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DIMENSIONALITY AND DISORDER 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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* * * * *

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1995

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The importance of dimensionality and disorder in understanding the magnetic properties of molecule-based magnets is examined through the study of two classes of materials. The V/TCNE/solvent class (TCNE = tetracyanoethylene, solvent = CH₂Cl₂, THF, or MeCN) includes the first molecule/organic-based compounds that are magnetic at room temperature. Magnetization studies reveal a wide range of behavior consistent with variations in local order and sensitivity to synthetic conditions. In particular, the source of the vanadium cation is found to play a crucial role in determining the final magnetic state. The [MnTPP][TCNE] class (TPP = meso-tetraporphyrinato) are crystalline quasi-one-dimensional ferrimagnets with direct metal-TCNE bonds similar to V/TCNE. The parent compound of this class, [MnTPP]⁺⁺[TCNE]⁻⁻·2PhMe, exhibits low-temperature magnetic properties that are novel for a quasi-1D molecular material. A reentrant spin glass phase, metamagnetism, and a broad temperature region of short-range ferrimagnetic order are revealed through studies of magnetization, dynamic and harmonic susceptibility, and specific heat. The results are compared with the expectations of a model of strongly interacting superparamagnetic clusters. The structural anisotropy in [MnTPP][TCNE] is reflected in the high-temperature susceptibility, which is found to deviate significantly from the predictions of current theories of ferrimagnetic chains. The dipole interaction between chains is considered as a viable candidate to explain
the long-range order in metal-TCNE chains as well as the lower-temperature glassy behavior in [MnTPP][TCNE].
For Nguyễn Hoài Thu.
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CHAPTER I

Introduction

While an ultimate understanding of the origin and distribution of matter in the universe may require a unification of the four fundamental forces of nature,\(^1\) the properties of matter we observe in our everyday lives arise primarily from electromagnetic interactions between electrons and nuclei. One of the most intriguing and yet, for all the recent advancements in condensed matter physics, still mysterious, properties is the bulk magnetism of certain solids. Magnetic materials are essential to the most basic elements of modern technology (motors, switches, and recording, to name three), but a fundamental understanding of the origin of their magnetism has not been readily forthcoming. This is not to say that the study of magnetism has been unproductive! It could be argued that the need to overcome classical physics’ inability to account for magnetism was the central driving force in the development of the quantum theory of solids. Once the concept of spin grasped hold, successful modern many-body theories of magnetic behavior began to multiply. Progress has increased quite significantly in the past decade, and the time may indeed be ripe

\(^{1}\text{gravitational, electromagnetic, strong nuclear, and weak nuclear forces}\)
for a "unification" of band and localized pictures into a general field theory of bulk magnetism in the near future.

The phenomenon of superconductivity is often cited as an example of a long incubation period (40 years) between the discovery and eventual explanation of a physical phenomenon. As magnetite was first discovered and utilized by the ancient Greeks and Chinese, the incubation period for magnetism is on the order of 5000 years. However, no scientific attempt at understanding magnetism was made until Gilbert's *De Magnete* of 1600, and that was only a qualitative and somewhat anthropomorphic account [1]. A quantitative theory did not arise until the mid- and late-1800s. That electricity and magnetism are inextricable facets of the same coin was first understood by Maxwell [2], who combined the observations of Oersted and Faraday to formulate a general theory of electromagnetism. For most of the current practical uses of magnetic materials, such as in transformers, computers, and other electronic applications, the classical theory of Maxwell has proven adequate. The underlying quantum origins of these material properties has not manifested itself as a major design problem.

The development of molecule-based magnetism in the past decade has changed this attitude drastically. With the desire and ability to fabricate magnetic materials molecule by molecule has come the absolute necessity to face quantum mechanics in the microcosm with courage and, what is more, ingenuity. As an analogy, consider having used a computer productively for several years, and then coming upon a new goal which first requires building a computer from scratch. The challenge to design and fabricate novel electromagnetic materials for the next generation of materials technologies requires an overlap of physical, chemical, and engineering expertise. Moreover, this synergy has led, and will continue to lead, to structures that provide unprecedented opportunities for the study of idealized or otherwise fascinating
physics.

The materials studied in this thesis are examples of such opportunities. The V/TCNE/solvent materials were the first of their kind to display magnetism at room temperature, and offer the physicist a rare problem of simultaneously fundamental and technological importance. These are the study of bulk magnetism in a highly disordered matrix of metal and organic-based spins, and the development of practical uses for a light-weight, "tunable" magnetic material. The [MnTPP][TCNE] class represent excellent examples of quasi-one-dimensionality, also of current theoretical and practical interest. These chain-like systems are tunable through ordinary solid-state chemistry techniques, yielding derivative complexes with varying amounts of interchain magnetic coupling. Additionally, [MnTPP][TCNE] and similar anisotropic magnets open up new areas of physics investigation. Two that are considered in this thesis are 1) the relative importance of dipolar coupling in ferrimagnets where little or no superexchange overlap is present and 2) the behavior of systems in the "middle ground" between traditional spin glass behavior and traditional superparamagnetism.

Before the data on these molecule-based magnetic compounds is discussed, it is important to firmly establish the basic precepts of magnetism, and particularly the effects of dimensionality and disorder on magnetic behavior. This task is accomplished, it is hoped, in Chapter 1. Chapter 2 will serve to briefly introduce the experimental techniques used, which include d.c. and a.c. magnetic susceptometers and a specific heat cryoprobe, designed to accomodate air-sensitive samples (a common feature in molecular systems). Chapters 3 and 4 present the results and analysis of investigations on the V/TCNE/solvent and [MnTPP][TCNE] magnets, respectively. In Chapter 5, some initial results on the effects of ligand substitutions in the [MnTPP][TCNE] chain systems are given to further illustrate the effects of low dimensionality.
1.1 Origins of Magnetism

1.1.1 Spin

Magnetism is essentially the study of the angular momenta of charged particles. The magnetic (dipole) moment \( \mu \) of a particle with mass \( m \) and charge \( q \) is proportional to its angular momentum \( \mathbf{G} \) according to \( \mu = \gamma \mathbf{G} \), where \( \gamma \), typically called the gyromagnetic ratio, is of order \( q/mc \). Since the nuclear magnetic moment is typically much smaller than that of the electron, the observed magnetic properties of matter are, to a very good approximation, due solely to electronic angular momenta.

As a result of the work of Stern and Gerlach [3], Uhlenbeck and Goudsmit [4], and Dirac [5], it was discovered that electrons (and many other subatomic particles) have an excess of angular momentum that cannot be attributed to orbital degrees of freedom alone. This additional "intrinsic" angular momentum \( \mathbf{S} \) is quantized with a quantum number \( s \) which takes on half-odd integral values, rather than integral values as is the case with orbital momentum. For the electron in particular, it is found that \( s = \frac{1}{2} \) only. The only attempt at a classical analogue for this non-orbital angular momentum was to think of the electron as spinning on its axis, like a top. As a result, the intrinsic momentum was named "spin", although the analogue has since proven inadequate.\(^2\)

The spin angular momentum \( \mathbf{S} \) of the electron has been the basis for our modern

\(^2\text{In order for a sphere with uniform mass } m_e, \text{ charge } e, \text{ and radius } r_e = a_e a^2 \text{ to have angular momentum } S_z = h/2, \text{ a point on its surface must have the speed } v = \omega r_e = S r_e / I = \frac{1}{2} h r_e / (\frac{2}{5} m_e r_e^2) = \frac{2}{5} h / (e^2 / c^2) = (\delta / 4a) c >> c. \)
understanding of the magnetic properties of matter. As with the orbital momentum \( \mathbf{L} \), for any electron state \( |\psi\rangle \) the total spin \( \mathbf{S} \), with \( S^2|\psi\rangle = s(s + 1)\hbar^2|\psi\rangle \), and \( z \)-component \( S_z|\psi\rangle = m_s|\psi\rangle \) commute with the Hamiltonian and are constants of the motion.

Aggregates of electrons, whether in an idealized gas, an atom, or a delocalized molecular or crystalline orbital, must possess total wave functions which are antisymmetric with respect to the exchange of any two electrons. This requirement is a consequence of the indistinguishability of electrons and the particular quantization of \( \mathbf{S} \), via the spin-statistics theorem. Electrons are thus said to obey Fermi-Dirac statistics and are called fermions. Alternately, the symmetry of a wavefunction can be observed experimentally by measuring quantities dependent on the interference between electrons. Ensembles with minimal interference consist mainly of fermions, which tend to avoid one another. Ensembles with maximal interference (more than even distinguishable particles) consist mainly of bosons,\(^3\) which tend to conglomerate.

These peculiar statistics of ensembles of electrons are central to understanding the observable properties of matter, especially magnetic properties. The source of their indistinguishability is the fact that when their wave functions overlap, their identities become undefined. For the purposes of this thesis, the primary consequence of Fermi-Dirac statistics is the so-called exchange interaction between electrons. The concept of exchange is used to explain the many-body magnetic effects in solids, such as long-range order, and will be discussed in section 1.3.

\(^3\)Bosons are particles for which \( s \) is integral.
1.1.2 The Magnetic Hamiltonian

The Hamiltonian for an ensemble of electrons in a magnetic field may be written

\[ \mathcal{H} = \left[ \sum_i \left( \frac{\mathbf{p}_i^2}{2m} - e\phi_i \right) + \sum_{ij} \frac{e^2}{r_{ij}} + \lambda \mathbf{L} \cdot \mathbf{S} \right] + \frac{\mu_B}{\hbar} \mathbf{H} \cdot (\mathbf{L} + g_s \mathbf{S}) + \sum_i \frac{e^2}{8mc^2} (\mathbf{H} \times \mathbf{r}_i)^2. \]  

(1.1)

The quantities \( \mathbf{r}_i \) and \( \mathbf{p}_i \) are respectively the position and momentum of electron \( i \). The orbital and spin angular momenta of the ensemble are defined as \( \mathbf{L} = \sum_i \mathbf{l}_i \) and \( \mathbf{S} = \sum_i \mathbf{s}_i \). The static Coulomb potential of electron \( i \) arises from the nucleus and neighboring ions \(-e\phi_i\) and from the other electrons \( (\sum_j e^2/r_{ij}) \). This last contribution is neglected when considering only noninteracting moments. The term \( \lambda \mathbf{L} \cdot \mathbf{S} \) represents the spin-orbit coupling. The terms in brackets, then, comprise the Hamiltonian in the absence of any magnetic field. Coupling to the external magnetic field is made with the last two terms in 1.1.

The third term is the Zeeman interaction. The Bohr magneton \( \mu_B \) is a basic unit of angular momentum, defined as

\[ \mu_B = \frac{e\hbar}{2mc} \approx 5.79 \times 10^{-9} \text{ eV} \cdot \text{G}^{-1}. \]

(1.2)

The "g-factor" \((g_e \approx 2)\) in front of \( \mathbf{S} \) represents the fact that the gyromagnetic ratio for spin angular momentum is almost precisely twice that for orbital angular momentum \((\gamma_S = 2\gamma_L = 2\mu_B)\). This factor follows from the Dirac theory of the electron, in which a four-component wave function is required to preserve the relativistic invariance of the equations of motion \([5, 6, 7]\). The necessity of the spin degree of freedom and its half-odd integral statistics appear naturally. The operator \( \mathbf{\mu} = -\mu_B(\mathbf{L} + 2\mathbf{S})/\hbar \) may be conveniently regarded as the "intrinsic" magnetic moment of the ensemble (typically an atom) because it exists in the absence of any applied field \([7]\).
1.1.3 Magnetization and Susceptibility

The most important thermodynamic quantities for characterizing the magnetic behavior of a compound are the magnetization \( \mathbf{M} \) and the magnetic susceptibility \( \chi \). The magnetization, which is the magnetic moment per unit volume, originates from the definition of \( \mathbf{H} \):

\[
\mathbf{B} = \mathbf{H} + 4\pi \mathbf{M}.
\]  

(1.3)

\( \mathbf{M} \) thus indicates the difference between the external (applied) field \( \mathbf{H} \) and the internal induction \( \mathbf{B} \). The magnetic susceptibility, which directly characterizes the response \( \mathbf{M} \) to the field \( \mathbf{H} \) is defined through the constitutive relation

\[
\mathbf{M} = \mathbf{M}[\mathbf{H}] = \chi \cdot \mathbf{H}
\]  

(1.4)

from which the relation \( \chi_{\alpha\beta} = \partial M_\alpha/\partial H_\beta \), or simply \( \chi = \partial M/\partial H \) for isotropic media, can be obtained. The assumption of isotropy is appropriate for polycrystalline (powder) samples. In general, the susceptibility is a function of field \( \chi = \chi(H) \). In the limit \( y = 2\mu_B H/k_B T \ll 1 \), the magnetization is a linear function of \( H \), and the initial susceptibility \( \chi_0 = (\partial M/\partial H)_{H=0} \) can be defined. Alternately, one can define the \textit{d.c.} susceptibility as \( \chi_{\text{dc}} = M/H \), which is a function of \( H \). The \textit{nonlinear d.c. susceptibility}, then, may be written

\[
\chi_{\text{dc}}^{\text{nl}}(H,T) = \chi_0(T) - M(H,T)/H.
\]  

(1.5)

The inherent nonlinearity of magnets will be elucidated in the sections to follow. In any case, the powder susceptibility can be expanded in powers of \( y \), giving the necessary nonlinear contribution to arbitrary precision.

The question of units often arises in experimental magnetism. While the SI is the uniform standard, most researchers chose the cgs system for its convenience (as was
used in (1.3)). In this system, the susceptibility is expressed in \textit{electromagnetic units} (emu). The emu is defined as a cm$^3$ so that the volume susceptibility, which appears in (1.4) is unitless. Therefore, since the volume magnetization has units of Gauss, the molar magnetization has the units emu·G·mol$^{-1}$. However, some researchers define the emu differently, which can lead to confusion in comparing experimental values. Although the definition presented here will be used in this thesis, the issue of units can always be made unambiguous by expressing the magnetization in units of \textit{NqPb}. For conversion purposes, each mole of Bohr magnetons ($S = 1/2$) has magnetization $M = 5585$ emu·G·mol$^{-1}$.

Even in the absence of interactions, the net magnetization of a classical system of moments must be zero. This result, known as \textit{Miss van Leeuwen's theorem} [1, 8], establishes the absolute necessity of quantum mechanics to account for all magnetic phenomena. An electron in a classical orbit \textit{does} give rise, of course, to a magnetic field, but the use of classical statistics for thermal equilibration eliminates any net magnetism in an ensemble. Since the force exerted by an adiabatic magnetic field is always perpendicular to the classical velocity, it can do no work and the electron energy must be independent of $\mathbf{H}$. The division of electrons into energy states thus cannot be affected by a magnetic field. That is, the classical partition function is

$$Z = \int_{-\infty}^{\infty} dx dy dz \int_{-\infty}^{\infty} dp_x dp_y dp_z e^{-\beta[p_x-(e/c)A_x]^2/2m+...}, \quad (1.6)$$

where $\beta = 1/k_B T$ ($k_B \approx 8.62 \times 10^{-5}$ eV·K$^{-1}$ is Boltzmann's constant). Because the momenta are integrated from $-\infty$ to $\infty$, the contribution from the vector potential may be transformed away by setting $u_i = p_i - \frac{e}{c} A_i$ for $i = x, y, z$:

$$Z = V \int_{-\infty}^{\infty} du_x du_y du_z e^{-\beta(u_x^2+u_y^2+u_z^2)/2m}, \quad (1.7)$$

which is independent of $\mathbf{A}$. Therefore, the magnetization, which is proportional to $\partial Z/\partial H$, vanishes identically in a classical system.
In quantum mechanics, the momenta are discrete and the energies are affected by a magnetic field. So, the magnetization does not necessarily vanish:

\[ M = N k_B T \left( \frac{\partial \ln Z}{\partial H} \right) \]

\[ = N k_B T \frac{\partial}{\partial H} \ln \sum_n e^{-\beta E_n} \]

\[ = N \frac{\sum_n \left( -\frac{\partial E_n}{\partial H} \right) e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}. \]  (1.9)

Detailed knowledge of the eigenvalue spectrum \( \{E_n\} \) is required to determine \( M \), as is the case with any thermodynamic quantity. The energies \( E_n \) are obtained by solving the Schrödinger equation with \( \mathcal{H} \) as given in (1.1) under various assumptions about \( L, S, H \), and the electronic environments in the system of interest.

In the following sections, the eigenvalue problem \( \mathcal{H} |\psi\rangle = E |\psi\rangle \) for electrons in a solid is considered. The properties of isolated moments are considered first (Sec. 1.2, leading to diamagnetism and paramagnetism. Next a brief treatment of the pertinent effects of the chemical environment of the moments is presented (Sec. 1.2.2). Ligand field and spin-orbit coupling effects modify the eigenvalue spectrum in the absence of a field. In some molecular systems, the impact of the chemical environment on magnetic properties may be very significant. Finally, many-body effects due to electron-electron interactions are considered (Sec. 1.3). The primary tool for explaining these effects is the exchange interaction, and its ability to induce long-range magnetic order in solids is discussed. Throughout, an emphasis will be placed on insulating solids with fairly localized ionic magnetic moments as this picture applies most readily to the molecule-based magnets studied in this thesis.
1.2 Properties of Isolated Moments

Before undertaking any study of magnetic materials possessing long-range order, it is necessary to understand the behavior of isolated magnetic moments. The simplest example of such a moment is an individual electron with orbital and spin angular momenta $l_i$ and $s_i$. Net moments are also associated with atoms, molecules, and more complicated structures. In these cases, the total orbital and spin momenta $L$ and $S$ are determined by considering the overall wavefunction of the constituent electrons. However, determining, or even approximating, this wavefunction requires knowledge not only of the intra-atomic interactions, but also of the moment's chemical environment. Even if the moment is well isolated from other moments, its magnitude still depends on the crystal or ligand fields of neighboring atoms.

In general, one must consider the internal structure, nonmagnetic environment, and neighboring moments all together to get a clear estimate of the magnetic moment of interest. The question of the survival of these local moments in a solid is thus a great challenge of current interest in condensed matter physics. Since the analysis of this question is intimately tied to the exchange interaction, it is postponed until Sec. 1.3. In the present section, the moments are taken as given and their behavior in a magnetic field is considered.

For convenience, the effect of a magnetic field $H$ will be considered for the ground state of a collection of independent atomic ions, each with orbital and spin angular momenta $L$ and $S$. The results can be applied more generally to any ensemble of isolated moments. It will be shown that the effect of $H$ is to magnetize the system, linearly in low field (Curie's Law), then nonlinearly toward saturation as $H$ increases.
1.2.1 Effect of $H$

Treatment of magnetic field effects is facilitated by explicitly dividing the Hamiltonian into two parts ($\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$), where

\[
\mathcal{H}_0 = \sum_i \left( \frac{p_i^2}{2m} - e\phi_i \right) + \sum_{ij} \frac{e^2}{r_{ij}} + \lambda \mathbf{L} \cdot \mathbf{S}, \quad \text{and} \quad (1.10)
\]

\[
\mathcal{H}_1 = \frac{\mu_B}{\hbar} \mathbf{H} \cdot \left( \mathbf{L} + g_e \mathbf{S} \right) + \sum_i \frac{e^2}{8mc^2} (\mathbf{H} \times \mathbf{r}_i)^2. \quad (1.11)
\]

A logical first approximation in determining the eigenvalues of $\mathcal{H}$ is to assume that the excited states $|\psi_n^{(0)}\rangle$ of $\mathcal{H}_0$ lie well above the ground state $|\psi_0^{(0)}\rangle$, out of the range of any reasonable temperature and field. The primary level splittings of $\mathcal{H}_0$ in transition metals (crystal field) and rare earths (spin-orbit) are typically on the order of 1 eV. Since the thermal factor $k_B T \approx 1/40$ eV at room temperature, and the field factor $2\mu_B H \approx 1.16 \times 10^{-3}$ eV at $H = 10$ T, the assumption of isolation is usually very accurate. Accordingly, $\mathcal{H}_1$ may be regarded as a perturbation. Taking the H-field along the z-axis, the perturbation energy $\Delta E$ may be written

\[
\Delta E = E^P + E^D; \quad (1.12)
\]

\[
E^P = \mu_B H (L_z + 2S_z), \quad (1.13)
\]

\[
E^D = \frac{e^2}{8mc^2} H^2 \sum_i (x_i^2 + y_i^2), \quad (1.14)
\]

where $E^P$ and $E^D$ are the paramagnetic and diamagnetic energies, respectively. In (1.14) and hereafter, the constant $\hbar$ is taken as unity. For simplicity, it is assumed that no two states of $\mathcal{H}_0$ have the same energy so that nondegenerate perturbation theory may be used. The explicit identification of the small, or expansion, parameter for this problem is often glossed over in texts. It should be emphasized that it is not $y = g\mu_B H/k_B T$; this approximation comes in optionally at a later point. The expansion parameter is the relative size of the splittings expected to be induced by
H as compared to the smallest energy differences of $\mathcal{H}_0$, such as the above-mentioned spin-orbit or crystal-field splittings. Each $(J,L,S)$ manifold of $\mathcal{H}_0$ will in general have its own $g$-value and field-dependence. A schematic illustration of this important point is given in Fig. 1. The expansion parameter $\eta$ may be defined as

$$\eta = \left| \frac{\langle \psi_m^{(0)} | \mathcal{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \right| \ll 1. \quad (1.15)$$

The perturbation series is then written

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \eta |\psi_n^{(1)}\rangle + \eta^2 |\psi_n^{(2)}\rangle + \cdots \quad (1.16)$$

$$E_n = E_n^{(0)} + \Delta E_n \quad (1.17)$$

$$= E_n^{(0)} + \eta E_n^{(1)} + \eta^2 E_n^{(2)} + \cdots. \quad (1.18)$$

It is noted that $\eta$ appears here only as a convenience for the bookkeeping of terms which are presupposed to be successively smaller.

Langevin Paramagnetism

In the first-order approximation, the paramagnetic term $E^p$ will split the $J_z$-degeneracy of a "total-$J$" basis state of $\mathcal{H}_0$. (Taking total-$J$ states presupposes Russell-Saunders coupling.) To see this splitting explicitly, though, $E^p$ must be cast into a diagonal form,\(^4\) since $L_z + 2S_z$ is not a constant of the motion. That is, the energy will be determined by the projection of $\mu$ onto $J = L + S$:

$$\mu \cdot J = -\mu_B \{ (L + 2S) \cdot (L + S) \},$$

\(^4\)Diagonalizing $\mathcal{H}_1$ within a total-$J$ manifold is permitted by the Wigner-Eckart theorem, which states that the matrix elements of any vector operator in the $(J^2,J_z)$ subspace are proportional to the matrix elements of $J$ itself.
Figure 1: The splitting of $^3\text{H}_4$ and $^3\text{F}_4$ states of a free ion by an applied field. The separation of $\sim 7000 \text{ cm}^{-1}$ is appropriate for a Pr$^{++}$ ion; the splitting by the field is not drawn to scale being of order $1 \text{ cm}^{-1}$ only for fields of a few kilo-oersteds. From Martin (1967) [9].
\[
\begin{align*}
\{ &-\mu_B \left\{ \frac{3}{2}J^2 - \frac{1}{2}L^2 + \frac{1}{2}S^2 \right\}, \\
&= -\mu_B \left\{ \frac{3}{2}J(J+1) - \frac{1}{2}L(L+1) + \frac{1}{2}S(S+1) \right\}.
\end{align*}
\]

Now \( E^p \) can be written

\[
E^p = \mu_B H(-g(J_z)) \equiv -g\mu_B m_J H,
\]

where the Landé \( g \)-factor

\[
g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}
\]

is defined as the fraction of the intrinsic atomic magnetic moment parallel to the total angular momentum. Since \( g \) is constant, \( J \) must precess about \( H \), and \( \mu \) about \( J \), as depicted in Fig. 2. The quantum number \( m_J \) for the \( z \)-component of \( J \) takes on the \( 2J+1 \) values \(-J, -J+1, \ldots, J-1, J\) which must either be integers or half-odd integers.

Substituting into (1.9), the first order paramagnetic magnetization of an ensemble of isolated moments term is obtained by summing over the \( 2J+1 \) values of \( m_J \),

\[
M = Nk_BT \frac{\partial}{\partial H} \ln \sum_{m_J} e^{\beta g\mu_B m_J H},
\]

\[
= Ng\mu_B \frac{\partial}{\partial y} \ln \left( \frac{\sinh(J + \frac{1}{2})y}{\sinh y/2} \right),
\]

\[
= N\mu_{\text{max}} B_J(\mu_{\text{max}} H/k_BT),
\]

where \( \mu_{\text{max}} = g\mu_B J \) is the maximum \( z \)-component of \( \mu \) and \( B_J \) is the Brillouin function:

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

This first-order result defines the \textit{Langevin paramagnetic response} to a static applied field. The dependence of \( M \) on the argument \( x \) for various total angular momentum
Figure 2: The relationships between the angular momenta and the magnetic moment. From Martin (1967) [9].
quantum numbers $J$ is shown in Fig. 3. In the limit of small $y$ (low field and/or high temperature), $B_J(y) \to y(J+1)/3J$ is linear in $y$ and yields

$$\chi_0 = \left( \frac{\partial M}{\partial H} \right)_{H=0} = \frac{N g^2 \mu_B^2 J(J+1)}{3k_B T} \equiv \frac{C}{T},$$

(1.23)

which is known as Curie's Law. $C$ is the Curie constant and is used to determine the sizes of the moments through (1.23). In the limit of large $y$, $B_J(x) \to 1$ and $M$ saturates to its maximum value $N\mu_{\text{max}}$, a quantity which is also used to determine $J$.

As the main contribution to the first-order term, the Langevin paramagnetic susceptibility usually dominates the response of any collection of ions with intrinsic magnetic moments. It is always positive and $C$ is typically of the order 1 emu·K·mol$^{-1}$, so that $\chi_0 \approx 10^{-3}$ emu·mol$^{-1}$ at room temperature. In the case of 3d transition metal complexes, when $L \approx 0$, plotting $(M/H)T = \chi_0 T = C = N g^2 \mu_B^2 S(S+1)/3k_B \approx \frac{1}{2} S(S+1)$ versus $T$ at high temperatures (say, approaching room temperature $T_R \approx 300$ K) gives the Curie constant which should yield the net unpaired spin $S (= \frac{1}{2}\cdot\text{(number of unpaired electrons)})$ on each atomic/molecular unit. A collection of different species of ions, each with a particular net spin, will give a paramagnetic susceptibility which is the sum of $\chi_0$ from each species: $\chi_0 = \chi_0(S_1) + \chi_0(S_2) + \cdots$. The Curie constant for some typical combinations of atomic spins is listed in Table 1.

Larmor Diamagnetism

Keeping with the first-order approximation, the diamagnetic term $E^D$ may be written

$$E^D = \frac{e^2}{8mc^2} H^2 \langle \psi_n^{(0)} | \sum_i (x_i^2 + y_i^2) | \psi_n^{(0)} \rangle$$

(1.24)
Figure 3: The dependence of the magnetization of a collection of isolated moments on $g\mu_B H/k_B T$ for various $J$. 
Table 1: Approximate paramagnetic $C = \chi_0 T$ values at high temperature used to identify the spin species of a particular compound. Examples are "pure" Curie Law systems (PC) with well isolated moments or interacting systems (IC) which obey Curie's Law at temperatures much larger than the scale of the interactions and/or ordering temperatures.

<table>
<thead>
<tr>
<th>Spin Species</th>
<th>$C \approx \frac{1}{2} \sum_i S_i (S_i + 1)$ (emu·K·mol$^{-1}$)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>0.375</td>
<td>NO$_2$ClO$_2$</td>
</tr>
<tr>
<td>1</td>
<td>1.000</td>
<td>O$_2$ (gas or liquid)</td>
</tr>
<tr>
<td>3/2</td>
<td>1.875</td>
<td>KCr(SO$_4$)$_2$·12H$_2$O (PC)</td>
</tr>
<tr>
<td>2</td>
<td>3.000</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>4.375</td>
<td>(NH$_4$)$_2$Mn(CO$_4$)$_2$·6H$_2$O (PC)</td>
</tr>
<tr>
<td>3</td>
<td>6.000</td>
<td></td>
</tr>
<tr>
<td>7/2</td>
<td>7.875</td>
<td>Gd$_2$(CO$_4$)$_3$·8H$_2$O (PC)</td>
</tr>
<tr>
<td>1/2 + 1/2</td>
<td>0.750</td>
<td>CuNi(fsa)$_2$en(H$_2$O)$_2$·H$_2$O</td>
</tr>
<tr>
<td>1/2 + 1</td>
<td>1.375</td>
<td></td>
</tr>
<tr>
<td>1/2 + 3/2</td>
<td>2.250</td>
<td></td>
</tr>
<tr>
<td>1/2 + 2</td>
<td>3.375</td>
<td>[MnTPP]$^+$[TCNE]$^-$ (IC)</td>
</tr>
<tr>
<td>1/2 + 5/2</td>
<td>4.750</td>
<td>FeCu(fsa)$_2$en(CH$_3$OH)(Cl)·CH$_3$OH</td>
</tr>
<tr>
<td>1 + 5/2</td>
<td>5.375</td>
<td>FeNi(bpmp)(C$_3$H$_7$O)$_2$</td>
</tr>
</tbody>
</table>
The molar susceptibility is

\[ \chi^D = \frac{e^2}{12mc^2} H^2 (\langle \psi^{(0)}_n | \sum_i r_i^2 | \psi^{(0)}_n \rangle). \]  

(1.25)

The calculation of the expectation value of the square radius of a given electron is a fairly complicated affair. The result for a particular molecule or solid is very sensitive to the shape of electron orbits, especially their spatial variations at large distances. To a first approximation, one can use the simple expression for hydrogenic

\[ \langle r^2 \rangle = \sum_i \langle \psi^{(0)}_0 | r_i^2 | \psi^{(0)}_0 \rangle / Z \]  

where \( Z \) is the number of electrons per ion and \( N_0 \) is Avogadro's number (the number of ions in a mole). The last line results from the very good assumption that, in thermal equilibrium at reasonable temperatures, the occupation of excited states is negligible.

