wavefunction. The second term can be expanded as

\[
\sum_{i=x,y,z} (\mu_B H_i + \lambda S_i) \langle 0|L_i|0 \rangle = 0,
\]  

(2.26)
since the matrix elements vanish due to the orbital momentum quenching. Proceeding to the second-order perturbation theory, and defining $\Lambda_{ij}$ as

$$\Lambda_{ij} = \sum_n \frac{\langle 0|L_i|n \rangle \langle 0|L_j|n \rangle}{E_n - E_0},$$

we obtain for the second-order correction to the energy:

$$\Delta E_0^{(2)} = - \sum_{i,j=x,y,z} [\lambda^2 \Lambda_{ij} S_i S_j + 2\lambda \mu_B \Lambda_{ij} H_i S_j + \mu_B^2 \Lambda_{ij} H_i H_j].$$

Adding $\Delta E_0^{(1)}$ and $\Delta E_0^{(2)}$ we obtain the spin Hamiltonian for a nondegenerate ground state split off by the crystal field:

$$H_S = \sum_{ij} [2\mu_B H_i (\delta_{ij} - \lambda \Lambda_{ij}) S_j - \lambda^2 S_i \Lambda_{ij} S_j - \mu_B^2 H_i H_j] =$$

$$= \mu_B S \cdot g \cdot H - \lambda^2 S \cdot \Lambda \cdot S - \mu_B^2 H \cdot \Lambda \cdot H.$$

Here $\Lambda$ and $g$ are tensors, the latter having components: $g_{ij} = 2(\delta_{ij} - \lambda \Lambda_{ij})$.

The first term in (2.30) represents an effective Zeeman energy, and it is responsible for the paramagnetic behavior. This means that the effective $g$-factor becomes a tensor, where the term $-2\lambda \Lambda_{ij}$ is due to the induced orbital moment that arises from the mixing with the high-energy orbital states due to the LS coupling. The second term in (2.30) is the single-ion anisotropy term, and the last, spin-independent term, is responsible for the Van Vleck paramagnetism.

The single-ion anisotropy term lifts the $(2S + 1)$-fold degeneracy of the spin. With a choice of basis that diagonalizes $\Lambda$, we obtain

$$H_{SIA} = -\lambda^2 (\Lambda_{xx} S_x^2 + \Lambda_{yy} S_y^2 + \Lambda_{zz} S_z^2) = D[S_z^2 - \frac{1}{3} S(S + 1)] + E[S_z^2 - S_y^2],$$

where

$$D = -\frac{3}{2} \lambda^2 \Lambda_{zz}, \quad E = -\frac{1}{2} \lambda^2 (\Lambda_{xx} - \Lambda_{yy}).$$
Note that the single-ion anisotropy constants $D$ and $E$ are proportional to the square of the spin-orbit coupling constant $\lambda$.

In the case of axial symmetry $E = 0$ and, omitting the constant term, we have

$$H_{\text{SIA}} = DS_z^2.$$  (2.33)

For octahedral symmetry $D = 0$ and the anisotropy shows up only in the fourth order of the perturbation theory. The same is the case for ions with half-filled $d$ shell (e.g., Fe$^{3+}$ and Mn$^{2+}$), which have $L = 0$. For $S = 1/2$ the anisotropy is zero even in the crystal fields of low symmetry.

The single-ion anisotropy is one of the main causes of the magnetic hysteresis. Systems in which this anisotropy is small are expected to have narrow hysteresis loops (i.e., small coercivity).

### 2.3 Magnetic Interactions

#### 2.3.1 Direct Exchange

By far the most important interactions between magnetic moments in solids are various forms of the exchange interaction. The exchange interaction is a purely quantum mechanical phenomenon. It results from the electrostatic interaction in conjunction with the requirement for antisymmetrization of the total wave function for a many-electron system (this requirement is a direct consequence of the indistinguishability of electrons).

One of the simplest theoretical approaches to the problem of interatomic exchange is the Heitler-London method, originally developed for the hydrogen molecule [42, 43, 32]. The Hamiltonian for the system of two nuclei ($a$ and $b$) and two electrons (1 and
2) is written as

\[
\mathcal{H} = \left( -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{r_{1a}} - \frac{e^2}{r_{22}} \right) + \left( \frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}} \right),
\]

(2.34)

where \( R_{ab} \) and \( r_{ij} \) denote the respective interparticle coordinates. The terms in the first and second parentheses are the one- and two-electron parts of the Hamiltonian, respectively.

The wavefunction of a two-electron system must be antisymmetric with respect to the interchange of the two electrons. This requirement can be satisfied if the orbital part of the wavefunction is symmetric, while the spin part of the wavefunction is antisymmetric (singlet state, with total electron spin zero), or if the orbital part is antisymmetric, while the spin part is symmetric (triplet states, with total spin of 1).

In the Heitler-London approach the orbital parts of the two-electron wavefunctions for the singlet \((s, +)\) and triplet \((t, -)\) states are given by

\[
\Psi_s = \frac{1}{\sqrt{2(1 \pm S^2_{ab})}} [\psi_a(1)\psi_b(2) \pm \psi_b(1)\psi_a(2)],
\]

(2.35)

where the one-electron wavefunctions \( \psi_a \) and \( \psi_b \) are solutions of the respective one-electron Schrödinger equations, for instance

\[
\left( -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{r_{1a}} \right) \psi_a(r_1) = E_1 \psi_a(r_1), \quad \psi_a(r_1) \equiv \psi_a(1).
\]

(2.36)

The energy difference between the singlet and triplet states is given by

\[
\Delta E = E_s - E_t = 2 \frac{K_{ab} - C_{ab}S_{ab}^2}{1 - S_{ab}^4}.
\]

(2.37)

Here \( S_{ab} \), \( C_{ab} \), and \( K_{ab} \) are integrals given by

\[
S_{ab} = \int \psi_a(1)^*\psi_b(1) d^3r_1.
\]

(2.38)
\[ C_{ab} = \int \psi_a(1)^* \psi_b(2)^* V \psi_a(1) \psi_b(2) d^3r_1 d^3r_2 \]  
(2.39)

\[ K_{ab} = \int \psi_a(1)^* \psi_b(2)^* V \psi_a(2) \psi_b(1) d^3r_1 d^3r_2 \]  
(2.40)

where \( V \) is the two-electron part of the Hamiltonian

\[ V = e^2 \left( \frac{1}{R_{ab}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}} \right). \]  
(2.41)

\( S_{ab} \) is called the overlap integral, \( C_{ab} \) the Coulomb integral, and \( K_{ab} \) the exchange integral.

It is convenient to construct a Hamiltonian that explicitly expresses the energy dependence of a two-electron system on the spin states of the two electrons ('spin Hamiltonian') [28]. In order to construct the spin Hamiltonian for a two-electron system, one starts by noting that the electron spin operator for a single electron satisfies \( S_i^2 = \frac{1}{2}(\frac{3}{2} + 1) = \frac{3}{4} \). Consequently, for the total spin operator \( S \) we have

\[ S^2 = (S_1 + S_2)^2 = \frac{3}{2} + 2S_1 \cdot S_2. \]  
(2.42)

As \( S^2 \) has the eigenvalue \( S(S+1) \) in the state of spin \( S \), it follows that the operator \( S_1 \cdot S_2 \) has eigenvalue -3/4 in the singlet \((S = 0)\) state and +1/4 in the triplet \((S = 1)\) states. Consequently, the operator

\[ h_{\text{spin}} = \frac{1}{4} (E_s + 3E_t) - (E_s - E_t)S_1 \cdot S_2 \]  
(2.43)

has eigenvalue \( E_s \) in the singlet state and \( E_t \) in each of the three triplet states, and it is the desired spin Hamiltonian. The additive constant is usually omitted to give the Heisenberg exchange Hamiltonian

\[ h_{\text{spin}} = -JS_1 \cdot S_2, \quad J = E_s - E_t. \]  
(2.44)
Evidently the interaction described by (2.44) will favor (have minimum energy for) parallel spins if the exchange constant $J$ is positive, and antiparallel if $J$ is negative. For many cases of interest the form of the spin Hamiltonian for the entire solid is simply that for the two-spin case, summed over all pairs of spins

$$H^{\text{spin}} = -\sum_{i<j} J_{ij} S_i \cdot S_j.$$

(2.45)

According to (2.37), in the Heitler-London formalism the exchange constant (for not too large overlaps, i.e. $S_{ab}^4 << 1$) is given by

$$J_{ab} \approx 2K_{ab} - 2C_{ab}S_{ab}^2.$$

(2.46)

The Heitler-London approach, initially applied to the H$_2$ molecule, is often used as the first approximation in considerations of exchange in more complex systems, such as molecule-based magnets. For instance, in the case of exchange interaction between two organic radicals, the one-electron wavefunctions $\psi_a$ and $\psi_b$ would correspond to the magnetic orbitals (atomic or molecular orbitals carrying unpaired spins) localized on the two radicals $a$ and $b$. The exchange is described by an expression analogous to (2.46) [44]. The Heitler-London approach, devised for well-localized electrons, becomes inappropriate in the case of metals.

It can be shown that the exchange integral $K_{ab}$ is always positive, i.e., it favors parallel (ferromagnetic) alignment of spins [30]. The term $2K_{ab}$ is usually referred to as the potential exchange. The second term in (2.46), $-2C_{ab}S_{ab}^2$, is usually negative and favors antiparallel (antiferromagnetic) alignment of spins [30]. It is usually called the kinetic exchange. If there is no overlap between the magnetic orbitals only the potential exchange is present, and the expected ordering of spins is ferromagnetic. If the magnetic orbitals overlap, both terms in (2.46) are present, and the sign of
$J_{ab}$ depends on the relative magnitudes of the two terms. In most cases the kinetic exchange term is dominant and the total exchange interaction is antiferromagnetic. In molecule-based systems the antiferromagnetic ordering is present in the vast majority of cases. In the cases in which ferromagnetism is observed, it usually cannot be explained as a result of solely potential exchange, but requires consideration of additional effects, like the exchange (spin) polarization and the charge transfer interaction, that involve not only the 'magnetic' electrons, but also the 'core' electrons [30, 44].

2.3.2 Indirect and Itinerant Exchange

The magnetic interactions discussed above are different forms of the direct exchange, arising from the direct Coulomb interaction between electrons from the two centers. It often happens that two magnetic centers are separated by a nonmagnetic unit, i.e., by an ion or an organic radical with all electronic shells filled. It is then possible for the magnetic centers to have a magnetic interaction mediated by the electrons in their common nonmagnetic neighbors, which is more important than their direct exchange interaction. This type of magnetic interaction is called superexchange. Useful criteria for estimating the sign of the superexchange are given by the Goodenough-Kanamori rules [45, 46]. As a first step, one should determine the orbital symmetry of the magnetic orbitals. For instance, in the case of the transition metal ions, one considers populations of the $e_g$ and $t_{2g}$ levels according to the ligand field theory. Then, based on the orbital symmetry and the geometry of the system (in particular, the angle between the lines connecting the interacting magnetic centers via the nonmagnetic unit), one can estimate the sign and strength of the superexchange.
In essence, the rules state that non-overlapping (orthogonal) orbitals lead to positive \textit{potential superexchange}, causing ferromagnetic ordering, while overlapping orbitals generally lead to predominant negative \textit{kinetic superexchange} and antiferromagnetic coupling.

Yet another mechanism for magnetic interaction occurs between localized spins in metals, which are coupled through their interactions with the conduction electrons. This mechanism is particularly important in rare earth metals, which have spins in partially-filled \textit{f}-shells. As the \textit{f}-shells of the neighboring ions generally overlap very little, the direct exchange coupling is relatively weak, and the indirect exchange may be the dominant magnetic interaction. This indirect exchange is described by the RKKY model (Ruderman, Kittel, Kasuya, and Yoshida [47, 48, 49]). The RKKY indirect exchange between ions \textit{i} and \textit{j} is given by

\[ J_{ij} = \frac{J^2 m^*}{4(2\pi)^3 R_{ij} R_{ij}^2} \left[ 2k_F R_{ij} \cos(2k_F R_{ij}) - \sin(2k_F R_{ij}) \right], \]  

where \( J \) is the hyperfine interaction constant (the interaction between the ionic and conduction electron spins), \( m^* \) the effective electronic mass, \( R_{ij} \) the interionic distance, and \( k_F \) the Fermi wavevector. The RKKY exchange thus has oscillatory behavior, and can lead to both ferromagnetic and antiferromagnetic alignment of spins.

In metals there is also an important exchange interaction among the conduction electrons themselves, usually referred to as \textit{itinerant exchange}. In the independent electron approximation, the ground state of the electron gas is the state in which all states below the Fermi level are occupied with a pair of spin-up and spin-down electrons. When the Coulomb repulsion among electrons is included, two separate Fermi spheres emerge, one corresponding to spin-up electrons, the other to spin-down electrons. It can be shown that the total energy of the system is lowered with respect
to the noninteracting case if the number of spin-up electrons is greater than the number of spin-down electrons, thus a nonvanishing (ferromagnetic) magnetization is obtained [28, 41].

2.3.3 Anisotropic Exchange

In all the cases discussed above, the exchange Hamiltonian can be expressed in the Heisenberg form (2.44), thus the coupling is isotropic, i.e., it depends only on the relative orientation of the two spins, not on their directions with respect to the line connecting the two spins. For this reason the discussed interactions are all referred to as the isotropic exchange. This isotropy is a consequence of the spin independence of the original Hamiltonians and holds without any assumption about the spatial symmetries of these Hamiltonians. One must include terms that break rotational symmetry in spin space, such as dipolar interactions or spin-orbit coupling, in the original Hamiltonian, in order to produce a spin Hamiltonian with anisotropic coupling.

Based purely on symmetry considerations, Dzyaloshinskii [50] predicted that in crystals of low symmetry an interaction of the form [41]

$$\mathcal{H}_{DM} = D_{ij} \cdot (S_i \times S_j)$$

(2.48)

may exist (Dzyaloshinskii-Moriya (DM) exchange). Here $D_{ij} = -D_{ji}$ is a pseudovector related to the matrix elements of the orbital angular momentum. Moriya [51] found a microscopic mechanism for this interaction: the indirect coupling of spins through the spin-orbit interaction. The DM vector $D_{ij}$ is zero when the crystal field acting on the magnetic ions has inversion symmetry with respect to the center between the two magnetic ions. When $D_{ij}$ is nonzero the DM interaction favors
the perpendicular alignment of the two spins. The strength of the DM interaction is about an order of magnitude smaller than the isotropic exchange. Therefore the equilibrium spin configurations are canted, i.e., the spin orientations are somewhere between the two extremes of colinear (parallel or antiparallel) and perpendicular orientations.

Another important source of magnetic anisotropy is single-ion anisotropy, discussed in Section 2.2. If the single-ion anisotropy term $DS_i^2$ is included into Heisenberg exchange Hamiltonian, the total spin Hamiltonian becomes

$$\mathcal{H} = -J \sum_{i<j} S_i \cdot S_j + \sum_i DS_i^2.$$  \hspace{1cm} (2.49)

If $D$ is very large and negative, the energy is minimized by an axial spin configuration $S || \hat{z}$, and the spin Hamiltonian can be reduced to

$$\mathcal{H} = -J \sum_{i<j} S_{i,z} S_{j,z}.$$ \hspace{1cm} (2.50)

This simplified expression for the spin Hamiltonian is referred to as the Ising model, and it is widely used in the theory of magnetism because it significantly simplifies calculations compared to the Heisenberg ($D = 0$) model. If $D$ is very large and positive, planar configuration $S \perp \hat{z}$ is favored, and the Hamiltonian is reduced to

$$\mathcal{H} = -J \sum_{i<j} (S_{i,x} S_{j,x} + S_{i,y} S_{j,y}),$$ \hspace{1cm} (2.51)

referred to as the planar, or the XY model.

### 2.3.4 Magnetic Dipolar Interaction

While the discussed exchange interactions are quantum effects, the last interaction considered in this section, the dipole-dipole interaction, is of classical origin. The
interaction between two magnetic dipole moments $\mu_i$ and $\mu_j$ a distance $r_{ij}$ apart, is given by

$$H_{dip}^{ij} = \frac{\mu_i \cdot \mu_j - 3(\mu_i \cdot \hat{r}_{ij})(\mu_j \cdot \hat{r}_{ij})}{r_{ij}^3},$$

(2.52)

where $\hat{r}_{ij}$ is the unit vector along the line connecting the two dipoles. In solids the dipolar interaction is usually not considered as an important factor in magnetic ordering, as its strength is typically about three orders of magnitude lower than the Heisenberg exchange [28]. However, in certain cases, in which dipolar coupling between larger magnetic units rather than between atomic moments is considered, the effect of this coupling may be important, especially considering its long-range character. For instance, for materials composed of magnetic chains with strong intrachain exchange and very weak interchain exchange, the interchain dipolar interactions may lead to sizable ordering temperatures [52]. Furthermore, for a system consisting of single-domain magnetic nanoparticles (with the average magnetic moment per particle exceeding 1000 $\mu_B$), substantial dipolar interactions were obtained, leading to spin glass ordering at $T \sim 10$ K [53]. The dipole-dipole interaction is anisotropic, and can lead to both parallel orientation of magnetic moments (if the moments are oriented along $\hat{r}_{ij}$) and their antiparallel orientation (if the moments are perpendicular to $\hat{r}_{ij}$).

2.4 Types of Magnetic Ordering

In the absence of magnetic interactions, individual magnetic moments in the system are (in the absence of external field) thermally disordered at any temperature, and the average value of each vector moment is zero, giving zero total magnetization. In the presence of magnetic interactions, at sufficiently low temperatures these interactions may exceed the disordering effect of temperature and lead to nonvanishing
average vector moments (even in zero external field), and cooperative behavior of the moments, referred to as the magnetic order. The transition to a magnetically ordered state has properties of a second-order phase transition, at a well-defined critical temperature (or magnetic ordering temperature) $T_c$.

The best known examples of magnetic ordering are ferromagnetic (in which the moments have parallel alignment), antiferromagnetic (with antiparallel alignment of the neighboring moments), and ferrimagnetic (in which the neighboring moments are antiparallel, but nonequal, so that a net total magnetic moment is produced), Fig. 2.3. In the case of ferromagnets, the critical temperature is referred to as the Curie temperature $T_C$, while for antiferromagnets it is referred to as the Néel temperature $T_N$. For ferrimagnets both terms have been used, Curie temperature because of the existence of the net magnetization, like in ferromagnets, Néel temperature because of the antiferromagnetic ordering. To avoid confusion, the term 'ferrimagnetic Néel temperature' has been proposed [39]. As in any second-order phase transition, the state below the critical temperature $T_c$ is characterized by the occurrence of nonzero mean values of a quantity that had zero mean value in the disordered state; such a quantity is called the order parameter. In the case of ferro- and ferrimagnets the order parameter is (spontaneous) magnetization

\[ M = \frac{1}{N} \sum_i \langle \mu_i \rangle, \quad (2.53) \]

where the sum goes over $N$ magnetic moments $\mu_i$ in the system, and $\langle \rangle$ stands for the statistical mechanics average. In the case of antiferromagnets the magnetization is zero even below $T_N$, but the order parameter can be defined as [54]

\[ M_Q = \frac{1}{N} \sum_i \langle \mu_i \rangle e^{iQ \cdot r_i}, \quad (2.54) \]
Figure 2.3: Linear arrays of spins illustrating possible configurations: (a) ferromagnetic; (b) antiferromagnetic; (c) ferrimagnetic; (d) canted antiferromagnetic; (e) helical; (f) paramagnetic; (g) spin glass. The paramagnetic and spin glass states are compared by depicting the spin configurations at two different instants $t_0$ and $t_1$. 
(the 'staggered magnetization'), where the wavevector \( Q \) specifies the spatial periodicity of the antiferromagnetic state.

If anisotropic magnetic interactions are present, the ordered state may be characterized by non-collinear ground-state configurations of spins, including canted and helical (Fig. 2.3).

### 2.4.1 Mean Field Theory of Magnetic Ordering

The simplest theoretical approach to the problem of magnetic ordering is the mean field theory (MFT). It is based on the approximation in which the complex interaction of a given spin with its neighbors is replaced by an effective magnetic field acting on the spin. Here the MFT formalism will be illustrated [28] on the example of ferromagnetism. The results can be readily generalized to describe antiferromagnetism and ferrimagnetism.

If one considers the Heisenberg Hamiltonian, (2.45), and keeps only the part of the Hamiltonian that describes interaction of a particular spin \( S_i \) with its neighbors, one gets (in the presence of external field \( H \))

\[
\Delta \mathcal{H}_i = -S_i \cdot \left( \sum_{i<j} J_{ij} S_j + g \mu_B H \right). \tag{2.55}
\]

This equation has the form of the energy of a spin in an effective external field

\[
H_{\text{eff}} = H + \frac{1}{g \mu_B} \sum_{i<j} J_{ij} S_j. \tag{2.56}
\]

However, the 'field' \( H_{\text{eff}} \) is an operator that depends on the detailed spin configurations at sites different from \( i \). In the MFT this operator is replaced by its thermal equilibrium mean value. For a ferromagnet every spin has the same mean value,
which can be expressed in terms of the total magnetization $M$ as

$$\langle S_i \rangle = \frac{V M}{N g \mu_B}. \quad (2.57)$$

If each spin in (2.56) is replaced by its mean value, the expression for the effective field becomes

$$H_{\text{eff}} = H + \lambda M, \quad (2.58)$$

with

$$\lambda = \frac{V}{N (g \mu_B)^2}, \quad J_0 = \sum J_j. \quad (2.59)$$

The magnetization is determined by solving the equation

$$M = M_0 (H_{\text{eff}} / T), \quad (2.60)$$

where $M_0$ is the magnetization in the absence of interactions. This magnetization was calculated in the first section of this chapter (Equation (2.13)) and it depends on $H$ and $T$ only through their ratio, which is taken into account in (2.60). If there is a spontaneous magnetization $M(T)$ (magnetization in the absence of field, the ferromagnetic order parameter) at a temperature $T$, it will be given by a nonzero solution to (2.60) when $H = 0$. For $H = 0$ the effective field becomes $H_{\text{eff}} = \lambda M$, therefore

$$M(T) = M_0 (\lambda M(T) / T). \quad (2.61)$$

This equation can be solved graphically. Equation (2.61) can be written as a system of equations

$$M(T) = M_0 (x), \quad M(T) = \frac{T}{\lambda} x. \quad (2.62)$$

For each $T$ the solution to (2.61) (if any) is given by the intercept of the straight line $T x / \lambda$ with the graph of $M_0(x)$ (Fig. 2.4). The solution will exist if and only if the
Figure 2.4: Graphical solution to the mean-field theory equations 2.62 (after Ref. [28]). For $T > T_c^{MF}$ there are no solutions with nonzero spontaneous magnetization $M(T)$. For each temperature $T_i < T_c^{MF}$ there is a solution with nonzero $M(T_i)$. $M_s$ denotes the saturation magnetization.

The slope of the straight line, $T/\lambda$, is less than the slope of $M_0(x)$ at the origin, $M'_0(x = 0)$.

The MFT critical temperature $T_c^{MF}$ is defined by the limiting case $T_c^{MF}/\lambda = M'_0(0)$.

The slope $M'_0(0)$ can be expressed in terms of the susceptibility calculated for zero field and in the absence of interactions, $\chi_0$:

$$\chi_0 = \left(\frac{\partial M_0}{\partial H}\right)_{H=0} = \left(\frac{\partial M_0(H/T)}{\partial(H/T)}\right)_{\mu=0} = \frac{M'_0(0)}{T}. \tag{2.63}$$

By comparing this result with the explicit form of $\chi_0$, given by the Curie law:

$$\chi_0(T) = \frac{N(g\mu_B)^2 S(S+1)}{V 3 k_B T}, \tag{2.64}$$

one obtains for the limiting case

$$\frac{T_c^{MF}}{\lambda} = M'_0(0) = T_c^{MF} \chi_0(T = T_c^{MF}), \tag{2.65}$$
and finally

\[ T_c^{MF} = \frac{N (g \mu_B)^2 S (S + 1)}{3 k_B} \lambda = \frac{S (S + 1)}{3 k_B} J_0. \]  

(2.66)

The MFT susceptibility is obtained by differentiating (2.60):

\[ \chi = \frac{\partial M}{\partial H} = \frac{\partial M_0}{\partial H_{eff}} \frac{\partial H_{eff}}{\partial H} = \chi_0 (1 + \lambda \chi), \]  

(2.67)

which gives

\[ \chi = \frac{\chi_0}{1 - \lambda \chi_0}, \]  

(2.68)

where \( \chi_0 \) is calculated in the field \( H_{eff} \). Above \( T_c^{MF} \) and in the limit of zero applied field, \( H_{eff} \) vanishes, and \( \chi_0 \) assumes the Curie law form. The last equation then gives for the zero-field susceptibility above \( T_c^{MF} \):

\[ \chi = \frac{N (g \mu_B)^2 S (S + 1)}{V 3 k_B} \frac{T - T_c^{MF}}{T - T_f}. \]  

(2.69)

This expression is known as the Curie-Weiss law. It can be shown [28, 39] that the MFT gives a spontaneous magnetization that varies as \( (T_c^{MF} - T)^{1/2} \), regardless of the dimensionality of the lattice. Near \( T = 0 \) the MFT predicts the deviation of the spontaneous magnetization from its maximum value by a term of order \( \exp(-J_0 S/k_B T) \).

The mean-field theory fails to accurately predict much of the behavior experimentally observed, and determined by more accurate treatments, especially in the vicinity of the critical temperature. The critical temperatures in ferromagnets are lower by as much as a factor of 2 than the MFT prediction. This disagreement, however, reduces with increasing lattice dimensionality and coordination number. Near \( T_c \) the measured and calculated susceptibilities of three-dimensional ferromagnets diverge as \( (T - T_c)^{-\gamma} \), with critical exponent \( \gamma \) between 5/4 and 4/3, rather than 1 given by Eq. 2.69. The spontaneous magnetization near \( T_c \) varies as \( (T_c - T)^{\beta} \), with \( \beta \) depending on the lattice dimensionality, and being close to 1/3 for most three-dimensional
systems, rather than 1/2 predicted by the MFT. The exponential deviation of the spontaneous magnetization from the saturation value is replaced by a $T^{3/2}$ behavior in the more accurate treatment. However, the first-order correction to the high-$T$ Curie law, given by Eq. (2.69), does agree with the more exact result.

The main reason for these failures of the MFT is the fact that it completely neglects the thermodynamic fluctuations, i.e., it replaces the actual configurations of the local variables (e.g., spins) by their average value [55]. The more spins that interact with a particular test spin, the more appropriate is the approximation of this interaction by an effective field acting on the test spin. The number of spins producing the effective field increases with the range of interaction and with the lattice dimensionality. Consequently, the MFT becomes more accurate in higher dimensionalities and for long-range interactions.

Despite its inadequacy, the mean-field theory has been widely used as a starting point for more sophisticated calculations. It has an advantage of being mathematically simple, and it is usually the first approach taken to predict phase diagrams and properties of new experimental systems.

The MFT approach analogous to the one for ferromagnets, summarized above, is applied to antiferromagnets and ferrimagnets. In these cases, the ordered state is viewed as consisting of two interpenetrating magnetic sublattices (A and B), with neighboring spins belonging to different sublattices, oriented in opposite directions. The analysis similar to the one for ferromagnets gives the following expression for the zero-field susceptibility above the critical temperature

$$\chi = \frac{C}{T + \theta}, \quad \theta > 0, \quad (2.70)$$
for both the antiferromagnetic and ferrimagnetic case. The expression is called the Curie-Weiss law, as in the ferromagnetic case. Here the Curie constant is given by

$$C = \frac{(g\mu_B)^2}{3NV_{kB}} [N_A S_A(S_A + 1) + N_B S_B(S_B + 1)],$$

(2.71)

where $N_A, N_B$ are the numbers of spins in sublattices A and B, and $S_A, S_B$ are spin values for the sublattices (equal in the case of antiferromagnetism, different in the ferrimagnetic case). The constant $\theta$ (the Weiss constant or Weiss temperature) is given by a complicated expression involving the exchange coupling constants within and between the sublattices [39]. The critical temperature also can be calculated, and in general it is different from $\theta$, in contrast to the ferromagnetic case [39].

Thus, the deviation of the high-$T$ susceptibility from the paramagnetic behavior (the Curie law) is expressed with a positive constant $T_{cMF}$ in the denominator in the case of ferromagnetism, and with a negative constant $-\theta$ in the case of antiferro- and ferrimagnetism. In more accurate theoretical treatments the same expressions are obtained for the first-order corrections to the Curie law. In general, the higher the temperature, the more accurate the Curie-Weiss law becomes. As a rule of thumb, fitting of the experimental susceptibility data to the Curie-Weiss law should be done at temperatures at least five times higher than the magnetic ordering temperature for the material studied. In practice, high-$T$ data for $\chi^{-1}$ are plotted versus $T$, and constants $C$ and $\theta$ ($T_{cMF}$) determined from the slope and abscissa intercept of the linear fit. The Curie constant $C$ thus obtained can give useful information about the nature of the independent spins present (effective $g$-factor, total $S$, presence of the single-ion anisotropy), while the Weiss constant gives a qualitative estimate of the strength of exchange interactions in the system.

41
2.4.2 Critical Region: Scaling and Universality

As noted above, the practical applicability of the mean field theory is in most cases limited to a qualitative predictions of the types of magnetic ordering and the high-\(T\) behavior in the material studied, while it completely fails to accurately describe the critical behavior (singular behavior in physical quantities near \(T_c\)). A theory that successfully accounts for the critical phenomena relies on the scaling hypothesis. In this approach the most relevant physical quantity is the spin correlation function, which describes the spatial correlations of spins (it can be understood as a measure of the 'degree of order' in the system). The scaling hypothesis is based on the assumption that the only relevant length scale in the system near \(T_c\) is the spin correlation length \(\xi\), which is a characteristic length for the spatial decay of the spin correlation function. According to this hypothesis all physical quantities in the critical region are scaled with one parameter \(\xi\). Thus the singular temperature dependence of the meaningful physical quantities enters the equations only through \(\xi(T)\), and any additional dependence on \(T\) is smooth near \(T_c\), and can be neglected.

The physical meaning of the scaling hypothesis can be found in the argument that near \(T_c\) the system becomes long-range ordered, which means that spins are correlated over large distances (the correlation length diverges). Thus the structure on the length scales shorter than \(\xi\) is unimportant for critical phenomena [41]. The independence of the critical behavior on the microscopic details of the particular system is reflected in the fact that the critical exponents depend only on the spatial dimension, the symmetry of the order parameter, and the symmetry and range of interactions, but not on the detailed form and magnitude of interactions [55]. This constancy of exponents over a wide range of systems with the same dimensionality...
and symmetry properties is called universality, and systems with the same critical exponents are referred to as the universality classes.

The spin correlation function is defined as \[ C(r) = \langle S(r) \cdot S(0) \rangle. \] (2.72)

For a paramagnet (in zero field), \( C(r) \) decays exponentially to zero in the large separation limit \( r \to \infty \), while in the ferromagnetic phase it tends to \( \langle S^2 \rangle \). The Fourier transform of the correlation function is given by

\[ C(k) = \int C(r) e^{-ikr} dr, \] (2.73)

and it diverges as \( k \to 0 \) and \( T \to T_c \) \[41\]. Since \( C(k) \) has a sharp peak at \( k = 0 \), one can define the correlation length as the inverse of the width of this peak \[41\]:

\[ \xi^2 = -\frac{1}{2} C^{-1}(0) \left( \frac{d^2 C(k)}{dk^2} \right)_{k=0}. \] (2.74)

Experiments show that the transition into an ordered state at \( T_c \) is characterized by a power-law divergence of \( \xi \): \( \xi \propto |\mathcal{T}|^{-\nu} \), where \( \mathcal{T} \) is reduced temperature, defined as

\[ \mathcal{T} = \frac{T - T_c}{T_c}. \] (2.75)

Furthermore, the specific heat \( c_V \) and susceptibility \( \chi \) diverge as \( c_V \propto |\mathcal{T}|^{-\alpha} \) and \( \chi \propto |\mathcal{T}|^{-\gamma} \), while the critical behavior of the order parameter (magnetization) is described by \( M \propto |\mathcal{T}|^{\beta} \). These relations are referred to as the scaling laws, and the exponents \( \alpha, \beta, \gamma, \) and \( \nu \) are examples of the critical exponents.

In order to illustrate the application of the scaling hypothesis, let us consider the scaling of the free energy density \( f \). In \( d \)-dimensional space, \( f \) has units of energy\((\text{length})^{-d}\). Near \( T_c \) the energy scale is given by \( k_BT_c \), while, according to the
scaling hypothesis, the only relevant length scale is given by $\xi$. Thus we can write, for $T \to 0$

$$f \propto T\xi^{-d} \propto T^{\nu d}.$$  \hfill (2.76)

The specific heat is given by

$$c_V = -T \frac{\partial^2 f}{\partial T^2} \propto T^{\nu d-2} = T^{-d}.$$  \hfill (2.77)

Based on the scaling hypothesis the free energy density as a function of temperature and external field $H$ obeys a homogeneity relation [55]

$$f(T, H) = \xi^{-d} f(T \xi^{1/\nu}, H \xi^\lambda).$$  \hfill (2.78)

This equation allows us to calculate the order parameter and the susceptibility as

$$\langle M \rangle = \frac{\partial f}{\partial H} = \xi^{-d+\lambda} f'(T \xi^{1/\nu}, H \xi^\lambda) \propto T^{\nu - \nu}$$  \hfill (2.79)

$$\chi = \frac{\partial^2 f}{\partial H^2} = \xi^{-d+2\lambda} f''(T \xi^{1/\nu}, H \xi^\lambda) \propto T^{2\nu - \nu}$$  \hfill (2.80)

According to Equations (2.77), (2.79), and (2.80) the following relationships hold between the critical exponents

$$\alpha = 2 - \nu d, \quad \beta = d\nu - \Delta, \quad \gamma = -d\nu + 2\Delta,$$  \hfill (2.81)

where $\Delta \equiv \lambda \nu = \beta + \gamma$. Thus the scaling hypothesis reduces the number of the independent critical exponents.

The scaling hypothesis is also applied to dynamic properties. Similar to the static case, the relaxation time, and the dynamic variables in general, have their singular behavior in the vicinity of $T_c$ determined by the correlation length. For instance the
Figure 2.5: The single-domain (a) and multiple-domain (b) structures. A ferromagnetically ordered solid reduces its dipolar energy by breaking up into a complex structure of magnetic domains.

scaling law for the relaxation time $\tau$ is given by $\tau \propto \xi^z$, where $z$ is the dynamical critical exponent.

The firm theoretical basis for the scaling hypothesis and a method to calculate the critical exponents were given by the renormalization group theory of K. Wilson [56, 57].

2.4.3 Magnetic Domains

It was stressed in Section 2.3 that the magnetic dipolar coupling can in most cases be neglected in considerations of the microscopic mechanisms for magnetic ordering. However, this interaction has a profound effect on the magnetic response of a bulk ferro- or ferrimagnet. While the exchange interaction is much stronger than the dipolar interaction, it is quite short-ranged. In contrast, the dipolar interaction is
long-ranged, and consequently dipolar energies become significant when large num-
bers of spins are involved, which can considerably alter the spin configuration favored
by the exchange interaction.

A configuration with uniform magnetization throughout the bulk of a ferromag-
netically ordered material would be exceedingly uneconomical in dipolar energy. The
dipolar energy can be reduced by dividing the specimen into uniformly magnetized
domains of macroscopic size (such that long-range ferromagnetic order exists within
each domain), with domain magnetization vectors pointing in different directions
(Fig. 2.5). For spins near the boundary between two domains this subdivision is en-
ergetically unfavorable, since they experience ferromagnetic exchange coupling with
spins from the neighboring misaligned domain. However, as the exchange interaction
is short-ranged, this increase in the exchange energy will be limited to the spins near
domain boundaries. In contrast, the decrease in magnetic dipolar energy is a bulk
effect: the dipolar energy of every spin drops when domains are formed. Thus, unless
the domains are too small, domain formation will minimize the total energy.

While Fig. 2.5 suggests abrupt boundaries between domains (domain walls), in
reality this is not the case, as it would be unnecessarily costly in exchange energy.
The surface energy of a domain wall can be reduced by spreading out the reversal of
spin direction over many spins, each spin differing in orientation from its neighbor by
a small angle. Thus the domain wall has a finite width $l_d$. This width is determined
by a balance between the exchange energy and the magnetic anisotropy energy. The
magnetic anisotropy causes dependence of the energy of spins on their absolute ori-
entation with respect to the crystal axes (single-ion anisotropy, discussed in Section
2.2), as well as their relative orientation with respect to each other (due to, e.g., the
Dzyaloshinskii-Moriya interaction). Within the domain wall the anisotropy energy will, on average, contribute a fixed energy per spin to the energy of a line of deviant spins, and will for a sufficiently thick wall outweigh the reduction in the exchange energy made possible by the gradual reversal of the spin direction within the wall. Assuming that the only source of magnetic anisotropy is the single-ion anisotropy, described by the (phenomenological) anisotropy constant $K_1$, the total energy of a domain wall per unit area is given by

$$E_w = \frac{\pi^2 J S^2}{a l_d} + K_1 l_d,$$

(2.82)

where $a$ is the lattice constant. The first term in (2.82) is the contribution of the exchange energy to the total energy, while the second term describes the contribution of the anisotropy energy. The wall thickness $l_d$ is found from the condition that $E_w$ is minimum and it is given by

$$l_d = \sqrt{\frac{\pi^2 J S^2}{K_1 a}}.$$

(2.83)

If magnetic anisotropy in the system is very small, $l_d$ can become comparable to the size of domain itself. In these cases the domain picture becomes inapplicable.

2.4.4 Spin Glass Ordering

Spin glasses are systems exhibiting cooperative magnetic behavior fundamentally different from that of conventional magnetically ordered systems discussed above. At sufficiently low temperatures, spins in these systems become 'frozen' in random directions. By this it is meant that each individual spin has a specific orientation that varies very little in time, but these spin orientations vary randomly throughout the material, thus producing a state with little or no spatial order. A contrast between the spin glass and paramagnetic states is illustrated in Fig. 2.3.
From the experimental point of view, spin glasses are characterized by the following properties:

- The magnetic susceptibility \( \chi \) measured in zero dc field (static field) shows a cusp or a peak at a characteristic temperature ('the freezing temperature'). The freezing temperature \( (T_f) \) depends on the time scale of the experiment; the shorter the time scale, the higher \( T_f \). This means that if \( \chi \) is measured in alternating magnetic field ('ac' field), the position of the peak in \( \chi \) shifts to higher temperatures with increased frequency \( f \) of the applied ac field.

- Neutron diffraction pattern shows no magnetic Bragg peaks at any wavenumber and any temperature, indicating that no long-range spatial magnetic order is present.

- Below \( T_f \) the magnetic response is strongly history-dependent. The magnetization measured after cooling to \( T < T_f \) in finite applied dc field \( H \) (field-cooled magnetization, \( M_{fc} \)) is nearly reversible upon subsequent warming and cooling. In contrast, the magnetization measured after cooling in zero applied magnetic field, and subsequently applying a nonzero \( H \) (zero-field-cooled magnetization, \( M_{zfc} \)) is irreversible under subsequent temperature changes. Furthermore, \( M_{zfc} \) is much reduced compared with the \( M_{fc} \) value for the same applied field, and it exhibits a very slow increase towards \( M_{fc} \). The dynamics of this \( M_{zfc} \) increase depends not only on temperature and the applied field, but also on the time spent below \( T_f \) before the field was applied. The \( M_{fc}(T) \) and \( M_{zfc}(T) \) curves meet at the bifurcation temperature, which is strongly \( H \)-dependent, and which is for low \( H \) values close to \( T_f \) observed in the ac susceptibility measurements.
Figure 2.6: Examples of frustration (after Ref. [14]). (a) Frustration due to random exchange; (b) Geometric frustration.

- Upon field-cooling below $T_f$ and subsequently reducing $H$ to zero, spin glasses exhibit remanent magnetization, similar to ferromagnets. However, the remanent magnetization exhibits a slow decay with time.

- Below $T_f$ spin glasses exhibit magnetic hysteresis, with shape of the $M(H)$ hysteresis curve depending on the magnetic history and field sweeping rates.

- The magnetic contribution to the specific heat shows a broad maximum at temperatures somewhat above $T_f$.

Two conditions considered necessary for a physical system to exhibit spin glass behavior are randomness (positions of spins in the material should be random) and frustration. A spin system is said to be frustrated if the interaction between spins is such that no configuration can simultaneously satisfy all bonds and minimize the energy at the same time. Frustration can be produced by competition between interaction of different kinds (e.g., competing ferro- and antiferromagnetic interactions, or competing nearest-neighbor and next-nearest-neighbor interactions) or by the lattice
topology (e.g., triangular, kagomé, pyrochlore lattices with antiferromagnetic nearest-neighbor interactions). Two examples of frustrated Ising spin systems are shown in Fig. 2.6. The first system (Fig. 2.6(a)) shows frustration due to randomly distributed antiferro- and ferromagnetic exchange, while the second system (Fig. 2.6(b)) shows geometry-produced frustration in a two-dimensional triangular lattice with purely antiferromagnetic exchange. In both cases the ground state for the given group of spins is degenerate; for the entire lattice this degeneracy becomes exceedingly large.

The peculiar experimental behavior of spin glasses is a consequence of two properties that characterize the frozen state: extremely long (macroscopic) relaxation times, which cause the system to fall out of equilibrium, and very ‘rough’ free energy surface, with many local energy minima (metastable states) and, according to some theories, highly degenerate ground states.

The spin glass phenomenon was first discovered in magnetic alloys, like CuMn, AuFe, YDy, YEr, etc., in which d or f magnetic ions are randomly distributed through the crystal lattice. These ions interact through the long-range RKKY indirect exchange interaction (Eq. 2.47), which can be either ferro- or antiferromagnetic, depending on the interionic distance. Thus both randomness and frustration (resulting from competing ferro- and antiferromagnetic RKKY interactions of an ion with its neighbors) are present, and the alloys, in a certain range of concentrations of the magnetic ions, exhibit spin glass properties. These metallic spin glasses are often referred to as the canonical spin glasses. Subsequently, the spin glass state was also found in insulating systems, in which the origin of frustration can be found in competing nearest-neighbor and next-nearest neighbor superexchange interactions, or in
the lattice geometry. Another possible source of frustration are magnetic dipolar interactions, the sign of which can be positive or negative, as discussed in Section 2.3.

After years of controversy, it is now almost generally accepted that the transition into the spin glass state is a phase transition, although an unconventional one, characterized by an order parameter, critical (divergent) behavior of the spin glass correlation length $\xi_{\text{SG}}$ at the spin glass transition temperature $T_g$, and appropriate scaling relations. The spin glass transition temperature is to be distinguished from the freezing temperature $T_f$, the latter being the temperature at which spins appear to be frozen at the experimental time scale. The relaxation in the system begins to slow down even at $T > T_g$ and, instead of a single relaxation time, a broad distribution of the relaxation times develops, extending from the typical spin flip time $t_{\text{min}}$ (of the order of $10^{-9} - 10^{-13}$, depending on the system), to the maximum relaxation time $t_{\text{max}}$ (which rapidly increases as $T_g$ is approached). $T_f$ corresponds to the temperature where $t_{\text{max}}$ just extends out of the experimental time window, and it is the upper bound on $T_g$: $T_g = T_f(f \to 0)$, where $f$ is the experimental frequency [59].

The spin glass transition is characterized by an unconventional order parameter. Both the magnetization $M$ and any staggered magnetization $M_Q$ (Eqs. 2.53 and 2.54) remain zero below $T_g$, reflecting the lack of spatial long-range order. The first attempt to theoretically describe the spin glass transition was the Edwards and Anderson (EA) model [60]. The order parameter in the EA model is defined as

$$q_{\text{EA}} = \lim_{t \to \infty} \lim_{N \to \infty} \langle (S_i(0) - S_i(t)) \rangle_{\text{av}},$$

(2.84)

where $\langle \rangle$ denotes the statistical mechanics average and $\langle \rangle_{\text{av}}$ denotes ‘configurational’ average, i.e., average over the distributions of random interactions in the system. This order parameter can be understood as the time autocorrelation function for a spin,
averaged over all possible realizations of disorder in the system. The EA model uses the standard spin Hamiltonian

\[ \mathcal{H} = -\sum_{i<j} J_{ij} S_i \cdot S_j, \] (2.85)

and assumes a regular three-dimensional square lattice with the exchange couplings \( J_{ij} \) taken to be independent random variables symmetrically distributed about zero, according to a Gaussian distribution

\[ P(J_{ij}) \propto \exp\left(-\frac{J_{ij}^2}{2\Delta_{ij}^2}\right), \] (2.86)

where \( \Delta_{ij} \) depends only on the lattice vector separation \( \mathbf{R}_i - \mathbf{R}_j \). Edwards and Anderson, and subsequently Sherrington and Kirkpatrick (SK) [61], constructed the mean-field solutions to the EA model, finding that \( q_{EA} \) indeed develops a nonzero value at a finite temperature \( T_g \), as expected for an order parameter, accompanied by the occurrence of a cusp in the susceptibility, consistent with experiments. Furthermore, this model predicts that, while the linear susceptibility remains finite at \( T_g \), the nonlinear susceptibility diverges [62]. However, the model has significant flaws, including unphysical predictions for entropy (becomes negative below \( T_g \)) and free energy (in this model it is lower for \( q = 0 \) than for \( q \neq 0 \)). De Almeida and Thouless [63] showed that that the SK mean-field solution is invalid (unstable, i.e., has negative eigenvalues) at low temperatures, and that in the presence of applied field \( H \) the instability line \( T_{AT}(H) \) below which the SK solution is unstable behaves as [64]

\[ T_g - T_{AT}(H) \propto H^{2/3}, \] (2.87)

(de Almeida-Thouless, or AT instability line). An experimental consequence of this is that below the AT line irreversible magnetic behavior appears [64].
The problem with the SK solution is in the way the statistical averaging is performed. In the frozen state one is faced with the problem of *nontrivial broken ergodicity*. The ergodic hypothesis implies that in the long-time limit the time average and the statistical average over ensemble are the same, in other words for long enough times the system probes the entire phase space. However, it was shown that in the case of spin glasses this assumption ceases to hold below the $T_g$ line. Thouless *et al.* derived equations that avoided problems of the nontrivial broken ergodicity, and obtained physically meaningful results for the entropy and free energy [66]. Their equations turned out to have a large number of physical and stable solutions below
the AT line with different free energies. The number of these solutions \( N_s \) increases very rapidly as \( T \) is lowered: 
\[
N_s = \exp\left(\frac{8}{31}NT^6\right),
\]
with \( T = 1 - T/T_g \) [65], and \( N \) the total number of spins. Each of the solutions can be interpreted as a locally stable thermodynamic state, the free energy of which is not necessarily a global minimum [64]. The work of Parisi [67, 68] supported this picture of multiple free energy minima below \( T_g \). The situation can be visualized by a diagram in Fig. 2.7.

The scheme shows the free energy hypersurface, the horizontal axis representing the multi-dimensional phase-space coordinate. Above \( T_g \) there is only one free energy minimum. When \( T \) is decreased below \( T_g \), new local minima appear. As \( T \) is decreased further, each of these 'valleys' subdivides into others, and, simultaneously, the heights of the energy barriers separating the valleys rapidly increases [65]. Upon cooling below \( T_g \), the system finds itself in one of these valleys. As the system subsequently explores more of the phase space, it encounters ever increasing barrier heights; the time it takes for the transition from one valley to another increases exponentially with the barrier height [65], thus it takes infinite time for the system to explore the entire phase space (ergodicity is broken). Consequently, the system will in experiments reflect properties which are specific to one specific valley, which differ from true equilibrium properties that involve averages over all valleys with appropriate relative thermal weights [54].

Starting from this picture, strongly supported by the experimental work [65, 69], we can understand the large difference between the field-cooled and zero-field-cooled magnetizations observed in experiments. Upon zero-field-cooling below \( T_g \), and subsequently applying the external field, the system attempts to relax into a new equilibrium configuration that would minimize its free energy in the presence of the field. However, due to very large energy barriers below \( T_g \), within the experimental times
available the system can explore only a small part of the phase space in the vicinity of the local free energy minimum it occupied before the field was applied. Thus it relaxes very slowly towards the new equilibrium configuration (indicated by the slow increase in \(M_{fc}\)), being unable to reach it during the experimental times. In contrast, when cooled in applied field below \(T_g\), the system can effectively explore much larger part of the phase space, as the energy barriers for \(T \sim T_g\) are still not too high, and find a configuration close to the equilibrium one. Moreover, the slower the cooling is, the more time for phase space exploration the system has. Thus, the field-cooled state is much closer to the equilibrium state than the zero-field-cooled one, which is reflected in the higher magnetization \(M_{fc}\), as well as a nearly reversible behavior of \(M_{fc}\) upon heating and cooling.

As every second-order phase transition, the spin glass transition is characterized by scaling laws. The spin glass correlation function can be defined as [62]

\[
C_{SG}(R_i - R_j) = \langle (S_i S_j)^2 \rangle_{av},
\]

and it decays exponentially with distance in the paramagnetic phase, as

\[
C_{SG}(R_i - R_j) \propto \exp(-|R_i - R_j|/\xi_{SG}),
\]

where \(\xi_{SG}\) is the spin glass correlation length.

At \(T_g\) the correlation length diverges as

\[
\xi_{SG} \propto |T|^{-\nu},
\]

where \(T = (T - T_g)/T\) is the reduced temperature, while the relaxation time \(\tau\) diverges as

\[
\tau \propto \xi_{SG}^z \propto |T|^{-\nu z}.
\]
It is convenient to define the spin glass susceptibility (also called the order parameter susceptibility) \[54]\:

\[ x_{SG} = \frac{1}{(k_B T)^2}[(\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle)^2]_{av}, \tag{2.92} \]

which is directly related to the nonlinear susceptibility \(x_{nl}\) as

\[
x_{nl} = \frac{1}{k_B T} \left( x_{SG} - \frac{2}{3} \frac{1}{(k_B T)^2} \right). \tag{2.93} \]

The critical behavior of \(x_{SG}\) is given by the scaling law \[54]\]

\[ x_{SG} \propto |T|^{-\gamma}. \tag{2.94} \]

Thus the critical behavior that characterizes the spin glass transition can be experimentally detected by measuring the nonlinear susceptibility, which is defined as the coefficient of \(-H^3\) in the expansion of the magnetization in powers of the external field:

\[
M = xH - x_{nl}H^3 + \cdots \tag{2.95} \]

\(x_{nl}\) can be determined if the dc magnetization near \(T_g\) is measured at different applied dc magnetic fields \(H\). The deviation from linearity of the \(M(H)\) plot gives \(x_{nl}\). Alternatively, \(x_{nl}\) can be measured in the ac susceptibility experiment, as it can be shown (Ch. 3) that, for small applied ac fields, it is equal to the third harmonic susceptibility.

In some case spin glass behavior develops not from the paramagnetic, but from ferromagnetic phase. This somewhat counter-intuitive behavior (implying that the spatially ordered ferromagnetic phase has greater entropy than the spin glass phase \[13]\) is referred to as reentrance. Reentrance is often observed in alloys of transition metals and rare earths. A schematic phase diagram of such an alloy (very similar
Figure 2.8: Schematic magnetic phase diagram of a dilute alloy $M_xA_{1-x}B$, where $M$ is magnetic and $A$, $B$ nonmagnetic ions (e.g., $\text{Eu}_x\text{Sr}_{1-x}S$). PM, FM and SG denote paramagnetic, ferromagnetic and spin glass phases. The vertical dashed line denotes a concentration $x$ for which reentrant transition PM$\rightarrow$FM$\rightarrow$SG upon cooling is expected.

to the real phase diagram of $\text{Eu}_x\text{Sr}_{1-x}S$, see Ref. [54]) is shown in Fig. 2.8. Here the horizontal axis corresponds to the fraction $x$ of the magnetic ions in the alloy, while the vertical axis displays temperature. For a very diluted magnetic alloy (small $x$) the magnetic moments are decoupled and the alloy shows paramagnetic behavior. For high enough concentrations, and not too low temperatures, the paramagnet-ferromagnet transition occurs (the concentration $x_p$ at which ferromagnetic long-range order occurs is called the percolation limit). However, at lowest temperatures and for a limited range of $x$ the alloy shows spin glass properties. It is thus possible, for some $x$, that upon cooling the alloy undergoes successive transitions from paramagnetic to ferromagnetic to spin glass state (vertical line in Fig. 2.8).
Some of the experimental indications of reentrance are frequency-dependent peak in the ac susceptibility at $T_f$ usually considerably below the Curie temperature (the latter being indicated by a frequency-independent susceptibility peak), and nearly constant or decreasing field-cooled magnetization as $T$ is decreased below $T_f$ [70, 71].

Current models of the reentrance suggest that the observed behavior is not due to true transition from a pure ferromagnet to a pure spin glass, but rather that a longitudinal ferromagnetic order develops at higher temperature, followed by a freezing of the transverse spin components at a lower $T$, resulting in a magnet with randomly canted spins [13, 70].

Two examples of molecule-based magnets exhibiting reentrance are $V(\text{TCNE})_x\cdot y(\text{solvent})$ and $\text{Mn(TCNE)}_x\cdot y(\text{CH}_2\text{Cl}_2)$ [13, 72].