The quantity \( \langle r^2 \rangle = \sum_i \langle \psi^{(0)}_i | r_i^2 | \psi^{(0)}_i \rangle / Z \) is the mean square ionic radius.

This negative susceptibility is known as the Larmor diamagnetic response to a static applied field. Diamagnetism is the tendency for matter to be repelled by a magnetic field (i.e., to move into a region of lower field strength). This effect is always present since it relies only on local orbital characteristics of electrons and not the presence of unpaired spins. The negative sign arises from Lenz's Law, which states that a changing magnetic flux will induce current loops with an electromotive force (EMF). The current loops are oriented so that their (induced) flux is opposed to the derivative of the external flux.

The calculation of the expectation value of the square radius of a given electron is a fairly complicated affair. The result for a particular molecule or solid is very sensitive to the shape of electron orbits, especially their spatial variations at large distances. To a first approximation, one can use the simple expression for hydrogenic
For the purposes of this thesis, an order of magnitude estimate will suffice. Following Ashcroft and Mermin (1976, p.649) [10],

\[ \chi^D \approx -Z\alpha^2 \frac{N_0 a_0^3}{6} (r/a_0)^2 = -0.79Z \times 10^{-6} (r/a_0)^2 \text{ emu/mol,} \]

which is of order \(10^{-5}\) emu·mol\(^{-1}\), minute in comparison to the paramagnetic susceptibility as given by Curie's Law. However, some molecules are enormous, such as metalloproteins with molar masses \(M_m\) of \(\sim 10^4\) g·mol\(^{-1}\). Even in reasonable molecule-based magnets, molar masses can be on the order of \(10^3\) g·mol\(^{-1}\). In these cases, \(\chi^D\) shows up at room temperature as a significant fraction of the total susceptibility. Since the diamagnetic susceptibility is negative and independent of temperature, having only to do with electron orbits, one might expect to always see a high-temperature \(\chi T\) product with a clearly visible negative slope (\(\chi T = C - \chi^D T\)) in most molecule-based magnets. In fact, the major contribution to the large molar masses of molecule-based magnets is the "chicken fat" (organic ligand matrix), for which significant, positive constitutive corrections to \(\chi^D\) must be made. Such corrections account for the fact that molecules with multiple or conjugated bonds are less diamagnetic than similar molecules with single bonds [11], and tend to reduce the high temperature slope somewhat. For a system with \(S = 2\) and \(M_m = 10^3\) g·mol\(^{-1}\), the diamagnetic correction amounts to a few percent. Some constitutive corrections are listed in Table 2.
Table 2: Constitutive corrections to the diamagnetic susceptibility $\chi^D$ for molecules with multiple bonds. Values given are in units of emu·mol$^{-1}$ and are additive. From (Kahn, 1993) [11]

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>$\Delta\chi^D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C=C}$</td>
<td>5.5</td>
</tr>
<tr>
<td>$\text{C=C}$</td>
<td>0.8</td>
</tr>
<tr>
<td>$\text{C in aromatic ring}$</td>
<td>-0.25</td>
</tr>
<tr>
<td>$\text{C=N}$</td>
<td>8.1</td>
</tr>
<tr>
<td>$\text{C=N}$</td>
<td>0.8</td>
</tr>
<tr>
<td>$\text{N=N}$</td>
<td>1.8</td>
</tr>
<tr>
<td>$\text{N=O}$</td>
<td>1.7</td>
</tr>
<tr>
<td>$\text{C-Cl}$</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Van Vleck Paramagnetism

For a system with $S = L = J = 0$, the Langevin paramagnetic susceptibility is zero, so $\chi^D$ is usually the dominant contribution. In some cases, however, the second-order contribution to $E^p$ is significant. It arises from the coupling between the ground and excited states of $\mathcal{H}_0$ through the Zeeman interaction:

$$E_0^{(2)} = (\mu_B H)^2 \sum_{L'S'J'mJ'} \frac{|\langle 0 : LSJmJ | (L_z + g_e S_z) | n : L'S'J'mJ' \rangle|^2}{E_0^{(0)} - E_{n}^{(0)}}, \quad (1.32)$$

$$\approx -(\mu_B H)^2 \sum_{J'=J\pm1} \frac{|\langle LSJmJ | (J_z + S_z) | LSJ'mJ' \rangle|^2}{E(LSJ'mJ) - E(LSJmJ)}, \quad (1.33)$$

$$= -(\mu_B H)^2 \sum_{J'=J\pm1} \frac{|\langle LSJmJ | S_z | LSJ'mJ' \rangle|^2}{E(LSJ'mJ) - E(LSJmJ)}, \quad (1.34)$$

$$= -(\mu_B H)^2 \left\{ \frac{|f(J+1)|^2[(J+1)^2 - m_f^2]}{\lambda(J+1)} - \frac{|f(J)|^2[J^2 - m_f^2]}{\lambda J} \right\}, \quad (1.35)$$

where the function $f(J)$, which couples $J$ and $J-1$ levels, is given by

$$f^2(J) = \frac{[J^2 - (L - S)^2][(L + S + 1)^2 - J^2]}{4J^2(4J^2 - 1)}. \quad (1.36)$$
The denominators are the energy differences between successive $J$-levels of $\mathcal{H}_0$, which are known to arise from the $LS$-coupling as $E(J) - E(J - 1) = \lambda J$ (see Sec. 1.2.2). No further simplification exists for the general case.

Like $E^D$, the second-order paramagnetic energy $E_0^{(2)}$ is of order $H^2$. The quantity

$$\chi^{VV} = N_0 k_B T (\partial^2 \ln Z / \partial H^2)$$

(1.37)

is the *Van Vleck temperature-independent response* to an applied field. Since the denominators are always negative, $\chi^{VV}$ is positive. In cases where the energies of successive $J$-levels are not too widely separated, $\chi^{VV}$ can be of order $10^{-5}$ emu-mol$^{-1}$, and therefore compete with $\chi^D$. Physically, this term reveals the presence of the component of $\mu$ perpendicular to $J$.

To summarize, a magnetic field affects a collection of isolated moments by defining a preferred axis of spin quantization. For most molecular systems such as those in this thesis, the effects in decreasing order of importance are Langevin paramagnetism ($\chi > 0$), Larmor diamagnetism ($\chi < 0$), and Van Vleck paramagnetism ($\chi > 0$). It must be cautioned, however, that the dominance of Langevin paramagnetism only exists at sufficiently low temperatures and for systems with a high density of moments (such as one spin per unit cell). At high temperatures, an experimental susceptibility datum will incorporate many comparable contributions, and care must be taken in extracting physics. This line of caution will be taken up further in the experimental techniques section.
1.2.2 Ligand Fields and LS Coupling

In this final section concerning the properties of isolated moments, the possibility of detectable magnetic phenomena in the absence of an applied field is briefly considered. This topic is fundamentally important because it establishes the “unperturbed” states of $\mathcal{H}_0$, and thereby both the validity of the assumption of well-separated total-J levels and the appropriate wavefunctions entering into the exchange interaction.

The effects that split the $J$-levels of $\mathcal{H}_0$ are ligand fields and LS-coupling. The symmetry of the chemical environment of an atomic or molecular moment will, through the Coulomb interaction and orbital hybridization, determine its preferred magnitude and direction. In this context the “chemical environment” is assumed to be a diamagnetic collection of ligands surrounding an atomic ion. If the effect of the ligands is to weakly perturb the ionic states, the ligands are said to produce a crystal field and the net moment remains associated with the ion. If the effect is strong enough to require \textit{ab initio} consideration of the ion-plus-environment molecular states, the more general term of ligand field is used. The ligand field view is especially important in understanding the magnetic properties of molecular systems; several are what are called charge-transfer compounds, in which a 3d transition metal-based complex donates one or more electrons to its ligands, separate from those involved in any bonding. The metal ion and (previously diamagnetic) anion are then individual spin-carrying units whose identities are stabilized by the relatively high energies that would be required to excite them. Excitations between redox levels are observed in the charge-transfer bands of UV-VIS spectra $\sim 1 - 6$ eV ($\sim 10^4$ K).

On lower energy scales, the charge transfer can be thought of, in a first approximation for the magnetic properties, as yielding a static starting configuration for a
treatment with crystal fields. A 3d metal cation in the crystal field of six nitrogen or carbon atoms, possibly with a distortion has an essentially ionic the magnetic moment, and a simple description of the level splittings is possible. With no ligands present, the five d-orbitals are degenerate atomic states. When placed in an octahedral carbon "cage," the metal levels will be split by the preference of d-lobes to orient diagonally between the metal-ligand bonds. As such, the $d_{xy}$, $d_{yz}$, and $d_{zx}$ levels will form their own $T_2$ level at a lower energy than the $d_{z^2}$ and $d_{x^2-y^2}$ level which has $E$ symmetry. The $T_2$ level acts as an effective p-state with a partially quenched orbital momentum, while the higher $E$ level acts as an s-state. The first three electrons will fill the $T_2$ states, yielding $L = 1,1,0$ ($S = 1/2,1,3/2$) respectively. The placement of the subsequent electrons depends on the $T_2$-$E$ separation, commonly named $10Dq$. If $10Dq \gg U$, where $U$ is the on-site Coulomb repulsion, the subsequent electrons (fourth through sixth) will tend to reside in the $T_2$ level with spins opposing the original three. If $10Dq \ll U$, or in $d^6$ and higher configurations in either case, subsequent electrons will begin to fill the $E$-level, which has $L = 0$ rigorously. All octahedral $d^n$ configurations therefore have their orbital angular momentum partially or fully quenched. Further ligand field effects such as axial or trigonal distortions of the basic octahedron will further lower the symmetry and tend to fully quench $L$.

Energy level excitations between d-based molecular levels, such as the $T_2$ and $E$-levels mentioned here, are on the order of $\sim 0.1$ eV ($\sim 10^3$ K). They show up as deviations from Curie's law at high temperatures or, when the splittings are smaller, in high-field magnetization and high-frequency electron paramagnetic resonance (EPR) spectra.

The other zero-field effect on spin states is LS-coupling, which must be considered together with ligand fields. In complexes of transition metals, the last term $H_{SO} =$
\( \lambda L \cdot S \) in \( H_0 \) is of order \( \sim 10^{-2} - 10^{-1} \) eV, depending on oxidation, producing splittings that are perturbations of the ligand field levels but usually much larger than the magnetic field effects. \( H_{SO} \) depends on the angular momenta, and thus, insofar as \( \lambda \) and \( L \) are nonzero, there is a zero-field splitting of the spin states with quantization axis \( \hat{L} \).

LS-coupling arises as an effective term quantity from an ensemble of single-electron \( l - s \) dipole interactions

\[
\lambda L \cdot S = \sum_i \zeta(r_i) l_i \cdot s_i = \begin{cases} +\zeta/2S, & \leq \text{half-filled shell} \\ -\zeta/2S, & > \text{half-filled shell} \end{cases}
\]

where \( \zeta(r) = \frac{\hbar^2}{2m^2} \frac{\partial U(r)}{\partial r} > 0 \) is the usual spin-orbit interaction for an electron in a central field \( U(r) \) [5, 12], and \( \zeta = \int dr R(r)\zeta(r) \). The matrix elements of \( L \cdot S \) are nonzero only when \( m_l + m_s = m'_l + m'_s = m_j \), i.e., diagonal and \( \Delta S = 1 \) elements. Since \( 2L \cdot S = J^2 - L^2 - S^2 \), the energy difference between diagonal states of different \( J \) is simply

\[
\Delta E_{LS} = E_{LS}(J) - E_{LS}(J - 1) = \lambda J,
\]

called the Landé interval rule. Thus, LS coupling lifts the degeneracy of states with the same \( L \) and \( S \) quantum numbers but different \( J \), where \( J = L + S \).

If the orbital momentum is completely quenched, the LS coupling must vanish and the magnetic behavior is referred to as “spin-only.” However, the previous arguments about the quenching of \( L \) by ligand fields are only as valid as the approximation (\( \lambda \ll 10Dq \)) that LS-coupling is a perturbation. This is because if \( \lambda \neq 0 \), the wave-functions cannot be factorized into spin and orbital components: \( L \) and \( S \) are no longer good quantum numbers. The assumption \( J = S \) in the Curie law is then seen as a first approximation, to be corrected by terms in increasing powers of \( \lambda/10Dq \). Although this theory, as applied to various complexes and symmetries, can
become quite involved (some of the details can be found in Figgis [13] and Tsukerblat [14]), a simple "experimentalist's relation" for the correction can be mentioned. To first order the corrections to $g$ and $\chi_0$ have the form

$$g = g_0 (1 - k\lambda/10Dq),$$  \hspace{1cm} (1.40)  

$$\chi_0 = \chi_0^{so} (1 - 2k\lambda/10Dq),$$  \hspace{1cm} (1.41)  

where s.o. stands for "spin-only" and $k$ is a constant of order unity. The quenching of $L$ may also be represented by a smaller, effective orbital momentum $L_\Gamma$ for the particular irrep $\Gamma$, the degree of reduction taken as an experimentally determined parameter.

1.3 Properties of Interacting Moments

The most important magnetic properties, such as ferro- and ferri-magnetism, arise from the very strong interactions between neighboring magnetic moments. These interactions must be of sufficient magnitude to explain magnetic order in solids at even very high temperatures (e.g., the critical temperature of Fe is 1043 K). The strongest available forces are, of course, the Coulomb repulsion between electrons, and dipole forces. From a classical point of view, it would make sense to look to the strongest magnetic interaction to explain magnetic behavior. However, the dipole potential,

$$H_{dip} = \sum_{\langle ij \rangle} \frac{1}{r_{ij}^3} [\mu_i \cdot \mu_j - 3(\mu_i \cdot \hat{r}_{ij})(\mu_j \cdot \hat{r}_{ij})],$$  \hspace{1cm} (1.42)  

is of order $\sim (g\mu_B)^2/r^3 \approx \alpha^2(a_0/r)^3$ Ry $\approx 10^{-4}$ eV $\sim 1$ K, in units of $k_B$. This energy is not nearly large enough to account for the observed long-range order. The needed interaction must be electrostatic.
The strongest coupling between moments is actually due to the so-called \textit{exchange interaction}, which is an effective interaction between local moments that emulates the complicated statistical effects imposed externally by the Pauli Exclusion Principle. The total wave function $\Psi$ of an ensemble of electrons must be antisymmetric with respect to the exchange of any two electrons. This requirement restricts the permissible spin states of the ensemble. For instance, in the absence of LS-coupling, the wavefunction for two electrons can be separated into spatial ($\psi$) and spin ($\chi$) parts,

$$\Psi(r_1, r_2, s_1, s_2) = \psi(r_1, r_2)\chi(s_1, s_2), \quad (1.43)$$

so that the antisymmetry of $\Psi$ requires $\psi$ and $\chi$ to be of definite and opposite symmetries. Therefore, a symmetric $\psi$ corresponds to the antisymmetric $\chi$,

$$\chi_A = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \quad (1.44)$$

which is a singlet ($S = 0$), while an antisymmetric $\psi$ corresponds to the symmetric $\chi$ manifold,

$$\chi_S^1 = |\uparrow\uparrow\rangle,$$

$$\chi_S^0 = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle),$$

$$\chi_S^{-1} = |\downarrow\downarrow\rangle, \quad (1.45)$$

which is a triplet ($S = 1$). Thus the correspondence between symmetry and spin is evident.

Which of all the possible $2^N$ spin configurations of an ensemble of $N$ electrons is preferred? This is a very difficult question. What is known is that the ordering of the configurations into energy levels is done by considering their relative \textit{Coulomb energies}. Since certain symmetries favor certain spatial configurations (i.e., interelectron
distances $r_{ij}$, the level splittings will be determined by the differing Coulomb repulsions between electrons with differing spin symmetries. The strength of the exchange interactions are given by these level splittings.

To see explicitly how these relationships work out, the problem of the $H_2$ molecule will be discussed first. Simple two-electron exchange leads to the Heisenberg Hamiltonian. The extension to molecules and solids will be considered next. It may seem surprising, but in most cases the simple two-electron exchange is already of sufficient complexity to describe the observed magnetic behavior of solids. Among these, ferro-, antiferro-, and ferri-magnetism will be examined.

### 1.3.1 The Hydrogen Molecule

The spatial, or orbital, states of $H_2$ are determined by solving the Schrödinger equation for the Hamiltonian, in atomic units,

$$\mathcal{H} = \frac{1}{2} \nabla_1^2 + \frac{1}{2} \nabla_2^2 + \frac{1}{r_{12}} - \left( \frac{1}{r_{a1}} + \frac{1}{r_{b1}} \right) - \left( \frac{1}{r_{a2}} + \frac{1}{r_{b2}} \right),$$

where $r_{12}$ is the interelectron distance, and $r_{i\alpha} (i = 1, 2; \alpha = a, b)$ are the distances between electrons 1 or 2 and nuclei a or b. The difficulty with solving $\mathcal{H}\psi = E\psi$, of course, is that insidious term in $r_{12}$. (Indeed, some might say that term is the main problem with condensed matter physics.) Since no closed-form solution exists even in this simple case, it is of interest to write approximate solutions based on series expansions. However, this procedure is not plausible computationally for anything other than the simplest molecules. As the main goal is to understand effects in solids, a more uniform (and devastating) approximation is used as the starting point – the one-electron (or independent electron) approximation (OEA).
The One-Electron Approximation

In the OEA, the total spatial wavefunction $\psi$ is made up from a combination of one-electron eigenstates $\varphi_i$ of a noninteracting Hamiltonian. The total Hamiltonian for $H_2$ is then written

$$H_{\text{OEA}} = H_1 + H_2 + H_{12},$$

(1.47)

where $H_i$ is the noninteracting Hamiltonian for electron $i$,

$$H_1\varphi_1 = E_1\varphi_1,$$

(1.48)

$$H_2\varphi_2 = E_2\varphi_2,$$

(1.49)

and $H_{12}$ is the interaction Hamiltonian, which can be taken as a perturbation.

It should be clarified here that the rewriting of $H$ as $H_{\text{OEA}}$ does not assume a particular mapping of their terms. That is, $H_{12}$ is not necessarily just $1/r_{12}$. In fact, it is the particular assignment of these terms that embodies an actual calculation with the OEA. The general procedure goes like this. First, $H$ is divided up into $H_1$, $H_2$, and $H_{12}$. There are two ways of doing this for $H_2$, corresponding to an itinerant ("molecular") picture or a localized ("atomic") picture. Second, the one-electron eigenfunctions $\varphi_i$ are combined into total (approximate) spatial wavefunctions in such a way as to satisfy the requirements of exchange symmetry. This can be done explicitly, by simply writing down the symmetric (+) and antisymmetric (−) forms

$$\psi_\pm = N_\pm [\varphi_1(r_1)\varphi_2(r_2) \pm \varphi_2(r_1)\varphi_1(r_2)].$$

(1.50)

The normalization constants $N_\pm$ are determined by

$$1 = \int d\tau_1 d\tau_2 \psi_\pm^* \psi_\pm,$$
\[
\begin{align*}
\rho^2 & = N_+ \int d\tau_1 d\tau_2 \{ \phi_1^*(r_1)\phi_2^*(r_2)\phi_1(r_1)\phi_2(r_2) + \phi_2^*(r_1)\phi_1^*(r_2)\phi_2(r_1)\phi_1(r_2) \\
& \quad + \phi_2^*(r_1)\phi_1^*(r_2)\phi_1(r_1)\phi_2(r_2) \pm \phi_1^*(r_1)\phi_2^*(r_2)\phi_2(r_1)\phi_1(r_2) \}, \quad (1.51) \\
\rho^2 & = 2N_+^2[1 \pm \int d\tau_1 d\tau_2 \phi_1^*(r_1)\phi_2^*(r_2)\phi_2(r_1)\phi_1(r_2)], \quad (1.52) \\
& \equiv 2N_+^2(1 \pm \alpha^2), \quad (1.53)
\end{align*}
\]

where the overlap integral \( \alpha \) is
\[
\alpha = \int d\tau \phi_1(r)\phi_2(r). \quad (1.54)
\]

Third, the energies are evaluated by taking the expectation values of the full Hamiltonian \( \mathcal{H} \) in these combined states. It can be shown that the OEA energies \( E_{\pm} = \langle \psi_{\pm} | \mathcal{H}_{\text{OEA}} | \psi_{\pm} \rangle \) may be written
\[
E_{\pm} = E_1 + E_2 + \frac{V \pm W}{1 \pm \alpha^2}, \quad (1.55)
\]
where
\[
\begin{align*}
V & = \langle \phi_1^*(r_1)\phi_2^*(r_2) | \mathcal{H}_{12} | \phi_1(r_1)\phi_2(r_2) \rangle, \quad \text{and} \quad (1.56) \\
W & = \langle \phi_1^*(r_1)\phi_2^*(r_2) | \mathcal{H}_{12} | \phi_2(r_1)\phi_1(r_2) \rangle, \quad (1.57)
\end{align*}
\]

are called the Coulomb and exchange integrals, respectively. The symmetric-antisymmetric splitting, which defines the exchange energy \( J \), is then
\[
2J \equiv \Delta E,
\]
\[
\begin{align*}
& = 2V(N_+^2 - N_1^2) + 2W(N_+^2 + N_1^2), \quad (1.58) \\
& = \frac{2W - V \alpha^2}{1 - \alpha^4}. \quad (1.59)
\end{align*}
\]

If \( J \) is positive, \( \psi_+ \) is higher in energy than \( \psi_- \), so the symmetric (triplet) spin state is favored. Similarly, if \( J \) is negative, the singlet spin state is favored. Thus, electrons with positive \( J \) tend to align parallel, and electrons with negative \( J \) tend to align antiparallel.
The two ways of separating the Hamiltonian (and viewing the physics) mentioned above are the Heitler-London and Molecular Orbital models. The energy splittings in these models can both be interpreted as exchange energies. Following this, it will be straightforward to determine an explicit exchange interaction between spins, and thereby a model to understand exchange effects in many-body systems.

**Heitler-London Model**

In the Heitler-London (HL) approximation, the electron repulsion is considered to be sufficiently strong for the H$_2$ molecule to look primarily like two H-atoms; the electrons tend to stay at opposite end of the molecule. Thus, following the OEA scheme, the Hamiltonian may be divided as

\[
\mathcal{H}_1 = \frac{1}{2} \nabla^2_1 - \frac{1}{r_{a1}},
\]

\[
\mathcal{H}_2 = \frac{1}{2} \nabla^2_2 - \frac{1}{r_{b2}}, \quad \text{and}
\]

\[
\mathcal{H}_{12} = \frac{1}{r_{12}} - \left( \frac{1}{r_{a2}} + \frac{1}{r_{b1}} \right).
\]

The one-electron wavefunctions \( \psi_i \) are the atomic orbitals (AO) \( \phi_a \) and \( \phi_b \), so written to emphasize the localization of the electrons on nuclei a and b. The molecular wavefunctions (1.50) are

\[
\psi_\pm = N_\pm [\phi_a(r_1)\phi_b(r_2) \pm \phi_b(r_1)\phi_a(r_2)].
\]

The Coulomb and exchange integrals may be simplified to

\[
V = \int \frac{\rho_{aa}(1)\rho_{bb}(2)}{r_{12}} d\tau_1 d\tau_2 - \int \frac{\rho_{aa}(1)}{r_{b1}} d\tau_1 d\tau_2 - \int \frac{\rho_{bb}(2)}{r_{a2}} d\tau_1 d\tau_2, \quad \text{and}
\]

\[
W = \int \frac{\rho_{ab}(1)\rho_{ab}(2)}{r_{12}} d\tau_1 d\tau_2 - 2\alpha \int \frac{\rho_{ab}(1)}{r_{b1}} d\tau_1
\]

(1.64)  

(1.65)
where $\rho_{xy} = \phi_x \phi_y$. Because it places the electrons in well-defined AOs, the HL model is asymptotically accurate for widely separated nuclei. Through (1.59), $J$ can be calculated with Hydrogen 1s functions. The details are not presented here, but it turns out that $J$ is negative, corresponding to an embryonic form of antiferromagnetism. This result is in agreement with experiment, and with the elementary theorem that the ground state $\psi$ of two-electron systems must be symmetric [10]. The dependence of the singlet and triplet energies on internuclear distance is shown in Fig.4. A thorough critique of the HL model is given by Herring (1962) [15].

### Molecular Orbital Model

In the Molecular Orbital (MO) approximation of Hund and Mulliken [16], the unperturbed electrons are shared equally between the nuclei; each is independently as likely to be in orbit around either nucleus. The interelectron repulsion proper is the perturbation:

$$
\mathcal{H}_i = \frac{1}{2} \nabla_i^2 - \left( \frac{1}{r_{ai}} + \frac{1}{r_{bi}} \right),
$$

$$
\mathcal{H}_{12} = \frac{1}{r_{12}},
$$

(1.66)

(1.67)

In this case, the one-electron wavefunctions $\varphi_i$ are not the AOs, but a linear combination of atomic orbitals (LCAO). In other words, the basis functions are molecular in character:

$$
\varphi_s = N_s (\phi_a + \phi_b),
$$

$$
\varphi_u = N_u (\phi_a - \phi_b),
$$

(1.68)
Figure 4: The variation of the energy of $H_2$ as a function of internuclear separation in the Heitler-London (HL) and Molecular Orbital (MO) schemes. The dotted lines are the energy of a more sophisticated (nearly exact) calculation. Lower curves are singlets (ground state), upper curves are triplets (excited). Energies plotted include internuclear Coulomb repulsion. The equilibrium separation is about 1.7 atomic units. From Martin (1967) [9].
where
\[ N_{g/u}^2 = \frac{1}{2(1 \pm S)}, \quad (1.69) \]
with \( S = (\rho^2/3 + \rho + 1)e^{-\rho} \) \((\rho = r/a_0)\). The MOs \( \varphi_g \) and \( \varphi_u \) are depicted schematically in Fig. 5. These orbitals approximate the even (gerade) and odd (ungerade) eigenfunctions of \( H_2^+ \), and correctly predict the formation of a stable bond. Now, in the MO model, there is no restriction to prevent both electrons from orbiting the same nucleus (the ionized states), as there was in HL. Consequently, there are now \textit{four} possible two-electron spatial wavefunctions:

\[
\begin{align*}
\psi_- &= N_-[\varphi_g(r_1)\varphi_u(r_2) - \varphi_u(r_1)\varphi_g(r_2)], \\
\psi_{+1}^1 &= \varphi_g(r_1)\varphi_g(r_2), \\
\psi_{+2}^2 &= \varphi_u(r_1)\varphi_u(r_2), \\
\psi_{+3}^3 &= N_+[\varphi_g(r_1)\varphi_u(r_2) + \varphi_u(r_1)\varphi_g(r_2)].
\end{align*}
\]

The ground state for the equilibrium nuclear separation turns out to be \( \psi_{+1}^1 \), which when expanded is

\[
\begin{align*}
\psi_{+1}^1 &= N_g^2[\phi_2(r_1)\phi_u(r_2) + \phi_u(r_1)\phi_2(r_2) + \phi_u(r_1)\phi_2(r_2) + \phi_2(r_1)\phi_u(r_2)], \\
&= \psi^{\text{IONIC}} + \psi^{\text{HL}}. \quad (1.74)
\end{align*}
\]

Evidently, the ionized states are equally as probable as the neutral states. While the singlet ground state is also correctly predicted with the MO model, for reasonable distances \((5 \leq r/a_0 \leq 12)\), it fails completely at large distances where the electrons reside on isolated atoms. For large distances, \( J \) is forced positive by a logarithmic term in \( r \) which arises from the neglect of electron interactions in the unperturbed molecular wavefunctions, incorrectly predicting ferromagnetism as \( r \to \infty \). The dependence of the MO energies on separation is shown in Fig. 4.
Figure 5: Molecular wavefunctions as formed by a linear combination of atomic orbitals (LCAO). The dotted lines are the individual atomic orbitals. The symmetric case (right) is *bonding*: the electron density between nuclei screens the internuclear repulsion and lowers the energy.
Embryonic CI: Admixing Higher States

The HL and MO schemes represent two extremes in estimating the wavefunction of two electrons. The actual situation must lie somewhere between the localized (HL) and delocalized (MO) limits. One way to attain a compromise is through configuration mixing (CM) or configuration interaction (CI). With CI, the singlet ground state of HL (also called valence bond (VB) in this context) is made more accurate by admixing only a small amount of purely ionic (delocalized) state as a perturbation,

$$\psi^{CI} = \psi^{HL} + \delta \psi^{IONIC},$$

which is qualitatively a "relaxed" MO wavefunction. In the spirit of the Hubbard model, the ionic state is taken to be at an energy $U$ above the HL ground state. Then $\delta = -t/U$, where $t = \langle \psi^{HL} | H_{12} | \psi^{IONIC} \rangle$, and the (second-order) energy shift is $-t^2/U$. This effect, then, acts to further stabilize the singlet ground state (antiferromagnetism). The finite probability $\delta^2/(1 + \delta^2)$ of finding both electrons around the same nucleus is also referred to as a virtual charge transfer or kinetic exchange. Admixture of excited states is a general theme used to account for the types and strengths of exchange couplings seen in solids, and has proven especially useful for molecule-based magnets, where delocalized states tend to be high in energy.

For completeness, it should be mentioned that there is a powerful related method which focuses on obtaining improved basis functions $\varphi_i$ from the outset. The idea is not to write the interaction term $H_{12}$ explicitly, but to model the electron interaction in $H_i$ by having each electron respond to the average motion of the other electron(s). (This averaged interaction is called the Hartree or mean-field term.) In the two-electron case, electron 1 responds to the averaged motion of electron 2, which of course is in turn an average of the averaged motion of electron 1. If this averaged
motion can be made to depend on some small quantity (which can be simply the term $1/r_{12}$), a self-consistent perturbation series develops for the total interaction. The *imposition* of symmetry in this more explicitly interacting model, called the Hartree-Fock approximation, can then lead to improvements over simpler schemes.

### Spin Hamiltonian and Hund’s Rules

To make the connection between magnetism and symmetry computationally and aesthetically useful, a Hamiltonian describing the spin degrees of freedom alone is needed. This was originally accomplished by Heisenberg [17] and Dirac [18], who “noticed” that the singlet-triplet energy splitting of two electrons could be written as a function of the scalar product of their spins. That is, the four spin states of two electrons span a subspace described by a new *spin Hamiltonian*:

$$
\mathcal{H}_{ij} = -J_{ij} \left( \frac{1}{2} + 2s_i \cdot s_j \right).
$$

(1.76)

It is straightforward to see that this Hamiltonian reproduces the singlet-triplet splitting, since $2s_i \cdot s_j = S^2 - \frac{3}{2}$, and

$$
\Delta E = \langle \chi_A | \mathcal{H} | \chi_A \rangle - \langle \chi_S | \mathcal{H} | \chi_S \rangle \\
= -2J [\langle \chi_A | S^2 | \chi_A \rangle - \langle \chi_S | S^2 | \chi_S \rangle] \\
= -2J.
$$

(1.77)

The validity of this association relies on two important assumptions, ones which must especially be reevaluated in analyzing the magnetic properties of a new class such as molecule-based magnets. The first is the restriction to a nondegenerate orbital subspace described by $\mathcal{H}_{ij}$. The Coulomb interaction will always couple to higher
orbital states to some extent. The second assumption is the orthogonality of the spanning basis functions. It should be valid for electrons on the same atom (when using atomic wavefunctions), but breaks down when considering the exchange between electrons centered on different atoms or molecules.

If the one-electron orbitals are mutually orthogonal, then \( \alpha = 0 \) and \( N_+ = N_- = 1/\sqrt{2} \). The exchange interaction is then \( J = W > 0 \) (\( W \) is necessarily positive definite when \( \alpha = 0 \)). Concerning the simple expression (1.59) for \( J \), it is seen that a positive \( W \) favors ferromagnetism. So, the triplet state is always favored for orthogonal orbitals. This is the origin of Hund's rule, which states that the ground state of an atom has maximum multiplicity [6, 10]. At the simple OEA level, the effect of nonorthogonality is seen in the \( V \) term of (1.59), which favors antiferromagnetic coupling for \( V > 0 \). However, things are more complicated in solids, and both signs of exchange are realized in molecular systems. Specific cases will be analyzed at the appropriate points.

It is useful to think of the spin Hamiltonian as representing a real interaction between spins. Indeed, if one were able to manipulate electrons individually, the Pauli Exclusion Principle could be thought of as a kind of force field which tends to anti-align spins as they are brought closer together, or equivalently to cause parallel spins to have a stronger Coulomb repulsion than antiparallel ones. The true nature of this tendency remains, however, a great mystery.
1.3.2 Exchange in Solids

To extend the concept of exchange to moments in solids, at least in insulators, what is usually done is to simply assume that the Heisenberg exchange form is still valid, and that only the pairwise exchange effects are ultimately of importance. With these assumptions, the spin Hamiltonian is

\[ H = -2 \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \]  

where the sum is taken over all pairs of spins. The allowance of \( S \) as the net spin of an atom or molecule as well as that of an electron is also an assumption – that orthogonal orbitals of electrons in the same spatial region can be logically separated from the (possibly nonorthogonal) orbitals of those at some distance. Although making these assumptions requires no great effort, justifying them certainly does. Imagine \( N \) spins, either electrons, atomic ions, or molecular radicals, infinitely far apart. There is no overlap of their wavefunctions and the exchange is zero; the ground state is \((2S + 1)^N\)-fold degenerate. As the moments are brought slightly closer together, it can be shown [19, 20] that, in many cases, the initial splittings are exactly described by (1.78). The source of, and thereby the radial and angular dependence of, the exchange parameter may vary with the local chemical environment of the spin pair, however. The next correction is the biquadratic term \( \sum_{ij} J_{ij}^2 (\mathbf{S}_i \cdot \mathbf{S}_j)^2 \), following Anderson [21, 22], which is insensitive to issues of ferromagnetic versus antiferromagnetic coupling. In this thesis, it is assumed that the simple bilinear Heisenberg form (1.78) is generally applicable. The states of this Hamiltonian are sufficient complexity to (potentially) explain most experimental observations in molecule-based magnets. The main concern, to reemphasize, is the ultimate sign of \( J \), taken in an average sense, which leads to the tendency for a particular long-range ordering.
1.3.3 Long-Range Order in Solids

Magnetism would not have even a small fraction of its current stature in modern science and technology if certain materials did not possess the strong bulk properties known as ferromagnetism and ferrimagnetism. Below a certain critical temperature \( T_c \), such materials are very easily saturated in modest fields, so that molar magnetization is \( M_{SAT} = N\mu_{\text{max}} \), where \( \mu_{\text{max}} \) is the microscopic magnetic moment (per unit cell, say). To quantify "easily" and "modest," consider that according to the Brillouin function, a paramagnet saturates in the limit \( g\mu_B H \gg k_B T \), or \( H \) (in Tesla) \( \gg 0.74T \) (in Kelvin). At 100 K, a field much greater than 74 T would be required. In contrast, only a few Oersted are required to saturate ferromagnetic Fe at the same temperature. Of even greater value for current magnetics technology, when the saturating field is removed, a ferromagnet\(^5\) will retain a remanent magnetization, \( M_R \), which is a significant fraction of \( M_{SAT} \). The material is then said to have been "magnetized," and is useful for data storage technologies and attaching favorite recipies to refrigerator doors. Examples of such materials are listed in Table 3.

The various kinds of magnetic order are summarized in Fig.6. Ferromagnetic (b), antiferromagnetic (c), and ferrimagnetic (d) materials all undergo a transition to collinear order below \( T_c \), while others may have more complex orderings. There is also the possibility of materials displaying several types of order depending on the field, temperature, or other conditions.

The body of literature concerning properties of magnetic compounds and theo-

\(^5\)For convenience, the term "ferromagnet" will be used to refer to any material possessing a net magnetization below some \( T_c \), including ferrimagnets.
Table 3: Examples of Various Magnetic Systems

<table>
<thead>
<tr>
<th>Curie-Law Paramagnets</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{KCr(SO}_4\text{)}_2 \cdot 12\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2\text{Mn(SO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{Gd}_2(\text{SO}_4\text{)}_3 \cdot 8\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Ferromagnets</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
</tr>
<tr>
<td>$\text{Co}$</td>
</tr>
<tr>
<td>$\text{Fe}$</td>
</tr>
<tr>
<td>$\text{CrBr}_3$</td>
</tr>
<tr>
<td>$[\text{FeCp}_2][\text{TCNE}]$</td>
</tr>
<tr>
<td>$\text{GdCl}_3$</td>
</tr>
<tr>
<td>$\beta-p-\text{NO}_2\text{C}_6\text{H}_4\text{NIT}$</td>
</tr>
<tr>
<td>Antiferromagnets</td>
</tr>
<tr>
<td>$T_N$ (K)</td>
</tr>
<tr>
<td>$\text{NiO}$</td>
</tr>
<tr>
<td>$\text{Cr}$</td>
</tr>
<tr>
<td>$\text{FeCl}_2$</td>
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<tr>
<td>Ferrimagnets</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
</tr>
<tr>
<td>$\text{Fe}_3\text{O}_4$</td>
</tr>
<tr>
<td>$\text{MnFe}_2\text{O}_4$</td>
</tr>
<tr>
<td>$\text{Y}_3\text{Fe}<em>5\text{O}</em>{12}$</td>
</tr>
<tr>
<td>$V(\text{TCNE})_2 \cdot \frac{1}{2}(\text{CH}_2\text{Cl}_2)$</td>
</tr>
<tr>
<td>$[\text{MnTPP}][\text{TCNE}]2\text{PhMe}$</td>
</tr>
<tr>
<td>Metamagnets</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
</tr>
<tr>
<td>$\text{FeCl}_2$</td>
</tr>
<tr>
<td>$[\text{MnCp}_2][\text{DDQ}]$</td>
</tr>
<tr>
<td>$[(\text{CH}_3)_3\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$[\text{FeCp}_2][\text{TCNQ}]$</td>
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<tr>
<td>Superparamagnets</td>
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<tr>
<td>Ferritin</td>
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<td></td>
</tr>
<tr>
<td>$a-(\text{Ho}_2\text{O}_3)(\text{B}_2\text{O}_3)$</td>
</tr>
<tr>
<td>Spin Glasses</td>
</tr>
<tr>
<td>$T_f$ (K)</td>
</tr>
<tr>
<td>$\text{Au}<em>{0.98}\text{Fe}</em>{0.02}$</td>
</tr>
<tr>
<td>$\text{Au}<em>{0.99}\text{Fe}</em>{0.01}$</td>
</tr>
</tbody>
</table>
Figure 6: Various types of spin ordering in magnetic materials. (a) paramagnet, (b) ferromagnet, (c) antiferromagnet, (d) ferrimagnet, (e) metamagnet, (f) superparamagnet, (g) spin glass, (h) helimagnet, (i) domain magnet, (j) correlated spin glass, (k) ferromagnet with wandering axis.
retical models to describe them is enormous. This enormity is the result of several factors, foremost of which is that magnetism is a fascinating and vital scientific subject. Its “attraction” is only increased by the difficulty of explaining fully even some of the simplest many-body magnetic properties of materials, such as the survival of a transition metal’s local moment when dissolved in a nonmagnetic host. The bulk ferromagnetism of the transition metals is another area not completely understood.

In this section, only the simplest aspects of magnetism will be discussed, i.e., those deriving from mean-field theory and/or the intuition of an experimentalist. The practical subject of domains and hysteresis is presented briefly first. Then the gross behavior of the three basic classes of collinear magnets as described by mean-field theory will be analyzed.

**Domains and Hysteresis**

The strong magnetic properties of ferromagnets, ferrimagnets, antiferromagnets, and other materials with long-range order are due to the exchange interaction between microscopic moments. It would seem then that such materials should order naturally in zero applied field, as $J$ is not dependent on $H$. However, most pieces of iron, nickel, or magnetite laying around are nonmagnetic – they don’t attract each other or other metals. There is spontaneous ordering in these materials, but it occurs on length scales smaller than the size of the whole solid. The small regions of aligned spins, called domains, each possess a net (saturated) moment, but the net moments of domains point in different directions and average to zero. The reason that domains exist is that the alignment of moments over large length scales in real materials is
not solely determined by $J$. Structural anisotropies, chemical defects, and the simple dipole interaction favor a situation which breaks the magnet into domains separated by "Bloch" walls within which a rotation of local moments occurs. A schematic drawing of domains in a ferromagnet is shown in Fig. 6 (i). The application of an external field allows neighboring domains to overcome their divisive energy barrier and lock into alignment, forming a larger domain. As the field increases, domains merge together. Since crystalline magnets have a finite number of possible domain orientations, the final, macroscopic domain is not, in general, aligned with the field, but rather with the crystalline axis closest to the field direction. Further increases in $H$ will coherently rotate the spins in the macro-domain toward the field direction.

When the field is removed, the material does not break into domains in the exact reverse order in which they originally merged. This intrinsic irreversibility, called hysteresis, is due to the fact that force on a Bloch wall in the region of an imperfection is nonmonotonic [23]. The bulk magnetization will be $M_R$ at $H = 0$, and reduces to zero only when a negative coercive field $H_c$ is applied. Consequently, the $M(H)$ will trace out an irreversible path – the hysteresis loop – whose shape depends on the intrinsic structural and magnetic properties of the material, as well as on the conditions of measurement. A typical hysteresis loop is shown in Fig. 7. The total magnetic energy dissipated in this irreversible cycle is the area of the loop. Magnets are classified as "soft" and "hard" if they have small or large hysteresis loops, respectively.
Figure 7: A typical hysteresis loop. From Jiles [24].
Ferromagnetism

It was shown above that the actual magnetic field generated by neighboring spins is far too small to account for ferromagnetism at reasonable temperatures. P. Weiss [25] was the first to model the exchange effect as an "effective" magnetic field, although at the time not knowing what the exchange effect was. The strength of this effective field must be on the order of $10^6$ Oe. The Heisenberg Hamiltonian for the spin $S_i$ on site $i$ in a magnetic field $H$ is rewritten as

$$\mathcal{H}_i = -g\mu_B S_i \cdot H_{\text{eff}},$$  \hspace{1cm} (1.79)

where

$$H_{\text{eff}} = H + \frac{1}{g\mu_B} \sum_{j \neq i} 2J_{ij}S_j.$$  \hspace{1cm} (1.80)

In the mean-field approximation, $H_{\text{eff}}$, which depends instantaneously on the states of all spins $j \neq i$, is replaced by its mean, or equilibrium, value. Such an assumption is hardly justified in reality, but may serve as an initial guess upon which to base more sophisticated treatments which include the fluctuations about that mean value. Now, the mean value of $H_{\text{eff}}$ is determined by the mean value of $S_j$, since $H$ and $J_{ij}$ are fixed. The mean value of $S_j$ in a solid with bulk magnetization $M$ is simply the site magnetization

$$\langle S_j \rangle = \frac{M}{Ng\mu_B}.$$  \hspace{1cm} (1.81)

The problem is then reduced to solving, self-consistently, for the behavior of an isolated spin in the effective field $H_{\text{eff}} = H + \lambda M$, where

$$(g\mu_B)^2 \lambda = \frac{1}{N} \sum_{j \neq i} 2J_{ij} \approx \frac{1}{N} \sum_j 2J_{ij}.$$  \hspace{1cm} (1.82)

The solutions are therefore given through the Brillouin function (1.21)

$$M(T, H) = N\mu_{\text{max}} B_S \left( \frac{\mu_{\text{max}}(H + \lambda M)}{k_B T} \right),$$  \hspace{1cm} (1.83)
considered, for \( H \to 0 \), as the graphical intersection of a pair of functions

\[
m = B_s(x), \tag{1.84}
\]
\[
m = T x / \lambda, \tag{1.85}
\]

where \( m = M / N \mu_{\text{max}} \) is the reduced magnetization. Consulting Fig. 8, it is clear that there is a solution for nonzero \( x \) only if the slope \( \lambda / T \) is less than the initial slope of \( B_s(x) \). Since this initial slope can be obtained from Curie's law,

\[
\left( \frac{\partial B_s(x)}{\partial x} \right)_0 = \left( \frac{\partial H}{\partial x} \right)_0 \left( \frac{\partial B_s(x)}{\partial H} \right)_0 = T \chi_0 = C, \tag{1.86}
\]

there is a simple condition \( T < T_c \) for a nonzero solution, where

\[
T_c = \frac{2 J_0 S (S + 1)}{3 k_B}, \tag{1.87}
\]

is the critical temperature and \( J_0 = \sum J_{ij} \).

In addition to estimating a critical temperature, it is important in any treatment of ferromagnetism to work out the behavior for \( T \to 0 \), \( T \to T_c^\pm \), and \( T \to \infty \). In mean-
Figure 8: Graphs for solution of transcendental equation for the reduced magnetization of a ferromagnet in mean field theory. From Ashcroft and Mermin [10], p.716.
field theory (MFT) these are

\[ m(T) = 1 - \exp \left( -\frac{3}{S+1} \frac{T_c}{T} \right) \], \quad T \to 0 \\

\[ m(T) = \left[ \frac{10}{3} \frac{(S+1)^2}{S^2 + (S+1)^2} \right]^{1/2} \sim t^{1/2} , \quad T \to T_c^- \\

m(H) = m_0 |h|^{1/3} + \text{(nondivergent terms)} \quad T = T_c \\\n
\[ \chi(T) = \chi_0 |t|^{-1} + \text{(nondivergent terms)} \quad T \to T_c^\pm \\\n
C(T) = 5Nk_B \left[ \frac{S(S+1)}{S^2 + (S+1)^2} \right] \quad T < T_c \\\n
\[ \xi(T) = \xi_0 |t|^{-1/2} + \text{(nondivergent terms)} \quad T \to T_c^+ \\\n
\[ \chi(T) = \frac{C}{T - T_c} \quad T \gg T_c \]

where \( t = (1 - T/T_c) \) is the reduced temperature and \( \xi \) is the correlation length.

The limitations of MFT are evident in these relations. In real ferromagnets, the
low temperature magnetization actually follows a power-law rather than the exponential predicted by MFT. The particular form of this Bloch-\( T^{3/2} \) law is \( m(T) = 1 - BT^{3/2} \)
where

\[ B = \frac{1}{S} \left( \frac{k_B}{8\pi JS} \right)^{3/2} \xi \left( \frac{3}{2} \right) \], \quad (1.88) 

and arises from the \( \sim k^2 \) dispersion of low-temperature magnons. In the region
near \( T_c \), MFT necessarily misses the critical exponents (corresponding as it does to \( d \geq 4 \)). Table 4 summarizes the critical exponents for some experimental systems
and the predictions of various models. The essential result of MFT is its ability to
accurately predict the first-order correction to Curie's Law at high temperatures –
the so-called Curie-Weiss Law. In general, independently of MFT, magnetic systems
with exchange interactions have $\chi^{-1}$ vs. $T$ relations which diverge from linearity as $T$ decreases, according to

$$\chi = \frac{C}{T - \theta}$$  \hspace{1cm} (1.89)

where $\theta$ is the Curie-Weiss temperature, typically slightly greater than $T_c$. Figure 9 shows how this relation behaves for the three main classes of magnets. In particular, ferromagnets have a positive $\theta$, corresponding to their positive exchange $J$. Of course, as $T \to T_c^+$, the Curie-Weiss behavior gives way to scale-invariant critical behavior. The width of this “critical region” near $T_c$ depends sensitively on the dimensionality of the chemical environment and of the local order parameter, as well as on the degree and type of disorder in the material.

For a detailed exposition of ferromagnetism, the reader is referred to the copious literature [1, 8, 9, 34, 6, 35].

**Antiferromagnetism and Ferrimagnetism**

Antiferromagnetic (AF) and ferrimagnetic (FI) materials, like ferromagnets, undergo a transition to long-range order below $T_c$, but in these cases, neighboring spins tend to antialign. If every spin is identical (magnitude and chemical environment), the “up” spins and “down” spins, residing on two logically separate sublattices, will exactly cancel, giving no net magnetization. This is antiferromagnetism. When the magnitudes or chemical environments of the spins on the two sublattices are different, there can be a net moment at low temperatures – the ferrimagnetic state. Actually, ferrimagnetism is a more general term which applies to spins on possibly more than just two sublattices, with different magnitudes, and possibly a mixture of ferro- and
Figure 9: The Curie-Weiss behavior $\chi = C/(T - \theta)$ used to characterize the initial corrections to paramagnetism ($P, \theta = 0$) due to magnetic interactions of ferromagnetic ($F, \theta > 0$) or antiferro- (AF) /ferri- (FI) magnetic ($\theta < 0$). In mean field theory, $\theta \propto J$. 
Table 4: Critical exponents of magnetic systems. Values for MFT, RMA MFT (RMA = Random Magnetic Anisotropy), and 2D Ising models are exact. Values of $\alpha$ for the pure metals are from direct scaling of specific heat data. Values of $\nu$ for Co, Gd, and typical amorphous magnets were calculated from Josephson's scaling law $\nu d = 2 - \alpha$, with $d = 3$. Values for V/TCNE and [MnTPP][TCNE] magnets are discussed in Chs. 3 and 4, respectively.

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\delta$</th>
<th>$\gamma$</th>
<th>$\nu$</th>
<th>Ref.</th>
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<td>3</td>
<td>1</td>
<td>1/2</td>
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<td>5/3</td>
<td>1/2</td>
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<td>7/4</td>
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<td>4.3</td>
<td>1.33</td>
<td>0.69</td>
<td>[26, 27]</td>
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<td>3.4</td>
<td>1.23</td>
<td>0.7</td>
<td>[28, 27]</td>
</tr>
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<td>1.33</td>
<td>0.64</td>
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<td>1.2</td>
<td>0.73</td>
<td>[28, 27]</td>
</tr>
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<td>1.4</td>
<td>0.72</td>
<td>[27, 29]</td>
</tr>
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<td></td>
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<tr>
<td>V/TCNE/THF</td>
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<td>[MnTPP][TCNE]</td>
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<td></td>
<td>1.7</td>
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<td>[33]</td>
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</table>
antiferro-magnetic intersublattice couplings. In this sense, antiferromagnetism is a special case of ferrimagnetism when the spins are antialigned but otherwise identical. Schematic arrangements of spins in antiferromagnets and ferrimagnets are depicted in Fig. 6. Examples of such systems are given in Table 3. Antiferromagnetism, aside from its intrinsic interest for fundamental magnetism, has been found to be of great importance in some areas of modern research, such as high-temperature superconductivity. Ferrimagnets have been technologically important for some time - the spinel and garnet (REG, GdIG, and YIG) ferrites have found applications in high-frequency electronics, data storage, and magneto-optical devices.

In the mean-field picture, it is hard to imagine a physical "external" field with the spatial variation necessary to give rise to antialigned order, but such a staggered field is postulated mathematically to oscillate with the periodicity of the magnetic lattice. One may directly introduce such a field in the form \( H \sim \sum h(k)e^{ikr} \) and solve the MFT for an effective oscillating exchange, following White [6]. It is initially more intuitive to instead look at a simple two-sublattice model wherein each sublattice is treated separately until their interaction is worked in self-consistently.

The magnetization of a binary ferrimagnetic alloy \( A_pB_{1-p} \) may be written, in analogy with the ferromagnetic MFT,

\[
M = M_A + M_B = N[pm_A + (1 - p)m_B],
\]

(1.90)

where

\[
m_A = S_A B S_A (S_A H_A/k_B T),
\]

(1.91)

\[
m_B = S_B B S_B (S_B H_B/k_B T),
\]

(1.92)

and the effective fields for each sublattice are

\[
H_A = H + 2J_{AA} Z pm_A + 2J_{AB} Z (1 - p)m_B,
\]

(1.93)
\[ H_B = H + 2J_{BB}Z(1-p)m_B + 2J_{AB}Zpm_A, \] (1.94)

or more simply,

\[ H_A = H + \lambda_{AA}M_A + \lambda_{AB}M_B, \] (1.95)
\[ H_B = H + \lambda_{AB}M_B + \lambda_{BB}M_A, \] (1.96)

where \( Z \) is the number of nearest neighbors and \( \lambda_{xy} \) is the Weiss field constant accounting for the \( x \)-sublattice ↔ \( y \)-sublattice exchange interaction. The magnetization is obtained by solving these fairly complex coupled equations in various limits.

**Low Temperatures**  One simplification that is often made, especially in dealing with the antiferromagnetic limit \( p = 1/2, S_A = S_B = S \), is to assume that \( \lambda_{AA} = \lambda_{BB} = 0 \). That is, the ordering is entirely due to the (presumably nearest-neighbor) intersublattice interaction. In this case the magnetization for \( J_{AB} < 0 \) is \( M = N_A S_A - N_B S_B \) at absolute zero, while near \( T_c \), also called the Néel temperature \( T_N \) for \( J_{AB} < 0 \), expansion of the Brillouin function yields

\[ M_A = \frac{nC_A M_B}{T}(1 - \theta_A M_B^2), \] (1.97)
\[ M_B = \frac{nC_B M_A}{T}(1 - \theta_B M_A^2), \] (1.98)

where

\[ C_x = \frac{N_x S_x(S_x + 1)}{3k_B T}, \quad \theta_x = \frac{2S_x^2 + 2S_x + 1}{30S_x^2} \left( \frac{S_x n}{k_B T} \right)^2, \quad (x = A, B). \] (1.99)

\( C_x \) is the Curie constant for sublattice \( x \). Thus the final solution for \( M_x^2 \) is the root of a quadratic equation and may be written

\[ M_x^2 = \frac{2C_x}{C_A \theta_B + C_B \theta_A} \frac{T_c - T}{T_c}, \] (1.100)
where the mean-field critical temperature $T_c$ is found to be

$$T_c = \lambda_{AB}(C_A C_B)^{1/2} = \frac{2JJ_{AB}[S_A(S_A + 1)S_B(S_B + 1)]^{1/2}}{3k_B}.$$  (1.101)

For $J_{AB} < 0$, the total magnetization is the difference of the positive roots, so $M \propto C_A^{1/2} - C_B^{1/2}$, which vanishes for antiferromagnets ($C_A = C_B$) for all $T < T_c$.

Between $T = 0$ and $T = T_c$, the behavior of even this simplified ferrimagnet can be quite complex. Néel [36] identified five distinct types of temperature dependence, depicted in Fig. 10. Among these is the interesting possibility of compensation, where at some temperature $T_{comp}$, the total magnetization vanishes due to a geometric cancellation of the $M_x(T)$ curves of each sublattice. Compensation is observed in several crystalline and amorphous alloys [27].

**High Temperatures** At higher temperatures, the inverse susceptibility may be written, for general $\lambda_{xy}$, as the Néel Hyperbola:

$$\frac{1}{\chi} = \frac{T}{C} - \frac{1}{\chi_0} - \frac{\Delta}{T - \theta},$$  (1.102)

where $C = C_A + C_B$ and

$$\theta = -\frac{C_A C_B}{C}(\lambda_{AA} + \lambda_{BB} - 2\lambda_{AB}),$$  (1.103)

$$\frac{1}{\chi_0} = \frac{\lambda_{AA}C_A + \lambda_{BB}C_B - \theta}{C},$$  (1.104)

$$\Delta = \frac{C_A C_B(\lambda_{AA}\lambda_{BB} - 1)}{C} + \frac{\theta}{\chi_0}.$$  (1.105)

The zero of this relation defines $T_c$, which is found to be

$$T_c = \frac{1}{2}\{\lambda_{AA}C_A + \lambda_{BB}C_B + (\lambda_{AA}C_A - \lambda_{BB}C_B)^2 + 4\lambda_{AB}^2 C_A C_B\}^{1/2}.$$  (1.106)
Figure 10: Possible temperature dependences of a ferrimagnet below $T_c$, as categorized by Néel [36]. The four cases are determined by the conditions (I) $N_A S_A > N_B S_B$, $C_A > C_B$; (II) $N_A S_A > N_B S_B$, $C_A < C_B$; (III) $N_A S_A = N_B S_B$, $C_A > C_B$; (IV) $N_A S_A > N_B S_B$, $C_A = C_B$. From Kaneyoshi [27].
Curie-Weiss Limit  The expression for $\chi$ presented here depends hyperbolically on temperature. The first step in evaluating any new magnetic compound, however, is to look at the high-temperature limit, where the third term may be temporarily neglected. With the assumption that $\lambda_{AA} = \lambda_{BB} = 0$, the susceptibility may again be simply written

$$\chi = \frac{C}{T - \theta};$$

(1.107)

where $\theta = 2\lambda_{AB}C_A C_B / C$ is positive for FM coupling and negative for AF coupling. Therefore, antiferromagnets and AF-coupled ferrimagnets have a negative Curie-Weiss temperature. Its absolute value will give a fairly good "factor-of-two" estimate of $T_c$ for most magnets. The Curie-Weiss behavior for AF and FI systems is depicted in Fig. 9.