A number of experimentally studied systems exhibit properties that suggest a coexistence of short-range colinear (ferro-, antiferro- or ferrimagnetic) order and spin glass-like behavior. The colinear order is limited to 'clusters' of spins and, due to relatively small sizes of these clusters (much smaller than the domain size) the thermodynamic limit $N \rightarrow \infty$, cannot be assumed. Since this limit is a necessary condition for the critical (divergent) behavior that characterizes second-order phase transitions, the occurrence of the short-range order within clusters is not expected to show properties of a real phase transition. Cluster glass systems (or 'mictomagnets', as they were called in the earlier literature) are found among alloys of transition and rare-earth metals, for relatively high concentration of magnetic ions, as well as insulating systems, including molecule-based magnets. In the literature the term cluster glass has been inconsistently used both for systems that show signatures of cooperative spin glass-like freezing of clusters, and for systems in which cluster magnetic moments
appear to be poorly correlated and undergo progressive blocking (like in superparamagnets). In this thesis we define cluster glass as a system that exhibits a short-range colinear order within clusters of spins below a 'quasicritical temperature' $T_c$, and in which the cluster moments undergo cooperative freezing, like individual spins in 'normal' spin glasses, at a lower temperature $T_f < T_c$. Thus cluster glasses are considered a special case of spin glasses [62]. Cluster glasses are difficult systems to study or to model, therefore theoretical work on this topic is very scarce. Among the few attempts to address the issue, worth mentioning is the work of Soukoulis et al. [73, 74], who developed a 'cluster mean field theory' of concentrated spin glasses, in which spin clusters, rather than individual spins are the basic entity. This model predicts that the basic spin glass properties (a cusp in the susceptibility, a rounded peak in the specific heat, etc.) are preserved even in the concentrated regime. The model, however, assumes that the cluster sizes are independent on temperature, which is not likely to be realistic, as the decrease in temperature is expected to lead to a more effective clustering of spins.

2.4.5 Superparamagnets

The term superparamagnet (SP) refers to a system consisting of fine (single-domain) magnetic particles, in which interparticle magnetic interactions can be neglected. The spins within each particle are magnetically ordered (with spontaneous magnetization) and their ordering has already occurred at a temperature far above our considerations.

At relatively high temperatures, the vector magnetic moments of the particles undergo thermal fluctuations analogous to the fluctuations of individual spins in the case
of paramagnets. Thus the high-$T$ magnetization of the SP follows the paramagnetic law, given by the Brillouin function (identical particles are assumed)

$$M \propto (s + \frac{1}{2}) \coth \left( \left( s + \frac{1}{2} \right) \frac{g_\mu_B H}{k_B T} \right) - \frac{1}{2} \coth \left( \frac{g_\mu_B H}{2k_B T} \right),$$  \hspace{1cm} (2.96)

where $S$ denotes the total spin of a particle. Since $S$ is a large number (typically $> 10^3$), the Brillouin function has very slow saturation with increased $H$.

Each particle in the system has inherent magnetic anisotropy, which has origin in the single-ion anisotropy and the *shape anisotropy*. The shape anisotropy is a consequence of the fact that the magnetostatic energy of a body depends on the body's shape; for an ellipsoidal body magnetized along one of the principal axes, the shape anisotropy constant is given by: $K_s = 2\pi M^2 (D_\perp - D_\parallel)$, where $D_\perp$ and $D_\parallel$ are the demagnetization factors (the demagnetization effects and demagnetization factors are discussed in Ch. 3) perpendicular and parallel to the principal axis. The total anisotropy energy of a particle with volume $V$ is given by $E_a = KV$, with the total anisotropy constant $K = K_1 + K_s$ being the sum of the single-ion and shape anisotropy constants.

The energy of a particle has two minima (corresponding to the two magnetization directions along the principal axis), separated by the energy barrier $E_a$. At a finite temperature, thermal fluctuations give some probability of overcoming the energy barrier. The transition of the magnetization between the two states is described by the characteristic time $\tau$, given by

$$\tau = \tau_0 \exp \left( \frac{E_a}{k_B T} \right),$$ \hspace{1cm} (2.97)

where $\tau_0$ is a microscopic relaxation time. This formula is known as the *Arrhenius law*. Below a characteristic temperature, called the *blocking temperature* (given by
\( T_B = K V/25k_B \) \([75]\), the particle magnetic moment is blocked in one of the energy minima, as thermal fluctuations are insufficient to overcome the anisotropy barrier. The transition between the superparamagnetic and blocking regimes is characterized by a peak in the magnetic susceptibility, which is strongly frequency-dependent (much more so than in spin glasses). Moreover, the magnetic hysteresis occurs below \( T_B \). The behavior of superparamagnets thus shows similarities with spin glasses and it is sometimes not a trivial matter to distinguish between the two classes, particularly when one deals not with a pure SP, but a system with non-negligible interparticle interactions. A detailed analysis of the dynamic magnetic response in those cases is required, as will be shown on the example of Prussian blue magnets in Ch. 4.
CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 Sample Synthesis and Preparation

The polycrystalline samples of Prussian blue analogs $K_xCo_y[Fe(CN)_6]zH_2O$ were prepared by Dr. Jamie L. Manson at the University of Utah, following the literature method [3]. The starting compounds $CoCl_2$ and $K_3Fe(CN)_6$ were purchased and used as received. An aqueous solution of $CoCl_2$ was slowly added to a vigorously stirred aqueous solution of $K_3Fe(CN)_6$. The reaction produces precipitate of $K_xCo_y[Fe(CN)_6]zH_2O$, which is filtered and washed with methanol and diethylether. The synthesis was done at room temperature. The stoichiometry depends on the concentrations of solutions of the starting compounds. The thesis presents results for three different samples, denoted as samples A, B, and C in the text to follow. Stoichiometry was determined on the basis of elemental analyses done in Shwartzkopf Analytical Labs, Inc. The concentrations of starting solutions used and respective stoichiometries for the three samples used are given in Table 3.1.

The samples of $Mn(TCNE)_2 - y(CH_2Cl_2)$ were prepared by Dr. Jie Zhang and Dr. Chitoshi Kitamura at University of Utah, following the method from Ref. [26]. The starting material $MnI_2$ was prepared by stirring $Mn$ chips in $I_2/Et_2O$ solution at...
Table 3.1: Chemical compositions of Co-Fe Prussian blue analogs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>mol/l CoCl₂</th>
<th>mol/l K₂Fe(CN)₆</th>
<th>Formula</th>
<th>µ₆/unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.72</td>
<td>1.43</td>
<td>K₀.₆Co₁.₂[Fe(CN)₆]·4.₉H₂O</td>
<td>1.5</td>
</tr>
<tr>
<td>B</td>
<td>0.50</td>
<td>0.17</td>
<td>K₀.₄Co₀.₃[Fe(CN)₆]·4.₆H₂O</td>
<td>1.8</td>
</tr>
<tr>
<td>C</td>
<td>0.83</td>
<td>0.43</td>
<td>K₀.₂Co₁.₄[Fe(CN)₆]·6.₀H₂O</td>
<td>2.4</td>
</tr>
</tbody>
</table>

room temperature. The resulting solid was filtered, washed with Et₂O and dissolved in CH₃CN. The solution was cooled to -35°C, and yellow crystals were obtained. This solid was dried under vacuum at 135°C for 6 h. The material synthesis then proceeded as follows. A solution of MnI₂ (279 mg) in CH₂Cl₂ (20 ml) was prepared and ca. 2 ml of CH₃CN was added in this solution until the mixture became clear. The mixture was then added slowly to 293 mg (2.29 mmol) of TCNE in 30 ml of CH₂Cl₂. This produced an immediate precipitation. The reaction mixture was then stirred at room temperature for 24 h. The precipitated powder was filtered and washed with 150 ml of CH₂Cl₂ until the filtrate was colorless. The solid was dried at room temperature under vacuum for 2.5 h. The elemental and thermogravimetric analyses gave values of stoichiometric coefficients of x ≈ 2 and y ≈ 0.8. Several batches of the material were prepared. While samples from different batches exhibit nearly identical values of 75 K for the ferrimagnetic ordering temperature, as well as qualitatively the same magnetic and PIM behavior, the position of the low-temperature peak varies from batch to batch (in the range ~5-10 K), which is attributed to the variation of the solvent content y.
As both materials studied are in the form of fine powders, their specific surface area is very large, which greatly enhances sensitivity to oxygen exposure, adsorption of water from atmosphere, and loss of solvent. After exposure to air of several hours the materials show a decrease in magnetic moment. For $\text{K}_x\text{Co}_y\text{[Fe(CN)$_6$]}\_z\text{H}_2\text{O}$ this is accompanied by a decrease in the characteristic transition temperatures. For $\text{Mn(TCNE)$_x$} \cdot \gamma(\text{CH}_2\text{Cl}_2)$ the reentrant transition peak temperature quickly decreases, while $T_c$ is more robust. Upon several days of exposure to air both materials lose signatures of magnetic order, and their colors change (from deep purple to black for $\text{K}_x\text{Co}_y\text{[Fe(CN)$_6$]}\_z\text{H}_2\text{O}$, from dark green or dark yellow to brown for $\text{Mn(TCNE)$_x$} \cdot \gamma(\text{CH}_2\text{Cl}_2)$). In order to prevent degradation, materials were stored in glass tubes sealed in argon atmosphere. Magnetic measurements of bulk samples (>10 mg) were also done on samples sealed in glass tubes. All manipulation of samples was done in a VAC dry box with argon atmosphere ($\text{O}_2$ and $\text{H}_2\text{O}$ content < 10$^{-6}$).

For optical studies of $\text{Mn(TCNE)$_x$} \cdot \gamma(\text{CH}_2\text{Cl}_2)$ samples were prepared by grinding the powders and mixing them with viscous transparent liquids and placing thus obtained paste between two transparent slides (mull method). For the UV-Vis-NIR spectral region Nujol mineral oil and and quartz slides were used, while Fluorolube liquid polymer and KBr plates were used in the MIR region. The KBr pellet method was not used because of the known property of Br$^-$ ion to replace ligand in some organometallic compounds [76], thus giving false spectral data.

For the experimental studies of photoinduced magnetic effects samples need to be prepared so that their thickness in direction of the incident visible light is of the order of the penetration depth of visible light (typically ~1 µm for an insulating solid). This enables conversion into the photoexcited state throughout the bulk of
the sample studied. Samples prepared in this way have small mass and produce very small magnetic signals, which sometimes approach the sensitivity limits of the SQUID magnetometer and ac susceptometer. Prussian blue samples were prepared by encapsulating the powders in Stycast transparent nonmagnetic epoxy resin and shaping the resin into tablets before it cures. No signs of chemical reaction between the Prussian blue analogs and the resin were detected. Thus obtained samples were transparent for visible light, while containing sufficient amount of $\text{K}_2\text{Co}_3[\text{Fe(CN)}_6] \cdot \text{zH}_2\text{O} \ (\sim 1 \text{ mg})$ to achieve good signal/noise ratio in low-temperature magnetic measurements. Samples of $\text{Mn(TCNE)}_x \cdot y(\text{CH}_2\text{Cl}_2)$ were prepared by applying a small amount ($\sim 50 \mu\text{g}$) of powder in a thin layer on a piece of adhesive tape. The tape was placed in a transparent gelatin (or, alternatively, quartz) capsule, and the capsule sealed with teflon powder, in order to prevent significant exposure to air while transferring the sample from the drybox to the magnetometer/susceptometer. Samples prepared in this way are still relatively thick, since estimated penetration depth of blue-green light in $\text{Mn(TCNE)}_x \cdot y(\text{CH}_2\text{Cl}_2)$ is only about $\sim 0.4 \ \mu\text{m}$, therefore very long illumination period (2-3 days) was needed to achieve saturation of the PIM effect. For the presented SQUID study of PIM in which saturation was achieved in about six hours (Fig. 5.9), the sample was prepared by dispersing the $\text{Mn(TCNE)}_x \cdot y(\text{CH}_2\text{Cl}_2)$ powder in Nujol mineral oil, filtering the dispersion to select the smallest particles, and subsequently sealing it in a quartz capsule.

While the above described preparation methods for PIM measurements did not change the general magnetic behavior of the materials (compared to bulk samples sealed in glass tubes), the following minor differences were detected. Peaks in the magnetic susceptibility vs. temperature curves were more rounded than in the bulk
samples, which is attributed to different demagnetization factors for a bulk sample and a thin-layered or encapsulated sample. The $M_{sfe}$ and $\chi_{ac}$ peaks for Prussian blue samples and the low-$T$ $\chi_{ac}$ peak for Mn(TCNE)$_x$ - $y$(CH$_2$Cl)$_2$ shifted by 0.5-1 K to lower temperatures compared to bulk samples. This may be attributed to a minor loss of solvent and/or oxidation that may have occurred in spite of the extreme precautions taken in handling the samples. Alternatively, the origin of these shifts may possibly be found in the fact that the preparation methods used selected the smallest particles from the bulk, which may have somewhat different magnetic behavior from larger particles. (e.g., due to the approach to the single-domain limit). As a consequence of these effects, random from sample to sample, a quantitative comparison between different samples prepared for PIM is not possible. For Prussian blue analogs, comparison of samples with different composition, given in Ch. 4 (Table 4.1), is based on the data obtained for bulk samples. Another limitation of the samples prepared for PIM is that masses of the magnetic components were impossible to determine with certainty in most cases. Therefore magnetization and susceptibility on most of the graphs showing PIM data are displayed in the units of magnetic moment (emu).

3.2 Sample Illumination

Illumination of Prussian blue samples was done using a halogen lamp and interference filters, while for Mn(TCNE)$_x$ - $y$(CH$_2$Cl)$_2$ an argon ion laser (Coherent Innova 300C) was also used. In optical experiments samples were illuminated directly by laser beam through the window of the optical cryostat. SQUID magnetometer was equipped with a Fiber Optics Sample Holder (FOSH), manufactured by Quantum Design, while a home-made fiber optics sample holder was made for the
ac susceptometer. These accessories allow illumination of samples inside the magnetometer/susceptometer. Light from lamp/laser was directed to the sample holders by optical fiber guides. The reported power of light was measured by a pyrometric power meter at positions approximately corresponding to the positions of samples during the measurements. Polarization of light was random in all measurements.

### 3.3 SQUID dc Magnetometry

Superconducting Quantum Interference Devices (SQUIDs) are magnetic flux detectors with unparalleled sensitivity, which are based on the Josephson effect. This effect consists of the occurrence of electric current between two pieces of superconductor separated by a 'weak link,' a small region in which the superconductivity is weakened (for instance, a very thin insulating layer). Such configuration is called Josephson junction. A SQUID consists of a superconducting ring interrupted by either one (rf SQUID) or two (dc SQUID) Josephson junctions. In the absence of weak links no extra magnetic flux can enter the ring, as superconducting current would be induced to compensate the extra flux. When a weak link is added a change in flux is allowed, the variation being one flux quantum \( \Phi_0 \) at a time. If a coil is inductively coupled with the superconducting ring then a voltage pulse is induced in the coil at each ring current jump corresponding to a flux variation. This voltage pulse can be used to measure the magnetic flux density [77, 58].

In the Quantum Design Magnetic Property Measurement System (MPMS-5) [78] the detection system consists of an rf SQUID inductively coupled to a set of three coils configured as a second-order (second-derivative) gradiometer. The three coils consist of a single piece of superconducting wire, the upper coil having a single turn.
wound clockwise, the center coil having two counter-clockwise turns, and the bottom
coil a single clockwise turn (Fig. 3.1).

The detection coils are positioned at the center of a 5.5 T superconducting magnet,
outside the sample chamber. The gradiometer configuration is used to reduce the
noise in the detection circuit, caused by the fluctuations in the large magnetic field
of the superconducting magnet and other sources. If the background field is changing
randomly with time but in a spatially uniform manner over the region occupied by
the coils, no change will be detected [77].
Figure 3.2: Response of MPMS to dipole point source moving through the second-derivative system of coils.

The measurement is performed by moving the sample along the common axis of the detection coils. The change in the sample position causes a change in the magnetic flux density, which is detected in the coil as a variation in current. The system finally measures voltage as a function of position and determines the magnetic moment of the sample by fitting the response to that of an ideal dipole (Fig. 3.2).

The MPMS-5 system enables measurements in the region of dc fields $0 \leq H_{dc} \leq 55$ kOe, at temperatures between 1.7 and 400 K. Magnetic moments as low as $10^{-8}$ emu are detectable.

While MPMS-5 is fully automated and easy to operate, it poses several limitations which require precautions in order to obtain reliable data.
The MPMS response depicted in Fig. 3.2 is given for an ideal dipole, the vertical dimension of which is negligible with respect to the dimensions of the gradiometer. The samples used that are too long (> 1.5 cm) will produce a significantly distorted response curve. Fitting such curve with functional form describing the ideal dipole response will give false values of magnetic moment. In the extreme case, when a homogeneous object moving through the gradiometer is longer than the gradiometer itself, no signal will be detected at all. This feature is sometimes advantageous because it enables mounting of samples on probes with non-negligible magnetic susceptibilities, which are not being detected by the coils. Typically, a sample is placed inside a long plastic straw. While the straw has diamagnetic susceptibility that in some cases may present an appreciable fraction of the sample’s susceptibility, no signal from the straw is detected, as long as it is homogeneous. In the FOSH probe used for PIM measurements, samples are placed in a void of a quartz sample holder. While the bulk of the sample holder has a (negative) diamagnetic susceptibility, the detected magnetic signal of the empty probe, produced by the void in the diamagnetic background, is positive (‘antidiamagnetic’).

Before measurements the sample centering needs to be performed. Due to temperature variations during the measurements the sample position may significantly change. Thus, during measurements over large $T$ ranges, an automatic centering routine should be performed at every 5-10 K.

As the MPMS superconducting magnet is based on a type-II superconductor, once the applied current drives the magnet above the lower critical field $H_{cl} \sim 100$ Oe, the magnet will retain a remanent field $H_{rem}$ upon removal of the current. The remanent fields may exceed 10 Oe when the magnet is ramped to the maximum
field of 55 kOe and back to zero. This makes the real value of the subsequently applied field uncertain. The method used to reduce $H_{\text{rem}}$ is oscillation of the applied field from the maximum field available to zero, in progressively smaller steps, for instance: $H_0, -H_0/2, H_0/4, -H_0/8, ... 0$. The remanent field trapped in the magnet after this procedure is below 1 Oe, and it can be determined with precision of $\sim 0.1$ Oe by measuring the $M(H)$ dependence for a Pd paramagnetic standard in the region $-10 \leq H \leq 10$ Oe. The correction for this small remanent field should then be taken into account when setting the nominal field values. In the coercivity measurements presented in Ch. 4, $H_{\text{rem}}$ was determined by measuring the hysteresis loop for the Pd standard. This hysteresis loop is an artifact produced by the presence of $H_{\text{rem}}$, and values of $H_c$ measured for the sample were corrected for $H_{\text{rem}}$.

3.4 AC Susceptometry

In contrast to dc magnetometry, the principle of operation of ac susceptometry involves subjecting the sample material to a small alternating magnetic field. The flux variation due to the sample is picked up by a sensing coil surrounding the sample and the resulting voltage induced in the coil is detected by a lock-in amplifier. This voltage is directly proportional to the magnetic susceptibility of the sample [79]. Using phase-sensitive lock-in detection, this simple yet powerful method allows both the real ($\chi'$) and imaginary ($\chi''$) parts of the complex susceptibility $\chi_{ac} = \chi' - i\chi''$ to be determined. Furthermore, nonlinear contributions to the susceptibility can be measured, by detecting the output signal at integer multiples of the driving frequency, as will be explained in the text below.
Figure 3.3 shows schematically how the principles of ac susceptometry are incorporated into the Lake Shore Cryotronics 7225 ac Susceptometer/dc Magnetometer system [79]. The alternating magnetic field $H_{ac}$ (up to 25 Oe RMS) is generated by a solenoid which serves as the primary in a transformer circuit. Two identical, but counterwound, pick-up coils connected in series are positioned symmetrically within the primary coil and serve as the secondary coils in the measuring circuit. The two pick-up coils are wound in opposition in order to cancel the voltages induced by the ac field itself or by unwanted external sources. Assuming perfectly wound coils and perfect symmetry, no voltage will be detected by the lock-in amplifier when the coil assembly is empty. However, the electronic sensitivity of the measurement system exceeds the physical capability of manufacturing two identical secondary coils. As a result, a slight offset voltage $v_{off}$ is read even when no sample is present. The compensation for $v_{off}$ is provided by the ability to move the sample between the two pick-up coils and make measurements in these two positions.

Besides ac susceptibility measurements the Lake Shore instrument provides the option of dc magnetization measurements, as well as $\chi_{ac}$ measurements in the presence of dc field ($H_{dc}$). As these options were not used in the presented studies, they will not be discussed. The $\chi_{ac}$ data can be taken in the ranges $1.5 < T < 325$ K, $0 \leq H_{dc} \leq 50$ kOe, $0 \leq H_{ac} \leq 25$ Oe, and $1 \leq f \leq 11,000$ Hz, with maximum sensitivity of $2 \times 10^{-8}$ emu in terms of equivalent magnetic moment.

The measured voltage due to the sample placed within one of the pick-up coils is given by $v = (1/\alpha)VfH\chi$, where $v$ is the measured RMS voltage, $V$ sample volume, $f$ frequency of the ac field, $H$ RMS magnetic field, $\chi$ volume susceptibility of the sample, and $\alpha$ calibration coefficient. The coefficient $\alpha$ depends on the coil
Figure 3.3: Lake Shore 7225 ac Susceptometer/dc Magnetometer block diagram.
configuration and sample geometry, the latter dependence being rather weak [79] and therefore neglected in our measurements. Rearranging the previous equation gives the relationship used in determining the sample susceptibility from the experimental parameters

\[ \chi = \frac{\alpha v}{\sqrt{f H}}. \] (3.1)

In order to eliminate the offset \( v_{\text{off}} \) the signal is measured with the sample in both the bottom and top pick-up coils (voltages \( v_b \) and \( v_t \), respectively), then subtracted and divided by two to get the signal due to the sample \( v_s \)

\[ v_t = v_s + v_{\text{off}} \] (3.2)
\[ v_b = -v_s + v_{\text{off}} \] (3.3)
\[ v_s = \frac{v_t - v_b}{2}. \] (3.4)

In the linear regime, the driving ac field \( H_{\text{ac}} = h_0 \cos \omega t \) (\( \omega = 2\pi f \)) induces the magnetization in the sample given by \( M(t) = \chi' h_0 \cos \omega t - \chi'' h_0 \sin \omega t \). To detect the real (in-phase) and imaginary (out-of-phase) parts of the susceptibility, the lock-in amplifier is directed to pick up the voltage signals that are exactly in phase (\( v_0 \) at \( \Theta = 0 \)) and out of phase (\( v_{\pi/2} \) at \( \Theta = \pi/2 \)) with the driving field \( H_{\text{ac}} \). The in-phase and out-of-phase susceptibilities are calculated as

\[ \chi' = \frac{\alpha v'}{\sqrt{f H_{\text{ac}}}}, \] (3.5)
\[ \chi'' = \frac{\alpha v''}{\sqrt{f H_{\text{ac}}}}, \] (3.6)

where

\[ v' = v_0 \cos \Theta + v_{\pi/2} \sin \Theta, \] (3.7)
\[ v'' = v_{\pi/2} \cos \Theta - v_0 \sin \Theta. \] (3.8)
By driving the primary coil at frequency \( f \) and detecting the output signal at integer multiples of \( f \), the harmonic susceptibilities can be measured. For small driving fields the harmonic susceptibilities correspond to the nonlinear magnetic susceptibilities. In general (nonlinear) case, the magnetization can be expanded in powers of the applied field \( H \) as

\[
M = M_0 + \chi_1 H + \chi_2 H^2 + \chi_3 H^3 + \chi_4 H^4 + \ldots
\]  

(3.9)

where \( M_0 \) is the spontaneous magnetization and \( \chi_n \) (\( n > 0 \)) are nonlinear susceptibilities. It is important to note that the even terms in this expansion \( \chi_2, \chi_4, \ldots \) are observed only if there is a spontaneous magnetization in the system, because in that case \( M \) has no inversion symmetry with respect to the applied field [80]. For a spin glass the expansion of \( M \) contains only odd terms and no spontaneous magnetization [64, 81]. For zero dc magnetic field and an ac field with magnitude \( h_0 \) one gets

\[
M = M_0 + \chi_1 h_0 \cos \omega t + \chi_2 \frac{1}{2} h_0^2 (1 + \cos 2\omega t) + \chi_3 \frac{1}{4} h_0^3 (3 \cos \omega t + \cos 3\omega t) + \ldots
\]  

(3.10)

By grouping the terms with the same frequency dependence (i.e., \( \omega t, 2\omega t, 3\omega t, \) etc.), one obtains for the various harmonics

\[
\chi_1 = \chi_1 + \frac{3}{4} \chi_3 h_0^2 + \frac{5}{8} \chi_5 h_0^4 + \ldots
\]  

(3.11)

\[
\chi_2 h_0 = \chi_2 h_0 + \chi_4 h_0^3 + \chi_6 h_0^5 + \ldots
\]  

(3.12)

\[
\frac{3}{4} \chi_3 h_0^2 = \frac{3}{4} \chi_3 h_0^2 + \frac{15}{16} \chi_5 h_0^4 + \ldots
\]  

(3.13)

\[
\frac{1}{2} \chi_4 h_0^3 = \frac{1}{2} \chi_4 h_0^3 + \frac{3}{4} \chi_6 h_0^5 + \ldots
\]  

(3.14)

The quantities on the left-hand sides are the ones actually measured in the ac susceptibility experiment. In the limit of small ac fields \( h_0 \) the measured susceptibilities coincide with the nonlinear susceptibilities \( \chi_n \). The last set of equations holds for
Demagnetization factors

<table>
<thead>
<tr>
<th>Specimen Shape</th>
<th>D (SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>1/3</td>
</tr>
<tr>
<td>Long Needle, H perpendicular</td>
<td>1/2</td>
</tr>
<tr>
<td>Long Needle, H parallel</td>
<td>0</td>
</tr>
<tr>
<td>Thin Film, H perpendicular</td>
<td>1</td>
</tr>
<tr>
<td>Thin Film, H parallel</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.2: Demagnetization factors for some simple sample geometries.

both the real and imaginary parts of the respective susceptibilities. However, usually only the magnitudes of the nonlinear susceptibilities are displayed.

For precision measurements or when the susceptibility is large, the measured susceptibility must be corrected for the demagnetization effect in order to obtain the actual intrinsic susceptibility. This effect is a geometric one and accounts for the fact that the internal field in the sample $H_{int}$ in general differs from the externally applied field, due to the magnetic dipole induced in the sample. The internal field is given by $H_{int} = H - DM$, where $D$ is the demagnetization factor, determined by the sample geometry. For the intrinsic susceptibility one obtains

$$H_{int}/M = H/M - D$$  \hspace{1cm} (3.15)

$$1/\chi_{int} = 1/\chi - D$$  \hspace{1cm} (3.16)

$$\chi_{int} = \frac{\chi}{1 - D\chi}$$  \hspace{1cm} (3.17)

Table 3.2 lists the demagnetization factors for some common geometrical configurations. The demagnetization correction is properly made using the last equation when $\chi$ is (volume) susceptibility, expressed in the SI units (dimensionless).
It is noted that the demagnetization correction also should be done in the dc magnetization measurements. In the case when both the in-phase and out-of-phase susceptibilities are measured, the corrections are given by

$$\chi_{\text{int}}' = \frac{\chi'(1 - D\chi') - D\chi''^2}{(1 - D\chi')^2 + D^2\chi''^2}$$  \hspace{1cm} (3.18)$$

$$\chi_{\text{int}}'' = \frac{\chi''}{(1 - D\chi')^2 + D^2\chi''^2},$$  \hspace{1cm} (3.19)$$

which means that the real and imaginary intrinsic susceptibilities are interdependent on both the real and imaginary measured susceptibilities.

As for the powder samples studied here the correct demagnetization factors were impossible to determine, the demagnetization corrections were not done. Since the volume magnetic susceptibilities of the studied materials are small ($\sim 10^{-1}$), due to their large molar masses and low densities, the demagnetization corrections are of the order of several percent. The demagnetization effect is manifested by a slight rounding of the peaks in the experimental $\chi$ vs. $T$-curves with respect to the intrinsic susceptibility peaks, while the peak positions do not have detectable shifts.

In order to correctly separate the real and imaginary components of the susceptibility, the phase calibration of the system needs to be performed periodically. The calibration is done by measuring $\chi'$ and $\chi''$ of a standard sample, $\chi''$ of which is expected to be zero (usually a paramagnetic salt, e.g., HgCo(SCN)$_4$) in the temperature region of interest, and subsequently adjusting the phase so that $\chi''$ is as close to zero as possible.

Diamagnetic backgrounds were measured and subtracted for all magnetic measurements.
3.5 UV-Vis-NIR Spectroscopy

Perkin Elmer Lambda 19 is an automated, double-beam, double-monochromator dispersive spectrophotometer with operating range from 2500 nm (4000 cm\(^{-1}\)) to 190 nm (55,000 cm\(^{-1}\)). Schematic of the Lambda 19 optical system is displayed in Fig. 3.4 [82].

Two light sources are used: deuterium lamp (DL) (190-340 nm) and halogen lamp (HL) (300-2500 nm). By a set of mirrors (M1-M4) polychromatic light from the respective source is directed to the entrance slit of monochromator 1. The light is dispersed at the monochromator’s grating to produce a spectrum. The rotational position of the grating effectively selects a segment of the spectrum, reflecting this segment to mirror M5 and through the exit slit. The exit slit restricts the spectrum segment to a nearly monochromatic radiation beam. The light then enters the monochromator 2 which further improves the spectral purity. Thus obtained monochromatic light is directed to the chopper assembly (C). As the chopper rotates, a mirror segment, a window segment, and dark segments are brought alternately into the light beam. When a mirror segment enters the beam, light is reflected from mirror M9 to form the sample beam (S), while window segment produces the reference beam (R). A dark segment in the beam path permits the detector to create the dark (background) signal. As detectors, a photomultiplier is used in the UV/Vis range (190-900 nm), while PbS detector covers the NIR range (900-2500 nm). For the transmission measurements, samples are placed in the optical path of the sample beam (position S), and measured quantity is the ratio of intensities of the transmitted and incident light. Before the sample measurement, background spectrum (without sample in the position S)
Figure 3.4: Schematic of the optical system of Lambda 19 UV-Vis-NIR spectrophotometer.
needs to be measured. The instrument can also measure reflectance, by using Perkin-
Elmer RSA-PE-90 reflectance accessory based on the Labsphere DRTA-9a integrating
sphere. The integrating sphere provides total hemispherical collection of the reflected
energy.

The transmission coefficient (transmittance) $T$ is defined as

$$T = \frac{I(r)}{I_0} = e^{-Kr}, \quad (3.20)$$

where $I_0$ is the intensity of light penetrating the medium, $I(r)$ is the intensity of the
transmitted beam a distance $r$ apart from the surface of the medium, and $K$ is the
absorption coefficient, related to the extinction coefficient $k$ (the imaginary part of
the complex refraction index) by

$$K(\omega) = 2\frac{\omega}{c}k \quad (3.21)$$

For a sample of thickness $d$ one gets $T = e^{-Kd}$. Absorbance ($A$) is defined as

$$A = -\log \frac{I}{I_0} = -\log T = Kr \log e \quad (3.22)$$

Strictly speaking, the measured transmittance is equal to $T$ defined above only
when no light is being reflected or scattered at the sample. As this is never the case,
the measured quantity is in fact a lower limit of $T$. If the interference effects can be
neglected, the measured transmittance $T_{exp}$ and reflectance $R_{exp}$ for normal incidence
are given by [83]

$$T_{exp} = \frac{(1 - R)^2T}{1 - R^2T^2} \quad (3.23)$$

$$R_{exp} = R(1 + TT_{exp}), \quad (3.24)$$

where $T = e^{-Kr}$ is the ‘real’ transmittance and $R = [(n-1)^2+k^2]/[(n+1)^2+k^2]$ is the
‘real’ reflectance between air and the sample with complex index of refraction $n + ik$.  

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Figure 3.5: Experimental absorbance $A_{\text{exp}}$ and calculated "real" absorbance $A$ for a sample of Mn(TCNE)$_x$·y(CH$_2$Cl$_2$). Sample was prepared as Nujol mull. The measurement was done at room temperature.

By measuring both $T_{\text{exp}}$ and $R_{\text{exp}}$ for a sample, both $T$ and $R$ can be determined. In order to estimate the error introduced by neglecting reflection, we measured $T_{\text{exp}}$ and $R_{\text{exp}}$, room temperature spectra for a Mn(TCNE)$_x$·y(CH$_2$Cl$_2$) sample and calculated $T$ and $A = -\log T$. The measured reflectance is in the range 5-13%. The comparison between $A_{\text{exp}} = -\log T_{\text{exp}}$ and $A$ (Fig. 3.5) shows that deviation between them is insignificant for the qualitative analyses presented in the thesis. The absorption spectra in Ch. 5 therefore show only the directly measured $A_{\text{exp}}$.

In the experiments presented here, samples were prepared as Nujol mulls, as described in the first section (Nujol oil is transparent for wavelengths above ~250 nm),
and mounted on the cold head of the APD Cryogenics Heli-Tran LT-3-110 continuous-flow optical cryostat. The sample plane formed a 45° angle with the sample beam, which allowed laser illumination of the sample through the cryostat quartz window in the direction perpendicular to the sample beam. For absorbance vs. time measurements (Ch. 5) an interference filter (peak transmission at $\lambda_{\text{peak}} = 600$ nm, 80 nm bandwidth) was placed in the sample beam path between the cryostat and detector, in order to filter out the stray laser light that would saturate the detector. The background spectrum was measured at room temperature, with empty cryostat in the S position. Temperature was controlled by the Oxford ITC 503 temperature controller. The photoinduced absorption measurements were done at the lowest attainable temperature of about 13 K.

The photoinduced absorption spectra were obtained by subtracting the spectra measured before laser excitation from spectra measured after excitation. As the spectrometer exhibits a slow drift of the baseline over extended periods of time that can effect the PA spectra, the time period between the successive measurements was limited to about 15 min. During this period the drift was negligible. In a typical measurement, laser excitation was done for 10 min, and after illumination was stopped, the sample temperature was allowed to re-stabilize for 5 min before the next measurement. It is noted that $T$ measured by the temperature sensor increased by only about 0.01-0.02 K during illumination and returned to the value measured in the dark within 10 s after laser was turned off. However, longer time period was allowed for re-stabilization of temperature, having in mind that sensor temperature may be somewhat different from the local sample temperature (the sensor is mounted at the cryostat's cold head, about 1 cm away from the sample). As in any PA experiment,
it is important to estimate the effect that heating by laser excitation may have on the spectrum. As in the present experiments the spectra were measured in the dark before and after excitation, at the same temperature, this problem is less important than in the time-resolved PA experiments, where PA spectra are taken during laser excitation. As indicated above, a very small increase in $T$ during illumination was measured during illumination, indicating that the increase in the sample $T$ is not substantial either. As an additional check, the sample was warmed up to 20 K above the lowest temperature and cooled back to 13 K, then the measurement of A repeated. Nearly perfect reproducibility of spectrum was obtained. When this cycle was repeated for higher upper temperatures, small differences in spectrum were observed (possibly due to thermal dilatation and subsequent contraction of the sample assembly), but the difference spectrum showed only a uniform drift, with no structure.

3.6 FTIR Spectroscopy

The basic components of any FTIR spectrometer are a light source, a Michelson interferometer, and a detector. The Michelson interferometer is a device that divides a light beam into two paths and then recombines them so that the intensity variations of the exit beam can be measured by a detector as a function of the path difference $x$. The simplest form of interferometer (Fig. 3.6) consists of two mutually perpendicular plane mirrors (E and F), one of which can move along the axis perpendicular to its plane. The moving mirror E is either moving with a constant velocity or is held at equally spaced points for fixed short periods of time and rapidly stepped between these stops. Between the fixed and moving mirrors is a beamsplitter (B), at which the beam of radiation from the light source (A) is partially reflected to the fixed
mirror and partially transmitted to the moving mirror. The beams reflect from the mirrors back to the beamsplitter, where they are recombined to form a single beam which is directed through the sample (C) and towards detector (D). Due to the light interference the intensity of the beam passing towards the detector depends on the path difference of the beams in the two arms of interferometer. The variation of the intensity as a function of the path difference yields the spectral information in a Fourier transform spectrometer.

Referring to Fig. 3.6, let us denote by $l$ the optical path between the light source A and a point P of the beam just before the detector D, for the beam which is reflected at the fixed mirror F, and by $E_1$ the electric field of this beam at P. Similarly, $l + x$ and $E_2$ are the optical path and the electric field of the beam reflected at the moving mirror E. For a monochromatic light source of frequency $\omega = 2\pi c \tilde{u}$ we have [84]

$$E_1(\tilde{u}) = A_1(\tilde{u})A_S(\tilde{u})e^{2\pi i c \tilde{u} t} e^{ikl}$$ (3.25)

$$E_2(\tilde{u}) = A_1(\tilde{u})A_S(\tilde{u})e^{2\pi i c \tilde{u} t} e^{ik(l+x)}.$$ (3.26)

$A_1(\tilde{u})$ depends on instrumental conditions of the interferometer (source efficiency, losses by transmission of beam splitter, lenses, filters, windows and by reflection at mirrors, etc.), and $A_S(\tilde{u})$ depends on the optical properties of the sample. For a transmission experiment $A_S(\tilde{u}) = \xi_S(\tilde{u})$ is the complex amplitude of the beam transmitted by the sample. Using $k = 2\pi/\lambda = 2\pi \tilde{u}$ and the expressions for $E_1$ and $E_2$, the intensity at point P is given by

$$I(x, \tilde{u}) = \frac{1}{2} |E_1 + E_2|^2 = S(\tilde{u})(1 + \cos 2\pi \tilde{u} x),$$ (3.27)

where $S(\tilde{u}) = |A_1(\tilde{u})|^2 |A_S(\tilde{u})|^2$ is the spectral density at wavenumber $\tilde{u}$. For a polychromatic source emitting light between $\tilde{u} = 0$ and $\tilde{u} = \infty$ the total intensity is given
Figure 3.6: Schematic of the optical system of Bruker IFS 66v/s FTIR spectrometer. (A) source, (B) beamsplitter, (C) sample position, (D) detector, (E) moving mirror, (F) fixed mirror.
by
\[ I(x) = \int_0^\infty S(\tilde{\nu})[1 + \cos(2\pi \tilde{\nu} x)]d\tilde{\nu} = \frac{1}{2} I(0) + \int_0^\infty S(\tilde{\nu}) \cos(2\pi \tilde{\nu} x)d\tilde{\nu}, \] (3.28)

where \( I(0) \) is the intensity at zero path difference. Function \( I(x) \) is called interferogram. Applying the real form of Fourier's integral, we obtain for the desired spectrum
\[ S(\tilde{\nu}) = 4 \int_0^\infty [I(x) - \frac{1}{2} I(0)] \cos(2\pi \tilde{\nu} x)dx. \] (3.29)

In practice, \( S(\tilde{\nu}) \) is approximated by the sum
\[ S(\tilde{\nu}) = 4 \sum_{x=0}^{D} [I(x) - \frac{1}{2} I(0)] \cos(2\pi \tilde{\nu} x)\Delta x. \] (3.30)

Here \( D \) is the maximum optical path difference and equals twice the total moving mirror displacements. \( I(x) \) is sampled at discrete intervals \( \Delta x \) between \( x = 0 \) and \( x = D \) and the sum \( S(\tilde{\nu}) \) calculated by computer. Let \( G \) and \( D(\tilde{\nu}) \) be the gain of the amplifier and the detector sensitivity, respectively. Then the actual computed transmission spectrum of the sample is
\[ P_S(\tilde{\nu}) = G_SD(\tilde{\nu})|A_T(\tilde{\nu})|^2 T_S(\tilde{\nu}), \] (3.31)

where \( T_S(\tilde{\nu}) = |A_S(\tilde{\nu})|^2 = |\tilde{t}_s(\tilde{\nu})|^2 \) is the transmission of the sample. The spectrum of the background is
\[ P_B(\tilde{\nu}) = G_BD(\tilde{\nu})|A_T(\tilde{\nu})|^2, \] (3.32)

since \( T_B(\tilde{\nu}) = 1 \) for a hole at the place of the sample. It follows that
\[ T_S(\tilde{\nu}) = \frac{G_BP_S(\tilde{\nu})}{G_SP_B(\tilde{\nu})}. \] (3.33)

An obvious advantage of FTIR spectrometers over the grating ones is the high light throughput. They use the full intensity of the polychromatic light source, while
in the grating spectrometers light from the source is analysed by the narrow slits of the monochromator to obtain high resolution. Another major advantage of interferometric over dispersion spectroscopy lies in the fact that with an interferometer the whole spectral range of interest is incident on the detector at one time, rather than a single resolution width. Assuming otherwise comparable efficiency, the interferometer can obtain the whole spectral range in the same time taken by the monochromator to obtain one resolution width. If there are \( N \) elements in the spectrum the interferometer will show an improvement of the order of \( \sqrt{N} \) in its signal/noise ratio, as compared to a single channel spectrometer of the same luminosity and resolving power.

The Bruker IFS 66v/S FTIR spectrometer features evacuable optical compartment, which prevents pollution by air and moisture that can produce spurious spectral lines, as well as damage the moisture-sensitive optical components (e.g., KBr windows and beamsplitter). The low-\( T \) absorption and photoinduced absorption spectra were measured using the APD Cryogenics Heli-Tran LT-3-110 continuous flow optical cryostat and Oxford ITC 503 temperature controller in a setup analogous to the one used for UV-Vis-NIR experiments. For mid-infrared absorption and PA measurements, KBr beamsplitter, KBr cryostat windows, MCT (mercury cadmium telluride) detector, and Glowbar light source were used. Samples were prepared as Fluorolube mulls, as described in the first section of this chapter. Fluorolube is transparent at energies above 1300 cm\(^{-1}\), which limited measurements to the region 1300-7000 cm\(^{-1}\). The lower energy region can be covered by preparing samples as Nujol mulls (Nujol oil is transparent below 1300 cm\(^{-1}\)), however the sensitivity of the MCT detector rapidly decreases at these energies and the signal/noise ratio becomes too large to
permit the sensitive PA measurements. Thus Nujol mull method was used only for
a room-temperature survey spectrum between 600 and 1300 cm\(^{-1}\). The PA spectra
were obtained by subtracting the spectra before and after illumination, analogously
to the UV-Vis-NIR experiments. As in the UV-Vis-NIR case, instrumental drift poses
a significant problem in the PA experiments, and same measures of precaution were
taken to exclude a significant contributions of the drift to the PA signal. The effect of
warming by laser excitation was accounted for in the same way as in the UV-Vis-NIR
experiments, and it will be discussed in more detail in Ch. 5.
CHAPTER 4

PHOTOINDUCED MAGNETISM IN Co-Fe PRUSSIAN BLUE ANALOGS

Comprehensive experimental studies of magnetic ordering and its optical control in Co-Fe Prussian blue magnets are presented in this chapter. An overview of the previous studies of photoinduced magnetism in Prussian blue analogs is given in the first section. The next section presents magnetic studies that determine cluster glass state in the materials. The chapter proceeds with dc and ac magnetic susceptibility studies of the photoinduced magnetic effects. Finally, a cluster glass model is presented, which on a qualitative level accounts for all experimentally observed magnetic and PIM phenomena.

4.1 Overview of Previous Studies

One of the most interesting recent advances in the field of molecule-based magnetism is recently discovered photoinduced magnetization (PIM) in Co-Fe Prussian blue-based magnets [3]. While photoinduced low-spin to high-spin transition in paramagnetic spin crossover complexes (LIESST effect) has been known since 1984 [37], the fundamentally novel aspect of the effects observed in the Prussian blue magnets
Figure 4.1: Schematic structure of cobalt-iron Prussian blue analogs. Solid (open) circles represent carbon (nitrogen) atoms. Alkali metal ions are interstitial.

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. 4.1. In general, significant structural disorder may be present, due to randomly distributed vacancies in the metal (Fe) sites. General formula for Co-Fe Prussian blue magnets is $\text{A}_x\text{Co}_y[\text{Fe(CN)}_6]z\text{H}_2\text{O}$ ($\text{A}=$ 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. 4.1) [85, 86].

Depending on the composition and preparation method, the materials are dia- or paramagnetic, or exhibit magnetic ordering at temperatures below 25 K [3, 85, 87, 88, 89, 90]. The metallic ions in the materials may have different oxidation states and, consequently, different magnetic behavior. Thus $\text{Fe}^{II}(t_{2g}^6, \text{Is})$ and $\text{Co}^{III}(t_{2g}^6, \text{Is})$ do not have
unpaired spins and give diamagnetic response, while Fe"^{III}(t_{2g}^5e_g^0\text{, ls}) and Co"^{II}(t_{2g}^5e_g^3\text{, hs}) carry spins S=1/2 and S=3/2, respectively and therefore have paramagnetic response. Here 'ls' and 'hs' stand for the low-spin and high-spin states (see Section 2.2). Predominantly antiferromagnetic superexchange coupling, mediated through the cyanide bridge between nearest-neighbor metallic spins, was proposed [3, 85]. The interaction between the $t_{2g}$ orbital of Fe"^{III}(ls) and the $e_g$ orbital of Co"^{II}(hs) is ferromagnetic, due to the orthogonality of these orbitals (potential superexchange, Ch. 2). The interaction between the $t_{2g}$ orbital of Fe"^{III}(ls) and the $t_{2g}$ orbital of Co"^{II}(hs) is antiferromagnetic, due to their nonorthogonality (kinetic superexchange). As the kinetic term usually dominates the potential term (Ch. 2), the total superexchange is expected to be antiferromagnetic.

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 [3]. 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 [3].

The mechanism for PIM in Prussian blue magnets has been the subject of a number of experimental and theoretical studies [85, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 86, 102, 103, 104, 105, 106, 107]. Infrared [85], Mössbauer [91] and X-ray absorption spectroscopy (EXAFS and XANES) [94, 95, 96] studies determined that the microscopic origin of PIM is in the light-induced electron transfer, followed by a spin flip, within the Fe-CN-Co moieties (Fig. 4.2). While in the initial state (a) Fe"^{II}(ls)(t_{2g}^5, S=0)—CN—Co"^{III}(ls)(t_{2g}^5, S=0) the metal ions have no unpaired electrons,
Figure 4.2: Scheme of the charge transfer transition in Co-Fe Prussian blue.

in the photoexcited state (b) \( \text{Fe}^{III}(ls)(t_{2g}^5, S=1/2) - \text{CN} - \text{Co}^{II}(hs)(t_{2g}^3e_g^2, S=3/2) \) both ions carry nonzero spin.

The increased number of spins is thus responsible for PIM. These studies also determined that in the photoexcited state the Co-N bond lengths are significantly increased (up to 0.18 Å [85]). 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 [85, 103].

As the initial and final spin states are different (one electron has to flip its spin), the direct photoinduced transition from state (a) to state (b) is spin-forbidden. It has been proposed that the transition from (a) to (b) is indirect, and proceeds through the intermediate state (i) \( \text{Fe}^{III}(ls)(t_{2g}^5, S=1/2) - \text{CN} - \text{Co}^{II}(ls)(t_{2g}^3e_g^1, S=1/2) \) [85]. In this scheme (Fig. 4.3), the first step in the transition is (spin allowed) photoinduced charge transfer from the state (a) to the state (i). Due to the spin-orbit coupling, a fraction of photoexcited states may undergo intersystem crossing into the higher-spin state (b). Due to the change in the Co-N bond length, the bottoms of potential wells
for states (a) and (b) are expected to be significantly separated, which introduces an energy barrier for the transition back to the state (a).

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 Fe(CN)$_6$ vacancies (e.g., for $A = K$, PIM is observed only for the Co/Fe ratios between 1.2 and 1.4) [93, 97]. This has been explained as a result of variation of the ligand field at the Co sites [85]. In the vicinity of a vacancy, substitution of CN by H$_2$O lowers the ligand field. Low ligand field favors the high-spin state Co$^{II}$(t$_{2g}^5$e$_g^2$), therefore materials with more vacancies are expected to have higher concentration of the Fe$^{III}$-CN-Co$^{II}$ moieties and, consequently, higher overall spin concentration, which has been experimentally confirmed [85, 90, 97].
However, materials with very high vacancy concentration do not exhibit PIM [85, 97], presumably because of an insufficient number of the diamagnetic moieties Fe\textsuperscript{II}-CN-Co\textsuperscript{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, which does not allow for the bond dilatation that accompanies PIM [97]. At optimum vacancy concentrations, a photoinduced transition from diamagnetic state to a magnetically ordered state can be obtained [87, 88, 97].

Even more profound role of the structural disorder was indicated by the quantum chemical cluster calculations of T. Kawamoto et al. [103]. The calculations 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 [85]. 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 [103]. 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.

The microscopic mechanism for PIM in Prussian blue analogs is similar to the LIESST effect observed in paramagnetic spin crossover complexes, and discussed in Ch. 2, with an important difference that the low-spin and high-spin states are states of
a single transition metal ion in the case of LIESST, while two different metal ions are involved in the transition observed in Prussian blue analogs. As for the spin crossover complexes the low-spin-high-spin transition can also be induced by the temperature increase, it is expected that similar transition is possible in Co-Fe Prussian blue. This thermally induced spin transition was indeed observed in Na$_{0.4}$Co$_{1.6}$[Fe(CN)$_6$]·5H$_2$O and thin films of K$_{0.4}$Co$_{1.3}$[Fe(CN)$_6$]·5H$_2$O, with the high-spin phase occurring above $T = 260$ K and 280 K, respectively [108, 95]. The X-ray absorption fine structure spectroscopy study determined that the local structure of this high-temperature phase was similar to the high-spin state induced by photoexcitation at lower temperatures, with increased concentration of the paramagnetic ions Fe$^{III}$ and Co$^{II}$(hs) [95].

4.2 Cluster Glass State of Co-Fe Prussian Blue Analogs

In this section detailed magnetic studies of the ground state (state before illumination) of Co-Fe Prussian blue analogs, K$_x$Co$_y$[Fe(CN)$_6$]·$z$H$_2$O are presented. Three different materials were studied, with their estimated chemical compositions given in Table 3.1. The approximate Co/Fe ratios for these three compositions are $y \approx 1.2$, 1.3 and 1.4, for samples A, B and C, respectively. As reported in Ref. [93], these values span most of the range of material compositions for which PIM effects can be observed. All three materials show very similar general low-$T$ magnetic response, suggestive of a cluster glass state. Different behavior of the materials will be emphasized, where applies.

Figure 4.4 shows the temperature ($T$) dependence of the reciprocal dc susceptibility for sample A ($\chi^{-1} = H/M$, where $H$ and $M$ are applied dc magnetic field and magnetization, respectively). The plot shows deviations from linear (Curie-Weiss)
Figure 4.4: Reciprocal dc susceptibility of Co-Fe Prussian blue (sample A).

behavior below $T \sim 50$ K. Linear fit in the region $50 \leq T \leq 205$ K gives values of $C = 2.66 \pm 0.01$ emuK/mol and $\theta = -8.0 \pm 0.6$ K for the Curie constant and Weiss temperature, respectively. The negative value of $\theta$ is consistent with predominantly ferrimagnetic ordering. Above 205 K deviations from linearity occur. For $T > 250$ K the $\chi^{-1}$ vs. $T$ dependence again becomes linear, with slope decreased from the one in the low-temperature linear region. The linear fit in the region $250 \leq T \leq 350$ K gives values of $C = 4.27 \pm 0.02$ emuK/mol and $\theta = -133 \pm 2$ K. The observed temperature-induced increase in $C$ implies that the number of spins is increased, while the increase in $\theta$ is an indication of enhanced spin-spin interaction. The result is suggestive of a spin transition, similar to the transition reported earlier for Na$_{0.4}$Co$_{1.3}$[Fe(CN)$_6$]-5H$_2$O and K$_{0.4}$Co$_{1.3}$[Fe(CN)$_6$]-5H$_2$O thin films [108, 95]. As noted in the preceding section,
this behavior has been attributed to a thermally-driven transition of diamagnetic sites Fe\textsuperscript{II}-CN-Co\textsuperscript{III} to the state Fe\textsuperscript{III}-CN-Co\textsuperscript{II} with unpaired spins on both metal ions.

For $T > 350$ K large deviations from the Curie-Weiss behavior occur. Heating above 350 K produces an irreversible reduction of the material's magnetic moment, suggesting that degradation/desolvation takes place.

While about the same value of $\theta$ was observed in samples B and C, these materials did not show behavior suggestive of spin transition below 350 K.

Figure 4.5 shows low-$T$ magnetic behavior at applied field $H = 10$ Oe for sample C. The magnetization was measured in three different ways. The field-cooled magnetization ($M_{fc}$) was recorded after cooling of sample from $T > 50$ K in applied magnetic field $H$. Upon reaching the lowest temperature of 4.6 K, $M(T)$ was measured on warming. The zero-field-cooled magnetization ($M_{zfc}$) was measured after cooling in zero applied magnetic field. Upon reaching 4.6 K, the field $H = 10$ Oe was applied, and data collected, again on warming. Remanent magnetization (remanence, $M_{rem}$) was collected after cooling in field $H = 10$ Oe, subsequent reducing $H$ to zero, and collecting data in zero field on warming.

The magnetization exhibits bifurcation between the $M_{fc}$ and $M_{zfc}$ curves below $T_b \sim 18$ K, indicating irreversible magnetic behavior. It also suggests some type of magnetic order below $T_b$, as in the paramagnetic regime $M$ is completely reversible and has no history-dependent behavior (i.e., the measured value of $M$ is a function of state, and depends only on the current values of $H$ and $T$, not on the way these $H$ and $T$ were reached). At about the same temperature, the increase in magnetization with decrease of $T$ becomes more rapid. While $M_{fc}$ monotonically increases as $T$ is
Figure 4.5: Field-cooled (squares), zero-field-cooled (triangles), and remanent (circles) magnetizations for sample C at $H = 10$ Oe. Inset: enlargement near $T_c$.

Lowered, $M_{zfc}$ exhibits a peak at $T_{max} = 12.2$ K, and rapidly decreases below this temperature, which produces much stronger $M_{fc}/M_{zfc}$ irreversibility.