1.4 Effects of Dimensionality

Due to the reduction of mathematical and conceptual difficulty, properties of condensed matter in lowered dimension are quite popular with physicists. In recent times, such studies have moved from the realm of "toy models" to practical applications, as numerous examples of highly anisotropic systems have now been realized. "Two-dimensional" (2D) physics is extremely important at present due to high-temperature superconductivity and the fabrication of extremely thin films in superlattices. "One-dimensional" (1D) systems have attained an equal stature from the growing number of potential applications using electronic polymers, quantum wires, and a now fairly extensive list of chain-like molecule-based magnets. Due to this last connection, the emphasis here will be placed on 1D and quasi-1D physics. In this section the basic ideas relating magnetism to dimensionality are briefly discussed. More detailed information on general low-D magnetism may be found pervading the
The most basic result in 1D magnetism is that the ground state of any number of electrons with arbitrary spin-independent interactions must have zero total spin—the Lieb-Mattis theorem [43]. From the phenomenological spin-Hamiltonian point of view, this result is reflected in the fact that the nearest-neighbor 1D FM Ising model

$$\mathcal{H} = -J \sum_i S_i S_{i+1}$$

(1.108)
cannot undergo a phase transition to long-range order below any finite temperature. (The factor of 2 has been absorbed into the definition of $J$). The reason for this is that spin-flip domain walls are much too easy to create in 1D. The energy cost of a single domain wall is $\Delta E = 2J$. However, in creating the kink the entropy increases by $\Delta S = k_B \log(N - 1)$, where $N$ is the number of spins. The free energy of one such defect is then $\Delta F = 2J - k_B T \log(N - 1)$, which is negative for $T > 0$ and arbitrarily large $N$. Domain walls will thus be created maximally. This argument also applies to each of the sublattices of an antiferromagnet or ferrimagnet, and therefore to these types of 1D spin chains as well. The idea of nucleating domains being energetically favorable can be extended to evaluate ordering in systems of arbitrary dimension $d$. For instance, Mermin and Wagner [44] have shown that the Heisenberg model orders only for $d > 2$. For completeness, it should also be noted that a 1D chain can order if the interactions fall off with distance slower than $r^{-2}$.

The issue of reduced dimensionality really has two faces. First there is the spatial dimensionality $d$, which describes the actual spatial arrangement of atoms. The term quasi-1D applies to systems which arrange as chains with physically significant inter-chain separations. The "significance" is the degree to which the spatial anisotropy is reflected in measured parameters and interactions. In electronic polymers, the delocalization length of the charge carrier, and thereby the conductivity, is much larger.
along the chains than between them ($\sigma_{||} \gg \sigma_{\perp}$). Similarly, in magnetism, there are different intrachain ($J_{||}$) and interchain ($J_{\perp}$) exchange parameters.

To introduce the second "face" of the dimensionality issue, consider the Hamiltonian for the so-called XYZ model, which elucidates another kind of anisotropy:

$$\mathcal{H}_{XYZ} = - \sum_{(ij)} \{ J_{ijx} S_{ix} S_{jx} + J_{ijy} S_{iy} S_{jy} + J_{ijz} S_{iz} S_{jz} \}. \quad (1.109)$$

In addition to the relative degrees of the exchange parameters $J_x$, $J_y$, and $J_z$ for intra- vs. inter-chain spins, one must also consider the number of spatial components granted to the spin variables themselves. Local crystalline, spin-orbit, or dipolar anisotropies will favor certain spin quantization axes to varying amounts. A single, strongly preferred direction will result in Ising spins $S_z = \pm S$. Similarly, a strong repulsion from a given axis results in easy-plane anisotropy (XY spins). Finally, a lack of any such anisotropies leads to the Heisenberg model. The dimensionality of the order parameter is thus logically separate from that of space.

To explicitly include both effects, the terms of $\mathcal{H}_{XYZ}$, can be written in the form $-(J_{ijz\perp} + J_{ijz||})S_{iz}S_{jz}$, etc. which simplifies in the uniform Heisenberg case to

$$\mathcal{H} = -J_{\perp} \sum_{[i,j]} S_i \cdot S_j - J_{||} \sum_{(i,j)} S_i \cdot S_j, \quad (1.110)$$

where $[i,j]$ and $(i,j)$ denote pairs of spins in separate chains and the same chain, respectively. The intra- to inter-chain exchange ratio is often expressed as the anisotropy parameter $\gamma = J_{\perp}/J_{||}$. Typical quasi-1D magnets have $\gamma \sim 10^{-2} - 10^{-4}$.

Of primary concern in systems of reduced dimensionality is the possibility of developing long-range order below some temperature. It is intuitive that all real quasi-1D compounds eventually must order, due to their small but finite interchain coupling. In other words, these systems must exhibit dimensionality crossover from 1D to 3D.
upon magnetic ordering. However, the type of order, the range of criticality, and the value of $T_c$ itself involve nontrivial, perhaps unsolvable, calculations. In a simple mean-field picture like that presented above for ferromagnets, the proportionality between $T_c$ and $J_0$, still holds, but $J_0$ is significantly reduced. For the quasi-1D analogue of the simple cubic lattice, obtained by increasing the interatomic spacing in the plane, the net mean-field exchange for nearest-neighbor coupling is $J_0 = 4J_1 + 2J_\parallel$, as opposed to $J_0 = 6J_\parallel$ in the 3D case, a reduction of nearly 66%. The general effect in mean-field is a reduction factor of $(Z + \gamma Z_\perp)/Z$.

The one exact example of a dimensionality crossover comes from the work of Onsager [45], who solved the 2D Ising model. In the case of anisotropic interactions $J_2 < J_1$, the transition temperature is lowered according to

$$\sinh\left(\frac{2J_1}{k_B T_c}\right) \sinh\left(\frac{2J_2}{k_B T_c}\right) = 1.$$  \hspace{1cm} (1.111)

In the 1D limit $\delta = J_2/J_1 \ll 1$, $T_c$ is given by

$$\frac{k_B T_c}{2J_1} \sim \left[\ln \frac{1}{\delta} - \ln \ln \frac{1}{\delta} + \cdots\right]^{-1},$$  \hspace{1cm} (1.112)

and can be applied [46] to the $d$-dimensional Ising crossover case with $\delta = (J_2 + J_3 + \cdots + J_d)/J_1 = (d - 1)\gamma$ for $J_2 = J_3 = \cdots = J_d = J_\perp$ and $J_1 = J_\parallel$. The expression for $T_c(\gamma)$ in 3D would then be

$$k_B T_c \sim \frac{2J_\parallel}{\ln 1/2\gamma}.$$  \hspace{1cm} (1.113)

Other qualitatively useful expressions for $T_c$ derive from essentially quasi-classical arguments, that is, solving the 1D problem quantum mechanically and treating the 3D interactions in mean field. For instance Imry et al. have obtained [47] the expression,

$$k_B T_c \sim 2S(S + 1)\left(\frac{Z}{3}\right)^{1/2} |J_\perp J_\parallel|^{1/2}.$$  \hspace{1cm} (1.114)

For ferrimagnetic chains a similar expression has been used [48]:

$$k_B T_c \sim 2S(S + 1)S'(S' + 1)|J_\perp J_\parallel|^{1/2}.$$  \hspace{1cm} (1.115)
The common theme of all treatments is that the exchange anisotropy in reduced dimensionality drastically reduces $T_c$.

The critical temperature region is also very sensitive to dimensionality. In quasi-1D magnets, short-range order builds up well above $T_c$, resulting in a small residual entropy associated with the 3D transition itself. For example, the magnetic specific heat of quasi-1D molecular systems has a broad excess above $T_c$, with only a small, if any, anomaly right at $T_c$ [39, 49]. For a fixed dimensionality $d$, an effective critical region may be defined as the reduced temperature range within which mean-field theory breaks down. This breakdown is predicted in Landau theory through the Ginzberg criterion,

$$|t|^\frac{d}{2} > (R/a)^d,$$

where $R$ is the characteristic range of interaction and $a$ is the atomic spacing. The mention of a reduced temperature in 1D ($T_c = 0$), as defined above, certainly gives one pause. Actually, in 1D the scaling toward $T_c = 0$ may be taken as having an effective reduced temperature of the form $t' = T/\Delta$. With such a modification, the Ginzberg criterion states that the critical region in $d$ dimensions is within $|t| < (a/R)^{2/3}$ in 1D, while in 3D it is much narrower $|t| < (a/R)^6$.

Quasi-1D magnets exhibit a crossover in their effective dimensionality, from 1D-like at high temperatures to 3D-like as $T \rightarrow T_c^+$. 1D fluctuations dominate at high temperatures before 3D fluctuations come into play. One way to think about criticality in quasi-1D magnets is that there is, necessarily, an inner or core critical regime representing true 3D long-range ordering hidden in a broad outer region of growing anisotropic correlations. The core may be extremely close to $T_c$, perhaps on the order of $|t| < 10^{-3}$ or less, normally experimentally inaccessible for low-$T_c$ systems.

The presence of such an inner critical region may also be related to the effect
of spin anisotropy on correlation length. In Fig. 11, the two-spin correlation length \( \xi \) is plotted for Ising, XY, and Heisenberg spins as a function of temperature for some fixed exchange \( J \). At a given \( T \), the correlation length is larger for lower spin-dimensionality \( n \) (\( \xi^I(T) > \xi^{XY}(T) > \xi^H(T) \)). Following Villain and Loveluck [50], the critical temperature is proportional to the correlation length and the interchain interaction (here \( E_i \)), that is, \( k_B T_c = E_i \xi(T_c) \). The dotted line intersects \( \xi(T) \) at \( T_c \). Ising magnets have higher \( T_c \) than Heisenberg magnets. Now, magnetic compounds with only a small amount of spin anisotropy will behave as Heisenberg systems at high temperatures, as measured by any anisotropy in thermodynamic parameters. Even as \( T \to T_c^+ \), the apparent critical exponents will be those of an isotropic order parameter. However, very close to \( T_c \), within the supposed core, the critical exponents will cross over to those of, say, an Ising system [38]. This "last-minute" selection of an easy-axis for the spontaneous magnetization in such systems corresponds to the onset of true long-range order.

The development of long-range order (LRO) in quasi-1D magnets must be, then, a subtle balance between spatial ('d') crossover and spin ('n') crossover. It is intuitive that \( n \)-crossover must accompany \( d \)-crossover, because the final crystalline and/or dipolar environment in which the chain spins will decide upon their ordering direction is established only when the effects of neighboring chains are felt fully. The progression of ordering in quasi-1D magnets may go something like: (1) build-up of 1D intrachain Heisenberg correlations, (2) build-up of 3D interchain Heisenberg correlations, and (3) crossover to much longer 3D Ising correlations and long-range order. Such a progression is an extreme view of what in reality must be a more complicated and delicate process. However, it does illustrate how the scaling of thermodynamic quantities such as \( M \) and \( \chi \) may be complicated in quasi-1D systems. For instance, a crossover of anisotropy can account for the observed temperature dependence of the
Figure 11: Spin-spin correlation length as a function of temperature for Ising (I), XY, and Heisenberg (H) magnets. The dotted line intersects the curves at the critical temperature. From Caneschi [51].
critical exponents even fairly close to \( T_c \) in some compounds. In fact, the "core" could be described as the range of reduced temperature within which the critical exponents become independent of \( T \).

Thermodynamic quantities, such as the magnetic susceptibility \( \chi \) and the specific heat \( C_p \), can be calculated analytically for 1D systems in many cases. From these expressions, a small 3D coupling can be brought in as a perturbation, at least at high temperatures. Near \( T_c \), the full 3D problem must be treated. Particular equations for 1D cases of different values and/or combinations of spins \((1/2, 1, 3/2, 2, 5/2, ...\)), \( g \)-values, and exchange constants \( J \) will not be given here. The reader is referred to the general literature on 1D magnets (above) and particularly to the reviews of Carlin [39], Bonner [38], Hatfield [52], Coronado [53], and Kahn [11]. Of particular interest for the high-temperature susceptibility of the [MnTPP][TCNE] class of quasi-1D magnets studied in this thesis is the work of Coronado et al., and references therein, concerning ferrimagnetic chains. Details will be discussed as these data are presented.

1.5 Effects of Disorder and Frustration

Depending on the unit of time or length used in a measurement, a physical quantity can be observed to change or to remain fixed. This may seem too obvious to have even mentioned. However, the concept of length and time scales is extremely important in science. What is more, the conceptual problems of how to probe processes on a given scale and how processes on different scales interact are, frankly, quite beautiful. At large enough length and time scales, everything appears fixed. As the technology of meter sticks and second hands is slightly refined, however, variations which were averaged out on larger scales become "visible." Working at the top of the list of scales, astrophysicists observe the "large-scale structure of space-time." The inter-
mediate size range, between galactic and atomic, is the realm of condensed matter. Macroscopic solids possess intensive properties such as temperature and molar magnetization which are thermodynamic averages of the microscopic quantities, kinetic energy and angular momentum. The reason such properties are well-defined is one of the basic tenets of statistical mechanics: the scale on which they are measured is far removed from the scale on which they fluctuate. All physical measurements have a characteristic length and time resolution. Bouncing basketballs from a colleague's head is not likely to reveal that person's identity.

What does all this have to do with disorder? A disordered quantity or collection of quantities is one which varies in time or space in a random way with respect to the time or length scale used to define it. For instance, the magnetic moment of an atom is thermally disordered at high temperatures in that it fluctuates on microscopic time scales (< ps). Similarly, at a fixed time, the magnetic moments of a collection of atoms at high temperatures are random from atom to atom. In this paramagnetic case, a spatial average over one configuration at a fixed time is equivalent to a temporal average of one spin. In the ferromagnetic phase, this is also the case, although now the averages are nonzero. Now imagine a situation where the spins are frozen, as in the FM, but with random orientations, as in the PM. In this case, the temporal average of a single spin is nonzero but the spatial average over many spins vanishes. Such a state is called a speromagnet, from the Greek διασπερω, for "I scatter in all directions" [54], and depicted in Fig. 6.

The realization of a speromagnet, as a manifestation of a certain kind of disorder, depends on the probe used to measure, and therefore define it. In this section, two kinds of speromagnets are considered - superparamagnets and spin glasses. In superparamagnets (SPM), the moments are assumed to be noninteracting, but are
frozen below certain time scales due to internal anisotropy. In spin glasses (SG), the moments are strongly interacting, and this interaction is the source of the frozen state.

1.5.1 Superparamagnets

Consider a collection of atomic or molecular magnetic moments which collect together into mesoscopic clusters of various sizes (say, up to $\sim 10^2 \text{Å} \text{diameter}$). This clustering may be thought of as the result of various structural defects (chemical clustering) and/or spatial anisotropies (dimensional clustering). Below the Curie temperature, the spins within a cluster will acquire a net moment. If each cluster is thought of as a domain, the cluster moment will be $\mu = g\mu_B(NS)$, but over the whole collection of clusters, these net moments will be randomly oriented. If the clusters do not interact with each other, then below the Curie temperature they will behave as a classical paramagnet with a distribution of large moments, called a superparamagnet. Let the distribution of cluster moments be described by $P(\mu)$. Then

$$M = N_c \int_0^\infty d\mu \mu P(\mu) \mathcal{L}(\mu H/k_B T)$$

(1.117)

where $\mathcal{L} = B_\infty$ is the Langevin function. For small values of the argument $y = \mu H/k_B T$, $\mathcal{L}(y) \rightarrow y/3$, giving the Curie Law:

$$\chi = \frac{N_c \langle \mu^2 \rangle}{3k_B T},$$

(1.118)

where

$$\langle \mu^2 \rangle = \int_0^\infty d\mu \mu^2 P(\mu).$$

(1.119)

Now consider the dynamics of a single cluster. For one reason or another, there may be an energy barrier to the uniform rotation of the moment $\mu$ due to a local or
intrinsic anisotropy. For instance, an axial distortion of the local crystal field will tend to align $\mu$ along the axis; nonzero perpendicular components of $\mu$ are energetically unfavored. As another example, a cluster with an elongated shape will tend to favor orientation parallel to the long axis for collinear spins and perpendicular to the long axis for anticollinear spins in order to minimize the internal dipolar energy. Suppose, in general, that the energy spectrum as a function of the orientation of $\mu$ can be modeled as a simple degenerate two-level system, separated by an energy barrier $E_\mu = K\mu$, as depicted in Fig. 12. The characteristic time for the magnetic field to reorient a cluster is given by the Arrhenius expression [55]

$$\tau_\mu = \tau_0 \exp(K\mu/k_B T),$$

where $\tau_0^{-1}$ is called an "attempt frequency." This characteristic time scale, as a function of $\mu$ and $T$, determines whether the system will appear fluctuating and paramagnetic ($t > \tau_\mu$) or frozen and speromagnetic ($t < \tau_\mu$). Mathematically speaking, the susceptibility will therefore depend on the time scale of measurement. To use the paramagnetic form (above), only those clusters that are able to reorient (i.e., respond) on a time scale less than $t$ should be included in the response $\chi(t)$. That is,

$$\chi(t) = \frac{N_c}{3k_B T} = \int_{0}^{\mu_{\text{max}}} d\mu \mu^2 P(\mu),$$

where $\mu_{\text{max}} = (k_B T/K) \ln(t/\tau_0)$ is the largest cluster moment included, taking time $t$ to activate. Qualitatively, it is easy to see from the form of (1.121) that $\chi(t)$ will exhibit a maximum when the upper integration limit is in the region of the maximum of the integrand. As a simple test case, consider a normal, temperature independent distribution of cluster moments with zero mean and variance $\sigma^2$,

$$P(\mu) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp[-(\mu/\sigma)^2/2].$$
With the substitutions \( z = \mu^2 \) and \( a = 1/2\sigma^2 \), (1.121) becomes

\[
\chi(t) = \frac{N_c}{3k_B T} \frac{1}{2(\pi/a)^{1/2}} \int_0^{\zeta_{\text{max}}} dzz^{1/2}e^{-az},
\]

\[
\chi(t) = \frac{N_c}{3k_B T} \frac{\gamma(3/2, az_{\text{max}})}{2a\pi^{1/2}},
\]

where \( \zeta_{\text{max}} = \mu_{\text{max}}^2 \) and \( \gamma \) is the incomplete gamma function. The temperature dependences of \( \gamma \), whose argument is proportional to \( T^2 \), and of this form of \( \chi \), are tabulated in Appendix A. The peak is exhibited in a plot of the static \( \chi(T) \), Fig. 13. In the figure, the corresponding curves for \( \mu_{\text{max}} = \infty \) (PM) and a magnet with a continuous phase transition for a particular choice of exponent (\( \gamma = 1.7 \)), scaled to occur at the SPM peak temperature are also shown.

The frequency-dependent temperature of the peak in \( \chi \) is called the superparamagnetic blocking temperature \( T_B(\omega) \). This name arises because below \( T_B \), the system of clusters is thermally "blocked" from being excited into spin flips by its own anisotropies. \( T_B \) can also be referred to as a freezing temperature. The blocking temperature is expected to increase with frequency. Decreasing \( T \) and increasing \( \omega \) have the same effect: smaller and smaller clusters become blocked. So the superparamagnet, as a whole, will exhibit blocking sooner as \( T \) is decreased for higher frequencies. Assuming the peak in \( \mu^2 P(\mu) \) is on the order of \( \langle \mu^2 \rangle \), the blocking temperature will have the frequency dependence \( T_B^{-1}(\omega) \propto \text{const} - \ln(\omega\tau_0) \), which exhibits this trend. The frequency dependence of \( T_B \) can be quite pronounced. In \( a-(\text{Ho}_2\text{O}_3)(\text{B}_2\text{O}_3) \), a known SPM, the fractional shift in \( T_B \) per decade of frequency is \( (\Delta T_B/T_B)/\Delta \log \omega \approx 0.28 \).

For more details on superparamagnetism, and its relation to spin glasses, the reader is referred to Section III.G. of the excellent review by Binder and Young [55], and references therein.
Figure 12: Schematic energy vs. orientation for a degenerate two-level system such as that used to model a noninteracting superparamagnet with an anisotropy barrier. From Mydosh [56].
Figure 13: Magnetic susceptibility for a paramagnet (PM), noninteracting superparamagnet (SPM), and ferromagnet (FM) with $\gamma = 1.7$, scaled so the SPM peak and $T_c$ coincide.
1.5.2 Spin Glasses

In some magnetic systems, speromagnetic freezing can also occur with very small clusters and even with individual spins, but the mechanism is different than that of SPM. Any collection of spins of sufficient density will be dominated by spin-spin interactions (say, $J_{ij}$) below some temperature. In ferromagnets, the interactions are such that below $T_c$, the symmetry of the microscopic Hamiltonian is "spontaneously" broken and, in the thermodynamic limit, all subsequent evolution of the system is limited to one-half of the total phase space. This limitation is called broken ergodicity – $M_z$ will theoretically take infinite time to flip its sign and thereby explore all of phase space. Some spin systems, however, don't possess such a simple two-state symmetry/ergodicity breaking. The most important, and most complicated, example of nontrivial low-temperature phase space division occurs in compounds referred to as spin glasses.

As mentioned, spin glasses are speromagnets which freeze due to interactions. Qualitatively, for a given length scale, the dynamical picture for spin glasses is similar to SPM. A cluster of spins in a spin glass are frozen on time scales less than a characteristic spin-flip time. However, the "clusters" in spin glasses are more complicated – they are actually embedded. That is, a single spin is frozen on some time scale due to the interactions with its neighbors. The cluster containing that spin and its neighbors is frozen on some other (longer) time scale due to the interactions with its neighbors, which are similarly defined clusters themselves. This scale-invariant picture of renormalized spins is essential to understanding the behavior of a spin glass compound. Now here is the really nasty part. By scaling the clusters up to macroscopic sizes, by the SPM picture, longer and longer relaxation times would be included in the dynamics up to the spin-flip time of the whole solid. The dynami-
cal range would thus be fairly broad, but still finite and characterized by a simple relaxation function. However, spin glasses never completely equilibrate – their dynamics include, in principle, processes on all time scales up to $\tau \to \infty$! Whither this infinitely broad distribution of relaxation times? The answer lies in the interactions – the source of the freezing.

The freezing processes on different length scales in a spin glass are not independent. In fact, what is more correct to say is that the dependence of the dynamics of one length scale on those of all possible smaller length scales is exactly the source of the speromagnetism. By simply making such a statement, without any justification, one immediately begins to entertain visions of recursion, hierarchical data structures, and the Towers of Hanoi.\(^6\) (Well, at least one preson entertains such visions.) The time it takes for a given cluster of spins to, say, flip its spins is proportional to the ultrametric distance between the two configurations on a spin state “tree” of the sort depicted in Fig. 14. The leaves of the tree correspond to the states of individual spins. Each node at higher level corresponds to the spin state of a cluster containing the spins of the children of that node. Now consider a “toy” dynamics on this tree. Spins at the leaves go through a Monte-Carlo-like flip with some attempt frequency $\omega_0$ in an effort to find the lowest energy state with their neighbors. At the same time, the spin of the clusters just above the leaves undergo a trial shuffling as a result of the leaf-processes. These clusters are not really given a chance, as it were, to have their own identities and reorder directly as they would like; they relax solely as a result of their internal spin flips. Consequently, it may take many internal attempts before

\(^6\)The Towers of Hanoi is the name of a simple game. Three pegs are placed vertically on a base, and in the initial state three disks of decreasing size are slid down on one of the pegs. The object is to move all three disks to another peg given the rules that 1) the disks must be moved one at a time, and 2) no larger disk may sit on a smaller disk at any time. The solution requires recursive movements using the third peg as a buffer.
the intercluster energies are reduced. The individual spins are in a sense unaware of the energy battle between clusters.

Extending the cluster relaxations to the next and higher levels, it becomes fright- enly clear that minimizing the total spin energy on large length scales will take a very, very long time. In fact, in the thermodynamic limit, spin equilibrium of the whole system is never reached. Dynamics exist on all time scales in a spin glass.

So why does not such a thing occur in other concentrated magnetic systems, where the picture of embedded clusters should also hold? The reason is in the nature of the "many attempts" needed for groups of spins to relax. In, say, a ferromagnet, all of the interactions are in agreement \((J_{ij} > 0)\), so the spins of a cluster will quickly become collinear after only a few attempts (just think of the "majority wins" rule for realignment – the largest aligned subcluster will act as a nucleation site). In a spin glass, the interactions are not all in agreement. If neighboring spins transmit (via their spins \(S_j\) and the interaction \(J_{ij}\)) conflicting information about which orientation the spin \(S_i\) is supposed to take, they are said to be competing and the spin, or the collection of spins, is said to be frustrated. Frustration may occur in two possible ways. In random exchange frustration (Fig. 15a), a group of spins can find neither a configuration which simultaneously satisfies the collection of FM and AF bonds, nor a unique ground state configuration within the phase space that is available to them. The frustrated square plaquette in the figure has eight degenerate ground states. In geometrical frustration (Fig. 15b), a similar situation arises on a plaquette with an odd number of AF-only bonds.

If the exchange interactions between a collection of spins take a random mixture of positive and negative values (the extension of Fig. 15a), the ensemble comprises a random exchange spin glass. Such a situation apparently occurs in a large number
Figure 14: The hierarchical structure of spin and spin cluster states in a spin glass. Higher levels in the tree may be thought of as corresponding to larger and larger length scales. From Dotsenko [57].
of transition metal alloys, such as Cu$_{1-x}$Mnx, where magnetic impurities are of sufficient density $x$ to invoke strong exchange coupling but not so dense as to nucleate a ferromagnetic state. In this intermediate concentration regime, randomly located impurities coupling via the oscillating RKKY interaction leads to a distribution of FM and AF bonds and frustration. Spin glass behavior also occurs in insulating and non-alloy compounds, where the randomness and frustration arises from other sources such as competing nearest- and next-nearest-neighbor bonds, random anisotropy, and/or long-range dipole forces. A fairly general Hamiltonian for describing various kinds of disorder and anisotropy may be written

$$\mathcal{H} = -\sum_{(ij)} S_i \cdot \bar{J}_{ij} \cdot S_j - \sum_i D_i (\hat{n}_i \cdot S_i)^2 - g\mu_B H \cdot \sum_i S_i,$$  \hspace{1cm} (1.125)$$

where $\bar{J}_{ij}$ is a (potentially random) spin-spin interaction, and $D_i$ and $\hat{n}_i$ are the (potentially random) single-ion anisotropy strength and easy axis, respectively. The diagonal elements of the $J$-matrix are the isotropic Heisenberg exchange parameters,
while the off-diagonal elements account for anisotropic spin-spin interactions such as Dzyaloshinskii-Moriya (second-order spin-orbit) and dipolar couplings.

As in SPM, the susceptibility also goes through a maximum in spin glasses, but now it is much sharper and more divergent. This behavior suggests that freezing in spin glasses is actually a phase transition rather than a dynamical, or non equilibrium effect as it clearly is in SPM. Whether this distinction is supported rigorously has been the subject of vigorous and educational debate among researchers for some thirty years. The single question “Do spin glasses constitute a distinct thermodynamic phase with a continuous phase transition and well-defined order parameter?” has sparked such great interest, in fact, that it is now its own subfield of statistical mechanics. From the experimentalist’s point of view, the reassessment of the meaning of the term “phase transition” that has come out of this debate is of particular relevance. The experimentalist tends to say “If it looks like a phase transition, and it quacks like a phase transition (or whatever), then it must be a phase transition.” The reason the term “phase transition” is used at all in this context is that, within a fairly narrow temperature range, the dynamics of random, frustrated spin systems undergo an enormous and sudden change. That is, below some apparent freezing temperature $T_f$, the distribution of relaxation times of such compounds goes from being sharply peaked at some small mean time, like a few femtoseconds, to being peaked at macroscopic times and having a divergent width. By freezing in this way, spin glasses essentially preclude themselves from exhibiting equilibrium physics on experimentally accessible time scales and thus seem to undergo a phase transition. Whether $T_f$ represents a real discontinuity in $\partial^2 G/\partial T^2$ or corresponds to a revolutionary new statistical mechanics is a question for the theorists.