The remanent magnetization is an indication of spontaneous magnetic moment in the system. In the present sample $M_{rem}$ is reduced to zero (within the magnetometer’s sensitivity) at temperature $T_c$ that nearly coincides with the bifurcation temperature $T_b$ (inset, Fig. 4.5), indicating loss of spontaneous moment above $\sim 18$ K.

Measurements of $M_{fc}$ and $M_{zfc}$ were repeated for a range of applied magnetic fields between 2 Oe and 1 kOe. The data, presented in Fig. 4.6 for chosen $H$ values, show a systematic decrease of the $M_{fc}/M_{zfc}$ bifurcation temperature $T_b$ with increasing $H$. 
Figure 4.6: Field-cooled (open symbols) and zero-field-cooled (solid symbols) magnetization for different applied magnetic fields (sample C). Arrows indicate approximate positions of the $M_{fc}/M_{zfc}$ bifurcations.

The $M_{zfc}$ peak temperature $T_{max}$ also decreases and the peak becomes more rounded as $H$ is increased.

The irreversible magnetic behavior, indicated by the $M_{fc}/M_{zfc}$ bifurcation, is observed in many magnetically ordered materials. In conventional ferro- and ferrimagnets pinning of magnetic domain walls can produce irreversibilities at temperatures below the magnetic ordering temperature. However, in these systems the deviations between $M_{fc}$ and $M_{zfc}$ are usually small, and the bifurcation temperature is not $H$-dependent at low field values, in contrast to the present system [13, 109]. Strong irreversibility, with $H$-dependent bifurcation, is characteristic for
spin glasses [13, 109, 64, 110]. However, while in spin glasses the \( M_{fc} \) below \( T_b \) is nearly temperature-independent, in the present case it continues to monotonically increase below \( T_b \). Such behavior has been observed in cluster glasses: systems with coexisting short-range colinear order and spin glass-like order [64, 111]. The rapid increase in \( M \) below \( T_c \) (the 'quasicritical temperature') has been attributed to the occurrence of short-range colinear magnetic ordering, which forms clusters of spins [111]. In the case of Co-Fe Prussian blue this ordering is assumed to be predominantly ferrimagnetic, as suggested by the negative values of \( \theta \) and expected antiferromagnetic nearest-neighbor superexchange in the system. The peak in \( M_{fc} \) and strong irreversibility at \( T \) below this peak may be attributed to the freezing of the magnetic moments of spin clusters in random directions, similar to the freezing of individual spins in the case of spin glasses.

Figure 4.7 shows magnetic field dependence of the \( M_{fc} \) peak temperature, with \( T_{max} \) plotted versus \( H^{2/3} \). This plot shows nearly linear dependence of \( T_{max} \) on \( H^{2/3} \), which is reminiscent of the Almeida-Thouless (AT) instability line from the mean-field theory of spin glasses [64, 54]. The theory predicts that the spin glass transition temperature \( T_g \) and the field-dependent temperature below which the irreversible behavior occurs \( T_{AT}(H) \) are related as \( T_g - T_{AT}(H) \propto H^{2/3} \). In the present case \( T_{AT}(H) \) is identified with \( T_{max} \), the temperature that marks the onset of the strong irreversibility. A good fit with the functional form \( T_{max}(H) = a - bH^{2/3} \), shown in Fig. 4.7, is obtained, with parameter values \( a = 12.28 \pm 0.02 \) K and \( b = (4.62 \pm 0.05)10^{-2} \) K/Oe\(^{2/3} \). When the data are fitted with the triparameter functional form \( T_{max}(H) = a - bH^4 \), the obtained parameter values are \( a = 12.31 \pm 0.04 \) K, \( b = \)
Figure 4.7: Magnetic field dependence of the $M_{z_{fc}}$ peak temperature (sample C). Solid line is fit with function $T_{\text{max}} = a - bH^{2/3}$.

$(5.3 \pm 0.7) \times 10^{-2}$ K/Oe$^{2/3}$, and $\delta = 0.65 \pm 0.02$, with $\delta$ coinciding with the predicted mean-field theoretical value of $2/3$, within the error interval.

Figure 4.8 shows the time dependence of the magnetization, measured after zero-field cooling to 5 K and applying the field $H = 20$ Oe after a waiting period of $t_w = 300$ s. After the field is applied (time $t = 0$), the magnetization exhibits a slow nonexponential increase, indicative of a nonequilibrium nature of $M_{z_{fc}}$. The long-time relaxation of the thermoremanent magnetization, measured after cooling in field and subsequently reducing the field to zero, also was recorded. The slow nonexponential relaxation of magnetization is another signature of glassiness [64]. The relaxation rate $S \equiv dM_{z_{fc}}/d(\ln t)$ does not exhibit a maximum at $t = t_w$, in contrast with canonical spin glasses [64], but similar to data reported for a cluster glass [112].
Figure 4.8: Time dependence of the zero-field-cooled magnetization for sample C.

The curves of initial magnetization, measured after zero-field cooling, are displayed in Fig. 4.9. Magnetization does not show full saturation even at fields as high as 55 kOe and temperature of 2 K. The curves in the low-\(T\) region are S-shaped (inset, Fig. 4.9). Both the lack of saturation and the shape of the \(M(H)\) curves are consistent with the spin glass-like order at low temperatures [62].

While the present system shows dc magnetic response consistent with the cluster glass ordering, it is important to clearly distinguish it from systems of small (single-domain) non-interacting magnetic particles (superparamagnets). The latter systems also exhibit slow relaxation and pronounced irreversible behavior below some 'blocking temperature,' related to the energy barriers induced by the shape and crystalline anisotropy [113]. The blocking temperature \(T_b\) also exhibits dependence on the magnetic field, and in some cases even \(T_b \propto H^{2/3}\) behavior is observed [114]. Thus it is
Figure 4.9: Curves of initial magnetization for temperatures of 2, 5, and 10 K (sample C). Inset: enlargement in the low-$H$ region.
not possible to determine with certainty that the system exhibits true cooperative
spin glass-like transition based solely on the dc magnetization studies.

The temperature dependence of the linear ac susceptibility \( \chi_{ac} = \chi' - i\chi'' \) for
sample C, measured for a wide range of frequencies (4 \( \leq f \leq 3330 \) Hz), is displayed
in Fig. 4.10. The in-phase component \( \chi' \) begins to exhibit frequency dependence
below \( \sim 18 \) K. This temperature nearly coincides with the temperature \( T_c \) at which the
vanishing of remanence and the onset of the weak irreversibility at low \( H \) are observed
(Fig. 4.5). At about the same temperature the nonzero out-of-phase component \( \chi'' \)
occurs. As \( T \) is decreased below \( T_c \) the \( f \)-dependence becomes more pronounced.
Both susceptibility components exhibit \( f \)-dependent peaks at temperatures close to
the \( M_{sfC} \) peak temperature \( T_{max} \) for the lowest values of \( H \). Both peaks decrease
in magnitude and shift to higher temperatures with increased \( f \). The frequency
dependence of \( \chi_{ac} \) indicates slow relaxation processes that characterize the glassy
behavior and freezing into a nonequilibrium state [64, 115]. For a material with long-
range ferro- or ferrimagnetic order no frequency-dependent behavior (particularly not
\( f \)-dependence of their magnetic ordering temperatures) is expected at relatively low
\( f \) values used in the ac susceptibility experiments, as the relaxation processes in these
materials are much faster than the experimental time scale \( 1/f \) [64].

The relative shift of the \( \chi' \) peak temperature \( T_f \) per decade of frequency is
\( \delta T_f \equiv (\Delta T_f / T_f) / \Delta (\log f) \approx 0.01 \). The value of this parameter has been used to
distinguish between the systems with cooperative (spin glass-like) freezing of mag-
netic moments, and the systems consisting of noninteracting or weakly interacting
magnetic particles, mentioned above, which also exhibit frequency dependence of
their blocking temperature. The value of 0.01 in the present system is in the range
Figure 4.10: Temperature dependence of the in-phase ($\chi'$) and out-of-phase ($\chi''$) linear ac susceptibilities at different frequencies between 4 and 3330 Hz (sample C).
Figure 4.11: Fit of the frequency dependence of the $\chi'$ peak temperature $T_f$ to the Arrhenius law: $f = f_0 \exp[-E_a/k_B T_f]$ (sample C).

typical for canonical spin glasses, suggesting strong cooperative behavior and spin glass-like freezing of the cluster magnetic moments. In contrast, in superparamagnet-like systems the values of $\delta T_b$ are typically an order of magnitude higher ($> 0.1$) [64, 116].

In a pure superparamagnet (assembly of noninteracting magnetic particles) the magnetic relaxation of a particle is described by the Arrhenius law of thermal activation over the anisotropy energy barrier $E_a$, $\tau = \tau_0 \exp(E_a/k_B T)$, where $\tau$ is the relaxation time for magnetization reversal of the particle and $\tau_0$ a characteristic microscopic relaxation time. This means that in the ac susceptibility experiment the dependence on the blocking temperature on the driving frequency $f$ is given by $f = f_0 \exp(-E_a/k_B T_b)$. By plotting $\log f$ versus $1/T_b$ the values of parameters $E_a$ and
Figure 4.12: Fit of the frequency dependence of the $\chi'$ peak temperature to the Vogel-Fulcher law: $T_f = T_0 - E_a/[k_B \ln(f/f_0)]$, with $f_0 = 10^{13}$ s$^{-1}$ (sample C).

$T_b$ can be obtained from the linear fit. Figure 4.11 shows an attempt to fit the $T_f(f)$ dependence for the $\chi'$ data from Fig. 4.10 with the Arrhenius law. While a good fit is obtained, the determined values of parameters are unphysical: $f_0 = 10^{93(3)}$ Hz and $E_a = 2700(90)$ K, confirming that the description of the frequency dependence of $T_f$ in the present system by a simple thermal activation of independent magnetic particles is completely inappropriate.

In cases when interparticle magnetic interactions are present, the frequency dependence of the $\chi'$ peak has been often described by the Vogel-Fulcher law, $f = f_0 \exp[-E_a/k_B(T_f - T_0)]$ [64, 114, 117, 118, 119, 116]. This expression has a form of the Arrhenius law modified with an additional parameter $T_0$. While the law, valid for $T > T_b$, is usually considered an empirical one, attempts have been made to relate
it to the interparticle interaction strength \cite{64, 116}. Furthermore, the value of the parameter $\alpha \equiv (T_f - T_0)/T_f$ has been proposed as a criterion to distinguish between different classes of materials, ranging from $\sim 1$ for superparamagnets to $\sim 0.1$ for spin glasses \cite{117, 116}. The Vogel-Fulcher law fit to the presented data for Co-Fe Prussian blue is displayed in Fig. 4.12, where $T_f(f)$ is plotted versus $1/\ln(f/f_0)$, and $E_a$ and $T_0$ obtained as the linear fit parameters. Good fits were obtained for different sets of values of the three parameters. It was therefore necessary to fix $f_0$ and vary the two remaining parameters, as in the earlier studies \cite{116, 119}. Figure 4.12 shows fit with $f_0 = 10^{13} \text{s}^{-1}$, a value adopted as a standard value for comparison of different systems \cite{116, 119, 117}. The fit gives the parameter values of $T_0 = 11.41(6)$ K, $E_a = 38(2)$ K, and $\alpha = [T_f(4\text{Hz}) - T_0]/T_f(4\text{Hz}) = 0.1$, with $\alpha$ being in the range characteristic for spin glasses. The values $E_a$ and $\alpha$ were found to decrease with decreasing $f_0$, while values of $f_0$ significantly higher than $10^{13}$ Hz are without physical meaning.

Thus, based on the dc magnetization behavior and the two empirical criteria for the $f$ dependence, the temperature $T_f$ can be identified as the temperature at which cluster magnetic moments undergo cooperative freezing in the experimental time window given by $1/f$ (the freezing temperature). The temperature of the spin glass transition $T_g$ is given by $T_g = T_f(f \to 0)$ \cite{64}. The freezing process is characterized by the dynamical slowing down of the spin fluctuations near the glass transition temperature $T_g$, and a power-law divergence of the critical relaxation time $\tau$ \cite{54, 64}

$$\tau = \tau_0 \left(\frac{T}{T_g} - 1\right)^{-\nu},$$

(4.1)
where \( z \nu \) is the dynamical critical exponent. In the language of experiment, one can write [64]

\[
\tau_{av} = \tau_0 \left( \frac{T_f}{T_g} - 1 \right)^{-z \nu},
\]

(4.2)

where \( \tau_{av} \) is the average relaxation time. A more convenient form for comparison with experiment is \( T_f = T_g \left[ 1 + (\tau_0 f)^{1/z \nu} \right] \). Again a fixed value of \( \tau_0 \) is commonly taken and fitting done with two parameters [120]. Figure 4.13 shows \( \log(T_f - T_g) \) plotted versus \( \log(\tau_0 f) \), with \( \tau_0 = 10^{-13} \) s, as in Ref. [120]. A good fit is obtained, with parameter values \( T_g = 12.47(4) \) K and \( z \nu = 7.6(2) \). The value of \( z \nu \) is within the range typical for spin glasses. Fitting with different values of \( \tau_0 \) was also done, having in mind that the experimentaly determined upper limit of \( T_g \) is the \( T_f \) value for the lowest frequency used (\( T_f(4 \text{ Hz}) = 12.75 \) K). For longer \( \tau_0 \), value of \( T_g \) was found to
increase, while $z\nu$ decreased. The opposite trend was observed with decreasing $\tau_0$. Maximum value of $\tau_0$ for which the condition $T_g < \min(T_f)$ still holds is about $10^{-8}$ s, and the corresponding value of $z\nu$ is about 3.1, still in the range characteristic for spin glasses. While values of $\tau_0$ significantly below $10^{-13}$ s lose physical significance, as they cannot correspond to any magnetic relaxation process in the material, even for $\tau_0$ as low as $10^{-16}$ s the corresponding value of $z\nu = 11.0(3)$ (with $T_g = 12.26(5)$ K) is still an acceptable value for a spin glass [64].

The second ($\chi_2$) and third ($\chi_3$) nonlinear susceptibilities, measured as the second and third harmonics in applied ac field of 5 Oe and at three different frequencies, are displayed in Fig. 4.14. Both harmonics exhibit an increase from near-zero values below $\sim 18$ K, and exhibit frequency-dependent peaks at temperatures close to the $\chi'$ peak temperature. One of the characteristic features of the spin glass transition is a power-law divergence of the nonlinear susceptibility $\chi_3$ at the transition temperature [64, 54]. In contrast, in a SP-like system with progressive blocking of magnetic moments $\chi_3$ is only weakly $T$-dependent [121]. Relatively sharp peak in the third harmonic at Fig. 4.14(b) suggests divergence of $\chi_3$ in Co-Fe Prussian blue. However, the occurrence of $\chi_2$ is not consistent with the spin glass behavior, as noted in Ch. 3. It may be associated with the spontaneous magnetic moment within spin clusters. As no theoretical guidelines for the behavior of nonlinear susceptibility in cluster glasses are available in the literature, these results are not analyzed further.

While the overview of the magnetic properties of Co-Fe Prussian blue in this section presented mostly data for one particular sample (C), the other two samples exhibit qualitatively the same low-$T$ magnetic behavior, suggestive of cluster glass state: irreversible magnetic behavior, with $H$-dependent bifurcation temperature;
Figure 4.14: Second (a) and third (b) harmonic ac susceptibilities at three different frequencies for sample C.
Figure 4.15: Field-cooled and zero-field cooled magnetizations (open and solid symbols, respectively) at $H = 10$ Oe for Prussian blue samples A (a) and B (b).
Table 4.1 gives comparison of some magnetic ordering parameters for the three Co-Fe Prussian blue analogs studied (bulk samples). The magnetic moment per $\text{K}_2\text{Co}_y[\text{Fe(CN)}_6]\cdot\text{zH}_2\text{O}$ unit was determined from the measured magnetization at $T = 2$ K and $H = 55$ kOe. As $M$ does not reach saturation at 55 kOe, these values are actually the lower limits of the magnetic moment per unit. The quasicritical temperature $T_c$ was estimated as the temperature at which $M_{\text{rem}}$ vanishes below the detection limit, thus the values given in the table present the lower limit of $T_c$. In all cases this temperature nearly coincided with the bifurcation temperature $T_b$ at very low fields. The upper limits for the spin glass transition temperature were determined as $T_f$ values for the lowest frequency used in the $\chi_{ac}$ measurements. While values of the magnetic moment per unit are consistent with the expected increase of the spin concentration with the amount of disorder (number of Fe(CN)$_6$ vacancies), the

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu_B$/unit&gt;</th>
<th>$T_c&gt;$</th>
<th>$T_g&lt;$</th>
<th>$\delta T_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.5</td>
<td>17.5</td>
<td>12.45</td>
<td>0.006(1)</td>
</tr>
<tr>
<td>B</td>
<td>1.8</td>
<td>17.5</td>
<td>12.60</td>
<td>0.010(2)</td>
</tr>
<tr>
<td>C</td>
<td>2.4</td>
<td>18.0</td>
<td>12.75</td>
<td>0.010(2)</td>
</tr>
</tbody>
</table>

Table 4.1: Comparison of magnetic properties of Co-Fe Prussian blue analogs.

non-saturated magnetization at $H = 55$ kOe; macroscopic-time relaxation of the remanent magnetization and $M_{\text{Fe}}$; $f$-dependent ac susceptibility, with $\delta T_f \sim 0.01$; sharp peaks in the harmonic susceptibilities. Fig. 4.15 shows magnetizations for $H = 10$ Oe for samples A and B, which exhibit very similar behavior to the one of sample C.
behavior of other parameters is less systematic and suggests a complicated role of the disorder in these systems.

4.3 Optical Control of Cluster Glass Order in Co-Fe Prussian Blue

The first part of this section presents data that confirm two basic PIM effects, reported by Sato et al. [3]: photoinduced enhancement of the magnetic hysteresis, and switching of magnetization by light of different wavelengths. The section then proceeds with the detailed studies of the photoinduced effects on the cluster glass ordering.

The room-temperature UV-Vis absorption spectrum of Co-Fe Prussian blue in Nujol, Fig. 4.16, shows a broad band in the region $\sim 500-800$ nm, and another peak

![UV-Vis Spectrum](image-url)
at 480 nm. The broad band has been assigned to the charge transfer transition from Fe$^{II}$(ls) to Co$^{III}$(ls) [3, 85]. By comparison with the spectrum of Co$_{1.5}$[Fe(CN)$_6$]-6H$_2$O, the peak at 480 nm may be assigned to the $d - d$ transition of Co$^{II}$(hs) [85].

The magnetic hysteresis for the ground and photoexcited states at 5 K is shown in Fig. 4.17. The sample was illuminated with red light from a halogen lamp (vide infra) at 5 K for one hour, and warmed to 30 K after illumination. A minor hysteresis loop between -5 kOe and 5 kOe was measured. In the photoexcited state the remanence is increased from about 7 emu/g to about 17 emu/g, while the coercive field is increased from about 400 Oe to about 850 Oe.

The optical switching of magnetization in Co-Fe Prussian blue is demonstrated in Fig. 4.18. The magnetization was measured at 50 Oe and 5 K after field-cooling. Two
Figure 4.18: Switching of magnetization with red light ($\lambda_{\text{peak}} = 650$ nm, bandwidth = 90 nm, $I \sim 10$ mW/cm$^2$) and blue light ($\lambda_{\text{peak}} = 470$ nm, bandwidth = 70 nm, $I \sim 8$ mW/cm$^2$) for sample C.

Different interference filters were used (red light: $\lambda_{\text{peak}} = 650$ nm, bandwidth = 90 nm, light intensity $I \sim 10$ mW/cm$^2$; blue light: $\lambda_{\text{peak}} = 470$ nm, bandwidth = 70 nm, $I \sim 8$ mW/cm$^2$). The data show that $M$ can be switched between two values using visible light of different energies, and that this switching cycle can be repeated. The result confirms the initial report from Ref. [3]. It is noted that, while the plotted data suggest equal rates for the two processes, this is actually not the case. The process of the magnetization increase with red light was found to be several times faster than the blue light-induced reverse process, possibly due to the stronger absorption of light in the blue region of spectrum (Fig. 4.16), i.e., smaller light penetration depth. In order
Figure 4.19: Effect of illumination on the magnetization of Co-Fe Prussian blue (sample C). Illuminated with red light, $\lambda_{\text{peak}} = 650$ nm, bandwidth = 90 nm, $I \sim 35$ mW/cm$^2$.

to achieve equal rates of the switching processes, the sample was initially illuminated with red light to a state with non-saturated PIM (vide infra), at which the increase rate of $M$ during illumination is comparable to the rate of the reverse process induced by blue light. Thus, the initial value of $M$ in Fig. 4.18 does not correspond to the ground state. The filters were quickly interchanged in the pause between two data points, without switching the lamp off. The abrupt changes in $M$ upon switching of red with blue filter and vice versa (see Fig. 4.19) were avoided by adjusting the power of light so that the heating effects for red and blue light were equal.

Figure 4.19 shows field-cooled magnetization $M$ measured in regular time intervals at $H = 50$ Oe and $T = 5$ K. Upon illumination with red light from a halogen lamp
(λ_{peak} = 650 nm, bandwidth = 90 nm, I \sim 35 \text{ mW/cm}^2), M \text{ rapidly increases. The increase rate gradually drops, and the PIM effect reaches saturation in about one hour. Upon turning the lamp off, } M \text{ abruptly increases by additional } \sim 6\%, \text{ which is attributed to the facts that the local sample temperature during illumination was higher than the nominal value of 5 K measured by the temperature sensor, and that the sample cools back to 5 K after illumination. The measurement of } M_{fc}(T) \text{ in the photoexcited state indicates that this local heating of the sample increases sample temperature by about 2 K. The total increase of } M \text{ after illumination is about 50 } \%\text{. The sample was subsequently warmed to 30 K (paramagnetic regime), and field-cooled back to 5 K. Interestingly, an additional 15 } \% \text{ increase in } M \text{ is observed after this thermal cycle. Repeated thermal cycles did not lead to further increase in } M.\]

This history dependence of PIM is shown in more detail in Fig. 4.20. The sample in the ground state was field-cooled to 4.5 K and } M_{fc} \text{ subsequently measured on warming up to 25 K (curve 1). The sample was afterwards slowly cooled back to 4.5 K, with } M(T) \text{ measurement continued during cooling (curve 2). Upon reaching 4.5 K, the sample was illuminated with red light to saturation. After illumination } M \text{ was measured, again both on warming (curve 3) and subsequent cooling (curve 4). While the curves 1 and 2 show very small difference, the difference between curves 3 and 4 is substantial, as expected from the data at Fig. 4.19, and it is observed for } T < 12 \text{ K. This behavior can be readily accounted for as a consequence of the cluster glass state at } T \text{ below } \sim 12 \text{ K, determined in the previous section. However, several remarks on the physical meaning of the field-cooled and zero-field-cooled magnetization will be made first.}
Figure 4.20: History dependence of the photoinduced magnetization at $H = 100$ Oe (sample C). The experiment was done in the following sequence: (1) Field-cooled to 4.5 K, $M$ measured on warming (open triangles); (2) $M$ measured on cooling (solid triangles); (2-3) Illuminated for one hour ($\lambda_{\text{peak}} = 650$ nm, bandwidth = 90 nm, $I \sim 35$ mW/cm$^2$); (3) $M$ measured on warming (open circles); (4) $M$ measured on cooling (solid circles). Arrows indicate the direction of $T$ change during the respective $M(T)$ measurement.

After zero-field-cooling below the freezing temperature, spin glass system finds itself in one of the many 'valleys' of the phase space (Section 2.4.4), in a state far from thermodynamic equilibrium [64, 62]. Due to extremely long relaxation times in the frozen state, it takes a macroscopic time (infinite time, for all practical purposes) for the system to reach the equilibrium. Upon applying magnetic field after zero-field cooling, $M_{\text{ZFC}}$ very slowly increases towards the corresponding $M_{\text{FC}}$ value and,
presumably, $M_{fc}(t \to \infty) \approx M_{fc}$ [64]. On the other hand, $M_{fc}$ reflects behavior of the system much closer to the equilibrium. Some authors even proposed that it corresponds to the real thermodynamic equilibrium, i.e., "averaging over all available states, the full Gibbs average" [122, 62]. It is usually considered that $M_{fc}$ is fully reversible, i.e., if after field-cooling temperature is cycled back and forth at constant $H$, $M_{fc}$ traces the same path. However, careful observations found a slight dependence of $M_{fc}$ on the cooling rate [123], as well small irreversibilities and slow changes with time [124, 125, 126], implying that it cannot correspond to a true thermal equilibrium [62]. For the purpose of interpretation of the data in Fig. 4.20 it will be sufficient to consider the field-cooled state a good approximation of the equilibrium state.

The imperfect reversibility of $M_{fc}$ in Fig. 4.20 is indicated by the small deviation between curves 1 and 2. This deviations may be attributed to the fact that, while the curve 1 was obtained after relatively quick direct field-cooling to 4.5 K, the curve 2 was measured during slow cooling (~0.2 K/min). Thus, in the latter case the time available for the system to equilibrate was longer, and it is closer to the true equilibrium. After illumination at 4.5 K new spins are introduced in the cluster glass matrix, and the system is expected to relax into a new 'equilibrium' configuration, corresponding to the changed spin distribution in the photoexcited state. However, due to the very slow dynamics, during the experimental time available it remains in some intermediate state (curve 3) between the previous 'equilibrium' (curve 2) and the new 'equilibrium' (curve 4). Only after warming to $T > T_g$ the magnetic moments 'melt down' and upon subsequent slow cooling (curve 4) the maximum values of $M_{fc}$ for the photoexcited state are achieved.
Figure 4.21: Field-cooled (squares) and zero-field-cooled (circles) magnetizations for the ground and photoexcited states (solid and open symbols, respectively) at $H = 10$ Oe (sample C). Inset: enlargement near the quasicritical temperature.

In all experiments to be presented in the rest of this section, illumination of samples was performed at 5 K, using halogen lamp and interference filter with $\lambda_{\text{peak}} = 650$ nm and bandwidth of 90 nm, as above. The intensity of light was $\sim$30-50 mW/cm$^2$, and samples were illuminated for the time period needed to reach saturation of PIM (1-2 hours). In order to avoid the relaxation effects discussed in the previous few paragraphs, illuminated samples were subsequently warmed to 30 K, which erased the magnetic ordering, while not significantly affecting the population of the photoexcited state.

The field-cooled and zero-field cooled magnetizations at 10 Oe for the ground and photoexcited states are shown in Fig. 4.21. The measurement sequences for the
Figure 4.22: Zero-field-cooled magnetization for the ground and photoexcited states (solid and open symbols, respectively) at different applied fields (sample C).

ground and photoexcited states were identical, with equal cooling rates and waiting times for temperature stabilization. In the photoexcited state, $M_{fc}$, the peak value of $M_{zfc}$, and the characteristic temperatures ($T_c \sim T_b$ and $T_{max}$) are increased. While decreased signal/noise ratio in the higher temperature region impedes determination of $T_c$ by a $M_{rem}(T)$ measurement, identification of $T_c$ with the low-field adopted in the previous section, leads to the conclusion that $T_c$ shifts from $\sim$18 K in the ground state to $T_c^{illum} \sim$ 20 K in the photoexcited state. The increase in $T_{max}$ is also about 2 K.
While the $M_{zfc}$ peak is increased in magnitude, at lower temperatures the zero-field-cooled magnetization for the photoexcited state ($M_{zfc}^{\text{illum}}$) is below the ground-state $M_{zfc}$. This crossover between the $M_{zfc}$ and $M_{zfc}^{\text{illum}}$ curves is observed for fields as high as 1 kOe (Fig. 4.22).

Magnetization measured at different applied fields (Fig. 4.23) shows that the photoexcited state exhibits irreversibility with $H$-dependent bifurcation, similar to the ground state. However, in the photoexcited state the irreversibilities are more pronounced.

The increased $T_{\text{max}}$ after illumination indicates that the freezing temperature in the photoexcited state is higher than in the ground state. Thus the entire dynamics of freezing (characterized by deepening of the local minima in the free energy hypersurface and, consequently, increased irreversibility as $T$ is lowered below $T_g$) is shifted to higher $T$. Therefore, at a given temperature below $T_g$ the illuminated material has increased irreversibility. In this particular sample this leads to a decrease in the low-temperature $M_{zfc}$ after illumination, a result that would be counter-intuitive for a material with a conventional magnetic order, considering that the spin concentration after illumination is increased. Thus the presented behavior can be understood as a direct consequence of the cluster glass state and the increased freezing temperature after illumination.

The magnetization for samples A and B, measured at 10 Oe, is displayed in Fig. 4.24. Similar to sample C, the characteristic temperatures $T_c$ and $T_{\text{max}}$ for these two samples are increased after illumination, as indicated by the respective shifts of the $M_{fc}/M_{zfc}$ bifurcations (insets in Fig. 4.24), and shifts in the $M_{zfc}$ peak.
Figure 4.23: Field-cooled and zero-field-cooled magnetization (solid and open symbols, respectively) for the ground (top) and photoexcited (bottom) states at different applied fields (sample C).
Figure 4.24: Field-cooled (circles) and zero-field-cooled (squares) magnetizations for the ground and photoexcited states (solid and open symbols, respectively) at $H = 10$ Oe, for samples A (a) and B (b). Insets: enlargements near the quasicritical temperatures.
Figure 4.25: Time dependencies of the zero-field-cooled magnetization (top) and the remanent magnetization (bottom) at 5 K (sample B). Solid symbols: ground state; open symbols: photoexcited state.
temperatures. In contrast to sample C, these two samples do not exhibit a crossover between $M_{zfc}$ and $M_{illum}$.

Figure 4.25 shows the time dependencies of the remanent magnetization (measured after cooling in $H = 10$ Oe and subsequently reducing the field to zero) and the zero-field-cooled magnetization (measured in $H = 20$ Oe) for the ground and photoexcited states of sample B. Both the $M_{rem}$ and $M_{zfc}$ exhibit relaxation over macroscopic time scales, characteristic for a frozen state. The absolute changes in $M_{zfc}$ within the elapsed time period are nearly equal for the ground and photoexcited states. However, when compared with the respective field-cooled magnetization, the relative increase
in $M_{zfc}$ (defined as $M_{zfc}/M_{fc}$) is about 1.6 times higher in the ground state than in the photoexcited state. It is noted that, for the illuminated sample, the decay of the remanent magnetization is partially due to the depopulation of the photoexcited state.

The measurement of the decay of the field-cooled magnetization for the illuminated sample showed a decrease of about 0.3 % on the time scale of $10^4$ s. No measurable time dependence of $M_{fc}$ was observed at this time scale for the material in the ground state.

Figure 4.26 shows the temperature dependence of the relative photoinduced increase in the field-cooled magnetization, $\delta M_{fc}$, defined as $\delta M_{fc} = (M_{fc}^{illum}/M_{fc}^0) - 1] \times 100\%$, where $M_{fc}^0$ and $M_{fc}^{illum}$ are the field-cooled magnetizations for the ground and photoexcited states, respectively. $\delta M_{fc}$ is determined for different applied fields between 5 Oe and 1 kOe. In the high-$T$ (paramagnetic) region, $\delta M_{fc}$ is essentially independent on $H$, reflecting the fact that no magnetic order is present, and therefore $\delta M_{fc}$ is determined solely by the photoinduced increase in the number of spins. For $T = 30K$ the value of $\delta M_{fc}$ is about 16 %, which may be taken as an upper limit for the relative increase in the total spin number. In contrast, at low temperatures $\delta M_{fc}$ has strong $H$-dependence, and decreases with increased $H$. $\delta M_{fc}$ rapidly increases below $\sim 19$ K, and exhibits a maximum around 16 K, as a consequence of the fact that in this temperature region the material undergoes a paramagnet-cluster glass transition.

Linear in-phase susceptibility for the ground and photoexcited states of sample B is displayed in Fig. 4.27. In the photoexcited state the peaks in $\chi'$ and $\chi''$ are increased in height and shifted to higher temperatures by about 2 K, confirming the increase of the freezing temperature suggested by the dc magnetization data. The
Figure 4.27: In phase (top) and out-of-phase (bottom) ac susceptibility at different frequencies for sample B. Solid symbols: ground state; open symbols and lines: photoexcited state. $\chi''$ data for $f = 11$ Hz were too noisy and they are not shown.
quasicritical temperature, indicated in the ac susceptibility data by the onset of \( f \) dependence of \( \chi' \) and occurrence of nonzero \( \chi'' \), is also increased by about 2 K after illumination. The relative frequency shift of the freezing temperature is decreased from \( \delta T_f = 0.010(2) \) in the ground state to 0.006(1) in the photoexcited state.

Similar photoinduced effects are observed in the linear ac susceptibilities of samples A and C. However, close inspection of the ac response of sample A, Fig. 4.28, reveals a feature that differs it from the other two samples. While \( T_f \) increases by about 2 K after illumination, both the \( f \) dependence of \( \chi' \) and nonzero \( \chi'' \) persist at temperatures as high as 23 K in the photoexcited state, suggesting that \( T_c \) increases by as much as 6-7 K. This contrasts the behavior of samples B and C, in which photoinduced increase in both \( T_c \) and \( T_f \) is about 2 K. The \( T_c^{\text{illum}} \) value of about 23 K is consistent with the \( M_{fc}/M_{zfc} \) bifurcation temperature, estimated as 22.5 K (inset, Fig. 4.24).

This peculiarity of sample A becomes particularly pronounced in the nonlinear susceptibility data. Figure 4.29 compares the second and third harmonic susceptibilities for the ground and photoexcited states of samples A and B. Both \( \chi_2 \) and \( \chi_3 \) are increased by illumination, as well as their peak temperatures. \( \chi_2 \) and \( \chi_3 \) for sample B each exhibit a single sharp peak in both the ground and photoexcited states. In contrast, the photoexcited state of sample A shows an additional shoulder in both harmonics, in the temperature region 18-23 K.

The presented behavior of sample A could in principle result from the existence of two distinct phases in the material, with one of them being in paramagnetic (or diamagnetic) state before illumination (thus not giving contribution to \( \chi_2 \) and \( \chi_3 \)), and upon illumination undergoing a transition into a magnetically ordered state. An
Figure 4.28: In phase (top) and out-of-phase (bottom) ac susceptibility at different frequencies for sample A. Solid symbols: ground state; open symbols and lines: photoexcited state. Frequencies that produced noisy $\chi''$ data are not shown in the bottom graph.
Figure 4.29: Harmonic susceptibilities for samples A (a) and B (b) at ac field of 15 Oe and frequency of 110 Hz. Solid symbols: ground state; open symbols: photoexcited state. Circles represent the second harmonic $|\chi_2 h_0|$. Triangles represent the third harmonic $(3/4)|\chi_3 h_0^2|$. 
Figure 4.30: Temperature dependence of the coercive field for the ground and photoexcited states (solid and open symbols, respectively) of sample A. Inset: same data, with $H_c$ on a logarithmic axis. Lines on both graphs are exponential fits: $H_c = a \exp(-T/b)$, with $a = 2270$ Oe ($2550$ Oe) and $b = 2.7$ K ($3.2$ K) for the ground (photoexcited) state.

argument against this explanation is the fact that such photoinduced transition from para(dia)magnetic to a magnetically ordered state has not been observed in any of the K$_2$Co$_y$[Fe(CN)$_6$]$\cdot$zH$_2$O magnets synthesized by the precipitation method, used here (however, it has been observed in several Co-Fe Prussian blue analogs synthesized via different routes [85, 97]). An alternative interpretation of this behavior can be proposed without employing the assumption of two separate phases. Sample A has
the lowest ground-state spin concentration of the samples studied here. Thus, when new spins are introduced into the lattice by photoexcitation, they likely couple into clusters more easily than spins in the more disordered samples. In other words, low level of structural disorder may lead to a higher level of local magnetic order, which explains unusually high $T_{c_{\text{illum}}}$. However, due to the low overall spin concentration, the clusters formed by photoexcitation may remain decoupled from one another. Their moments instead undergo progressive blocking, indicated by the broad shoulder in $\chi_2$ and $\chi_3$, weak frequency dependence, and weak $M_{fc}/M_{Lfc}$ irreversibility below $\sim 23$ K. Only at a $T$ significantly lower than $T_{c_{\text{illum}}}$ these spin clusters become strongly coupled with others and participate in the collective freezing process.

Figure 4.30 shows the temperature dependence of the coercive field ($H_c$) for the ground and photoexcited states of sample A. The values of $H_c$ were determined from the hysteresis loops measured between -55 kOe and 55 kOe. A correction for the remanent field in the superconducting magnet was performed (Ch. 3). The estimated maximum error in determination of $H_c$ is $\pm 3$ Oe. In the region below 8 K (10 K) the data for the ground (photoexcited) state can be fit to an exponential functional form $H_c = a \exp(-T/b)$. Fitting parameters are $a = 2270(4)$ Oe and $b = 2.70(6)$ K for the ground state, and $a = 2550(7)$ Oe and $b = 3.20(7)$ K for the photoexcited state. At higher temperatures deviations from this dependence occur (inset, Fig. 4.30). While in the literature to date there are no theoretical predictions for the temperature dependence of the coercivity in spin glasses or cluster glasses, the exponential decrease of $H_c$ with increased $T$ is not consistent with the existing simple models for coercivity in conventional magnetic systems. For instance, the weak pinning mechanism predicts a linear drop of $H_c$ with temperature increase; the
strong pinning mechanism predicts dependence of the form $H_{c}^{1/2} = H_{0}^{1/2} - \text{const}T^{2/3}$; for single-domain particles the dependence has form $H_{c} = a - bT^{1/2}$ [127, 75].

The photoinduced increase in $H_{c}$ in Prussian blue analogs has not been accounted for in the previous studies. Within the cluster glass model proposed here, this effect is readily explained as a consequence of the shift of the freezing dynamics to higher temperatures. More details are given in the following section.

The presented results demonstrate the cluster glass type of magnetic order in both the ground and photoexcited states. The formation of clusters and their cooperative freezing occur at higher temperatures in the photoexcited state. The three samples studied show similar general PIM behavior, with the exception of the "two phase-like" behavior of sample A.

4.4 Summary and Discussion

Based on the presented magnetic studies, the low-$T$ magnetic response of Co-Fe Prussian blue analogs 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 and form clusters of spins. The transition is characterized by: (i) rapid increase in $M$; (ii) onset of the weak $M_{fc}/M_{zfc}$ irreversibility; (iii) occurrence of magnetic absorption, indicated by a nonzero $\chi''$; (iv) rapid increase in $\chi'$ and onset of its frequency dependence; (v) occurrence of the nonlinear susceptibility.

It is proposed that the ferrimagnetic order is limited to spin clusters, the sizes of which increase as temperature is decreased, but always remain finite. At temperatures just below $T_{c}$ magnetic moments of individual clusters undergo progressive blocking.
due to energy barriers induced by crystalline and shape anisotropies, causing weak irreversibility and $f$-dependent behavior.

(2) At temperature defined as $T_g = T_f(\gamma \to 0)$ (the spin glass transition temperature) the cluster-cluster interactions produce transition into a spin glass-like state, in which the clusters' magnetic moments are frozen in random directions. The transition is indicated by:

(i) $f$-dependent peaks in $\chi'$, $\chi''$ and the nonlinear susceptibilities and (ii) onset of the strong $M_{fc}/M_{zfc}$ irreversibility and a peak in the low-field $M_{zfc}$. In contrast to the transition as $T_c$, the experiments suggest that this process is a real thermodynamic transition (with divergent spin glass correlation length, Ch. 2).

This qualitative model readily incorporates effects of light excitation on the low-$T$ magnetic behavior. Upon illumination new spins are introduced into the lattice, via the photoinduced charge transfer. It is proposed that increased spin concentration ($n_s$) in the photoexcited state has the following effects:

- Greater average number of magnetic neighbors of a given spin enables formation of the spin clusters at a higher temperature $T_{c\text{illum}} > T_c$. Furthermore, at a given temperature, higher $n_s$ leads to an increase in sizes of existing clusters and their magnetizations, as well as a decreased mean distance between clusters. The number of clusters of a given size at a given temperature is also expected to increase. These effects are all easily visualized if one considers a regular lattice in which new spins are (randomly) added (the approach known as the theory of percolation, see, e.g., Ref. [64]).
Figure 4.31: Scheme of the photoinduced magnetic effects in the cluster glass model. The meaning of the symbols is as follows: $n_s$—spin concentration; $M$—magnetization; $T_c$—quasicritical temperature; $\xi$—ferrimagnetic and spin-glass correlation lengths; $\tau$—relaxation times; $T_f$—freezing temperature; $\Delta$—energy barriers for rotation of cluster moments; $H_c$—coercive field. Arrows inside the ellipses indicate photoinduced increase in the respective quantities. Arrows between the ellipses indicate hierarchical order in the photoinduced effects within the cluster glass model.

- The correlation length for the colinear magnetic order is related to the sizes of clusters, thus this correlation length is increased after illumination. The shorter distances between clusters and their higher magnetic moments in the photoexcited state are expected to enhance intercluster interactions. Thus the intercluster correlations, characterized by the spin glass correlation length, are also expected to be enhanced.

- The relaxation times in the system are increased after illumination. This is directly observed in the experiments. Consider, for instance, the ac susceptibility
for the ground and photoexcited states at a fixed temperature (e.g., 17 K) between $T_c$ and $T_{c\text{illum}}$ (Fig. 4.27). While in the ground state $\chi'$ is frequency-independent, after illumination the $f$-dependence occurs, indicating that the maximum relaxation time has extended beyond the experimental time scale. Above temperatures at which the cooperative spin glass freezing begins to dominate the magnetic behavior, the lengthening of the relaxation times can be attributed to the changes in relaxation of individual, weakly coupled clusters. This relaxation is described by the Arrhenius law, in which the relaxation rate depends on the size of the anisotropy barrier. As cluster sizes increase after illumination, their anisotropy energies (proportional to the cluster volume, Section 2.4.5) also increase, leading to a slower relaxation. When intercluster interactions become strong enough, and the spin glass freezing sets off (critical regime, near the spin glass transition temperature), the relaxation time scales with the spin glass correlation length, which is expected to increase, as noted above.

- The increased spin glass correlation length 'accelerates' the freezing process, and leads to freezing of cluster moments at a higher temperature $T_{f\text{illum}} > T_f$. Here it is worth mentioning the experiments done on metallic spin glasses, in which higher magnetic impurity concentration led to increased freezing temperature, similar to the present case (see, e.g., examples given in Ref. [64]).

- Summarizing these arguments, increased $n_e$ leads to an increase of the relevant length and time scales in the material, and, consequently, to a shift of the entire dynamics of magnetic ordering to higher temperatures.

- Within the cluster glass model the following mechanism for the photoinduced coercivity is proposed. The process of cooperative, spin glass-like, freezing is characterized by the occurrence of a multi-valley free energy landscape, with energy barrier
heights rapidly increasing with decreasing temperature ('coarse graining' of the landscape, Ch. 2) [62, 64, 128]. Hence, as temperature is lowered, higher magnetic field is needed to change orientation of frozen magnetic moments and surmount the energy barriers, leading to a rapid increase in the coercivity with lowering of $T$. After illumination, the spin glass transition occurs at a higher temperature than in the ground state; thus, at a given temperature in the frozen state, the illuminated material has advanced further into the freezing process than the material in the ground state. Therefore the energy barriers for moment rotation are higher than in the ground state, leading to a higher $H_c$. It is noted that individual spin clusters are also expected to exhibit coercivity, due to the energy barriers related to the single-ion and shape anisotropies. It is possible that clusters decoupled from the cluster-glass matrix exist even below $T_g$, thus giving an additional contribution to the coercivity of the material.

The proposed model is presented schematically in Fig. 4.31. Here $\tau$ denotes the relaxation times in the system (both the average and maximum values). $\xi$ denotes both the ferrimagnetic (non-divergent) correlation length, related to the cluster sizes, and the spin glass correlation length, proposed to diverge at $T_g$. $\Delta$ denotes the energy barriers for cluster moment rotation in the frozen state. The arrows inside the ellipses indicate increases in the respective quantities.

According to the current state of understanding of spin glasses, the two necessary conditions for the occurrence of spin glass order are randomness and frustration (Ch. 2). In the studied Prussian blue analogs randomness is related to the structural disorder, i.e., randomly distributed vacancies that produce a random distribution of magnetic ions. However, the origin of frustration is an open question and macroscopic
magnetic studies cannot give an answer to it. Here two possible sources of competing interactions that could in principle give rise to frustration will be noted.

In the analyses of magnetic coupling in Co-Fe Prussian blue systems only the nearest-neighbor interactions have been considered. However, the next-nearest-neighbor interactions may have considerable strengths in a Prussian blue-based system. This is for instance suggested by a report of ferromagnetism at 5.6 K in the 'original' Prussian blue Fe₄[Fe(CN)₆]₃ · xH₂O [129]. In this system the uncompensated spins (S=5/2) are located on Fe^{III}(hs) ions. The spins are coupled with the next-nearest-neighbors through the superexchange interaction along the sequence Fe^{III}(hs)—NC—Fe^{II}(ls)—CN—Fe^{III}(hs). The Fe^{II}(ls) ions are nonmagnetic, thus the two Fe^{III}(hs) ions are not nearest neighbors, but they are nearest magnetic neighbors.

In Co-Fe Prussian blue the superexchange interaction between the two nearest Fe^{III}(ls) ions through the Fe^{III}(ls)—CN—Co^{II}(hs)—NC—Fe^{III}(ls) bridge is expected to be antiferromagnetic, as each ion has an unpaired electron in a t₂g orbital, with these orbitals being non-orthogonal (thus kinetic superexchange is expected to dominate). This interaction thus opposes the parallel alignment of the two spins on Fe^{III} ions, dictated by the stronger interaction between the neighboring Fe^{III} and Co^{II} spins. Similarly, the interaction between the nearest Co^{II} moments is expected to be predominantly antiferromagnetic, opposing their parallel alignment caused by the stronger nearest-neighbor superexchange. However, if there are irregular sequences in the system, of the form Fe^{III}(ls)—CN—Co^{III}(ls)—NC—Fe^{III}(ls) or Co^{II}(hs)—NC—Fe^{II}(ls)—CN—Co^{II}(hs), then the middle metal ion in the sequence is nonmagnetic, and the next-nearest neighbor interactions will cause antiparallel order of the spins. While speculative, the presence of such sequences, having in mind the significant disorder
in the system, cannot be excluded. In fact, the presence of Fe$^{II}$–CN–Co$^{II}$ units has been suggested by the infrared spectroscopy [85].

While the magnetic dipolar interactions usually present a negligible contribution to the magnetic coupling of individual atomic spins (compared to exchange), if relatively large entities of strongly coupled spins are present in the system (e.g., clusters or chains with colinear intracluster or intrachain order), the dipolar coupling between those entities may have substantial strength. As dipolar interactions can have both signs, i.e., can be both aniferromagnetic and ferromagnetic, depending on the relative orientation of the interacting dipoles, they have frustration as their inherent property. Spin glass order at $T \sim 10$ K in a system with only dipolar magnetic interactions has already been reported [53]. Furthermore, significant effects of dipolar interactions on the ordering of some molecule-based magnets was also proposed [52]. In the Co-Fe Prussian blue system the proposed freezing of spin clusters instead of individual spins may be at least in part affected by the dipole-dipole interactions between the cluster moments. Thus, while the source of frustration in the studied systems is not clear, some possible sources of competing magnetic interactions can be identified.
CHAPTER 5

PHOTOINDUCED MAGNETISM IN
Mn(TCNE)$_x$ · $y$(CH$_2$Cl$_2$)

This chapter presents magnetic and optical experimental studies of the photoin­
duced effects in Mn(TCNE)$_x$ · $y$(CH$_2$Cl$_2$) ($x \approx 2$, $y \approx 0.8$). The family of metal-
TCNE magnets is briefly introduced in the first section. The second section gives a
brief overview of the magnetic properties of Mn(TCNE)$_x$ · $y$(CH$_2$Cl$_2$) and proposed
magnetic ordering mechanisms. The magnetic studies demonstrating OCMO in the
material are presented next, followed by the direct and photoinduced absorption stud­
ies in the regions of electronic and vibrational optical transitions. Finally, a physical
mechanism for the photoinduced effects is proposed.

5.1 Metal-TCNE High-$T_c$ Molecule-Based Magnets

Tetracyanoethylene (TCNE) has been one of the most important building blocks
for organic-based magnets. Among TCNE-based magnets are [FeCp*$_2$][TCNE]$^-$ (Cp$_2^*$
= pentamethylcyclopentadienyl), the first magnet with spins residing in a $p$—orbital
[130, 131, 132, 133, 134, 135], [MnCp*$_2$][TCNE]$^-$ [136], and [MnTPP]$^+$[TCNE]$^-$
(TPP = meso-tetraphenylporphyrin) [137, 138, 139].
Figure 5.1: Schematic structure of tetracyanoethylene (TCNE). The molecule, as well as its monoanion $[\text{TCNE}]^{-}$, is planar ($D_{2h}$ symmetry) \cite{140}.

TCNE is a very strong electron acceptor. It can accept an electron in its antibonding $\pi^*$ orbital, forming charge transfer salts in which it is present as the $[\text{TCNE}]^{-}$ ion. This unpaired $\pi^*$ electron produces a net spin of 1/2 on $[\text{TCNE}]^{-}$. A single-crystal polarized neutron diffraction study of $[\text{Bu}_4\text{N}]^+[\text{TCNE}]^{-}$ ($\text{Bu}_4\text{N} =$ tetra-$n$-butylammonium) paramagnetic charge transfer salt determined the spin density distribution in $[\text{TCNE}]^{-}$ \cite{141}. The spin of 1/2 is delocalized over the entire $[\text{TCNE}]^{-}$ molecular ion, with 33 % of the total spin on each of the $sp^2$ hybridized carbon atoms (central C atoms in Fig. 5.1), 13 % of the spin on each of the four nitrogen atoms, and a negative corresponding to about 5 % of the total spin on each of the four $sp$ hybridized carbon atoms \cite{141,142}.

The family of molecule-based magnets $M(\text{TCNE})_x \cdot y(\text{solvent}) (M =$ transition metal) was introduced by the synthesis of $V(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$, the first room-temperature molecule-based magnet, with magnetic ordering temperature of $\sim 400$
The high magnetic ordering temperature was proposed to result from the direct bonding of the TCNE N atoms to V and a three-dimensional network structure in the solid [27]. This compound is amorphous, chemically unstable, and extremely air-sensitive [27]. Recently, thin films of V(TCNE)$_x$ (solvent-free) have been synthesized via chemical vapor deposition method, which have greatly diminished oxygen/moisture sensitivity and increased crystallinity compared to the powder samples [109, 143].

Recently, M(TCNE)$_x$-$y$(CH$_2$Cl$_2$) (M = Fe, Mn, Co, Ni) magnets have been synthesized [26]. These materials are also characterized by relatively high magnetic ordering temperatures, ranging form $\sim$ 44 K for M = Co, Ni to $\sim$ 121 K for M = Fe. The infrared absorption spectra in the region of CN stretching vibrations are consistent with metal-coordinated [TCNE]$_-$ for all the compounds.

In contrast to the disordered V(TCNE)$_x$-$y$(CH$_2$Cl$_2$), M = Mn, Fe compounds give sharp X-ray powder diffraction patterns, indicating that they are crystalline (Fig. 5.2). Furthermore, similarity of the diffractograms for these two compounds indicates that they are isostructural, although their structure is yet to be determined [26]. The M = Ni, Co compounds diffract poorly and do not appear to be isostructural with the Mn and Fe compounds. The $^{57}$Fe Mössbauer spectroscopy study of Fe(TCNE)$_x$-$y$(CH$_2$Cl$_2$) showed absorptions with large chemical shift and quadrupole coupling, characteristic of high-spin Fe$^{II}$ state [26, 145]. Based on this result, the elemental analysis, and the similarity between the M = Fe and M = Mn compounds, the metals in both materials are assigned as being divalent. The proposed compositions of these two compounds are Fe$^{II}$(TCNE)$_2$-$y$(CH$_2$Cl$_2$) and Mn$^{II}$(TCNE)$_2$-$y$(CH$_2$Cl$_2$) [26, 146, 145].

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Figure 5.2: X-ray powder diffraction pattern of Mn(TCNE)$_x \cdot y$(CH$_2$Cl$_2$) (from Ref. [144]).

5.2 Overview of the Magnetic Properties of Mn(TCNE)$_x \cdot y$(CH$_2$Cl$_2$)

As noted in the previous section, studies of Mn(TCNE)$_x \cdot y$(CH$_2$Cl$_2$) indicate that the oxidation states of manganese and TCNE in this compound are Mn$^{II}$ and [TCNE]$^-$. Both the manganese ion and the bridging organic ligand have partially filled orbitals, leading to nonzero magnetic moments: Mn$^{II}$ has half-filled $d$ shell, with spin $S=5/2$, while [TCNE]$^-$ molecular ion has a single unpaired electron ($S=1/2$) in a $\pi^*$ molecular orbital [26]. Elaborate magnetic studies and critical analyses revealed reentrant spin glass behavior, with a high-temperature transition to a three-dimensional Heisenberg ferrimagnet at $T_c = 75$ K, and a low-$T$ transition to a spin
glass-like state [13, 147]. It was proposed that the unusual low-$T$ behavior is a result of the random exchange in the system [13].

This section presents dc magnetization and ac susceptibility survey studies of Mn(TCNE)$_x$·y(CH$_2$Cl)$_2$ ($x \approx 2$, $y \sim 0.8$) that confirm the most important results reported in Refs. [13] and [147], and serve as a brief overview of the magnetic properties of the material.