In spin glass materials, the freezing temperature defined by the sharp maximum
in $\chi$ is found to increase with frequency, but much more weakly than in SPM. Typical values of $(\Delta T_f / T_f) / \Delta \log \omega$ are $\sim 0.05$. This fact may be related to the smaller fraction of the dynamical range accessible by lockin techniques. The susceptibility is very sensitive, however, to very small fields. In fact, in the phase transition picture, the susceptibility corresponding to the spin glass order parameter is actually the third harmonic $\chi_3(3\omega:\omega)$. This can be seen from the necessity that the order parameter of a speromagnetic state must be the temporal spin autocorrelation $q = \lim_{t \to \infty} [(S_i(0) \cdot S_i(t))]_{\text{ave}}$, where $\langle \rangle_\beta$ is a thermal average and $[\cdot]_{\text{ave}}$ is a configuration or disorder average. Diverging, or at least anomalous, third harmonic susceptibilities are observed in spin glass compounds. The specific heats of these compounds, on the other hand, do not exhibit the sharp anomalies at $T_f$ expected in a real phase transition, but rather broad maxima somewhat above $T_f$ are observed. It has been suggested that higher energy derivatives are required to see any anomalous behavior at $T_f$ [56].

The theory of spin glasses is fairly complex, and an exposition of even its basic results is inappropriate here. The main reason for this omission is that to even begin to describe theoretically what is going on in real spin glasses, treatments which go somewhat beyond mean field theory are required. Various features will be mentioned and referenced as they are required in discussing the spin glass-like behavior of some of the molecule-based magnets in this thesis. In addition to the above mentioned review by Binder and Young, extensive treatments of the spin glass field can be found in Mydosh [56], Fischer and Hertz [58], Dotsenko [57], Kaneyoshi [27], Diep [59], and Mezard, Parisi, and Virasoro [60]. It is worth mentioning that several of these and related monographs are published by World Scientific (Singapore), the editors of which seem to have assumed a sort of blanket responsibility for helping proliferate the study of random magnets.
The intent of this section has been to give a descriptive basis for some of the observed behavior in random, frustrated spin systems, and how their dynamics may vary from those of simple noninteracting superparamagnets. The main reason for this is to establish dynamics extrema between which some of the compounds studied in this thesis may be expected to lie. More boldly, it is proposed that molecular systems in general, because of their particular kinds of structural disorder and anisotropy, should open up the physics of the middle ground between superparamagnetism and spin glass behavior. This picture is discussed somewhat further in Sec. 1.6. Before then, it is necessary to review one final subject – that of reentrant spin glasses.

### Reentrant Spin Glasses

If any subfield of disordered magnetism presents a greater mystery than spin glasses, it would have to be reentrant spin glasses. These are compounds which go through two transitions as $T$ is lowered. First, at the critical temperature $T_c$ to a state of long range magnetic order such as FM, FI, or AF, and then at some lower temperature $T_f$ to a disordered, spin glass state. Such a possibility seems counterintuitive – doesn’t the spin glass state, by nature of its randomness, have more entropy than the ferromagnetic state? This intriguing puzzle, compounded with the underlying general spin glass problem, has made the subfield of reentrant spin glasses (RSG) a center of great activity and lively debate for two decades.

Traditionally, RSG compounds have been obtained from the “canonical” SG alloys, such as Cu$_{1-x}$Mn$_x$, by increasing the magnetic impurity concentration $x$ somewhat above the percolation threshold $x_c$ for the given lattice. The percolation thresholds for nearest-neighbor (nn) interactions are $x_c = 0.31$ for the simple cubic lattice and $x_c = 0.20$ for the fcc lattice. For couplings up to the next-nearest neighbors
(nnn), the respective thresholds are $x_c = 0.14$ and $x_c = 0.13$. In a small range of concentration above $x_c$, these alloys support what appears to be a FM state at intermediate temperatures and a SG state at the lowest temperatures. The $T-x$ phase diagram, then, looks qualitatively similar for all such alloys; the case of Eu$_x$Sr$_{1-x}$S, which follows the nnn fcc model, is shown in Fig. 16. The big question mark, of course, is the slope of the FM-SG phase boundary line (assuming that it can be called such). If it is vertical, then there is no reentrance. If drawn as in the figure, which schematizes real experimental results, there is a significant reentrant range of $x$.

Reentrance is actually predicted by some mean field theories of spin glasses. In the Sherrington-Kirkpatrick (SK) mean field theory of the undiluted random exchange Ising model [61], a rigorous reentrant phase is found for a sufficient degree of disorder. Specifically, reentrance occurs for $T < J_0/k_B$ and $1 < J_0/\Delta J < 5/4$, where $J_0$ and $\Delta J$ are the mean and standard deviation of a gaussian distribution $P(J)$ of exchange constants. The SK phase diagram is shown in Fig. 17. On the other hand, the Viana and Bray (VB) mean field theory of the dilute random exchange Ising model [62] is not as certain. Reentrance is admitted as possibility, depending on model parameters. In the case of the Heisenberg model, which applies more easily to real systems, Gabay and Toulouse (GT) showed [63] that mean field theory is not rigorously reentrant. However, two transitions of a non-continuous type were revealed below the PM-FM boundary, as depicted in Fig. 18. A new way to picture the onset of speromagnetism was proposed – that instead of thinking of clusters or embedded clusters, reentrant behavior may be the result of the freezing of the individual spin components transverse to the direction of spontaneous long-range order. In summary, the GT results are no rigorous RSG, but three transitions in weakly frustrated regime:
Figure 16: Temperature ($T$) - concentration ($x$) phase diagram for $Eu_xSr_{1-x}S$, illustrating the reentrant regime.
1. $T_c$: P - F, usual paramagnetic to ferromagnetic transition

2. $T_{xy}$: F - M1, freezing of transverse components $S_i^x, S_i^y$

3. $T_z$: M1 - M2, freezing of longitudinal component $S_i^z$

The three models mentioned here have two significant drawbacks. First, they are mean-field theories, and mean-field theory is notoriously overzealous in creating phase transitions where they may not actually exist. Second, they are all what is called in the SG field replica symmetric. A replica is simply a particular spin configuration of the spin glass. In the SK, VB, and GT mean field theories, all the possible replicas are treated on equal footing. More precisely, the fact that the energy barriers that one must traverse to go from one spin configuration to another are necessarily different for different pairs of configurations is ignored in these theories. Such a neglect makes the mathematics easy, but the physics wrong.

What is the correct way to treat different replicas? In fact it has already been presented. The cost to get from one replica to another is called variously the (inverse) replica overlap or “Hamming distance.” This distance is determined by the energy-space version of the heirarchical spin tree in the embedded cluster model. In energy, or replica overlap, space, each leaf corresponds to a different replica. Neighboring leaves have a large overlap (they may differ by only one spin flip). Thus the Hamming distance between them, the distance to their common ancestor node, is minimal. Widely-separated leaves correspond to replicas with little overlap, so many spin flips would be required to transform one into the other, and their common “ancestor” node is much closer to the root of the tree.

For a paramagnet in zero field, these overlaps are all zero because it costs nothing to rotate one configuration into another, and every configuration is an equilibrium
Figure 17: Phase diagram of the Sherrington-Kirkpatrick infinite-range (mean field) random exchange Ising model. $J_0$ and $\Delta$ ($\Delta J$) are respectively the mean and width of the Gaussian distribution of exchange $J_{ij}$. Reentrant spin glass behavior is predicted in the range $1 < J_0/\Delta J < 5/4$. From Sherrington [61].
Figure 18: Phase diagram of the Gabay-Toulouse mean field random exchange Heisenberg model. True thermodynamic phases of paramagnetism (PM), ferromagnetism (FM), and spin glass (SG) are predicted. M1 and M2 correspond to freezing of the transverse and longitudinal components of local spins, respectively, within the long-range order phase. From Gabay [63].
state. In a ferromagnet, there are two equilibrium states (+M and −M), with a particular overlap corresponding to a global flip. However, in a speromagnet, there is a vast spectrum of quasi-degenerate equilibrium states, and hence a continuous distribution of overlaps due to the frozen, or "quenched" disorder. The transition from a distribution that is a collection of delta functions to one that is continuous is called *replica symmetry breaking*. Parisi showed [64, 65, 60] that when this continuous distribution of replica overlaps is taken into account, the correct mean field phase line between FM and SG phases is in fact vertical. Reentrance is precluded by replica symmetry breaking in mean field theory.

Improving on MFT for RSGs is very difficult. Realistic 2D and 3D models which explicitly include short-range interactions and the concentration parameter x are poorly understood. Some significant numerical work has been done, much of which is reviewed by Gingras [66]. From the experimental standpoint, studies of reentrant spin glasses have focused heavily on the susceptibility of and neutron scattering from the metallic alloys. Insulating and/or non-alloy compounds are relatively unexplored. The general features observed in the a.c. susceptibility of RSGs are worth introducing here. As there are two transitions, two peaks are observed in the out-of-phase component \( \chi'' \) corresponding to the dissipative resonance of a phase transition. The real part \( \chi' \) also typically shows two features, unless their overlap is too great. Sorting out the origin of the anomalies in \( \chi \) in various cases has proved challenging, with other possible sources, such as SPM or impurities, competing to explain the anomalous behavior. If the lower transition is to a spin glass phase, an anomalous third harmonic should also be observed. Some of the RSG materials studied are listed in Table 5. At the bottom of the list are some of the molecular systems studied in this thesis, which are some of the first examples of nonmetallic RSG-like magnets with no obvious analogue of the concentration x. The next section introduces the general class
Table 5: Known reentrant spin glasses.

<table>
<thead>
<tr>
<th>Type</th>
<th>Compound</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>xtal met alloy</td>
<td>Au$_{1-x}$Fe$_x$</td>
<td>[67, 68, 69, 70, 71, 72]</td>
</tr>
<tr>
<td></td>
<td>Cu$_{1-x}$Mn$_x$</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>Ni$_{1-x}$Fe$_x$</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>(Ni$_{1-y}$Fe$<em>y$)$</em>{1-z}$Mn$_x$</td>
<td>[73, 74]</td>
</tr>
<tr>
<td></td>
<td>Ni$_{1-x}$Mn$_x$</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>Cr$_{1-x}$Fe$_x$</td>
<td>[76]</td>
</tr>
<tr>
<td></td>
<td>Al$_{1-x}$Fe$_x$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe$_{3-x}$Mn$_x$Si</td>
<td>[77]</td>
</tr>
<tr>
<td></td>
<td>Co$<em>{50}$Al$</em>{50-x}$T$_x$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Fe$_x$Cr$<em>y$Ni$</em>{1-(x+y)}$)$_2$P</td>
<td>[78]</td>
</tr>
<tr>
<td>amor met alloy</td>
<td>(Fe$<em>{1-x}$Mn$<em>x$)$</em>{75}$P$</em>{16}$B$_6$Al$_3$</td>
<td>[79, 75, 80]</td>
</tr>
<tr>
<td></td>
<td>Fe$<em>x$Mg$</em>{1-x}$Cl$_2$</td>
<td>[81]</td>
</tr>
<tr>
<td></td>
<td>Fe$<em>x$Mn$</em>{1-x}$TiO$_3$</td>
<td>[82, 83]</td>
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<tr>
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<td>Ce(Fe$<em>x$Al$</em>{1-x}$)$_2$</td>
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<tr>
<td></td>
<td>Fe$_{89}$Zr$_7$B$_4$</td>
<td>[85]</td>
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<tr>
<td>xtal ins alloy</td>
<td>Eu$<em>x$Sr$</em>{1-x}$S</td>
<td>[86]</td>
</tr>
<tr>
<td></td>
<td>KMn$<em>{x}$Zn$</em>{1-x}$F$_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[(CH$<em>3$)$<em>3$NH]Co$</em>{0.4}$Ni$</em>{0.6}$Cl$_3$·2H$_2$O</td>
<td>[87]</td>
</tr>
<tr>
<td>xtal ins nonalloy</td>
<td>CoCl$_2$·H$_2$O</td>
<td>[88]</td>
</tr>
<tr>
<td></td>
<td>[MnTPP]$^{3+}$[TCNE]$^-$·2PhMe</td>
<td>[33]</td>
</tr>
<tr>
<td>amor ins nonalloy</td>
<td>V/TCNE/Solvent</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td>Co$_3$BTCA$_2$(H$_2$O)$_n$</td>
<td>[89, 90]</td>
</tr>
</tbody>
</table>

of molecular systems to which the V/TCNE and [MnTPP][TCNE] magnets studied here belong. This introduction will suffice to put the data on these materials in the proper perspective.

### 1.6 Molecule-Based Magnets

A molecule-based magnet is a compound in which the magnetism is viewed as arising from molecular units. Such a definition may seem a bit circular. The molecular
character is the key, however: it separates molecule-based magnets from other, more conventional magnetic materials in which moments are associated with atomic units. This distinction is an important one for many reasons. First, the identification of a magnetic moment with a molecule supposes a molecular magnetic state that is well-defined and fixed relative to the chemical environment of the molecule. That is, the magnetic behavior of a molecule-based compound is to be determined by examining the interactions between molecular moments. Second, the now extremely refined synthetic techniques available for creating solids molecule by molecule in a chemistry laboratory at ordinary temperatures provide a great advantage to researchers interested in “tuning” the structural and magnetic properties of a desired material. In particular, nearly perfect examples of certain idealized structures of interest to physicists have been or can in principle be synthesized. As examples, consider the synthesis of certain polymeric compounds with vanishingly small values of $\gamma$, or of Kagomé-type structures with maximal geometrical frustration. Finally, molecule-based magnets have the potential to incite revolutionary developments in materials technology. Specific possible advantages, especially when increasing organic moieties are incorporated, are low densities, tunable magneto-optical properties (e.g., transparency), and biocompatibility. Several areas of practical development exploiting these advantages have already been initially investigated. Electromagnetic compatibility and shielding, molecular electronic switching, and magneto-optical data storage are three examples.

Molecule-based magnet (MBM) has been used here to refer to a material with essentially any kind of magnetic properties. The term more commonly in use for this purpose is molecular magnetism, while molecule-based magnet is normally reserved for compounds with a definite phase of three-dimensional long range magnetic order (below some $T_c$). Further, molecule-based is distinguished from molecule-bridged in
that the former is made up solely of individual molecules, each with some net spin, while the latter contains spin-carrying molecules connected by diamagnetic "bridge" ligands. It is hoped that the reader will forgive all this pedantry in the spirit of precision. These terms are all used fairly interchangeably in the field with few shed tears.

From a physics point of view, the interesting difference between molecular and atomic magnets is that, while atomic magnets rely on coupling between electrons in d and f orbitals, electrons in s and p orbitals play a crucial role in MBMs. As an illustration of this distinction, consider the first characterized molecule-based ferromagnet - the charge-transfer salt \([\text{FeCp}_2]^+\text{[TCNE]}^-\), which forms 1D chains of alternating donor-acceptor units and has \(T_c = 4.8\) K [91, 92]. In the tetracyanoethylene radial anion, the unpaired electron from the donor decamethylferrocenium is added to the LUMO of the (originally closed-shell) TCNE, creating a \(\pi^*\) "partially occupied" MO, or POMO, of \(b_{2g}\) symmetry. This essentially p-character electron has an associated spin-density which is distributed across the ion in an alternating fashion but with total \(S = 1/2\). Fig. 19 shows the results of a neutron scattering spin density map of \([\text{TCNE}]^-\) as measured in the salt of \([\text{Bu}_4\text{N}]^+\). The organic anion is thus seen to possess its own p-based moment and is a common component of MBMs.

The s- and p-based organic units play a passive or active role in the overall magnetism according to whether they form diamagnetic bridges or have their own unpaired spin, as in the case of \([\text{TCNE}]^-\). Examples of such "organic-bridged" and "organic-based" magnets are given in Fig. 20. In purely organic magnets, of which the only thoroughly characterized examples are the nitrophenyl-nitronyl-nitroxides of Kinoshita et al., no d or f orbitals are present to provide the basis for a strong exchange mechanism. The critical temperatures in these magnets \((T_c \sim 1\) K) are sufficiently
Figure 19: Neutron scattering spin density map of the organic radical cation [TCNE]$^-\,$ as measured in the tetrabutylammonium salt which possesses no net spin of its own. Regions of positive and negative spin density are indicated with plus and minus signs [93].
small that other mechanisms, such as dipole interactions, could be dominant. In other systems, the chemical structure will determine the relative importance of various interaction pathways. For close metal-based MOs \((r < 3 \text{ Å})\), direct exchange and/or kinetic exchange will dominate. For orbitals at greater separations \((3 < r < 6 \text{ Å})\), one has to rely on higher-order CI overlaps through multiple diamagnetic bridges, i.e. a superexchange pathway. If two metal atom-based MOs are separated by \(n\) diamagnetic “hops,” the effective exchange interaction will be at most \(t^n J\), where \(t\) is the orbital overlap between the metallic MO and a neighboring ligand. At larger distances \((r > 6 \text{ Å})\), where the superexchange interaction is likely quite ineffective, or in the absence of any superexchange pathway, dipole forces become important. Obviously, the various MBMs following this spatial trend will have lower and lower critical temperatures, on average.

Extensive reviews of molecular magnetism, its synthetic triumphs, mechanisms for stabilizing long-range ferromagnetic or ferrimagnetic order, and the crucial roles played by disorder and anisotropy have been written. The field of molecule-based magnets, now at least a decade old, is already quite large and grows continuously. The reader is referred to the reviews of Palacio [94], Miller and Epstein [95], Caneschi [51], and Kahn [11] for broad overviews of models and methods, and to a recent NATO ASI Proceedings [96] for details of current research. In this thesis the focus is on compounds from two very interesting subclasses of organic-based molecular magnets using the metal donor-TCNE acceptor anion motif to create strong magnetic interactions for long-range order and, as it turns out, some really fascinating physics as well.
• s- and p- orbitals play crucial role

Organic-bridged magnets

- bimetallic FI chains
  \( \text{MnCu(pbaOH)} \)
  Kahn \textit{et al.} (1988)

- Prussian blue
  \( \text{M}_x[\text{M}'(\text{CN})_y] \)
  Verdaguer \textit{et al.} (1994)

- metal-nitroxide chains
  \( \text{Mn(hfac)}_2 \text{NITEt} \)
  Gatteschi, Rey, \textit{et al.}

Organic-based magnets

- purely organic
  - \( \beta p\)-NPNN
    Kinoshita \textit{et al.} (1991)
  - \( \text{C}_{60}(\text{TDAE})_x \) (??)
    Wudl \textit{et al.} (1991)

- hybrids
  - [MCp\textsubscript{2}]\textsuperscript{+}[TCNE]\textsuperscript{-}
  - V(TCNE)\textsubscript{2}y(Solvent)
    [MnTPP]\textsuperscript{+}[TCNE]\textsuperscript{-}

\textbf{Figure 20:} Organizational scheme of molecule-based magnets. Hatched blobs correspond to organic ligands ("chicken fat") and dark centers to metallic ions.
CHAPTER II

Experimental Techniques

Three main experimental tools have been employed to study the effects of dimensionality and disorder in the molecule-based magnets presented in this thesis. The magnetization $M(T, H)$, or equivalently the d.c. susceptibility $\chi_{dc}(T, H) = M/H$, was measured with two methods: 1) Faraday Balance, 2) Superconducting Quantum Interference Device (SQUID). The a.c. magnetic susceptibility $\chi_{ac}(T, H_{dc}, H_{ac}, f)$ and its harmonics $\chi^{(1)}, \chi^{(2)}, ..., \chi^{(n)}$ were measured with a mutual inductance two-coil susceptometer. The specific heat $C_p$ was measured with a home-built 1K anaerobic dip-cryoprobe via both adiabatic and quasiadiabatic techniques. The details of these methods are described in the following sections, with an eye toward how such bulk thermodynamic probes are able to elucidate the novel and often fascinating properties of molecular systems that arise due to dimensionality and/or disorder.

2.1 DC Magnetic Susceptibility

The measurement of d.c susceptibilities is at once straightforward and complicated. It is straightforward in that the property directly recorded by a magnetometer is, in
principle, simply related to the moment of the sample in a magnetic field. It is complicated because, unless great care is taken in preparing the experimental conditions and accounting for apparatus limitations, what is measured may be more than simply the intrinsic magnetization of the material of interest. For example, heterogeneous samples, sample holders, misaligned or uncentered samples, and operation outside apparatus tolerances will all give results at odds with the expectations for $M$ of the bulk sample.

In this section, the Faraday Balance and SQUID techniques are described. By no means will the account be complete. Some details concerning the advantages and drawbacks of the specific instruments used in this study are mentioned in the hopes that they are more generally useful. The reader is forewarned that "no useful description of susceptibility [or other] experiments can be brief," [97] and encouraged to speak directly with experienced users to really become proficient with such measurements.

2.1.1 Faraday Balance

The Faraday Balance (FB) technique uses the fact that a magnetic sample placed in an inhomogeneous magnetic field will feel a force which can be detected as a change in weight. The force on a sample of volume $V$ and magnetization $M$ in a field $H$ is

$$ F = \int M \cdot \nabla H dV, $$

(2.1)

so the force in the $i$th direction on a differential volume $dV$ is

$$ dF_i = dV \chi_{jk} H_k \frac{\partial H_j}{\partial x_i}. $$

(2.2)

For the powder samples studied here, the scalar average $\chi = \frac{1}{3} \text{Tr} \bar{\chi}$ is measured and the expression for the differential force for $H = H\hat{z}$ is $dF = dV \chi H (\partial H/\partial z)$. If the
sample is placed in a region where \( H(\partial H/\partial z) \) is constant over \( V \), then the net molar susceptibility is simply \( \chi = F/[NH(\partial H/\partial z)] \), where \( N \) is the number of moles.

The present study employed an Oxford magnet dewar and a Perkin-Elmer AR-2 autobalance. The cryostat and connections are schematically pictured in Fig. 21. An outer vacuum jacket isolates the interior from heat flow from the atmosphere. In the first stage of cooling, liquid nitrogen is poured into a space just within the jacket. The inner space is filled with liquid helium cryogen in the second cooldown stage. Between stages, the helium space is precooled with liquid nitrogen and flushed with dry gas to minimize liquid helium boil-off during transfer.

Near the bottom of the helium space is an American Magnetics Inc. (AMI) superconducting magnet with vapor-cooled leads to an Oxford power supply capable of producing a field \( H_0 \) in excess of 8 T at an applied current of 71 A. A persistence switch removes lead connections after the magnet field has been set. The homogeneity of \( H_0 \) over a 1 cm length at the center of the magnet is 1 part in \( 10^4 \). The gradient of the magnetic field is supplied by a pair of Helmholtz coils whose field \( H_1 \) is superimposed coaxially on that of the main magnet. These coils are capable of producing a gradient as high as \( dH/dz = dH_1/dz = 10 \text{ T m}^{-1} \) (19 A) at the position of the sample, with a gradient homogeneity of 1 part in \( 10^3 \). Typical field gradients used during measurement were \( \sim 20 \text{ G cm}^{-1} \).

Samples were prepared by loading a few mg of powder into quartz capillary (Wilmad Glass 1.5 mm i.d. by 1.8 mm o.d.) in an inert (argon) atmosphere. The capillaries were capped with a length of dental tubing and a small hose clamp in order to bring them out of the glove box to a vacuum pump, where they were evacuated to \( \sim 10^{-5} \text{ mbar} \). The clamp was replaced and the holders sealed off with a torch applied as far from the sample end as possible. During the sealing, a small loop was made at
Figure 21: Schematic of Faraday Balance Magnetometer and its connections. From Oxford Instruments cryostat manual [98].
the top of the tube to provide a fixture for the tungsten hangdown wire of the balance. This wire is cut to a length (~ 0.9 m) which ensures the positioning of the center of the sample at the center of the magnet. In doing so, the small thermal contraction of the wire must be considered. Further, in lowering the sample into the sample tube of the cryostat care must be taken to ground all cryostat surfaces. The sample, tube, and hangdown wire are balanced at $H = 0$ with small metallic counterweights.

Sample temperature measurement and control was provided with a LakeShore CGR-1500 thermometer and Cu heater in conjunction with an Oxford ITC-4 temperature controller. A constant 100 mm of He exchange gas was maintained in the sample space for thermal anchoring. This gas and space could be pumped on from above, and by opening a capillary to the liquid helium space temperatures as low as 2 K could be attained.

After setting the field and temperature, a measurement sequence proceeded by alternating the gradient field in a trapezoidal wave with a WaveTek 75 Arbitrary Waveform Generator and amplifier. During the linear up- and down-ramps of the wave the gradient field moved from being aligned with $H_0$ to being antialigned, and vise-versa. The actual sample weight was recorded after $\pm H_1$ was set and constant. Since the weight from mass is independent of the direction of $H_1$, its effect was eliminated by subtracting the “up” and “down” $dH/dz$ total weights and dividing by 2: $\chi = [W(+) - W(-)]/2NH|dH/dz|$. Each such measurement period lasted approximately 40 s. As the mass resolution of the autobalance is $\sim 10^{-7}$ g (with $\pm 0.25\%$ accuracy), the ultimate sensitivity of the FB instrument is $\sim 10^{-11}$ emu or better. The Faraday Balance is thus a very sensitive technique available for measuring $\chi_{dc}$. The main drawbacks of the particular apparatus were the high helium consumption rate and the fact that attendance of the operator was required during most of the
2.1.2 SQUID

A second method for measuring $M$ and $\chi_{dc}$ employed a Quantum Design Magnetic Property Measurement System (MPMS) based on a superconducting quantum interference device (SQUID). A SQUID is based on the quantization of magnetic flux through a superconducting current loop. A signal may be induced in a normal current loop by varying the flux through it ($E = -d\Phi/dt$). The variation of $\Phi$ is accomplished by moving a magnetic sample through the loop in the presence of a uniform magnetic field. In a SQUID magnetometer, a superconducting loop, which encircles the path of the moving sample, is connected to a second loop a few cm distant. The second loop is placed coaxially within one of two bores of a solid niobium cylinder (Fig. 22). The bores are connected by a small empty channel which is traversed by a weak Josephson link. Now, when a persistent current exists in the loop, the niobium cylinder will support a current and field proportional to that produced by the sample. The current takes the shorter path around the second loop through the Josephson link. Due to the quantization of flux, the induced current in the SQUID will try to counter any attempts by the sample to change the flux through the bores, at least until the Josephson junction is saturated. At that point the SQUID goes normal just long enough to allow the flux to jump up by one quantum $\Phi_0$. The current temporarily takes the outer loop and the precise change in induced field due to the sample motion can be detected in units of $\Phi_0$ with a detector in the second bore.

In the QD system, a slightly more complicated configuration, using four current loops to cancel self-inductances, is employed but the basic concept is the same. Samples were prepared similarly to what was done for the FB. The quartz sample tubes
Figure 22: Schematic of Superconducting Quantum Interference Device (SQUID) magnetometer. The sample, represented by the diamond shape at left, is passed vertically through the loop, coaxially with the applied field. A top view of the Niobium core with its two bores appears at right. The triangle shape represents the weak Josephson junction. From Gerloch [99].
are attached to a sample rod with low-temperature Scotch tape and centered using a small applied field (typically 5 - 50 Oe). Centering, as well as any measurement scan, proceeded by moving the sample through 32 positions from well below the loop to well above with a stepper motor. The detected voltage signal \( V \propto \frac{\partial^2 \Phi}{\partial z^2} \) is fitted to the expected signal for an ideal point dipole and converted to absolute moment units (emu Oe). With the main magnet of 5.5 T, sensitivities of \( 10^{-10} - 10^{-11} \) emu are easily attained.

The sample temperature is controlled with helium exchange gas and a wound heater above 4.2 K and by thermal contact to a helium sub-pot in the range \( 1.7 \leq T \leq 4.2 \) K. The "black-box" nature of the QD system allowed unattended operation for most experimental runs – a great convenience. However, since the system is fully automated it is tempting to assume that things have proceeded normally during one's absence. At the lowest and highest temperatures available, this is rarely the case. At low temperatures, thermal stability is not maintained for long periods of time – detailed hysteresis loops below 4.2 K are not really feasible without "babysitting" the machine. Thermal instability can also result in unexpected and undesired changes in sample field history. It is of interest in disordered magnets to compare the zero-field cooled (ZFC) and field-cooled (FC) magnetizations to determine irreversibility points and long-time relaxations. If a ZFC \( M(H) \) curve is recorded below 4.2 K, care must be taken that no temperature spikes, which temporarily but unpredictably send the temperature above 5 K, occur between data recordings. Such a spike changes the field-history of subsequent data points from ZFC to FC, possibly resulting in discontinuities in \( M(H) \). By watching the low temperature runs personally and recording the \( T(t) \) information in detail, one can at least be aware of such occurrences. At high temperatures, it is the sample centering which can be in error. Due to the thermal contraction of the sample rod, shifts in the sample scan start and end positions rel-
ative to the loop occur and, since the high temperature signal for small samples is already noisy, a decay in signal may result. Although a first correction for this contraction is provided in the MPMS software, it is also advisable to take scans over wide temperature ranges in 50 K chunks, recentering between chunks. Alternately, sample centering plots may be recorded periodically to quantify the degree of degradation.