Figure 5.3(a) shows the linear ac susceptibility of Mn(TCNE)$_x$·y(CH$_2$Cl)$_2$ ($x \approx 2$, $y \sim 0.8$), measured at ac magnetic field $H_{ac} = 15$ Oe (zero dc applied field) and frequency $f = 333$ Hz. The in-phase susceptibility $\chi'$ exhibits a shoulder around 75 K, and a more rapid increase as $T$ is decreased below this temperature. Both $\chi'$ and the out-of-phase component $\chi''$ exhibit peaks at temperatures below 15 K. In the vicinity of the low-$T$ peak, the susceptibility becomes strongly frequency-dependent (Fig. 5.4), indicating lengthening of the relaxation times in the system. The $f$-independent high-$T$ shoulder was attributed to the paramagnet-ferrimagnet transition, while the $f$-dependent low-$T$ peak was attributed to the reentrant transition into a spin glass-like state [13].

The second and third harmonic susceptibilities (Fig. 5.3(b)) show an unusual behavior, exhibiting peaks in the intermediate temperature region between the ferrimagnetic and reentrant transitions, contrary to the expected peaks in the near vicinity of these transitions. This behavior is also consistent with the earlier report [147]. Close inspection, however, shows very weak peaks in both harmonics around $T_c$ (inset, Fig. 5.3(b)), unnoticed in previous reports. Magnitudes of both harmonic susceptibilities is three orders of magnitude lower than that of $\chi'$, indicating very small nonlinearities of the magnetic response at the applied ac field of 15 Oe.
Figure 5.3: AC susceptibility of Mn(TCNE)$_2$·y(CH$_2$Cl)$_2$, measured in ac field of 15 Oe, at frequency of 333 Hz.
Figure 5.4: Frequency dependence of the ac susceptibility of Mn(TCNE)$_x$-$y$(CH$_2$Cl$_2$).

The dc magnetization ($M$), measured in dc applied field of 10 Oe, is shown in Fig. 5.5. The magnetization exhibits a shoulder around $T_c = 75$ K, similar to $\chi'$. A weak irreversibility occurs below $T_c$, indicated by a slight deviation between the zero-field-cooled and field-cooled magnetization curves. The $M_{fc}/M_{zfc}$ irreversibility becomes much more pronounced in the vicinity of the reentrant transition ($< 20$ K) and $M_{zfc}$ exhibits a peak at $\sim 10$ K. Based on the field-independence of the $M_{fc}/M_{zfc}$ bifurcation at 75 K and the field-dependence of the low-$T$ peak, Wynn et al. understood the behavior of $M$ as additional indications of the reentrant behavior [13]. Finally, their static scaling analysis at the high-$T$ transition and dynamic scaling analysis at the low-$T$ transition provided strong evidence for ordering with a spontaneous magnetic moment at 75 K and spin glass-like ordering below 10 K [13].
Figure 5.5: Field-cooled (open symbols) and zero-field-cooled (solid symbols) magnetization of Mn(TCNE)$_x$·y(CH$_2$Cl$_2$) at $H = 10$ Oe.

Temperature dependence of the remanent magnetization, measured after field-cooling at $H = 10$ Oe and subsequently reducing the field to zero, is shown in Fig. 5.6. The remanence rapidly decays with temperature and becomes zero (within the magnetometer's sensitivity) at $T_c = 75$ K, indicating vanishing of the spontaneous moment above $T_c$.

The curve of initial magnetization at $T = 2$ K (Fig. 5.7(a)) shows a rapid approach to saturation, which occurs at $\sim 20$ kOe. The molar mass of Mn(TCNE)$_x$·y(CH$_2$Cl$_2$) is 343.4 g/mol (with $x = 2$ and $y = 0.8$, obtained from elemental analysis), which gives saturation moment of 15,450 emu/mol at 2 K and 55 kOe, equivalent to about 2.8 $\mu_B$ per a Mn(TCNE)$_2$ unit. This value is close to the expected value of 3 $\mu_B$ for a
ferrimagnetically ordered system in which a Mn$^{II}$ spin of 5/2 and two [TCNE]$^-$ spins of 1/2 per unit point in the opposite directions.

The material exhibits very narrow hysteresis and a small remanence (Fig. 5.7(b)). Even at lowest temperatures the coercive field is only several Oe. Small coercivity is not surprising, as system containing ions with half-filled d shells (Mn$^{II}$) have very low single-ion anisotropy (Section 2.2).
Figure 5.7: Top: curve of initial magnetization at $T = 2$ K. Bottom: portion of the hysteresis curve at 5 K.
Figure 5.8: Effect of illumination on the field-cooled magnetization of Mn(TCNE)$_x$ · $y$(CH$_2$Cl$_2$) ($x \approx 2$, $y \approx 0.8$). Sample was illuminated with filtered light from a quartz-halogen lamp (filter peak transmission at 470 nm, bandwidth 80 nm, light intensity $\sim 5$ mW/cm$^2$).

5.3 Photoinduced Magnetization in Mn(TCNE)$_x$ · $y$(CH$_2$Cl$_2$)

Figure 5.8 shows the magnetization of Mn(TCNE)$_x$ · $y$(CH$_2$Cl$_2$), measured at temperature of 5 K, in dc field of 100 Oe, after field-cooling. The sample was prepared by applying a thin layer of the material on a piece of adhesive tape, as described in Ch. 3. The magnetization was repeatedly measured in regular time intervals, and it is plotted versus time ($t$) elapsed from the beginning of the experiment. After about two hours illumination of the sample was started. Filtered light from a quartz-halogen lamp was used (filter peak transmission at 470 nm, bandwidth 80 nm, light
Figure 5.9: Effects of argon laser excitation on the field-cooled magnetization of Mn(TCNE)$_2$·$y$(CH$_2$Cl)$_2$ ($x = 2$, $y \sim 0.8$). Light intensity was $I \sim 10$ mW/cm$^2$ 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, $I \sim 10$ mW/cm$^2$).

intensity $\sim$10 mW/cm$^2$). Upon light excitation $M$ rapidly increases, the increase gradually slows down, but $M$ does not level off even after 40 h of illumination. After illumination has stopped, $M$ shows an additional increase, as the sample cools down ($M$ monotonically decreases with increased $T$, Fig. 5.5). The increased magnetization is maintained even in the dark after illumination.

The very slow photoinduced increase in $M$ without saturation reached after several days of illumination suggests that the sample thickness is large compared to the penetration depth of light $\lambda_p$. Thus only the portion of sample within $\sim \lambda_p$ from the surface receives appreciable photon flux, while the material far from the surface receives very small flux and consequently its conversion to the photoexcited state is
ineffective. In an effort to achieve more effective excitation of the bulk of the material, sample was prepared by dispersing the filtered powder in transparent mineral oil, as described in Ch. 3. Furthermore, argon ion laser was used for excitation, allowing use of higher light intensities. Figure 5.9 shows effects of Ar\(^+\) laser excitation on the field-cooled magnetization of this sample.

Upon excitation with 488 nm (2.54 eV) laser line the photoinduced magnetization (PIM) reaches saturation after about six hours. Upon stopping the illumination \(M\) is again additionally increased, indicating cooling of the sample that was warmed up by laser radiation above the nominal temperature of 5 K (stable during the entire measurement) measured by the magnetometer's temperature sensors. From the size of this discontinuity in the \(M(t)\) dependence and from the measured temperature dependence of \(M\) for the illuminated sample, it is estimated that the sample temperature increases by only about 2 K during illumination. Illumination with 514.5 nm (2.4 eV) laser line leads to a partial diminishing of the PIM (Fig. 5.9). Detailed study shows that the PIM nearly identical to the one obtained by the 2.54 eV laser line can be induced by excitation in the entire region \(\sim 400-488\) nm (\(\sim 2.54-3.00\) eV), with both monochromatic and broad-band light, while lesser values of PIM are obtained by excitation in the region \(\sim 490-530\) nm (\(\sim 2.3-2.53\) eV). Partial reduction of PIM is obtained upon excitation in the region \(\sim 500-700\) nm (\(\sim 1.8-2.5\) eV). The energies about 2 eV are the most effective and reduce PIM to about 60% of its maximum value (Fig. 5.9). In the region \(\sim 490-530\) nm both a partial PIM (less than the maximum PIM, achieved by 2.54 eV laser line) and a partial reduction of the maximum PIM can be obtained, depending on the illumination sequence. This behavior will be discussed in more detail in the next section.
Figure 5.10: Curves of initial magnetization for the ground and photoexcited states (solid and open symbols, respectively) at 5 K. Inset: ratio of the magnetizations in the ground ($M$) and photoexcited ($M_{\text{illum}}$) states.

The photoexcited state is extremely metastable at low temperatures. At $T = 5$ K the magnetization decreases from the stationary value reached by the 2.54 eV laser line excitation by less than 1 % within 60 h after illumination. Assuming that the relaxation of PIM is exponential, this gives a lifetime of the photoexcited state greater than $10^6$ s.

Curves of initial magnetization for the ground and photoexcited states are shown in (Fig. 5.10). Illumination of the sample (prepared as powder-on-tape) was done at 5 K for 60 h with 2.7 eV laser line. The comparison of the two curves shows that the photoinduced magnetization is effectively suppressed by static magnetic field.
At fields above the saturation field for the material no PIM is detected within the detection limit of the magnetometer. The magnetization curve after illumination is well reproducible upon repeated measurements, thus high field does not destroy the photoexcited state. The result is in contrast with behavior of Prussian blue analogs, where PIM persists even at a field of 50 kOe [3]. As in the saturation regime the spins are nearly alligned with the field, and the saturation magnetization 'counts' the total number of spins per unit \((5/2 - 2 \times 1/2)\), this suggests that in the photoexcited state the number of spins per unit is not altered.

Figure 5.11 shows temperature dependence of the ac susceptibility for the ground and photoexcited states, measured at frequency \(f = 333\) Hz and ac magnetic field \(H_{ac} = 15\) Oe. The sample was prepared as powder-on-tape. The susceptibility exhibits a shoulder around \(T_c = 75\) K and a low-T peak, similar to the data for the bulk sample presented in the previous section. Small deviations from the behavior of the bulk sample (relative magnitudes of the high-T and low-T peaks, position of the low-T peak) were discussed in Ch. 3. Illumination of the sample was done at 90 K, in the paramagnetic regime (illuminated with Ar\(^+\) laser, 457.9 nm (2.7 eV) line, \(f \sim 50\) mW/cm\(^2\)). In order to get large enough magnetic signal for good signal/noise ratio in the whole temperature region studied, a relatively thick sample had to be used. Therefore long illumination of 60 h was necessary to achieve complete conversion into the photoexcited state. After illumination the sample was cooled to 5 K, and susceptibility measurement was subsequently repeated in the same way as for the ground state.

The susceptibility in the photoexcited state exhibits a substantial increase in the temperature region below \(T_c\). The increase in \(\chi'\) is more than 50 % for temperatures
Figure 5.11: In-phase and out-of-phase ac susceptibilities, measured $f = 333$ Hz and $H_{ac} = 15$ Oe, for the ground and photoexcited states. Sample was illuminated with Ar$^+$ laser for 60 h at $T = 90$ K (2.7 eV line, $I \sim 50$ mW/cm$^2$).
Figure 5.12: Relative photoinduced increase in the in-phase susceptibility (calculated from the data in Fig. 5.11).

between 13 and 18 K (Fig. 5.12), while increase in $\chi''$ is more than fourfold in the same temperature region.

Increased $\chi_{ac}$ is accompanied with a shift of the low-$T$ peak to higher temperatures by about 2 K, indicating increased reentrant transition temperature in the photoexcited state. Increase in the out-of-phase susceptibility indicates enhanced magnetic hysteresis in the photoexcited state. The area of the minor hysteresis loop formed during one period of oscillation of the applied alternating magnetic field $H = h_0 \cos \omega t$ (energy loss per cycle, $W$) is given by $W = \pi h_0^2 \chi''$ [75]. This relationship holds only in the linear regime, which is a condition well satisfied for Mn(TCNE)$_x \cdot y$(CH$_2$Cl$_2$) at the applied ac field of 15 Oe; as noted in the previous section, nonlinear magnetic response at this field value is about three orders of magnitude lower than the linear
response. Direct measurement of the photoinduced changes in the hysteresis (dc magnetization measurement \( M(H) \)) was impeded by very low coercivity and remanence of the material, noted in the previous section, and by very small magnetic moments of the samples prepared for PIM measurements. These two factors produced large errors in the measurements of remanence and coercive field and made a trustworthy comparison of these quantities for the ground and photoexcited states impossible.

The fact that the PIM detected below \( T_c \) was obtained by excitation at 90 K indicates that the photoexcited state persists at temperatures above \( T_c \). However, no photoinduced effect in \( \chi_{ac} \) was detected at temperatures above \( T_c \) (Figs. 5.11 and 5.12). The susceptometer's sensitivity sets an upper limit to the possible photoiduced change in \( \chi' \) at \( T \) just above \( T_c \) to about 2%. Absence of PIM in the paramagnetic regime is in stark contrast with the PIM in Co-Fe Prussian blue analogs. It indicates that the number of spins in the system is not significantly changed in the photoexcited state, as a significant number of new spins would effect both the susceptibility above \( T_c \) and the magnetic ordering temperature itself. This result is consistent with the absence of PIM in the saturation regime discussed above. Thus the PIM in the system is produced by enhanced ordering of the existing magnetic moments.

The stability of the photoexcited state was studied in the following way. The susceptibility of the material was measured before illumination at \( T = 20 \) K. The sample was then brought to the photoexcited state with 488 nm laser line. Illuminated sample was warmed to a temperature \( T_i \) above \( T_c \), kept at \( T_i \) for 10 min, and subsequently cooled to 20 K, at which temperature the measurement of the susceptibility was repeated. This sequence was performed for different values of \( T_i \) between 100 K and room temperature. The study showed that upon warming to \( T_i \geq 100 \)
Figure 5.13: Effects of illumination and subsequent thermal treatment on the in-phase susceptibility, measured at 20 K. Solid arrows denote photoexcitation with 488 nm laser line. Dashed arrows denote warming to $T$ indicated and subsequent cooling to 20 K. Illumination was done at 20 K for 50 h in each sequence. The vertical interval in the plot indicates error due to non-reproducibility after thermal cycling.

Upon warming to 250 K the material fully relaxes to the ground state. The results are summarized in Fig. 5.13. It is noted that after thermal cycling over large $T$ intervals, such as warming-cooling sequences done in this experiment, the values of $\chi'$ are not completely reproducible. This irreproducibility is larger the larger the $T$ interval spanned, and it possibly has origin in a slight decentering of the sample due to thermal dilatation and subsequent contraction of the sample probe. The error
introduced by this irreproducibility is indicated in the graph by $\delta$. This effect prevented a more accurate determination of the temperature needed to completely erase the PIM. The presented studies place this temperature in the interval 200-250 K.

All the presented photoinduced effects were observed in four different batches of the material. While the PIM behavior is qualitatively the same for all the samples, variations in the magnitude of the effects were observed. Figure 5.14 shows the PIM effect in the in-phase ac susceptibility for one of the samples, different from the sample at Fig. 5.11. The plot shows $\chi'$ for the ground and photoexcited states, as well as for the state in which PIM was partially reduced by warming to 200 K. The
susceptibility curve after warming to 250 K nearly overlaps with the $\chi'$ measured before illumination.

5.4 UV-Visible Absorption and Photoinduced Absorption

The optical studies in the UV-Visible region of spectrum provide information about the electronic structure of the studied system. Each feature in this region of spectrum corresponds to a photon-induced electronic transition between different energy levels. In many cases these transitions are coupled with vibrational transitions (due to the electron-phonon coupling, in the case of a solid material, or the vibronic coupling, in the case of a molecule), that may produce vibrational overtones in the electronic spectrum. The goal of the optical absorption studies of Mn(TCNE)$_2$·y(CH$_2$Cl$_2$) was to identify the electronic transitions responsible for PIM and its partial reversal. The photoinduced absorption studies were aimed at detecting possible changes in the electronic structure concomitant with PIM.

The absorption spectrum of Mn(TCNE)$_2$·y(CH$_2$Cl$_2$) in Nujol, measured at 13 K, is displayed in Fig. 5.15. The spectrum shows several absorption bands between 1.5 and 5 eV. The strong, structured band in the region 2.4-3.5 eV is very similar to the reported absorption band of [TCNE]$^-$ [148, 140, 149], and assigned to the $\pi \rightarrow \pi^*$ internal transition of this ion [140]. The orbital occupancy for [TCNE]$^-$ (in terms of TCNE orbitals) is $(\pi)^2(\pi^*)^1$, whereas the lowest excited state should be $(\pi)^1(\pi^*)^2$ [140]. Based on this similarity we assign this band to the transition from an energy band formed primarily from $\pi$ [TCNE]$^-$ orbitals to a band with primarily $\pi^*$ character. This assignment is further supported by the fact that nearly identical band was
observed in the spectrum of the analog compound Fe(II)(TCNE)$_2$·x(CH$_2$Cl)$_2$). The conspicuous fine structure of this band (Fig. 5.16) is attributed to vibrational overtones due to the coupling of the electronic transition with a vibrational transition. The frequency of this vibration, estimated from the spacing of the vibrational sub-bands is ~550 cm$^{-1}$, similar to the previous report [140]. A totally symmetric vibrational mode was observed in the spectrum of [TCNE]$^-$ at 532 cm$^{-1}$ [150]. The mode was initially assigned to the C–C stretching mode [150]. Later the mode was reassigned to the C–C≡N bending vibration, and it was proposed that this vibrational mode for the excited electronic state is the mode observed in the UV-Vis spectrum of [TCNE]$^-$ [140].
Figure 5.16: Absorption band of Mn(TCNE)$_2$ - x(CH$_2$Cl$_2$) assigned to internal [TCNE]$^-$ transition.

The ligand [TCNE]$^-$ does not absorb at energies less than about 2.3 eV [148]. Furthermore, the $d$-$d$ transitions of Mn$^{II}$ are spin-forbidden, and therefore they are expected to give very weak absorptions (at least 2 orders of magnitude weaker than for symmetry allowed transitions [151]). Thus, the absorption band in the region 1.5-2.4 eV does not correspond to internal transitions of either metal or ligand. It thus may be assigned to a transition from a band with primarily metal character to a band with primarily ligand character, or vice versa, i.e., to a charge transfer (CT) transition between metal and ligand. Assuming that the only oxidation states present are Mn$^{II}$ and [TCNE]$^-$, this is a CT transition between these two units. As the [TCNE]$^-$-Mn$^{II}$-[TCNE]$^-$ moieties are formed via the complete charge transfer
of electrons from Mn $s$ orbitals to TCNE $\pi^*$ orbitals, the CT band observed may be due to either photoinduced back-transfer from the $\pi^*$ ligand orbital to the metal $s$ orbital, or photoinduced transfer between some other Mn$^{II}$ and [TCNE]$^-$ orbitals. However, it is noted that presence of a small fraction of other oxidation states cannot be excluded. For instance, it is possible that there are sites in the lattice at which local configurations (e.g., presence of solvent molecules) do not allow full CT and formation of TCNE anions. The band in question may then correspond to a photoinduced CT transition between neutral Mn and TCNE.

The ranges of excitation energies for which PEM and reversal of PIM are observed, given in the previous section, are indicated in Fig. 5.15. Assuming the assignment of optical transitions given above, the spectrum indicates that PIM is obtained by excitation at the $\pi \rightarrow \pi^*$ band, while partial reversal of PIM is obtained by excitation in energy region overlapping with the charge transfer band.

It is noted that neutral TCNE and dianion [TCNE]$^{2-}$ do not have electronic transitions at energies below 4.3 eV [140], thus even if trace amounts of these oxidation states were present in the material, they would not effect the spectral region discussed above.

The band in the region $\sim$ 3.8—4.6 eV, not significant for the present discussion, is possibly due to a higher energy charge transfer transition, or a higher energy [TCNE]$^-$ internal transition.

The photoinduced absorption (PA) spectra after excitation with Ar$^+$ laser light are displayed in Fig. 5.17(b). As a reference the direct absorption spectrum is again shown in Fig. 5.17(a). The PA spectra were determined by subtracting the ground state direct absorption spectrum from the absorption spectra measured after laser
Figure 5.17: (a) Absorption spectrum at 13 K. (b) Photoinduced absorption spectrum measured at 13 K, after 488 nm (2.54 eV) excitation (solid line), and after subsequent 514.5 nm (2.4 eV) excitation (dots). Light intensity ~ 10 mW/cm², 10 min illumination for both laser lines. The vertical axes show correct relative intensities of A and ΔA.
excitations, as explained in Ch. 3. After laser excitation 5 min was allowed for
temperature to re-stabilize.

After 10 min of excitation with 488 nm (2.54 eV) laser line, increased absorbance
(A) 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 (decrease in A) is detected. Subsequent illumination with the 514.5 nm (2.4
eV) leads to diminishing of the effects induced by the 488 nm line. Thus the pho­
toinduced effects are long-living, and partially reversible with excitation at different
energy, in full correspondence with the PIM effects presented in the preceding sec­
tions. The detected PA, maintained long after illumination, indicates formation of a
metastable electronic state. Assuming the assignment of the optical transitions given
above, the PA peak at ~ 2 eV indicates enhanced charge transfer in the metastable
state.

The origin of the PA peak at 3.4 eV is ambiguous. While it occurs in the energy
region that overlaps with the high-energy end of the \( \pi \rightarrow \pi^* \) band, it may result from
the enhanced absorption at a weak band unresolved due to its partial overlap with
the stronger \( \pi \rightarrow \pi^* \) band.

Figure 5.18 shows time dependence of the photoinduced absorbance \( \Delta A \), measured
at a fixed wavelength of 560 nm (~2.2 eV). Excitation with 488 nm laser line leads to
a rapid increase in absorbance, which reaches saturation in about 15 min. The \( \Delta A 
vs. time dependence shows that in the previously discussed PA spectrum measured
after 10 min illumination nearly complete conversion to the photoexcited state was
achieved. The reversal effect by the 514.5 nm line occurs on approximately equal time
scale. Very small changes in absorbance occurring upon turning the laser off indicate
that the effect of heating by laser radiation on the spectrum is insignificant.
Figure 5.18: Effects of argon laser excitation on the absorbance, measured at wavelength of 560 nm and \( T = 13 \) K. Light intensity was about 10 mW/cm\(^2\) for both laser lines.

As noted above, the data suggest that excitation at the \( \pi \rightarrow \pi^* \) band is responsible for the observed PIM and PA, while excitation in the region of the CT band leads to a partial reduction of PIM and PA. These two absorption bands have a large overlapping region, which hinders determination of exact widths of the bands. However, based on the earlier studies of [TCNE]\(^-\) [148, 140], and the similarity between the [TCNE]\(^-\) absorption spectra reported therein with the one presented here, no significant absorption by [TCNE]\(^-\) is expected for wavelengths above about 530 nm \( (E < 2.34 \text{ eV}) \). This is consistent with the fact that no significant PIM was observed above this wavelength, as noted above. Upon light excitation in the overlapping energy region between these two bands it is expected that the processes of conversion from the
Figure 5.19: Effects of argon laser excitation on the absorbance, measured at wavelength of 560 nm and $T = 13$ K. Light intensity was about 10 mW/cm² for both laser lines.

ground state to the photoexcited state and the opposite process will compete. Figure 5.19 shows again absorbance measured at 560 nm in regular time intervals. This time excitation with 514.5 nm laser line is performed first. The absorbance rapidly increases and reaches a stationary value $A_1$. Upon subsequent excitation with 488 nm line $A$ is increased to a new, higher stationary value $A_2$. Repeating illumination with 514.5 nm line reduces $A$ to a lower stationary value $A_3$, close to the value $A_1$.

It was noticed that the relative values of $A_1$ and $A_3$ vary from sample to sample, but their differences are always relatively small and comparable to the instrumental drift during the time elapsed in experiment, suggesting that $A_1$ and $A_3$ may correspond to the same stationary state. The PA response dependence on the excitation energy was probed further, by using other available argon laser lines. Figure 5.20
shows results of this study. The data show that PA induced by excitation at energies of 2.6 eV (476.5 line) and 2.7 eV (457.9 nm line) is nearly equal to the one obtained by the 2.54 eV (488 nm) line, the observed differences being attributable to the instrumental drift and different light penetration depths for these lines. Thus for energies of 2.54 eV and above the maximum value of PA is achieved. For excitation at energies below 2.54 eV the stationary states reached have PA progressively lower as the excitation energy is decreased. Thus the reduction of PA with 501.7 nm (2.47 eV) line is more effective than with 496.5 nm (2.5 eV) line, but less effective than with 514.5 nm (2.4 eV) line.
The presented results confirm that there are two electronic transitions responsible for the photoinduced transition into the metastable state and for the reversal process, i.e., relaxation back to the ground state. Assuming the assignment of optical transitions given above, the former process is due to the $[\text{TCNE}]^- \rightarrow \pi \rightarrow \pi^*$ transition, while the latter process is due to a CT transition between $[\text{TCNE}]^-$ and Mn$^{II}$. In the energy region where both these transitions have appreciable probability, their relative probabilities determine the population of the metastable state in the stationary state reached by illumination. The magnetic studies presented in Section 5.3 are consistent with this picture. It was noted therein that no PIM was detected at energies below $\sim 2.3$ eV, which is consistent with the lower energy limit for appreciable $[\text{TCNE}]^- \rightarrow \pi \rightarrow \pi^*$ absorption [148, 140]. It is thus expected that at energies below 2.3 eV only the reversal process is effective. At any finite probability of the reversal process, it is expected that illumination at energies $< 2.3$ eV leads to a complete conversion into the ground state and cancelation of PIM. This is inconsistent with the behavior observed in magnetic studies, where even upon excitation at energies about 2 eV no complete relaxation to the ground state is observed. This behavior may result from the different local configurations of energy levels, determined by local metal-ligand configurations, presence of disorder, etc. There may exist sites in the lattice at which only photoinduced conversion to the metastable state is effective, while the reversal process has zero probability. The remanent PIM after 2 eV excitation would thus be determined by the concentration of such sites.
5.5 Infrared Absorption and Photoinduced Absorption

Figure 5.21 shows room-temperature infrared spectrum of Mn(TCNE)$_2\cdot\pi$(CH$_2$Cl$_2$). For the spectral region 1300-7000 cm$^{-1}$ the sample was prepared as Fluorolube mull, while Nujol mull method was used in the region 650-1300 cm$^{-1}$.

The most prominent features in the spectrum are in the region 2150-2300 cm$^{-1}$: peaks at 2174, 2185, and 2226 cm$^{-1}$, and a shoulder at ~2255 cm$^{-1}$. These modes are readily assigned to the CN stretching vibrations of [TCNE]$^-$, previously reported in Mn(TCNE)$_x\cdot\pi$(CH$_2$Cl$_2$) at nearly the same energies [26].

The origin of the peak at ~1370 cm$^{-1}$ is more ambiguous. Earlier infrared studies of [TCNE]$^-$ reported a mode at ~1370 cm$^{-1}$, that was assigned to the stretching vibration of the central [TCNE]$^-$ carbon atoms, and this assignment is adopted here [152, 153, 150, 154]. The assignment is highly non-trivial and it requires a brief discussion, as this mode is totally symmetric and thus not expected to be infrared active.