With these two main caveats appreciated, the SQUID is a very convenient and rapid method to characterize new samples and to study $\chi_{dc}$ in general. A standard initial run on an uncharacterized sample incorporates three scans: 1) $M(H)$ at 5 K to obtain saturation magnetization, 2) $M(T)$ in 5000 Oe to room-temperature to obtain the Curie constant and Curie-Weiss temperature, and 3) $M(H)$ at room temperature to determine the presence of any ferromagnetic metal impurities such as Fe (Honda analysis). This full run takes about 10 hours and can be configured to execute unattended.

In both FB and SQUID techniques a type-II superconducting magnet is used. Once the applied current drives the magnet above the lower critical field $H_{c1} \sim 100$ Oe, the magnet will retain a remanent moment upon removal of the current. Subsequent low-field measurements are then fairly uncertain, in that the remanent moment may reach as high as 20 Oe and decay on the time scale of hours when the magnet is ramped to 5 T and back to zero. The best way to avoid the remanence is to do low- and zero-field data runs immediately following the initial cooldown of the cryostat, before $H_{c1}$ is traversed. Barring this option, a true field zero to within 0.5 Oe can be obtained by measuring $M(H)$ for a Pd standard paramagnetic sample from -20 to 20 Oe in steps of 1.0 Oe. The field zero for taking or interpreting data on the sample of interest is then offset by the y-intercept of the Pd curve. Additionally, the magnet may be degaussed by applying a current that approximates a geometrically-damped
cosine wave. For example, degaussing from 1000 Oe requires setting the field sequence (-500, 250, -125, 60, -30, 15, -8, 4, -2, 1, 0, corresponding approximately to a 50% amplitude factor) until the oscillations are much smaller than any coercive field in the sample.

2.2 AC Susceptibility

The a.c. magnetic susceptibility $\chi_{ac}$ measures the response of a sample to an oscillating magnetic field, in both zero and nonzero d.c. bias field. The addition of the frequency parameter $f$ (or $\omega = 2\pi f$) opens up a broad range of possible dynamics investigations, particularly in the determination of the frequency dependence of resonances or anomalies in $\chi_{ac}$. Recording ZFC data in zero d.c. field permits access to the true initial slope of $M(H)$, which relates to the initial permeability and to $H \rightarrow 0$ critical phenomena near some $T_c$. Similarly, applying a d.c. magnetic bias field allows investigation of the slope of $M(H)$ at higher fields and of the dynamics of the wide range of field-induced spin orderings in magnetic materials. Finally, because of the ability to probe dynamic response over a wide range of time scales, $\chi_{ac}$ is an essential tool for investigating spin glasses and spin glass-like systems.

A LakeShore Cryotronics 7225 A.C. Susceptometer/D.C. Magnetometer was used to collect $\chi_{ac}$ and $\chi_{dc}$ data in the ranges $1.25 \leq T \leq 325$ K, $0 \leq H_{dc} \leq 5$ T, $0 \leq H_{ac} \leq 20$ Oe, and $0 \leq f \leq 5 \times 10^4$ Hz. The Lakeshore system couples a superconducting d.c. field magnet (like those in the magnetometers) with a mutual inductance coil setup along the same axis and encircling the inner sample tube. The mutual inductance windings, pictured in Fig. 23, consist of a primary coil surrounding a pair of smaller, identical but counterwound secondary coils connected in series. A driving signal is set up in the primary coil with an a.c. current source. The oscillating induced field is picked up by the secondary coils via mutual inductance. Since the
secondary coils are counterwound, the net induced emf should vanish in principle. However, there will always be a small offset emf due to the fact that the coils cannot be counterwound perfectly. The voltmeter (an EG&G Princeton Applied Research 5209 lock-in amplifier) has a sufficiently high sensitivity to detect the offset. At $H_{ac} = 1$ Oe and $f = 125$ Hz, the offset voltage was found to be about 5 $\mu$V.

The change in induced voltage produced by placing a magnetic sample at the center of one of the secondary coils is directly proportional to the permeability (and susceptibility) of the sample. The relation $V = f H_{ac} \chi_{ac}/Na$, where $N$ is the number of moles and $a$ is a geometrical calibration constant, is used to convert induced voltage to molar susceptibility. To eliminate the offset, the signal is measured with the sample in both coils, then subtracted and divided by two, as in the FB technique. This process is done automatically with a stepper motor through the LakeShore ACS7000 software and IEEE-488 interface bus.

As the a.c. susceptibility is a dynamic response function, there may be a phase lag between a change in applied field and a change in susceptibility (voltage). The magnetization response to an oscillating field $H_{ac} = h_0 \cos \omega t$ may be written

$$M_{a.c.} = m_0 \cos(\omega t - \Theta), \quad (2.3)$$

$$= m_0 (\cos \omega t \cos \Theta + \sin \omega t \sin \Theta), \quad (2.4)$$

$$= \chi' h_0 \cos \omega t + \chi'' h_0 \sin \omega t, \quad (2.5)$$

where $\chi' = (m_0/h_0) \cos \Theta$ and $\chi'' = (m_0/h_0) \sin \Theta$. To detect these two components, 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 $H_{ac}$. The real and imaginary susceptibilities are calculated as

$$\chi' = \alpha V'/f H_{ac}, \quad (2.6)$$
Figure 23: Mutual inductance AC susceptibility setup. The sample is measured in both upper and lower secondary coil positions to eliminate coil offsets.
\[
\chi'' = \frac{\alpha V''}{f H_{ac}},
\]

where

\[
V' = V_0 \cos \Theta + V_{x/2} \sin \Theta,
\]

\[
V'' = V_{x/2} \cos \Theta - V_0 \sin \Theta.
\]

The same samples as used in d.c. magnetization could be measured in the a.c. susceptometer by adapting the a.c. sample probe rod and Delrin extension to the diameter of the quartz sample tubes. Alternately, samples could be loaded directly into small Delrin cups which screw right on to the extension. The drawbacks of this slightly more convenient configuration are that the cups are not airtight and contribute a larger diamagnetic signal. Because most a.c. measurements were done in zero d.c. bias field, the main magnet leads were usually left unattached. Centering was mainly accomplished by precisely initializing the sample position at the center of the bottom secondary coil using the known distance from the top of the probe load seal and the distance of the center of the sample from the end of the probe rod. Once centered, a temperature run at multiple frequencies and possibly multiple a.c. fields was set up and left to run unattended. A scan from 4 to 50 K, in increments of 0.25 K, at a fixed a.c. field and at an array of frequencies (5, 10, 20, 80, 125, 250, 400, 1000, 5000, 10000 Hz) took approximately 36 hours to complete.

The in-phase or real component corresponds to a dispersive response and in the limit \( f \to 0 \) is identical to \( \chi_{dc} \). The out-of-phase or imaginary component corresponds to dissipation – the energy absorbed by the sample from the a.c. field. The frequency dependences of \( \chi' \) and \( \chi'' \) are related through the Kramers-Kröning relations; a peak in \( \chi''(\omega) \) is associated with a maximum in the slope of \( \chi'(\omega) \).

As an additional option, the harmonic susceptibilities can be measured. By
driving the primary coil at frequency $f$ and detecting the output signal at integer multiples of $f$, any nonlinear magnetic responses can be analyzed. In zero d.c field, the magnetization may by expanded in powers of $H = h_0 \sin \omega t$,

$$M = \sum_{n=1}^{\infty} \chi_n H^n = \sum_{n=1}^{\infty} \chi_n h_0^n \sin^n \omega t$$

$$= \chi_1 h_0 \sin \omega t + \chi_2 h_0^2 \frac{1}{2}(1 - \cos 2\omega t) + \chi_3 h_0^3 \frac{1}{4}(3 \sin \omega t - \sin 3\omega t) + \cdots \quad (2.10)$$

where $\chi_n$ is the $n$th harmonic susceptiabilty, generally a function of $h_0$, $\omega$, and $T$. It is important to note that $\chi_2, \chi_4, \ldots$ can only be observed if there is a spontaneous magnetization because for a ferromagnet or ferrimagnet $M$ has no inversion symmetry with respect to the applied field [84]. In the absence of any even harmonics the expansion can be written

$$M = \sum_{n=0}^{\infty} \tilde{\chi}_{2n+1} h_0^{2n+1} \sin[(2n + 1)\omega t]$$

$$\tilde{\chi}_1 = \chi_1 + 3 \chi_3 h_0^2 + \frac{5}{8} \chi_5 h_0^4 + \cdots$$

$$-\tilde{\chi}_3 = \frac{1}{4} \chi_3 + \frac{5}{16} \chi_5 h_0^2 + \cdots$$

$$\tilde{\chi}_5 = \frac{1}{6} \chi_5 + \cdots$$

The quantities $\tilde{\chi}_n$ are the ones actually measured, so the intrinsic susceptibilities are related directly in the limit of zero a.c. field.

### 2.3 Specific Heat

The last experimental technique used was the low-temperature specific heat. The heat capacity $C$ of a system is the amount of heat energy input required to raise its temperature by 1 K. As it defines a variation with respect to a thermodynamic
quantity, the definition must specify which of each pair of conjugate quantities \((pV, MH, \text{etc.})\) is to be held constant. The experimental heat capacity naturally measured is at constant pressure \(p\) and magnetic field \(H\), defined as

\[
C_{p,H} = \left( \frac{\partial U}{\partial T} \right)_{p,H} = T \left( \frac{\partial S}{\partial T} \right)_{p,H}.
\]

The related intensive quantity of interest is the specific heat capacity, or simply specific heat, \(c_{p,H}\), defined as the heat capacity per mole, mass, or volume. A small notational confusion arises in the literature from the common use of both upper and lower case variables for specific heats. Here the variable \(C_p\) will be used to stand for the specific heat and context should clarify any ambiguity.

Knowledge of the specific heat \(C_p\) of a magnetic material is useful for several reasons. First, as a thermodynamic transformation of the quantum energy spectrum, the specific heat can give a fairly complete description of the density of states. Second, \(C_p\) is additive, being a sum of contributions from lattice (phonon), electronic, and magnetic processes. It is thus straightforward (in principle) to determine any one component experimentally by subtracting or suppressing the others. Third, specific heats can identify the presence or absence of a phase transition, much in the same way as magnetic susceptibility. An anomalous magnetic specific heat is expected at a traditional 3D continuous phase transition. Other processes can also contribute to or suppress peaks or anomalies in \(C_p\). The sharpness and relative magnitude of an anomaly is an indicator of the type of cooperativity involved.

The lattice specific heat of a 3D solid at constant volume is proportional to the cube of the temperature in the limit as \(T \to 0\) and approaches a constant at high temperatures. This behavior arises by treating the solid harmonic crystal of \(N\) atoms as a collection of \(3N\) independent oscillators whose energies are quantized according to \(E_s(k) = (n_k + \frac{1}{2})\hbar \omega_s(k)\), where \(s\) and \(n \in \mathbb{Z}^+\) specify different branches and
excitation numbers, respectively. A collection of such oscillators, or phonons, obeys
Bose-Einstein statistics; as such the specific heat may be directly written down as
[10]:

\[ C_V = \frac{1}{V} \frac{\partial}{\partial T} \sum_{k} \frac{\hbar \omega_s(k)}{e^{\beta \hbar \omega_s(k)} - 1} \]  

\[ \approx \frac{\partial}{\partial T} \sum_{k} \frac{d k}{(2\pi)^3} \frac{\hbar \omega_s(k)}{e^{\beta \hbar \omega_s(k)} - 1}. \]  

At very high temperatures \((\hbar \omega \ll k_B T)\), the specific heat is just the Dulong-Petit
constant \(C_V = 3Nk_B/V\). At low temperatures, modes with \(\hbar \omega_s(k) \gg k_B T\) contribute
negligibly to the specific heat. The dispersion relation may be approximated by a
linear form \(\omega_s(k) = c_s(\hat{k}) k\) corresponding to the region of the acoustic branches near
\(k = 0\). Then it is found that

\[ C_V(T) = \frac{\partial}{\partial T} \left( \frac{k_B T}{\hbar c} \right)^4 \frac{3}{2\pi^2} \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\partial}{\partial T} \frac{\pi^2}{10} \left( \frac{k_B T}{\hbar c} \right)^3 \]  

\[ = 2\pi^2 \frac{\hbar c}{5k_B} \left( \frac{k_B T}{\hbar c} \right)^3, \]  

where \(x = \beta \hbar c_s(\hat{k}) k\) and the quantity \(\bar{c}\) is an averaged long-wavelength velocity given
by \(3\bar{c}^{-3} = \sum_s \int d\Omega/4\pi c_s(\hat{k})^3\). Hence \(C_V\) is seen to vary as \(T^3\) at low temperatures.

In the intermediate temperature range, Debye's interpolation scheme may be used.
Replacing the upper limit of \(\infty\) on the integral with a finite Brillouin zone boundary
\(k_D\) where \(n = N/V = k_D^3/6\pi^2\) limits the number of wavevectors in the integral to \(N\).
Substituting the parameter \(\theta_D = \bar{c} k_D\), called the *Debye temperature*, the specific heat
is

\[ C_V(T) = 9nk_B \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2} \rightarrow 1944(T/\theta)^3 \text{ J mol}^{-1} \text{ K}^{-1}. \]  

The Debye temperature is on the order of \(\theta_D \sim 10^2 - 10^3\) K for most crystalline solids.
Molecular systems, especially ones with large organic groups, have more low-frequency
contributions and \(\theta_D \sim 10^1 - 10^2\). However, in most molecular systems the spectrum
of oscillating modes is quite complicated, with high-frequency intramolecular and
low-frequency intermolecular vibrations coming in at different temperatures, so that
detailed analysis with this simple Debye model is not appropriate.

The effect of dimensionality is manifested in the power of $T$. In $d$ dimensions,
$C_p \propto T^d$ at low temperatures. In real quasi-1D systems, a linear specific heat may be
visible in some low temperature range, but $C_V$ must obey the $T^3$ law at the very lowest
temperatures as transverse (interchain) vibrations become more and more important.
Therefore it may be possible to see a dimensionality crossover in the lattice as well
as the magnetic specific heat.

Since the Debye theory is developed for a harmonic crystal, the fitting to the
specific heats of disordered, especially amorphous, solids is dubious. In such cases the
Debye temperature is only defined for phonons with wavelengths within a crystalline
correlation length.

The two other major contributions arise from electronic and magnetic interac-
tions. Conduction electrons (a Fermi gas) has a characteristic specific heat that is
linear in temperature. As such, the low-temperature specific heats of metals is typ-
ically fit to $C_p = \gamma T + \beta T^3$: a plot of $C_p/T$ vs. $T^2$ should yield a line whose slope
gives the Debye temperature and whose intercept gives the density of states. As for
the magnetic contributions, a detailed summary will not be given here. The criti-
cal behavior at a long-range order transition was mentioned in Ch.I. Additionally,
the magnetic specific heat below $T_c$ should reflect the contribution of spin waves. In
ferromagnets and ferrimagnets, the low temperature magnetic specific heat varies as
$\sim T^{d/2}$, while that of antiferromagnets has the same temperature dependence as the
lattice specific heat ($\sim T^d$). The reader is referred to the review of Van Kronendonk
and Van Vleck [100], and a book by Gopal [101], or to any condensed matter text-
book, for a detailed exposition. Finally, spin glasses have a curious lack of anomaly in
the magnetic specific heat at $T_J$. The behavior of the magnetic component is similar to that of a two-level system – linear in $T$ at low temperatures, and passing through a broad maximum attributed to short-range order as $T$ increases. The maximum in spin glasses typically appears at temperatures 20-30% higher than the $T_J$ found from a.c. susceptibility.

In the remainder of this section, the experimental techniques used to determine $C_p$, "pulse" and "drift," are described. A calorimeter for measuring low-temperature specific heats of air-sensitive samples was constructed, and its design will be briefly summarized.

2.3.1 Pulse

The pulse technique isolates the sample of interest under conditions of (ideally) total adiabaticity. A heat-power $P$ is applied to the sample for a set pulse duration ($\Delta t$), and the subsequent temperature rise ($\Delta T$) is recorded, yielding the heat capacity as

$$ C = \frac{\Delta Q}{\Delta T} = \frac{P \Delta t}{\Delta T}. $$

(2.17)

In real experiments, the heating and thermometry are designed to affect the conditions of adiabaticity as little as possible. Nearly perfect adiabatic heating can be accomplished with a remote laser pulse through and optical cryostat window, however it is difficult to determine the total heat input due to reflection from window and sample, and from transmission through the sample. Much more reliable heat pulses are obtained from resistive, or Joule, heating through a wire coil affixed to the sample or its mount ($P = IV$). Remote thermometry is also very difficult to accomplish under the conditions of interest. Thus, a temperature diode or resistor is typically affixed to the sample directly. Both heater and thermometer solutions have the significant
drawback, however, that wires must run from the sample to the environment, nullifying the adiabatic state! Of course, experimental low-temperature physics is a science of degree (no pun intended), and as such a nearly- or quasiadiabatic state can suffice if the errors it admits are acceptably small. If the thermal conductivity of the wires linking sample to environment is very small, the sample will relax to the "bath" on a time scale much longer than a single heat pulse. For example, Constantan wire (60-40 CuNi alloy) has a relative thermal conductivity $k_{\text{Cu}}/k_{\text{Cu}} = 1/20$. A thin Constantan wire of 1 cm length will allow the sample to relax to the environment with a time constant on the order an hour, while a heat pulse may only last a few seconds. The error introduced by a small number of such links is negligible.

Pulse calorimetry has been the mainstay of specific heat measurement for decades. A modern method used for small, solid state samples at low temperatures was introduced by Morin and Maita [102]. It provides a true equilibrium measurement of the absolute heat capacity, something which is difficult with other, nonequilibrium methods. However, the pulse method in a given configuration requires a minimum sample size which may not be available. Also, very fine temperature steps may be precluded by the minimum $\Delta T$ available from the heater.

2.3.2 Drift

In the drift, or relaxation, technique [103], the sample is connected to the environment by a known heat link. Thermal relaxation proceeds in a predictable "isoperibol mode" that is approximately equivalent to the problem of one-dimensional heat flow. Consider a sample at temperature $T$ connected to a heat bath at constant temperature $T_0$ by a weak thermal link of thermal conductivity $k$, length $L$ and cross-sectional
area $A$. The 1D heat balance equation is

$$P_{in} = A k \frac{\partial T}{\partial z} + C(T) \frac{\partial T}{\partial t}.$$  \hspace{1cm} (2.18)

Integrating over the length of the wire,

$$C(T) = \left( \frac{dT}{dt} \right)^{-1} \left[ P_{in} - \frac{A}{L} \int_{T_0}^{T} k(T')dT' \right],$$  \hspace{1cm} (2.19)

which in steady state reduces to

$$C(T) = - \left( \frac{dT}{dt} \right)^{-1} \frac{A}{L} \int_{T_0}^{T} k(T')dT' = - \left( \frac{dT}{dt} \right)^{-1} P_{eq}(T),$$  \hspace{1cm} (2.20)

where $P_{eq}(T)$ is the heat input power required to raise the sample from $T_0$ to $T$ (in the limit $t \to \infty$). In a typical drift experiment, then, one first measures $P_{eq}(T)$ by applying an increasing heater current $I$ to the sample heater (resistance $R$, $P = I^2 R$) and recording the final equilibrium temperature attained at each $P$. At the highest temperature of interest, the applied power is turned off and the sample is allowed to drift back to $T_0$ via the thermal link. During the drift, the temperature is recorded as a function of time for subsequent differentiation.

The drift method is simple in principle and gives a continuous $C_p$ readout in a very short time at a $T$-density limited only by the thermometer response and electronic recording times. Other than the correction required for the specific heat of the addenda (thermometer, heater, sample mount, glue, etc.), the main source of error in the drift technique is the assumption that the sample itself has an infinite thermal conductivity. That is, the temperature sensor is assumed to respond instantaneously to the heater. In reality, applied heat takes time to diffuse through a bulk sample and complicated delayed effects can confuse the $T(t)$ interpretation. Resolutions of this problem take two forms – experimental and theoretical. An example of an experimental resolution is use a sample-bath link with a time constant ($\tau_1$) much longer than the
characteristic thermal time constant of the sample ($\tau_2$). Then $dT/dt \ll (T - T_0)/\tau_2$ for all temperatures of interest. To account for $\tau_2$ theoretically, the 1D heat flow equations can be generalized to model a heterogeneous system with two or more time constants. An exposition of such a model is given Bachmann et al. [103].

Further details are given in the following description of the calorimeter probe used, in which both pulse and drift experiments were conducted.

2.3.3 Construction of Calorimeter

The apparatus constructed is based loosely on the design in the excellent book *Techniques in Condensed Matter Physics at Low Temperatures*, by R.C. Richardson and E.N. Smith [104], adapted for the specific helium storage dewars used at Ohio State and modified to permit the measurement of specific heats, thermal conductivities, thermopowers, and d.c conductivities of small, air-sensitive samples. A schematic of the lower part of the probe appears in Fig. 24. The sample is mounted in a removable vacuum can ("glovebox stage") in an argon atmosphere. The sample mount consists of a thin, polished aluminum disk ($m = 30$ mg), on the underside of which is affixed the thermometer (a LakeShore TG-120PL diode, $m = 20$ mg). A small, precisely massed amount of IMI 7031 varnish is applied to the top side of the disk on which the sample pellet ($m \sim 200$ mg) is placed. A thin, polished aluminum strip wrapped with 20 $\Omega$ of 3-mil Constantan wire is then affixed to the top of the sample, creating a sample sandwich with aluminum bread. To facilitate the sample mounting, the thermometer and heater plates are connected to the cryostat wiring in atmosphere prior to bringing the sample stage into the glove box. Four sensor leads ($V_{ST}^\pm$, $I_{ST}^\pm$) and two heater leads ($I_{SH}^\pm$) are soldered to gold-plated copper electrical pins which plug into the sample stage chuck sockets (Fig. 25).
Figure 24: Specific heat cryoprobe design. Diagonally hatched region at center is helium sub-pot and pump line space. Cross hatched block (with screw hole) is Teflon compression brace.
PLEASE NOTE

Page(s) not included with original material and unavailable from author or university. Filmed as received.
The sample can is sealed with a small layer of vacuum grease applied to a polished metal taper. After removing the can from the glove box, it is evacuated to $< 10^{-6}$ mbar through a narrow hole at the bottom of the can. The hole is closed off with a awl-tipped screw sufficiently tight to remain sealed at low temperatures. The can is fitted onto an extended post of a copper helium sub-pot and clamped with a Teflon annulus (which has a much larger thermal contraction than Cu) to ensure intimate thermal contact. The sample leads emerge from the can through a Stycast feedthrough and are attached with more wire posts to leads running up to the top of the cryostat.

The sample can and sub-pot are both sealed from the liquid helium environment in a second vacuum can, with a taper seal and Stycast feedthrough similar to the sample can. In addition to the ST and SH wires, leads to a bath heater (BH) and bath thermometer (BT) are thermalized to the copper sub-pot with IMI varnish soaked into a layer of Kimwipe “cigarette” paper (for electrical insulation). The bath heater (~ 200 $\Omega$ Constantan coil) and bath thermometer (LakeShore DT470 diode) are affixed on the Kimwipe-covered sub-pot surface. Plumbing lines for pumping the vacuum jacket, pumping the sub-pot, and admitting liquid to the sub-pot from the storage cryostat run through the top of the outer can. All the electrical wires are twisted into fluxless pairs and snaked up to the top of the cryostat exposed to the helium liquid and/or gas. Although bringing the leads up in vacuum would minimize boiloff, vapor cooling minimizes the thermal conduction from room temperature to the experimental stage, which is a much more important problem.

Zero-field measurements are made by simply inserting the $\ell N_2$- precooled probe into a liquid helium storage dewar and allowing the sub-pot and sample can to cool to $\sim 4.2$ K via conduction through the plumbing lines at the top of the outer vacuum can. The initial thermal equilibration takes approximately 4-6 hours. The next
step is to calibrate the sample thermometer *in situ* with the sample. Although this must be done during a previous "addendum" run in the absence of the sample (with the aluminum plates pressed together), thermal cycling of the thermometer results in small but significant calibration shifts. Calibration consists of heating the bath (sub-pot and sample chuck) to a known temperature with a LakeShore DRC-82C temperature controller heater output, waiting for the sample thermometer voltage to equilibrate, and recording a \((T_B,V_{ST})\) point. With the bath heater coil used, bath temperatures between 4.2 and 40 K are obtained with the \((-3)\) and \((-2)\) scales on the 82C. Temperatures between 1.5 and 4.2 K are obtained by filling the sub-pot with liquid and pumping on it. If the needle valve is closed and the vacuum pump is fully open, the lowest temperature obtained is 1.2 K. However, with the heat load of the sample can in place the measurement of adiabatic or quasiadiabatic specific heats is not feasible below about 2 K because the pot empties fairly quickly in this range. If the needle valve is cracked open and the pot fully pumped, the cryoprobe is said to be running in continuous-flow mode, with a minimum temperature of 2 - 2.5 K. Manipulation of the needle and pump valves can provide stable long-time temperature control between 2 and 4.2 K. Calibration data points are input to a program entitled WFIT.C which provides the coefficients of a Chebychev polynomial fit to the \(T(V_{ST})\). These coefficients are used to generate the sample temperature in real time during the running of the data-taking program SPH5.C.

SPH5 allows the user to automate a sequence of GPIB (IEEE-488) commands and data processing commands for the measurement of pulse and drift specific heats. In pulse mode, a small sample current (~ mA) is turned on for a few seconds to heat the sample with a typical \(\Delta T\) of 0.1 K. The sample temperature profile is monitored before, during, and after the pulse to accurately determine the true temperature change. The pulse at a given bath temperature is repeated several times, waiting for
sample-bath equilibration between each pulse. This process is repeated at each of an increasing sequence of bath “base” temperatures. As $T_B$ increases, the heat input must be increased to keep $\Delta T$ above the background noise level. By programming increases in $\Delta t$ and in $I_{SH}$, $\Delta T$ can be controlled with linear and quadratic sensitivities. The ranges $0.5 \leq \Delta t \leq 10 \text{ s}$ and $0.5 \leq I_{SH} \leq 5 \text{ mA}$ give sufficient flexibility to maintain $1\% < \Delta T/T < 5\%$. In drift mode, the sample is heated incrementally to determine $T(P_{eq})$, then allowed to drift back to $T_B$, with the full drift range kept to within 20 K. Processing of $T(P)$ and $T(t)$ to calculate $C(T)$ is done with another routine in WFIT.
CHAPTER III

Magnetic Properties of V/TCNE/Solvent

3.1 Introduction to V/TCNE/Solvent Magnets

The V/TCNE/Solvent class of compounds includes the first example of a molecule-based magnet with a critical temperature near or above room temperature [105]. Previous work with metal-TCNE and metal-TCNQ molecular bonding had led to many interesting magnetic materials, but all had $T_c < 20 \text{ K}$ [92, 95]. Additionally, no other molecular system had yet produced any ordered magnetism much above this range either. So the discovery that $\text{V(TCNE)}_2 \cdot \frac{1}{2} (\text{CH}_2\text{Cl}_2)$ was magnetic at room temperature came as somewhat of a shock to the field of magnetic materials in general, and to researchers in molecule-based magnetism in particular. The proposed coupling between V-atoms via the $\text{trans-\mu}_2$ cyano bridges had been established previously, notably in the metalloporphyrin-TCNE class (see Ch.4), to lead to strong antiferromagnetic coupling. However, in the case of the vanadium compounds, this coupling seems to prevade into all three spatial directions, distinctly unlike what is obtained in other systems.

The underlying origin of the dramatic two-order of magnitude increase in the
critical temperature of this first ambient-temperature molecule-based magnet is intriguing for fundamental magnetism and also for the design of new materials. Future technological applications of molecule-based magnets, such as magnetic and electromagnetic shielding and novel digital components, will require a detailed understanding of their unconventional physics and precise control of necessary magneto-structural parameters. In this chapter, the magnetic properties of $V(TCNE)_2 \cdot \frac{1}{2}(CH_2Cl_2)$ are studied with d.c. magnetization as a function of temperature and field. Building on previous studies [105, 32, 106, 107, 108], it will be shown that, in addition to the solvent used, the source of the V-ion plays a crucial role in determining the resulting magnetic state. What is somewhat astonishing about this development is that there is no trace of the ligands comprising the different V sources in the final product. This sort of evanescent ligand influence is an example of a theme which underlies synthetic magnets in general – that very slight changes in synthetic conditions result in measurable and significant variations in local order, oxidation, and exchange coupling, almost, one might be so bold to propose, akin to the sensitivity of chaotic systems.¹

Following the analysis of $V(TCNE)_2 \cdot \frac{1}{2}(CH_2Cl_2)$ will be brief summaries of new developments in other members of the V/TCNE/Solvent class. An ageing effect in the most disordered compound, $V(TCNE)_2 \cdot y(MeCN)$, suggests the categorization as a kinetic phase, resulting from metastable structural states obtained through the synthetic “quench.” Dynamic susceptibilities will also be examined for further insight into the relation between local structural order and magnetic response in these systems.

¹This is hyperbole. The exponentially diverging trajectories of initially nearby states in a chaotic system cannot be expected to hold in a strict sense during the formation of a solid. The chemical restrictions on the variety of final states within what are controllably reproducible synthetic conditions are too strong. However, it is reasonable that the observed variations in magnetic properties of MBMs are to some extent due to synthetic deviations out of the range of macroscopic control.
Table 6: Properties of V(TCNE)$_x$ · $y$(solvent) for different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T_c$ (K)</th>
<th>$H_c^{RT}$ (Oe)</th>
<th>Proposed Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>350 - 400</td>
<td>15 - 60</td>
<td>spacer, possible ligand</td>
</tr>
<tr>
<td>C$_4$H$_8$O</td>
<td>190 - 205</td>
<td>20</td>
<td>spacer + ligand (V-O)</td>
</tr>
<tr>
<td>MeCN</td>
<td>80 - 150</td>
<td>0.2 - 0.5</td>
<td>spacer + ligand (V-CN)</td>
</tr>
</tbody>
</table>

3.2 Magnetization of V/TCNE/CH$_2$Cl$_2$

As mentioned above, the presence of disorder has an important effect on the bulk magnetic state as well as on the dynamic properties of molecule-based magnets, especially in the V(TCNE)$_x$ · $y$(solvent) class of ferrimagnetic materials [109, 32, 110]. Depending on the spinless solvent used, the structural correlation length varies, being $\sim$ 10 - 15 Å in the case of MeCN solvent and larger in the case of CH$_2$Cl$_2$ solvent [111]. By coordinating with V and/or acting as an interstitial spacer, the solvent directly affects the strength of the effective magnetic coupling between molecular units, leading to critical temperatures ranging from 80 to 400 K. Some of the results for three of the most thoroughly studied materials are summarized in Table 6.

3.2.1 $V(C_6H_6)_2$ and $V(CO)_6$ Comparison

In this section, it is shown that, in addition to the solvent used, the source of vanadium also has a profound effect on the resulting bulk magnetic state. The magnetization of the highest-$T_c$ version prepared via two routes, identified as V($C_6H_6)_2$/TCNE/-CH$_2$Cl$_2$ and V($CO)_6$/TCNE/CH$_2$Cl$_2$, have been studied. While both routes yield a room-temperature bulk ferrimagnet, the material derived from V($CO)_6$ has a higher saturation magnetization, depending on preparation, a slightly lower $T_c$, and a larger...
temperature range of validity of Bloch's Law than for the V(C_6H_6)_2-derived compound.

**Sample Preparation and Chemical Analysis**  The preparation of the V/TCNE magnets has been described in detail previously [105, 112]. The addition of V^0(C_6H_6)_2 or V^0(CO)_6 to an excess of TCNE in dichloromethane at room temperature results in a black solid precipitate that is highly sensitive to air and moisture. Though the x-ray diffraction pattern for V(CO)_6/TCNE/CH_2Cl_2 is very similar to that of the material derived from V(C_6H_6)_2, the relative intensities of the diffraction peaks differ, indicating a variation in structural order [111]. Infrared absorption spectra of V(TCNE)_2 • KCH_2Cl_2 prepared from V(C_6H_6)_2 and V(CO)_6 indicate similar elemental compositions but different binding modes. The carbonyl and benzene ligands are both absent from the products.

For the magnetization measurements both Faraday balance and Quantum Design MPMS SQUID magnetometers were used. The powder samples, usually ~ 2 - 3 mg, were loaded into quartz tubes in an argon atmosphere and sealed under vacuum. The dominant source of uncertainty in both techniques was the sample mass, estimated to be correct within 0.1 mg.

**Isothermal Magnetization**

Fig. 26 compares the isothermal magnetization $M(H)$ of the magnets prepared from V(CO)_6 and V(C_6H_6)_2. The saturation magnetization $M_0 \approx 10^4$ emu·Oe·mol$^{-1}$ of the V(CO)_6 - derived compound (estimated from the measured moment in an applied magnetic field of 3 T) is larger than that of the material derived from V(C_6H_6)_2,
$M_0 \approx 6000 \text{ emu-Oe-mol}^{-1}$. For comparison, $M_0$ for a magnet with a repeat unit of net spin per formula unit of $S = 1/2$ and $g = 2$ is $M_0 = 5585 \text{ emu-Oe-mol}^{-1}$. The magnetization of the $\text{V(C}_6\text{H}_6)\text{)}_2$-derived material is thus in accord with $V^{2+} (S = 3/2)$ antiferromagnetically coupled with two coordinating (TCNE)$^-$ anions ($S = 1/2$) per magnetic unit. However, such a coupling and stoichiometry does not account for the higher saturation of the $\text{V(CO)}_6$-derived material. Such a variation is possible in a more general model of a ferrimagnet, including TCNE-TCNE and V-V (nnn) couplings, or by assuming the existence of three sublattices. Due to the lack of structural information, however, the merits of such models cannot be argued in detail.

The approach to saturation varies among different preparations of $\text{V(CO)}_6$/-TCNE/CH$_2$Cl$_2$, consistent with the variability of earlier-studied V/TCNE magnets. The extreme insolubility of the product and reactivity of synthetic components likely leads to a range of local structural order, reflected in the differing $T_c$ values and magnetization characteristics. The data in Fig. 26 from two preparations of $\text{V(CO)}_6$/-TCNE/CH$_2$Cl$_2$ exhibit the full range of variability observed.

The room-temperature hysteresis loops, Fig. 27, show that the $\text{V(CO)}_6$-derived material saturates more quickly and has a smaller coercive field ($H_c \approx 15 \text{ Oe}$) than the magnet derived from $\text{V(C}_6\text{H}_6)\text{)}_2$ ($H_c \approx 60 \text{ Oe}$).

**Temperature Dependence**

The temperature dependence of the magnetization at low (100 Oe) and high (5000 and 2000 Oe) applied fields for the $\text{V(CO)}_6$ and $\text{V(C}_6\text{H}_6)\text{)}_2$-derived materials, respectively, is shown in Fig. 28. The curvature of $M(T)$ for the $\text{V(C}_6\text{H}_6)\text{)}_2$-derived system is highly suppressed consistent with disorder [32, 110]. At low fields, the variation between
Figure 26: Isothermal magnetization of V(TCNE)$_2$ · $\frac{1}{2}$(CH$_2$Cl)$_2$ from V(CO)$_6$ and V(C$_6$H$_6$)$_2$ sources. (SQUID magnetometer results).
Figure 27: Room-temperature hysteresis of $V(\text{TCNE})_2 \cdot \frac{1}{2}(\text{CH}_2\text{Cl}_2)$. (Materials from $V(\text{CO})_6$ and $V(\text{C}_6\text{H}_6)_2$ measured with SQUID and Faraday techniques, respectively).
preparations from V(CO)$_6$ is most pronounced. As the applied field is increased, the maximum magnetization obtained at low temperatures $M_S(T \to 0)$ increases.

The qualitative picture that emerges from the $M(T, H)$ data is that the magnetic behavior of the material derived from V(CO)$_6$ is that of a less-disordered magnet than the the data of the material from V(C$_6$H$_6$)$_2$, with variations occurring among different preparations. Insight into the "effective" increased order may be obtained via low-temperature spin-wave analysis and high-temperature analysis of the critical exponents.

Spin-Wave Analaysis

Information about excited states, exchange coupling, and molecular coordination can be extracted from the low-temperature magnetization. At temperatures well below $T_c$ the temperature dependence of the magnetization of a 3D ferro- or ferri-magnet generally is described by Bloch's Law, $M(T) = M(0)[1 - BT^{3/2}]$ [113, 114]. The constant $B$, deduced from the slope of $M$ versus $T^{3/2}$ at low fields (Fig. 29), is related to the noninteracting magnon energy dispersion. For a simple-cubic ferromagnet with $S = 1/2$ at each site, using (1.88),

$$
B^{FM} = \frac{1}{S} \left( \frac{k_B}{8\pi J^{FM} S} \right)^{3/2} \zeta \left( \frac{3}{2} \right) = 0.1173 \left( \frac{k_B}{J^{FM}} \right)^{3/2}; \quad S = \frac{1}{2}
$$

while for a two-sublattice (e.g., $S_1 = 3/2, S_2 = 1/2$) model of a simple-cubic ferri-magnet [100],

$$
B^{FI} = \frac{2}{S_1 - S_2} \left( \frac{k_B(S_1 - S_2)}{16\pi J^{FI} S_1 S_2} \right)^{3/2} \zeta \left( \frac{3}{2} \right) = 0.0226 \left( \frac{k_B}{J^{FI}} \right)^{3/2}; \quad S_1 = \frac{3}{2}, S_2 = \frac{1}{2}
$$

In these formulas, $\zeta$ is the Riemann zeta function and $J^{FM}$ and $J^{FI}$ are the ferro- and ferri-magnetic isotropic exchange couplings, respectively. Neither of these spin-wave
Figure 28: Temperature dependence of the magnetization at low (100 Oe) and high (5000 and 2000 Oe) applied fields for the V(CO)$_6$ and V(C$_6$H$_6$)$_2$-derived materials, respectively for V(TCNE)$_2$·$rac{1}{2}$(CH$_2$Cl)$_2$ samples. The progression of overlapping data-point symbols indicates the direction of temperature (warming or cooling) during measurement (e.g., the data presented for the V(C$_6$H$_6$)$_2$-derived material was taken during warming).
Table 7: Bloch coefficient $B$, exchange coupling $J$, and critical temperatures $T_c$ for V/TCNE and other magnets. See text for explanation of variables. Values for Fe and Ni are from Chen [35].

<table>
<thead>
<tr>
<th>Material</th>
<th>$B$ ($K^{-3/2}$)</th>
<th>$T_c^B$ (K)</th>
<th>$T_c^M$ (K)</th>
<th>$T_c^F$ (K)</th>
<th>$T_c^F$ (K)</th>
<th>$T_c^{exp}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V/TCNE/CH$_2$Cl$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- from V(CO)$_6$ #1</td>
<td>$15 \times 10^{-5}$</td>
<td>354</td>
<td>85</td>
<td>570</td>
<td>28</td>
<td>189 $\sim$ 370</td>
</tr>
<tr>
<td>- from V(CO)$_6$ #2</td>
<td>$8.5 \times 10^{-5}$</td>
<td>517</td>
<td>124</td>
<td>832</td>
<td>41</td>
<td>275 $\sim$ 370</td>
</tr>
<tr>
<td>- from V(C$_6$H$_6$)$_2$</td>
<td>$40 \times 10^{-5}$</td>
<td>184</td>
<td>44</td>
<td>295</td>
<td>15</td>
<td>101 $\sim$ 400</td>
</tr>
<tr>
<td>Fe</td>
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<td>205</td>
<td>2187</td>
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<td>n/a</td>
</tr>
<tr>
<td>Ni</td>
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<td>2610</td>
<td>230</td>
<td>920</td>
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<td>n/a</td>
</tr>
</tbody>
</table>

models are expected to exactly reflect the low-temperature behavior of V(TCNE)$_2$·$rac{1}{2}$-(CH$_2$Cl$_2$). However, as these compounds are strongly disordered, a three-sublattice model is unlikely to give substantial improvement.

The values of $B$ obtained by fitting $M(T)$ of V(TCNE)$_2$·$rac{1}{2}$-(CH$_2$Cl$_2$) prepared from V(C$_6$H$_6$)$_2$ and V(CO)$_6$ to Bloch's Law for temperatures between 4 and 35 K, and 2 and 100 K, respectively, are shown in Table 7, together with those for Fe and Ni. $T_c^B$ is the "critical" temperature predicted by setting $M = 0$ in Bloch's Law ($T_c^B = B^{-2/3}$). The exchange coupling calculated from the spin-wave equations (3.1) and (3.2) are tabulated, together with the critical temperature estimated from the mean-field equation $3k_BT_c = 2JZ[S_1(S_1 + 1)S_2(S_2 + 1)]^{1/2}$ ($Z \approx 6$ is the assumed average number of nearest neighbors). The observed values $T_c^{exp}$ are also tabulated.

It is noted that the predicted MFT $T_c$ is closer to the experimental value using the ferromagnetic model (3.1) for the V(C$_6$H$_6$)$_2$-derived material and the ferrimagnetic model (3.2) for sample #2 of the V(CO)$_6$-derived material. The observed $T_c^{exp}$ for sample #1 of the V(CO)$_6$-derived material is mid-way between $T_c$ predicted by the ferromagnetic and ferrimagnetic models.
Figure 29: Reduced low-field magnetization versus $T^{3/2}$ for spin-wave analysis.
The large values of $B$ are a general feature of disordered magnets; typically $B$ is a factor of two to four larger in amorphous ferromagnets than in related crystalline ferromagnets [27]. This trend is interpreted as a softening of the spin wave stiffness $D_a = 2JSa^2$, where $a$ is the lattice constant. In disordered magnets, small-q spin waves are more easily excited and $M$ decreases more quickly. The $B$-values of the V/TCNE magnets are consistent with such a description. The material prepared from V(CO)$_6$ does not simply behave as a "semi-crystalline" counterpart of the material from V(C$_6$H$_6$)$_2$. The temperature range of validity of Bloch's Law is usually a factor of two or more larger in amorphous ferromagnets than in crystalline counterparts [27]. These ranges for V(CO)$_6$- and V(C$_6$H$_6$)$_2$-prepared V/TCNE magnets ($\sim 150$ K and 60 K, respectively) are in opposition to this expectation. Despite these inconsistencies, the exchange constants $J$ lead to critical temperatures within 25% of the observed values for some samples, surprisingly close for mean-field theory.

The deviation of $M(T)$ of V(C$_6$H$_6$)$_2$/TCNE/CH$_2$Cl$_2$ from the usual Bloch's Law may reflect the role of random magnetic anisotropy (RMA). The RMA model has been applied [110] to the most disordered magnet in the V/TCNE class – V/TCNE/MeCN. Within RMA there are randomly oriented easy-axes of magnetization, correlated over a length scale which depends sensitively on local chemical structure [35, 27, 31]. In a small magnetic field and when the strength of the RMA effect is much less than the intermolecular exchange $J$, there is a nonzero (average) magnetization which aligns with the magnetic field. At short length scales, the local magnetization vectors tilt slightly from the field direction toward the easy axes, i.e., it is a ferromagnet with a "wandering axis" (FWA). In such a regime, Bloch's law fails due to the presence of a field-dependent gap $\Delta(H)$ in the magnon spectrum; spin waves are localized within the FWA correlation length. This localization results in highly suppressed magnetization curves, with $\Delta M \sim T$ in some cases, such as those observed in V/TCNE.
magnets [110]. The RMA model is also expected to apply to the present magnets made in CH$_2$Cl$_2$, with FWA correlation lengths larger than those made in MeCN. Further, spin-waves are likely more localized in the V(C$_6$H$_6$)$_2$-derived magnets than in the V(CO)$_6$-derived magnets, causing the increased deviation from Bloch’s law.

The presence of RMA in V/TCNE magnets may be viewed as an effect of local stoichiometric or chemical disorder induced by the random distribution of solvent molecules around the metal ion. Local stoichiometric variations may also give rise to a small variation in the exchange interactions between molecular units via a range of intermolecular distances. Such local effects may be present to varying degrees in the V(C$_6$H$_6$)$_2$- and V(CO)$_6$-derived magnets and lead to the strong differences in the $M(T)$ curves. On the other hand, variations in the average stoichiometry can give rise to the range of saturation magnetizations $M_S$ recorded in the $M(H)$ data.

Critical Analysis

The critical scaling of the magnetization near the transition temperature provides information about the nature of the magnetic disorder in a system. The critical temperature $T_c \approx 400$ K of the V(C$_6$H$_6$)$_2$-derived materials prepared in CH$_2$Cl$_2$ is well above the thermal decomposition temperature $T_d \approx 350$ K, making the critical regime inaccessible. The V(CO)$_6$-derived compound prepared in CH$_2$Cl$_2$ has a lower critical temperature $T_c \approx 370$ K, with the same $T_d$. The determination of $T_c$ and the availability of the critical regime below $T_c$ to measurement in this system depend upon the relative time scales of thermal decomposition and magnetization measurement. Above $T_d$, it is assumed that $M$ decays with an activated time constant $\tau$,

$$M(t) = M(0)e^{-t/\tau(T)}; \quad \tau(T) \sim \exp(\Delta E/k_BT),$$ (3.3)
where $t$ is time, $\tau^{-1}$ is the characteristic decomposition rate, and $\Delta E$ is an energy barrier related to the dissociation reaction kinetics that result in a loss of exchange coupling.

The magnetization was measured as a function of magnetic field at temperatures from 300 to 370 K. The time to increase the temperature between field runs was negligible compared to the duration of the $M(H)$ scans. The corrections needed to account for the degradation of $M$, as determined by following the time dependence $M(t)$ (at and above room temperature during field scans) were small, enabling estimation of the intrinsic magnetization in the range 350 - 370 K. The critical exponents $\beta$ and $\delta$, defined by

$$M \propto |t|^{\beta}, \quad T \to T_c^{-}; \quad (3.4)$$

$$M \propto |h|^{1/\delta}, \quad T = T_c, \quad (3.5)$$

were evaluated utilizing log-log plots near $T_c$. The results, as well as the value of the susceptibility critical exponent $\nu$ calculated with Widom’s scaling relation [115], are summarized in Table 4.

The very large values of $\beta$ in the V/TCNE magnets reflect the strong suppression of the magnetization near $T_c$ as compared to the behavior of more typical magnets. The small increase in $\beta$ expected when going from crystalline to amorphous systems may play a role in V/TCNE magnets but is not sufficient to explain the observed data. However, the effect of a weak random magnetic anisotropy is to increase $\beta$ by 50% over the non-RMA case [116]. The value of $\beta \approx 0.6$ observed in V(CO)$_6$/TCNE/-CH$_2$Cl$_2$ is consistent with the critical RMA effect on a typical disordered system with $\beta = 0.4$. The values of $\gamma$, which describe the divergence of the linear (in magnetic field) magnetic susceptibility near $T_c$ according to $\chi \propto |t|^{-\gamma}$, increase monotonically with correlation length. This trend is remarkable in that it describes sharper transitions
(larger $\gamma$) in V/TCNE magnets with increased local structural order. As the values for $\delta$ are near those observed in crystalline magnets, the large values of $\gamma$ likely reflect the enhancement of $\beta$ from RMA. The measured magnitudes of $\beta$ and $\gamma$ may also be increased in disordered magnets by scaling outside the experimentally inaccessible core critical region [28, 117].

3.2.2 Other V-Sources

Samples of V(TCNE)$_2 \cdot \frac{1}{2}$(CH$_2$Cl$_2$) using two other vanadium sources have also been studied. One is the result of using a combination of V(C$_6$H$_6$)$_2$ and V(CO)$_6$ sources simultaneously to create a single product. This compound will be indicated as (V(C$_6$H$_6$)$_2$ + V(CO)$_6$)/TCNE/CH$_2$Cl$_2$. The other compound obtains its vanadium from a tetraethylammonium variant of the V(CO)$_6$ source, and will be indicated as Et$_4$NV(CO)$_6$/TCNE/CH$_2$Cl$_2$. While V(TCNE)$_2 \cdot \frac{1}{2}$(CH$_2$Cl$_2$) materials from (V(C$_6$H$_6$)$_2$ + V(CO)$_6$) result in a room-temperature bulk magnet, as might be expected, the synthesis of Et$_4$NV(CO)$_6$/TCNE/CH$_2$Cl$_2$ yields a material with strong magnetic interactions only below $\sim$ 50 K. Again the source ligands are not present in the final compound, so fact that the latter material is is so drastically less magnetic than the other compounds is an extreme example of source dependent behavior.

(V(C$_6$H$_6$)$_2$ + V(CO)$_6$)

The compound made from (V(C$_6$H$_6$)$_2$ + V(CO)$_6$) strikes an interesting compromise between the behaviors of V(C$_6$H$_6$)$_2$- and V(CO)$_6$-derived magnets, as presented in the previous section. The d.c. SQUID magnetization at $T = 35$ K (Fig. 30) shows that (V(C$_6$H$_6$)$_2$ + V(CO)$_6$)/TCNE/CH$_2$Cl$_2$ has a saturation magnetization similar
to that of \(V(C_6H_6)_2/TCNE/CH_2Cl_2\), and consistent with a net spin of 1/2. However, the \(M(T)\) data for the \((V(C_6H_6)_2 + V(CO)_6)\)-derived compound at \(H = 100\) Oe (Fig. 31) is qualitatively much more like that of \(V(CO)_6/TCNE/CH_2Cl_2\). Taken together, the \(M(T)\) data on these three variants may be interpreted at resulting from a range of local order and a range of exchange and/or anisotropy. It is expected that the intermediate material from \((V(C_6H_6)_2 + V(CO)_6)\) is locally more ordered than \(V(C_6H_6)_2/TCNE/CH_2Cl_2\) like the \(V(CO)_6\)-derived compound. However, the lower saturation magnetization, in light of the variations observed in the previous section, seem to indicate that a mixture of AF and FM couplings may exist in these materials on length scales somewhat larger than the magnetic correlation length. That is, some regions, or domains, contain predominantly AF couplings which would lead to a local saturation magnetization of \(\sim 1\mu_B\). Other regions may contain significant amounts of FM couplings which would lead to local saturation magnetizations of up to \(\sim 5\mu_B\), given the proposed 2:1 \(V^{II}:TCNE\) stoichiometry. Since there are three possible values of \(S_z\) (1/2,3/2,5/2) in such a two-sublattice ferrimagnet, a range of domain moments is quite plausible and consistent with the data. Additionally taking into account the expected variation in local crystalline anisotropy resulting from random coordination by the spinless solvent \(CH_2Cl_2\) allows for local spin canting. The degree of canting may be decreasing as one goes from the \(V(C_6H_6)_2\)- to the \((V(C_6H_6)_2 + V(CO)_6)\)- to the \(V(CO)_6\)-derived compounds in constant applied field.

\textbf{Et}_4\textbf{NV(CO)}_6

The \(\chi T\) product and inverse static susceptibility \(\chi^{-1}\) of \(Et_4NV(CO)_6/TCNE/CH_2Cl_2\) are presented in Fig. 32. This compound is clearly not a room-temperature magnet. The Curie-Weiss temperature, estimated from a straight line through data above 200
Figure 30: Isothermal magnetization of $(V(C_6H_6)_2 + V(CO)_6)/TCNE/CH_2Cl_2$. 
Figure 31: Comparison of low-field magnetization $M(T)$ of $V(\text{TCNE})_2 \cdot \frac{1}{2}(\text{CH}_2\text{Cl}_2)$ from $V(\text{C}_6\text{H}_6)_2^-$, $(V(\text{C}_6\text{H}_6)_2 + V(\text{CO})_6)^-$, and $V(\text{CO})_6$ sources.
K in a field of $H = 1000$ Oe, is approximately $\theta \approx 65$ K. This value is used to estimate the room-temperature Curie constant $C = \chi(T - \theta) \approx 0.4$ emu K mol$^{-1}$. Such a value is consistent with the average $S = 1/2$ per magnetic unit found in the $V(C_6H_6)_2$- and $(V(C_6H_6)_2 + V(CO)_8)$-derived compounds from $M_S$. The strong increase (faster than $\sim T^{-1}$) in $\chi T$ below $\theta$ is indicative of the buildup to a lower temperature state of long-range order which may be expected to occur in the vicinity of the inflection in $M$ (not shown), or $T_c \sim 15$ K.

At $T = 3.5$ K, the magnetization of $Et_4NV(CO)_6/TCNE/CH_2Cl_2$ as a function of field was measured beginning from a ZFC state and traversing though a full hysteresis loop (Fig. 33). The initial, or "virgin" curve falls below the subsequent field-return data as expected in an irreversible state such as that of long-range magnetic order. The virgin curve also falls below the final section of the hysteresis loop, which is uncommon. It is possible that in the ZFC state, a highly disordered, frustrated magnetic state exists which resists the field's tendency to merge domains. However, once these domains have formed, the hysteresis loop indicates that $Et_4NV(CO)_6/-TCNE/CH_2Cl_2$ is very soft – the coercive field is approximately $H_c \approx 13$ Oe, as seen in the magnified plot of Fig. 34. The magnetization does not saturate, however, within the experimentally accessible field range (5 T). The relatively large initial susceptibility at 3.5 K ($\chi_0 \approx 0.5$ emu mol$^{-1}$, estimate from the initial slope of $M(H)$), followed by a slow approach to saturation is consistent with the presence of strong local anisotropies such as those produced by RMA.

The lack of high-temperature LRO in this compound remains a mystery. The chemical bonding, as indicated by an IR spectrum, is similar to that of other $V(TCNE)_2\cdot\frac{1}{2}(CH_2Cl_2)$ materials, so it remains to elucidate how the V-source prevents strong 3D magnetic coupling from nucleating during the very fast formation of the solid.
Figure 32: $\chi T$ (left scale) and $\chi^{-1}$ (right scale) for $\text{Et}_4\text{NV(CO)}_6/\text{TCNE/CH}_2\text{Cl}_2$. 
Figure 33: Isothermal initial magnetization and hysteresis loop of Et₄NV(CO)$_6$/TCNE/CH₂Cl₂ at 3.5 K. Arrows indicate direction of field scan.
Figure 34: Magnified hysteresis loop of Et₄NV(CO)₆/TCNE/CH₂Cl₂ at 3.5 K. Arrows indicate direction of field scan.
Conclusion

The magnetization $M(T, H)$ of the room-temperature molecule-based magnet V/-TCNE/CH$_2$Cl$_2$ has been compared for materials prepared from V(C$_6$H$_6$)$_2$, V(CO)$_6$, (V(C$_6$H$_6$)$_2$ + V(CO)$_6$), and Et$_4$NV(CO)$_6$. Significant differences in magnetic behavior are found which indicate the presence of a range of local order, ranging from the most ordered V(CO)$_6$/TCNE/CH$_2$Cl$_2$ to a material with possibly significantly increased local magnetic disorder Et$_4$NV(CO)$_6$/TCNE/CH$_2$Cl$_2$, although the metal ligands are not in the final compounds. Table 8 summarizes results of different vanadium source trials and their characteristic IR frequencies. The IR absorption spectra, shown in Fig. 35, underscore the key synthetic role different chemical complexes play in forming V(TCNE)$_2$ · $\frac{1}{2}$(CH$_2$Cl$_2$).

A low temperature spin-wave analysis of the V(C$_6$H$_6$)$_2$- and V(CO)$_6$-derived compounds supports the view of increased order, although the magnet derived from V(CO)$_6$ is not simply a more crystalline version of the V(C$_6$H$_6$)$_2$-derived magnet. The range of isothermal magnetization $M(H)$ data and the critical scaling analysis near $T_c$ suggests the presence of weak random magnetic anisotropy in V(CO)$_6$/TCNE/-CH$_2$Cl$_2$. Critical exponents are consistent with the trend of V/TCNE magnets with increasing structural order having decreasing RMA strengths. More magnetization and a.c. susceptibility studies must be carried out to further probe the critical regimes of the V/TCNE/solvent class.
Figure 35: IR absorption spectra of $V(\text{TCNE})_2 \cdot \frac{1}{2}(\text{CH}_2\text{Cl}_2)$. Different vanadium sources lead to similar stretch positions but varying intensities. Courtesy of Dr. J. Zhang.
Table 8: Sources of vanadium complex and corresponding IR stretches. Courtesy of Dr. J. Zhang.

<table>
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<tr>
<th>Vanadium Complex</th>
<th>FM at RT?</th>
<th>IR (CN stretch) cm⁻¹</th>
</tr>
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<tr>
<td>V(C₆H₆)₂</td>
<td>yes</td>
<td>2188  2088</td>
</tr>
<tr>
<td>V(CO)₆</td>
<td>yes</td>
<td>2187  2153  2090</td>
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<tr>
<td>V(C₆H₆)₂⁺[V(CO)₆]⁻</td>
<td>yes</td>
<td>2190  2154  2100</td>
</tr>
<tr>
<td>Na[V(CO)₆] · 2DiG</td>
<td>yes</td>
<td>2209  2183  2152  2098</td>
</tr>
<tr>
<td>Et₄N[V(CO)₆]</td>
<td>no</td>
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</tr>
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</table>
CHAPTER IV

Magnetic Properties of [MnTPP][TCNE]-2PhMe

4.1 Introduction to [MnTPP][TCNE]

The class of metalloporphyrin-TCNE electron-transfer compounds is of interest for its unusual structural and magnetic properties. The parent compound, [MnTPP]^{2+}+[TCNE]^{-}·2PhMe (TPP = meso-tetraporphyrinato) is comprised of chains of alternating [MnTPP] \((S_1 = 2)\) and [TCNE] \((S_2 = 1/2)\) molecular units with direct metal-CN bonds similar to those in V(TCNE). The structure of [MnTPP]^{2+}+[TCNE]^{-}·2PhMe is shown in Fig. 36. Also shown in the figure is a schematic of the Mn-porphyrin plane and the substitutions on the phenyl that are of interest in this thesis. By systematically varying the ligands \(Rx\), the interchain distances and registries may be varied and the resultant changes in magnetic behavior monitored.