A vibrational mode is observable in infrared absorption experiments ('infrared active') only if it induces a change in the dipole moment. A vibrational spectroscopy method complementary to the infrared absorption is light scattering, or Raman spectroscopy. A mode is observable in Raman scattering experiments ('Raman active') only if induces a change in at least one of the six independent components of the polarizability tensor [84]. For a system with a center of inversion (like TCNE and [TCNE]$^-$) all vibrational modes have a definite parity, i.e., they are either symmetric (have even parity, i.e., do not change) or antisymmetric (have odd parity, i.e., change their sign) with respect to the inversion symmetry. Even and odd parity modes are usually denoted as 'g' (from German: gerade) and 'u' (ungerade). It can be shown
Figure 5.21: Room-temperature infrared absorption spectra of Mn(TCNE)$_z$·$_y$(CH$_2$Cl$_2$) in Fluorolube (a) and in Nujol (b). The labels indicate modes assigned to the respective stretching vibrations of [TCNE]$^-$. 
that $g$ modes are infrared inactive, while $u$ modes are Raman inactive. The stretching vibration of the central carbon atoms (C=C) in [TCNE]$^-$ has $g$ symmetry [140] and it is therefore expected to be infrared inactive. However, it has been proposed that this mode becomes infrared active when [TCNE]$^-$ is in vicinity of a cation, through the following mechanism [152, 153]. The electron cloud of the [TCNE]$^-$ anion is highly polarizable and consequently distorted under the influence of the cation. The polarizability varies considerably with the inversion-symmetric (Raman active) C=C normal vibration. As the magnitude of the polarizability oscillates with the vibration, the distortion of the anion charge cloud by the cation varies such that the dipole moment directed between cation and anion oscillates. If the anion occupies a site of low symmetry in the crystal, this oscillation may lead to a net change of the dipole moment associated with the vibrational mode, which means that the mode is infrared-activated. Thus an intense infrared absorption may result, despite only minor distortion of the $D_{2h}$ molecular symmetry by the crystal field. It was proposed that this effect also was responsible for activation of several other [TCNE]$^-$ infrared-inactive modes [150].

The modes observed at 935 cm$^{-1}$ and 1200 cm$^{-1}$ (Fig. 5.21) may be tentatively assigned to the C-C vibrations of [TCNE]$^-$, following the assignment of modes at 970 cm$^{-1}$ and 1187 cm$^{-1}$ in K$^+$[TCNE]$^-$ from Ref. [150]. A broad peak around 1590 cm$^{-1}$ was observed to increase in magnitude with sample exposure to atmosphere, and may be assigned to vibrations of water molecules that may have adsorbed to the powder sample [155]. The peaks in the region 700-800 cm$^{-1}$ are not expected in the spectrum of [TCNE]$^-$ and are possibly due to the solvent CH$_2$Cl$_2$ that has strong absorption between 600 and 800 cm$^{-1}$ [156]. The vibrations of the metal-ligand bonds
Figure 5.22: (a) IR spectrum measured at 13 K. (b) IR photoinduced absorption after illumination with 2.54 eV Ar+ laser line (solid line), and after subsequent illumination with 2.4 eV laser line (dots). Light intensity ~10 mW/cm², 10 min illumination for both laser lines. The vertical axes show correct relative intensities of A and ΔA.
are expected to have energies lower than the energies covered here due to the large mass of the metal ion.

At $T = 13$ K the CN stretch peak positions are shifted to higher energies: 2185, 2191, 2236 and (shoulder) $\sim 2260$ cm$^{-1}$, respectively (Fig. 5.22(a)). The broad peak at $\sim 1370$ cm$^{-1}$ does not shift in energy but it appears to split into two poorly resolved peaks.

The spectrum of photoinduced absorption (PA) at 13 K after excitation with 488 nm (2.54 eV) laser line is shown in Fig. 5.22(b). The PA spectrum was obtained by subtracting the absorbance before illumination from the absorbance after illumination, as explained in detail in Ch. 3. The sample was illuminated for 10 min with light intensity of about 10 mW/cm$^2$.

In the region of the CN stretch modes 2170-2260 cm$^{-1}$ photoinduced absorption and bleaching are observed. 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 (Fig. 5.23).

Substantial photoinduced absorption is detected in the region of the 1370 cm$^{-1}$ mode (Figs. 5.22 and 5.24). In particular, as the PA has a single, symmetric peak at 1367 cm$^{-1}$, it appears that only the lower energy part of this poorly resolved doublet exhibits PA.

The photoinduced effects are maintained long after illumination; the spectrum after illumination remained unchanged one hour after illumination, within the instrumental drift. Illumination with 514.5 nm (2.4 eV) laser line leads to a partial reduction of the PA and bleaching induced by 488 nm laser line, Figs. 5.22-5.24, in full correlation with the magnetic and UV-Vis PA experiments.
Figure 5.23: Photoinduced absorption and bleaching of the CN stretch modes. Solid line: ground state. Dashed line: after excitation with 488 nm laser line. Dots: after 488 nm laser line excitation, followed by 514.5 nm line excitation.
Figure 5.24: Photoinduced absorption in the region of the C=C stretch mode. Solid line: ground state. Dashed line: after excitation with 488 nm laser line. Dots: after 488 nm laser line excitation, followed by 514.5 nm line excitation.

It is important to rule out the possibility that the observed PA is merely an effect of heating of the sample by laser radiation. The fact that the PA spectra were not measured during irradiation, but determined as a difference between the direct absorption spectra for the ground and photoinduced states that were measured at the same temperature, without laser irradiation, diminishes this problem. A good indication that the observed effect is truly a result of photon-induced transitions in the system rather than a heating effect, is well-defined structure of the PA spectrum, with near-zero values of PA in the whole energy region studied except in the nearest vicinity of the CN and C=C modes. Another such indication is the strong sensitivity of the PA signal on the excitation frequency, i.e., the partial reversal of...
Figure 5.25: (a) Difference between the absorption spectra measured at 13 K and subsequently at 25 K. (C=C stretch mode region). (b) Difference between the two absorption spectra measured at 13 K. The second spectrum was measured 30 min after the first one, during which period the sample was warmed to 25 K, kept at 25 K for 10 min, then cooled back to 13 K. (c) PA after 488 nm laser line excitation (10 min illumination, ~10 mW/cm²). The final A was subtracted from the initial A in all three cases.
the 488 nm laser line-induced PA by the 514.5 nm line. The magnetic studies of PIM indicate that the sample warms up by merely ~2 K during laser excitation. In the FTIR PA experiment this temperature increase may be different, as the sample preparation method and cryogenic system are different from the one used in magnetic measurements, and therefore the heat dissipation rate may significantly differ. The stable temperature measured in the FTIR measurements during laser irradiation (with a temperature sensor mounted at the cryostat’s cold head just above the sample) was typically only about 0.02 K higher than the temperature measured in the dark. While the local temperature on the illumination spot was impossible to determine this suggests that the increase in sample temperature was not substantial.

As an additional verification of insignificance of the heating effect, the IR spectrum was measured at 13 K, at an increased temperature (25 K), and subsequently again at 13 K. Figure 5.25 shows the differences between the initial spectrum at 13 K and the spectra at 25 K and at 13 K after cooling from 25 K, for the spectral region in the vicinity of the C=C mode. The PA spectrum after 488 nm excitation is also shown for comparison. The spectrum at 25 K shows almost no deviations from the 13 K spectrum, reflecting weak temperature-dependence of the C=C mode’s spectral lineshape. Upon cooling back to 13 K the initial spectrum at 13 K (measured 30 min before the second one) is well reproduced, except for a small shift attributed to the instrumental drift within the 30 min interval. Warming of the sample to higher temperatures (> 50 K) introduces larger irreproducibility of the initial spectrum, due to the larger time intervals needed to perform the warming-cooling cycle (and, consequently, larger drifts), and probably also due to slight changes in the sample
alignment during thermal dilatation and subsequent contraction of the sample assembly. However, only uniform shifts and distortions of the baseline were observed, with no structure reminiscent of the PA spectrum.

The presented photoinduced effects in the vibrational spectrum indicate that the PIM in Mn(TCNE)$_2$ - x(CH$_2$Cl$_2$) is accompanied with a lattice distortion, i.e., with changes in the chemical bond lengths and/or angles between the bonds. In particular, as the normal modes undergoing photoinduced changes are assigned to [TCNE]$^-$, it appears that a deformation of [TCNE]$^-$ occurs in the photoexcited state. At this point no details about the nature of this deformation can be deduced, as the details of structure, e.g., the symmetries of the particular CN modes, are yet to be determined. However, several observations can be made.

In the region of the CN stretch modes both PA and bleaching are observed, with areas above and below the $\Delta A=0$ line approximately equal, which indicates that the total oscillator strength of the CN modes is preserved. In contrast, only a very strong PA peak, with no bleaching was observed at 1367 cm$^{-1}$, indicating increased oscillator strength of this mode, assigned to the C=C stretch. This contrast suggests different mechanisms for PA in the two energy regions.

As noted above, the C=C symmetric stretch mode is infrared-activated through the interaction with cation, in this case Mn$^{II}$. The increased activity of this mode may result from increased interaction with cation, possibly due to changes in the Mn$^{II}$-[TCNE]$^-$ bonding. Thus, while the presented PA studies did not include metal-ligand vibrational modes, it is possible that the lattice distortion accompanying PIM also includes a change in the metal-ligand distances. One can go even further along
this line of argument. A free anion of TCNE is expected to have only two infrared-active CN stretch modes (of four total) [140], while for the present metal-coordinating [TCNE]$^-$ three peaks and a shoulder are observed in the CN stretch energy region. The other two CN modes may be activated if there is a symmetry breaking occurring due to different metal coordination of different CN groups in [TCNE]$^-$ (e.g., in a situation in which three CN groups coordinate to metal, while the fourth one is free). However, it is not likely that this weak static symmetry breaking would bring about a strong infrared absorption, like the ones here observed. Alternatively, these modes may become active through the same mechanism as the C=C mode, as was proposed earlier for K$^+$/[TCNE]$^-$ and Na$^+$/[TCNE]$^-$ [152]. If this is the case, a part of the PA observed in the CN stretch energy region may result from the changed metal-ligand interaction, similar to the mechanism for C=C mode enhancement discussed above.

The extremely long lifetime of the photoinduced effects indicates that the state with distorted lattice, determined in the FTIR PA experiments, is in a local energy minimum, separated by an energy barrier from the ground state. At low temperatures thermal excitations are insufficient to overcome the energy barrier and the system is trapped in the metastable excited state. Moreover, lattice distortion is here proposed as the origin of this metastability. Details of this model are presented in the following section.
5.6 Discussion and Model

The presented studies demonstrate optical control of magnetic order in organic molecule-based magnet Mn(TCNE)$_2$·CH$_2$Cl$_2$. The optical studies determine that photoinduced magnetization is accompanied by changes in the electronic and vibrational spectra, suggestive of transition into a metastable state with distorted lattice. While in the Co-Fe Prussian blue magnets PIM results from altered number of spins in the system, it appears that this is not the case in the present system. Significant change in the number of spins would lead to altered susceptibility above $T_c$, as well as to a shift in the ordering temperature itself, in contrast to the presented data.

Here a qualitative model is presented in which PIM results from locally enhanced exchange interaction at a fraction of sites in the lattice. The concentration of such sites must be below the percolation threshold for the lattice, so that $T_c$ is not affected.

It is assumed that the dominant magnetic interaction between neighboring Mn$^{II}$ and [TCNE]$^-$ spins is the direct exchange. The direct exchange integral between spins localized on sites $a$ and $b$ in Heitler-London formalism is given by (Section 2.3.1)

$$ J_{ab} = K_{ab} - C S_{ab}^2, $$ \hspace{1cm} (5.1)

where $K_{ab}$, $C$, and $S_{ab}$ are given by the expressions (2.38)-(2.40). As noted in Section 2.3.1, the potential exchange term is always positive, thereby favoring ferromagnetic ordering, while the kinetic exchange $-CS_{ab}^2$ is negative and favors antiferromagnetic ordering. If the spin-carrying orbitals have appreciable overlap $S_{ab}$, the kinetic exchange is usually a dominant term, thus the total exchange $J_{ab}$ favors antiferromagnetic ordering. The proposed ferrimagnetism in Mn(TCNE)$_2$·CH$_2$Cl$_2$ is thus consistent with the kinetic exchange as the dominant magnetic interaction.
The kinetic exchange term is strongly dependent on the overlap integral $S_{ab}$, thus any change in the system's geometry that produces enhanced overlap between the magnetic orbitals would lead to enhanced antiferromagnetic exchange. The presented infrared PA experimental data give strong indications that the geometry of the system is indeed different in the metastable photoexcited state. Moreover, as the intensity of CT bands strongly depends on the overlap between the ligand and metal orbitals involved in the CT transition [157], the increased CT absorption in the photoexcited state may be a result of the enhancement of this overlap. As discussed in the previous section, the increased oscillator strength for the C=C vibrational mode also suggest enhanced metal-ligand interaction in the metastable state. Thus the experimental results are consistent with the model in which stronger kinetic exchange results from the enhancement of the relevant orbital overlap integral in the presence of lattice distortion.

Furthermore, the lattice distortion possibly stabilizes the photoinduced state by introducing an energy barrier for relaxation into the ground state, thus causing metastability at low temperatures. Upon photoexcitation into an excited electronic state, the nuclei in the system may find a new equilibrium configuration, resulting in their rearrangement, usually referred to as 'lattice relaxation' [158]. Photoinduced structural defects and stabilization of photoexcited states by lattice relaxation (e.g., in the case of self-trapped excitons) in quasi-one-dimensional organic crystals, alkali halides, and other systems, have been subjects of extensive studies [159]. As noted in Ch. 4, presence of a lattice distortion as a key for stabilization of PIM also was proposed in the case of Prussian blue magnets. Diagram in Fig. 5.26 illustrates a general mechanism for these phenomena. The diagram displays adiabatic potential curves ($U$)
for the ground and excited electronic states (GS and ES, respectively) in a two-level system. Horizontal axis represents the relevant nuclear configuration coordinate Q. According to the Franck-Condon principle, an electronic transition between GS to ES corresponds to a vertical transition in such diagram (as electron mass is much less than the nuclear mass, an electronic transition takes place while nuclei are effectively stationary). The vertical arrow thus denotes a photoinduced transition from GS to

Figure 5.26: Energy diagram for the ground and excited states. (a) The excited state is unstable. (b) The excited state is metastable. $U$ and $Q$ denote the adiabatic potential and the internuclear distance, respectively.
ES. In the case (a) the nuclear displacement $Q_{\text{min}}$ at which the potential curve for ES has a minimum is such that the GS potential curve is below the ES potential curve at $Q = Q_{\text{min}}$. Thus, following the photoexcitation from GS to ES, an electron can decay to the GS (radiatively, by emitting a photon, or non-radiatively, through vibrational relaxation). In the case (b) the GS potential curve is above the ES curve for $Q = Q_{\text{min}}$, thus the minima for GS and ES are separated by an energy barrier $\Delta E$. If, following the photoexcitation, an electron relaxes to the minimum of ES, it cannot emit a photon because there is no lower electronic state at $Q_{\text{min}}$. Thus only the non-radiative decay channel remains. However, the non-radiative decay is effective only if vibrational excitations have sufficient energy to reach the crossing point between the two potential curves. At temperatures such that $k_B T \ll \Delta E$ the probability for this process becomes very small and the system becomes trapped in the minimum of the ES.

Based on this simple general scheme and the available experimental data, a schematic energy diagram for Mn(TCNE)$_2 \cdot x$(CH$_2$Cl$_2$) can be proposed, Fig. 5.27. Here GS denotes the adiabatic potential curve for the ground state in which the states of metal and ligand are assumed to be [TCNE]$^-$ and Mn$^{II}$, with both ions in their ground electronic states. PS denotes the state in which [TCNE]$^-$ is in its first excited electronic state. The vertical arrow marked with $'h\nu'$ represents the photoinduced $\pi \rightarrow \pi^*$ transition. The minima of the GS and PS are significantly separated along the configuration coordinate $Q$. This displacement of the PS minimum is suggested by the shape of the UV-Vis absorption spectrum. The long progression of vibrational overtones in the [TCNE]$^-$ absorption band indicates that the excited state minimum is appreciably shifted along the coordinate of the normal mode involved [160].
noted above, it was proposed that this mode is the C–C≡N bending vibration [140]. MS denotes the excited electronic state which has the minimum separated by an energy barrier $\Delta E$ from the crossover point with the GS curve.

Following the vertical photoinduced transition from GS to the photoexcited state PS, an electron can undergo a radiative or a non-radiative decay into MS. At temperatures $T \ll \Delta E$ the electron that reaches minimum of MS potential curve remains trapped in it. It is proposed that in this metastable state the electronic structure of $[\text{TCNE}]^-$ is not substantially different from that in the GS. This is suggested by the small changes in the $[\text{TCNE}]^-$ electronic spectrum, i.e., by small bleaching of the
The proposed model thus assumes inhomogeneity of the material, i.e., that the local configurations, both structural and electronic, somewhat vary from site to site in the lattice. While X-ray diffraction suggests significant crystallinity of the material, a moderate structural disorder, partly due to the presence of solvent molecules, is expected, similar to many other molecule-based magnetic materials. The inhomogeneity is also assumed in the proposed mechanism for PIM via enhancement of the kinetic exchange, as the concentration of sites with enhanced exchange should be below the
percolation threshold in order for $T_c$ to remain unaffected. These sites may be determined by local configurations that favor the lattice distortion needed for stabilization of the MS. Thus the energy barrier $\Delta E$ may vary from zero to $\Delta E \sim 250$ K, the upper limit being suggested by the temperature needed to erase PIM (Section 5.3).
CONCLUSIONS AND DIRECTIONS FOR FURTHER RESEARCH

6.1 Summary and Conclusions

6.1.1 Co-Fe Prussian blue analogs

Extensive experimental studies of magnetic properties and photoinduced magnetism (PIM) of Co-Fe Prussian blue magnets, $K_xCo_y[Fe(CN)_6]zH_2O$, ($0.2 \leq x \leq 0.4$, $y \sim 5$), have been presented. The experimental techniques included ac susceptibility, used in the studies of PIM for the first time. The experiments reveal a complex low-$T$ magnetic behavior with signatures of both short range collinear order and spin glass properties. We propose that materials are cluster glasses, in which short range ferrimagnetic ordering between spins leads to formation of spin clusters below the quasicritical temperature $T_g$, and intercluster interactions lead to cooperative freezing of the magnetic moments of clusters at a temperature $T_g < T_c$. Furthermore, materials in the photoinduced state also show cluster glass behavior, with indications of enhanced intra- and intercluster interactions. The absence of a long-range collinear order and cluster glass behavior in the materials are attributed to the significant presence of the structural disorder. The disorder thus controls both the PIM and the
type of magnetic ordering in these systems. We propose a qualitative model which accounts for all the observed PIM behavior. It is proposed that these effects are results of the increased spin concentration in the photoinduced state and the ensuing increase of the relevant length and time scales in the system. The significance of the results is twofold. First, they give one of the first examples of the optical control of the spin glass type of ordering. The second significant aspect concerns potential technological applicability of the optical control of magnetic order (OCMO) in Prussian blue magnets. Optimization of OCMO (in particular, enhancement of the stability of the photoexcited state) will include manipulation with the structural disorder in the material via various synthesis methods. The presented results suggests that one must take the effects of this disorder on the magnetic state into serious consideration, as they may produce highly unconventional magnetic behavior that may hamper, or promote, specific applications.

6.1.2 Mn(TCNE)$_x$·y(CH$_2$Cl$_2$)

Optical control of magnetic order (OCMO) in Mn(TCNE)$_x$·y(CH$_2$Cl$_2$) is demonstrated, at temperatures as high as 75 K. The magnetic susceptibility of the material is substantially increased upon optical excitation in the blue region of spectrum. The effect is partially reversible by visible light of lower energies, and fully reversible by thermal treatment. The photoexcited state is highly metastable, with lifetime $> 10^6$ s at low temperatures. The UV-Vis spectrum indicates that electronic transition responsible for PIM is the $\pi \rightarrow \pi^*$ internal transition of the [TCNE]$^-$ ion. The steady-state photoinduced absorption studies in the UV-Vis and infrared spectral regions detected photoinduced effects concomitant with PIM. The UV-Vis photoinduced absorption
confirms that PIM is accompanied with changes in the electronic configuration and a transition into a metastable electronic state. The infrared photoinduced absorption indicates presence of a lattice distortion in the metastable state, the distortion including an altered configuration of [TCNE]−. Based on the experimental results, we propose that PIM in the system results from trapping of the photoexcited charge into a metastable state with locally distorted lattice and locally enhanced exchange interaction. The exchange increase is explained as a consequence of the enhanced overlap between the spin-carrying orbitals that accompanies the local lattice distortion. The lattice distortion is also viewed as a source of the energy barrier between the ground and photoexcited states, i.e., of the metastability. The demonstrated reversible PIM in Mn(TCNE)x·y(CH₂Cl₂) presents a new mechanism for OCMO, and a promising new pathway towards high-Tc optically controllable magnets.

6.2 Proposed research

6.2.1 Prussian blue-based magnets

(i) The coexistence of cluster glass properties and PIM provides an interesting opportunity to study the evolution of magnetic order in a disordered magnet with an increase of spin concentration without changing the chemical composition of the sample. As noted in the text, Co-Fe Prussian blue analogs that exhibit paramagnet-ordered magnet transition have already been reported [87, 85, 88], and it would be interesting to study systematically the evolution of this transition as nₑ is gradually increased. The states with intermediate values of nₑ (between the non-illuminated state and the state with saturated PIM) could be obtained by illuminating the material to saturation and subsequently warming it to different temperatures to partially
erase PIM. This study could show different non-cooperative and cooperative behaviors at different \( n_s \), including paramagnetic (PM), superparamagnetic (SP), spin glass (SG), cluster glass (CG), etc., and the exact route along which cooperativity develops as a function of \( n_s \) (PM→SP→CG, PM→SG→CG, PM→CG, etc.). This would be an advance in understanding not only magnetism in Prussian blue analogs, but magnetic ordering in disordered systems in general.

(iii) From the point of view of the high-temperature OCMO, Prussian blue analogs are attractive systems, having in mind that high-\( T_c \) magnets in this family have already been reported, as noted in the text [22, 23, 24, 25]. While no PIM in these systems has been reported to date, it is possible that by their chemical modification a progress towards room temperature OCMO can be made.

### 6.2.2 Metal-TCNE-based magnets

(i) One of the key experiments for understanding the magnetism and OCMO in \( \text{Mn(TCNE)}_x \cdot y(\text{CH}_2\text{Cl}_2) \) would be the crystal structure determination. For this a deuterated material should be synthesized (H replaced by deuterium to reduce the neutron scattering cross section) to enable a neutron diffraction experiment. The experiment would determine the coordination of the Mn ions, as well as the possible multiple configurations within the coordination sphere and/or of \([\text{TCNE}]^-\). Neutron diffraction experiments can also ascertain the type of magnetic ordering in the material. The magnetic unit cell in a ferromagnet is identical to the unit cell of the crystal structure, while for an antiferromagnet or ferrimagnet the two are different.

(ii) Quantum chemistry calculations (e.g., by the cluster or density functional approaches) would be useful in determining the energy levels in the system, possibly
confirm the presence of metastable state(s), and help understand conditions for its formation.

(iii) An electroabsorption study would indicate which bands in the UV-Vis spectrum correspond to a charge transfer transition, as well as the direction of charge transfer (metal→ligand or ligand→metal). In this experiment absorption of material in externally applied static electric field is measured, and absorption bands responding to a change in the field identified as charge transfer bands [161]. The study would either confirm or refute the spectral assignment presented in this work and help elucidate the mechanism for OCMO.

(iv) A time-resolved photoinduced absorption (PA) study would complement the steady-state PA reported here and give important information on the mechanism of formation of the metastable state. The experiment would employ picosecond and millisecond PA setups, already existing in our lab. The PA signal during argon laser illumination would be measured at different temperatures between room temperature and liquid helium temperatures. While at low temperatures the photoexcited state responsible for PIM is metastable and has a macroscopic lifetime, as determined in the experiments here presented, at near-room temperatures a PA signal with microscopic lifetime is expected, the lifetime becoming longer as $T$ is decreased. The $T$-dependent evolution of energy and timescale for this PA would help understand mechanism for trapping of the photoinduced charge. For example, it would determine whether trapping occurs abruptly, i.e., in a narrow temperature region, which would suggest cooperative behavior, discussed in Chs. 4 and 5. In contrast, a gradual transition, over a wide range of temperatures, would indicate a range of different local metastable states, without significant cooperativity.
(v) It has been emphasized in the text that the novel class of $M(\text{TCNE})$-based magnets are promising targets for the OCMO research due to their high magnetic ordering temperatures ($T_e = 400$ K for $M = V$). While in the preliminary studies the $M = Fe, V$ materials did not show detectable PIM, it is possible that by chemical modifications of the existing magnets from this class new OCMO systems will arise, with possibly higher operating temperatures than in the $M = Mn$ magnet. It is a reasonable expectation that the understanding of the origins of OCMO in the $M = Mn$ system will improve, as a result of the above proposed and other studies to come, and that the structural aspects that promote OCMO will become known. This will enable planned synthesis of materials with enhanced OCMO properties. For example, the structure of $Mn(\text{TCNE})$ could be modified in such a way that the fraction of sites in the lattice that undergo transition into the metastable state with enhanced exchange is significantly increased. If this fraction reached the percolation limit for the lattice, an increase in $T_e$ would be achieved in the photoinduced state. Since the existing material magnetically orders at $T_e = 75$ K, a photoinduced increase of $T_e$ by only several kelvin would make the illuminated material magnetically ordered above the liquid $N_2$ boiling temperature of 77 K. Thus a photoinduced paramagnet-ferrimagnet transition at the boiling temperature of this inexpensive coolant would be possible for the first time.

Even at this stage of research several specific goals for synthetic chemists may be set:

- Synthesis of thin films of $Mn(\text{TCNE})_x$ would enable better control of sample thickness in PIM measurements, as well as greatly decreased air sensitivity. Furthermore, it would likely produce samples with decreased structural disorder, due to the
absence of solvent, which may have a favorable effect on the PIM properties, as well as increase the ferrimagnetic transition temperature over the liquid N\textsubscript{2} temperature limit. Thin films of V(TCNE)\textsubscript{x} obtained by chemical vapor deposition (CVD) have already been synthesized [143], and work on the CVD of Fe(TCNE)\textsubscript{x} and Mn(TCNE)\textsubscript{x} is in progress.

- Growth of single crystals of Mn(TCNE)\textsubscript{z} would enable much easier crystal and magnetic structure determination, as well as polarization-sensitive infrared and Raman studies that would determine the symmetries of the vibrational transitions. It would also greatly improve control of the crystal structure.

- Bimetallic materials M\textsubscript{1}M\textsubscript{2}(TCNE) would be an interesting extension of this family of magnets that would greatly increase their versatility and possibility for modification. In particular, a material with M\textsubscript{1} = Mn and M\textsubscript{2} = V may combine the OCMO properties of Mn(TCNE) and the high-\textit{T}_c property of V(TCNE).
BIBLIOGRAPHY


[156] NIST/EPA Gas Phase Infrared Database (NIST, Gaithersburg, MD, 2001).