[MnTPP][TCNE] is a crystalline compound with a small amount of structural disorder. Chains are aligned along the a direction of a primitive triclinic lattice \((P\bar{1})\) with parameters \(a = 10.116(1)\), \(b = 11.008(1)\), \(c = 12.489(1)\); \(\alpha = 108.15(1)\), \(\beta = 98.04(1)\), and \(\gamma = 67.92(1)\), as measured with x-ray diffraction by Miller et al. \([118]\). The x-ray data were further refined by Burkhart et al. \([119, 108]\), revealing a
subtle orientational disorder in the [TCNE] anion. A “minor” form of [TCNE], with 
\( \sim 16\% \) occupancy, is rotated about the Mn-Mn intrachain axis by approximately \( \pi \) radians, but with slight (internal) variations in the lengths of the bonds connecting the Mn atoms through the trans-\( \mu_2 \) [TCNE] bridge.

Initial investigations of the novel magnetic properties of this system determined the presence of long-range ferrimagnetic order below \( T_{\text{FI}} \approx 18 \text{ K} \) (by extrapolating the maximum slope of the magnetization \( M(T) \) to \( M = 0 \)) and thermal irreversibilities below \( T_f \approx 7 \text{ K} \), indicative of a “reentrant” spin-glass phase [118, 120, 108]. In this chapter, detailed measurements of d.c. magnetization \( M(T, H_{\text{d.c.}}) \), a.c. susceptibility \( \chi_{\text{a.c.}}(T, f, H_{\text{a.c.}}, H_{\text{d.c.}}) \), nonlinear a.c. susceptibility \( \chi^{(n)} \), and specific heat \( C_p \) for \([\text{MnTPP}]^{2+}[\text{TCNE}]^{-2}\text{PhMe}\) are presented. A state of long-range ferrimagnetic order builds up as \( T \) is decreased below \( \sim 20 \text{ K} \) toward a critical temperature of \( T_c \approx 13.5 \text{ K} \) as determined from a static scaling analysis. The broad temperature region of incipient ferrimagnetism above \( T_c \) may result from the presence of highly anisotropic coherent clusters of spins and the effects of disorder. The extreme anisotropy is also reflected in the lack of any measurable anomaly in the specific heat in this temperature range.

At lower temperatures (\( T < 10 \text{ K} \)), a distinct second peak appears in the out-of-phase a.c. susceptibility, suggestive of the “reentrant” transition to a spin-glass “phase” which coexists with ferrimagnetic order in the field-cooled state. The frequency dependence of this lower-temperature peak, however, is stronger than that observed in the canonical spin glasses[56] as well as known reentrant alloys [73, 86, 121]. The field dependence of the low-temperature state is similar to that of a metamagnet: spins of disordered ferrimagnetic chains reorient coherently over a temperature-dependent critical field range (\( \Delta H_c(T) \)) to a state with saturated ferrimagnetic order.
<table>
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Figure 36: Structure of $[\text{MnTPP}]^{2+}[\text{TCNE}]^{-2}\text{PhMe}$ and schematic of possible ligand substituents on the phenyl units.
These results are compared to the expectations of a model of anisotropic, interacting superparamagnetic clusters.

The relative intensities of the two maxima in $\chi_{a.c.}$ are found to vary between syntheses of $[\text{MnTPP}]^{3+}+[\text{TCNE}]^{-} \cdot 2\text{PhMe}$, ranging from a case where the lower temperature feature is hidden under the tail of the higher temperature maximum, to a case where the low-temperature feature is dominant. Such variation may arise from variations of local magnetic order, much in the same vein as was described for the V/TCNE compounds. These variations are analyzed within the interacting clusters model. Further support for such a picture is obtained in addition from the harmonic susceptibilities $\chi^{(n)}, n = 1, 2, 3$ of the range of samples studied.

Finally, the quasi-1D nature of $[\text{MnTPP}]^{3+}+[\text{TCNE}]^{-} \cdot 2\text{PhMe}$ is discussed and compared to current models concerning ferrimagnetic chains. A minimum in the high-temperature $\chi_T$ product is found in agreement with model predictions. Detailed comparison with theory shows variations which may arise from finite interchain coupling and disorder. The dipole interaction between chains is considered as the possibly dominant mechanism for stabilizing long range order as well as for nucleating a low-temperature random-exchange frustrated state in $[\text{MnTPP}]^{3+}+[\text{TCNE}]^{-} \cdot 2\text{PhMe}$.

### 4.2 Static Magnetization of $[\text{MnTPP}][\text{TCNE}]$

The basic preparation of $[\text{MnTPP}][\text{TCNE}]$ has been described earlier [118, 122]. Two synthetic variations of $[\text{MnTPP}][\text{TCNE}]$ were studied. Samples made via the traditional route consist of a fine black powder which tends to clump together. Extensive vacuum drying following reaction yields shiny, needle-like crystals, as well as some finer powder. The needle shapes range in length up to 1 mm. Samples, with masses
from 4.5 to 11.5 mg, were loaded into quartz tubes in argon and sealed under vacuum. The d.c. magnetization was measured with a Quantum Design MPMS5 SQUID magnetometer in the ranges $1.8 < T < 400$ K and $0 < H_{dc} < 5$ T. Prior to zero-field cooled (ZFC) and field-cooled (FC) magnetization runs, the (NbTi) superconducting magnet and sample were degaussed by slowly oscillating the applied current to zero at a temperature $T \geq 35$ K. Measurements at very low fields were made immediately following a full thermal cycle of the cryostat to room temperature to eliminate residual fields.

### 4.2.1 $M(T)$ and $M(H)$ - bulk characterization

The $\chi T$ product and inverse molar susceptibility $\chi^{-1}$ of $[\text{MnTPP}]^{2+}[\text{TCNE}]^{-2}\text{PhMe}$ at $H = 1000$ Oe is shown in Fig. 37. The value of $\chi T$ at 350 K is 3 emu K mol$^{-1}$ and increasing, consistent with molecular units with $S_1 = 2$ (MnTPP) and $S_2 = 1/2$ (TCNE). A minimum in this function is clearly evident with $T_{\text{min}} \approx 290$ K; its effect is seen clearly in the $\chi^{-1}$ curve, which, while fitting Curie-Weiss behavior in the intermediate temperature region of 200 - 300 K with a ferromagnetic $\theta \approx 60$ K, begins to turn over above room temperature. The data between 300 and 350 K do not fit Curie-Weiss behavior but do indicate that the true $\theta$ of $[\text{MnTPP}][\text{TCNE}]$ is large and negative, corresponding to the strong AF intrachain coupling.

### 4.2.2 ZFC and FC $M(T)$

The temperature dependence of the ZFC molar magnetization of $[\text{MnTPP}]^{2+}[\text{TCNE}]^{-2}\text{PhMe}$ for different applied fields is shown in Fig. 38. The lowest temperature state is demagnetized ($M$ is near zero at 5 K). The magnetization goes through a broad
Figure 37: $\chi T$ product (left axis) and inverse molar susceptibility $\chi^{-1}$ (right axis) of $[\text{MnTPP}]^{+}[\text{TCNE}]^{-}\cdot2\text{PhMe}$ at $H = 1000$ Oe. Due to the presence of a minimum in $\chi T$ at a high temperature ($T_{\text{min}} \approx 290$ K), Curie-Weiss behavior is not yet attained even above room temperature. Data taken on fine powder sample.
maximum centered between 8 and 11 K depending on field. As $T$ increases above 15 K, $M$ drops quickly, adjacent spins. The inset of Fig. 38 shows FC and ZFC magnetization data at two fields. While the ZFC curves are only obtained on warming, the FC magnetization, which lies above the ZFC magnetization at low temperatures, is reversible. The point where the FC and ZFC data merge is taken as the irreversibility temperature $T_f(H)$.

Isothermal magnetization data were recorded in a ZFC state (initial curves) for several temperatures $1.8 \leq T \leq 35$ K for the different preparations of [MnTPP][TCNE] (Figs. 39 and 40). the $M(H)$ behavior is similar for both preparations. The saturation magnetizations ($H > 4$ T) are $M_s \approx 17000$ emu Oe mol$^{-1}$ for both fine and needle powders. This value is consistent with the expected value ($M_s = 16755$ emu Oe mol$^{-1}$) for a ferrimagnet of net spin 3/2 per repeat unit. The 'S'-shaped approach to saturation occurs at lower fields as $T$ increases from 1.8 K.

4.3 Dynamic Susceptibility of [MnTPP][TCNE]

The a.c. susceptibility of both fine and needle-like powder samples of [MnTPP][TCNE] was measured via the mutual inductance technique with a LakeShore 7225 AC Susceptometer/ DC Magnetometer in the ranges $4 \leq T \leq 50$ K and $0 \leq H_{dc} \leq 1$ T. A d.c. bias current was applied to the primary coil for low-field measurements ($H_{dc} \leq 20$ Oe); larger fields were obtained with the main magnet. The real and imaginary components of the linear susceptibility were recorded for a.c. fields $0.1 \leq H_{ac} \leq 10$ Oe and a range of frequencies ($5$ Hz $\leq f \leq 40$ kHz). The dominant source of uncertainty in determining the magnitude of the molar susceptibilities was the sample mass, estimated to be accurate to within 0.1 mg.
Figure 38: Temperature dependence of zero-field cooled (ZFC) magnetization at various small applied fields. Inset: FC vs. ZFC magnetization at 50 and 125 Oe. Data taken on needle-like powder sample.
Figure 39: Zero-field cooled (initial) isothermal d.c. magnetization. Data taken on fine powder sample.
Figure 40: Zero-field cooled (initial) isothermal d.c. magnetization. (a) $2 \leq T \leq 7$ K, (b) $9 \leq T \leq 35$ K. Data taken on needle-like powder sample.
The results of zero-field, finite-field, and harmonic susceptibilities are presented in the next three sections. These results are best interpreted as part of the whole of magnetic data on [MnTPP][TCNE], and are therefore analyzed later in the Discussion.

4.3.1 Zero Field $\chi(T)$ Data

The zero d.c. field susceptibility data are presented in Figs. 41 ($H_{ac} = 1.0$ Oe) and 42 ($H_{ac} = 0.1$ Oe). The real $\chi'$ and imaginary $\chi''$ parts of $\chi_{ac}$ were recorded on warming from a ZFC state for $4 \leq T \leq 30$ K. At each temperature, the a.c. field was applied in a sequence of increasing frequencies ($5$ Hz $\leq f \leq 40$ kHz). For the small a.c. amplitude case ($H_{ac} = 0.1$ Oe), a low signal-to-noise ratio was obtained at certain frequencies. A limited frequency range ($20$ Hz $\leq f \leq 1$ kHz) is included in Fig. 42 to maximize the clarity of the dependence of $X_{ac}$ on $f$. The temperature dependence of the real part $\chi'$ becomes strongly frequency dependent below $\sim 14$ K. In addition, a distinct shoulder appears in $\chi'$ at lower temperatures. This feature is isolated in the imaginary part $\chi''$ as a separate peak, slightly narrower than the higher temperature maximum. The “double-peak” structure in these data is discussed below. In the figures, the $\chi''$ data for different frequencies are shifted vertically for clarity.

Variation with $H_{dc}$

Data were also recorded at finite d.c. bias fields $H_{dc} = 10, 100, 1000$ and $10000$ Oe. Data for $H_{dc} = 100$ Oe and $H_{dc} = 1000$ Oe are shown in Figs. 43 and 44, respectively. The out-of-phase component is anomalously large at $f = 10$ kHz, the size increasing with external field. (In Fig. 44, the 10 kHz data is scaled by 1/10 for clarity). At $H_{dc} = 1000$ Oe, the higher-temperature peak in $\chi'$ is enhanced with respect to the
Figure 41: Real ($\chi'$) and imaginary ($\chi''$) parts of the ZFC a.c. susceptibility in zero bias field $H_{dc}$ and excitation field $H_{ac} = 1.0$ Oe. $\chi''$ data are shifted upward for clarity; high temperature values show the approximate baseline for each curve.
Figure 42: Real ($\chi'$) and imaginary ($\chi''$) parts of the ZFC a.c. susceptibility in zero bias field $H_{dc}$ and excitation field $H_{ac} = 0.1$ Oe. $\chi''$ data are shifted upward for clarity; high temperature values show the approximate baseline for each curve.
lower-temperature peak (cf. Figs. 41 and 43), with very little dependence of the magnitude or peak position on $f$.

The dependence of $\chi$ on $H_{dc}$ at one frequency $f = 1000$ Hz is illustrated in Fig. 45. The qualitative effect of $H_{dc}$ is to enhance the susceptibility $\chi'$ at low applied field, then suppress $\chi'$ as the field increases, following the slope of $M(H)$. The d.c. bias field also suppresses the magnitude of the higher temperature peak in $\chi''$ relative to that of the lower temperature peak.

### 4.3.2 Harmonic Susceptibilities

Harmonics of $\chi_{ac}$ were measured by recording the induced coil voltages at integer multiple frequencies of the fundamental $f$. Setting the lock-in amplifier to record the $n$th harmonic presupposes that the system has been phased at frequencies $f$ and $nf$. For instance, to measure the 2nd through 5th harmonics of $f = 125$ Hz, the phase angle for each of the frequencies 125, 250, 375, 500, and 625 Hz must be set so that in the absence of sample, $\chi'' = 0$. Since the signal decreases as $n$ increases, larger a.c. fields are typically used to measure harmonic susceptibilities. The 1st through 5th harmonics of $f = 125$ Hz at $H_{ac} = 5$ Oe are shown in Figs. 46 and 47. For clarity, only the magnitudes $|\chi_n| = [(\chi')^2 + (\chi'')^2]^{1/2}$ of the 2nd through 5th harmonics are shown. At $H_{dc} = 5$ Oe, a sharp peak is observed in both $\chi_2$ and $\chi_3$ between 13 and 14 K. Any lower temperature peak is buried in noise at this field. The fourth $\chi_4$ and fifth $\chi_5$ harmonics are extremely small. No structure is seen in $\chi_4$, but $\chi_5$ exhibits a maximum in the region of 13 - 14 K.

The signal-to-noise ratio is enhanced at $H_{ac} = 10$ Oe. The second and third harmonics (Fig. 48) exhibit the same sharp peak seen at 5 Oe. Additionally, there
Figure 43: Real ($\chi'$) and imaginary ($\chi''$) parts of the ZFC a.c. susceptibility in bias field $H_{dc} = 100$ Oe and excitation field $H_{ac} = 1.0$ Oe.
Figure 44: Real ($\chi'$) and imaginary ($\chi''$) parts of the ZFC a.c. susceptibility in bias field $H_{dc} = 1000$ Oe and excitation field $H_{ac} = 1.0$ Oe. $f = 10$ kHz data scaled by 1/10 for clarity.
Figure 45: Real ($\chi'$) and imaginary ($\chi''$) parts of the ZFC a.c. susceptibility at $f = 1000$ Hz and excitation field $H_{ac} = 1.0$ Oe for different d.c. fields.
is a clear maximum in $\chi_3$ centered at $\sim 8$ K. No obvious feature exists in $\chi_2$ in this range.

A second preparation of [MnTPP][TCNE], also possessing the needle-like external morphology, was also measured. Although the synthesis of this second preparation was nearly identical to the previous one, possibly differing only in the amounts of starting materials, variations in its a.c. susceptibility were observed. The linear susceptibilities $\chi'$ and $\chi''$, and harmonics $|\chi_2|$ and $|\chi_3|$, of this preparation are shown in Fig. 49. The dependence on $T$ similar in that there are two peaks, but the lower peak is now enhanced in magnitude with respect to the higher-temperature peak. The 13 - 14 K peak occurs in $\chi_2$ and $\chi_3$ as before. As per the linear $\chi$ data, the lower-temperature maximum in $\chi_3$ at $\sim 8$ K is now greatly enhanced. At the same time, there is no similarly enhanced feature in $\chi_2$ at $\sim 8$ K, given the noise baseline of the entire $\chi_2$ curve. A small anomaly in $\chi_2$ may be present, but invisible due to noise and/or data density.

4.4 Specific Heat of [MnTPP][TCNE]

The zero-field specific heat $C_p$ of [MnTPP][TCNE] was measured in the quasadiabatic calorimeter described above. The sample was a pressed pellet from fine powder of mass $m \approx 137$ mg. The temperature range of measurement was limited to $6 \leq T \leq 27$ K. Due to an unresolved heat leak, the lowest bath temperature during drift runs was $T_0 = 5.1$ K. As the sample temperature relaxed below 6 K, an extremely slow temperature decay component dominated the drift. This slow component was unrelated to the sample specific heat, as it occurred in the absence of the sample as well. It is speculated that a poor thermal contact evolved below $\sim 6$ K, changing the link time constant. However, the obvious suspect – the critical temperature of a
Figure 46: Real ($\chi'$) and imaginary ($\chi''$) parts of the ZFC a.c. susceptibility, and magnitudes of 2nd $\chi_2$ and 3rd $\chi_3$ harmonics, at fundamental frequency $f = 125$ Hz in zero bias field $H_{dc}$ and excitation field $H_{ac} = 5$ Oe.
Figure 47: Real ($\chi'$) and imaginary ($\chi''$) parts of the ZFC a.c. susceptibility, and magnitudes of 4th $\chi_4$ and 5th $\chi_5$ harmonics, at fundamental frequency $f = 125$ Hz in zero bias field $H_{dc}$ and excitation field $H_{ac} = 5$ Oe.
Figure 48: Real ($\chi'$) and imaginary ($\chi''$) parts of the ZFC a.c. susceptibility, and magnitudes of 2nd $\chi_2$ and 3rd $\chi_3$ harmonics, at fundamental frequency $f = 125$ Hz in zero bias field $H_{dc}$ and excitation field $H_{ac} = 10$ Oe.
Figure 49: Real ($\chi'$) and imaginary ($\chi''$) parts of the ZFC a.c. susceptibility, and magnitudes of 2nd $\chi_2$ and 3rd $\chi_3$ harmonics, at fundamental frequency $f = 125$ Hz in zero bias field $H_{dc}$ and excitation field $H_{ac} = 10$ Oe. Data taken on second preparation of needle-like powder.
superconducting metal or alloy (below which the thermal conductivity is negligible) was not identified. All solder joints were made with PbSn or Indalloy, neither of which become superconducting in this range.\(^1\) Above 27 K, thermal noise increased quickly (as can be seen in the data), precluding reasonable statistical analysis on the same footing with the lower temperature data.

The \(C_p\) data for two sets of averaged \(T(t)\) drifts (\(T_0 = 6 \leq T \leq 16\) K and \(T_0 = 11 \leq T \leq 32\) K) are merged into a single plot in Fig. 50. Data for \(4.5 \leq T \leq 6\) K were recorded with adiabatic pulsing. There is no obvious anomaly (magnetic or other) over the full range of measurement. The data between 10 and 20 K appear very linear. Below \(\sim 10\) K, deviation from linearity becomes pronounced, and \(C_p\) has upward curvature (\(C_p \sim \text{superlinear power law}\)).

It is standard practice to plot \(C_p/T\) vs. various powers of \(T\) to elucidate the possible additive contributions from various processes, such as lattice, electronic, magnetic, etc. Graphs of \(C_p/T\) vs. \(T^2\) and \(C_p/T\) vs. \(T^{1/2}\) appear in Figs. 51 and 52, respectively. The parameters derived from these plots are analyzed in the Discussion below.

4.5 Discussion

Taken together, the data for [MnTPP][TCNE] differ significantly from the results expected of a traditional bulk 3D magnet. The differences reflect the significance of dimensionality and disorder for the magnetic behavior, and may be representative of a broad class of molecule-based magnets with donor-acceptor chain structures. In this section, different aspects of the magnetic behavior of [MnTPP][TCNE] are

\(^{1}\)The possibility of pure lead (\(T_c = 7\) K) is unlikely.
Figure 50: Zero-field specific heat $C_p(T)$ vs. $T$ of [MnTPP][TCNE], as measured with the quasiadiabatic drift technique.
Figure 51: Zero-field specific heat $C_p/T$ vs. $T^2$ of [MnTPP][TCNE].
Scaled Specific Heat [MnTPP][TCNE] 2PhMe

Figure 52: Zero-field specific heat $C_p/T$ vs. $T^{1/2}$ of [MnTPP][TCNE].
discussed, leading to the eventual emergence of a general model of quasi-1D donor-acceptor ferrimagnets. In this model, highly anisotropic clusters, "blocked" both internally (SPM) by dipolar barriers, and externally (interacting SG) by exchange and/or dipolar frustration, dominate the low-temperature magnetic response.

The discussion follows a logical progression from basic to more complex questions beginning posed concerning the magnetic state of [MnTPP][TCNE]. The first question — "Is the one dimensional character reflected at high temperatures, where interchain interactions should be small?" — is posed in light of the great current theoretical interest in 1D magnetic chains. The minimum in $\chi T$ is discussed in terms of the theories of Seiden, Drillon, Curély, Coronado, et al. for ferrimagnetic chains.

Second, the question "Is there a real phase transition to long-range order?" is discussed. The answer is a definite yes, however the nature of the build up of correlations above $T_c$ and the type of magnetic order below $T_c$ are nonconventional, reflecting the large anisotropy in magnetic interactions. The transition to long range order is analyzed with a static scaling analysis of the $M(T, H)$ and $\chi_{ac}$ data.

Next, the question "What is the origin of the long-range magnetic order?" is posed. It is shown that for the type of structure and bonding involved in [MnTPP]-[TCNE], direct exchange and superexchange between spins on neighboring chains must be extremely weak. Interchain dipolar interactions are considered as the dominant origin of interchain coupling. It is shown that only particular ferrimagnetic structures, of which [MnTPP][TCNE] is an example, are capable of stabilizing a state with net magnetic moment at low temperatures. However, this state is very sensitive to variations in canting angle, possibly leading to a spectrum of metastable states with a mixture of ferromagnetic and antiferromagnetic long-range orderings.
The low-temperature data are discussed next. It has been previously established [108] that [MnTPP][TCNE] displays spin-glass-like behavior at low temperatures $T < 8$ K. The questions of reentrance—"Is [MnTPP][TCNE] a reentrant spin glass?" and "What kind of spin state exists in [MnTPP][TCNE] at low temperatures?" are asked. Analysis of the frequency dependence and harmonics of the a.c. susceptibility in particular suggests the coexistence of spin glass and ferrimagnetic order. The data are compared to the expectations for an ensemble of interacting superparamagnetic clusters (ISPC) which exist over a large range of length scales. The possible origin of the spin-glass-like behavior is explored. The necessary ingredients of disorder and frustration may arise from the presence of "major" and "minor" [TCNE] orientations and partial geometric dipolar frustration.

4.5.1 Quasi-1D Magnetism

The minimum in the high temperature $\chi T$ of [MnTPP][TCNE] is consistent with predictions of current theories of 1D ferrimagnetic chains [123, 124, 125, 53, 126]. A minimum is expected due to the following physical argument. At the highest temperatures, $\chi T$ approaches the Curie constant $C \approx S(S + 1)/2$ for $g = 2$. Deviations from $\chi T = C$ arise from interactions. As $T$ decreases, the first interaction to come in is the strong antiferromagnetic coupling between nearest neighbor (NN) spins, such as the $S_1 = 2$ and $S_2 = 1/2$ in [MnTPP][TCNE]. As discussed in the Introduction, antiferromagnetic correlations cause $\chi T$ to decrease (curve downward) as $T$ drops—dimer formation reduces the moment. At lower temperatures, long range correlations tend to bring an increasing number of moments into coherent behavior, giving rise to quasi rigid and independent magnetic blocks of increasing amplitude [53]. The minimum represents a competition between short and long range correlations, which are
opposed in ferrimagnetic chains. The position $T_{\text{min}}$ of the minimum should increase with nearest-neighbor exchange $J$. The existence of a minimum relies on an initially slow build-up of long range correlations; For $d > 1$, correlations build up much more quickly and a minimum is not observed.

**Classical-Classical Chains**

The first, and simplest approach to the susceptibility of an isolated ferrimagnetic chain with $S_2 \neq S_1$ was given by Drillon, et al. [126], motivated by experiments performed on Mn-Ni chains. Treating both spins as classical vectors, the zero-field susceptibility per spin pair could be written as

$$\chi_0 T = \frac{N_0 \mu_B^2}{6k_B} \left( \frac{1-p}{1+p} g^2 + \frac{1+p}{1-p} \delta g^2 \right),$$

(4.1)

where

$$g = \tilde{g}_1 + \tilde{g}_2, \quad \delta g = \tilde{g}_1 - \tilde{g}_2,$$

(4.2)

$$\tilde{g}_i = g_i(S_i(S_i+1))^{1/2},$$

(4.3)

$$p = \coth \gamma - \gamma^{-1}, \quad \gamma = \beta \tilde{J},$$

(4.4)

$$\tilde{J} = J[S_1(S_1+1)S_2(S_2+1)]^{1/2}. $$

(4.5)

It is cautioned that in the references, $J > 0$ is typically taken as an antiferromagnetic parameter. Literature formulae have been adapted to follow the more standard sign convention ($J > 0$ is ferromagnetic) used in this thesis. The form (4.1) exhibits a minimum for $J < 0$ and $S_2 \neq S_1$, but cannot be expected to apply directly to real systems with either spin being less than about $S = 5/2$. 
Quantum-Classical Chains - Seiden Model

To account for several cases of experimental interest where one spin is large and the other small, such as in CuMn chains, Seiden proposed [123] a quasi-classical model for \((S,s = 1/2)\) chains where \(S\) is classical. By explicitly evaluating the three possibly types of pair correlations \((S \sim S, S \sim s, \text{and } s \sim s)\), the zero-field susceptibility per spin was found to be

\[
\chi_0 T = \frac{N_0 \mu_B^2}{3k_B} \left[ g_S^2 S^2 \left( \frac{S + 1}{S} + 2 \frac{\delta}{1 - \delta} \right) - \frac{4g_S g_s \Lambda S s}{1 - \delta} + g_s^2 \left( s(s + 1) + \frac{2\Lambda^2 s^2}{1 - \delta} \right) \right],
\]

where

\[
\delta = a_1/3a_0 \quad \Lambda = 2(b_1 + 3b_0)/3a_0, \quad (4.7)
\]

\[
a_0 = 4(\gamma^{-1} \sinh \gamma - \gamma^{-2} \cosh \gamma + \gamma^{-2}), \quad (4.8)
\]

\[
a_1 = 12[(\gamma^{-1} + 12\gamma^{-3}) \sinh \gamma - (5\gamma^{-2} + 12\gamma^{-4}) \cosh \gamma - \gamma^{-2} + 12\gamma^{-4}], \quad (4.9)
\]

\[
b_0 = \gamma^{-1}(\cosh \gamma - 1), \quad (4.10)
\]

\[
b_1 = 3[(\gamma^{-1} + 4\gamma^{-3}) \cosh \gamma - 4\gamma^{-2} \sinh \gamma + \gamma^{-1} - 4\gamma^{-3}]. \quad (4.11)
\]

The quantities \(a_i\) and \(b_i\) are coefficients of the Legendre polynomials used in the expansion of the chain partition function. In this mixed case, the exchange is normalized only by the classical spin: \(\tilde{J} = J[S(S + 1)]^{1/2}\). The equation (4.6) has been successfully used to fit high temperature data on CuMn \((S = 5/2)\) but has gone untested in the quantum-classical "border" case \((S = 2)\).

Pure Quantum Chains - Drillon Model

The fully quantum mechanical treatment of ferrimagnetic chains, essential for low-spin ions, has so far only been accomplished [126] with finite rings of \(n \leq 5\) pairs
(S, s) and extrapolated to n→∞. It is found that the (5/2, 1/2) case coincides with the (∞, 1/2) result within computational accuracy for k_BT/J > 0.5 As S decreases below 5/2, the χT minimum tends to get deeper and move to lower temperatures. Furthermore, for a certain critical ratio of g-values, depending on S, the susceptibility may vanish at some temperature below T_min, in analogy with the compensation seen in some 3D ferrimagnets.

**Effect of Interchain Interactions**

The χT curve for [MnTPP][TCNE] is compared to the quantum-classical and quantum-quantum models in Fig. 53. The χT data extend to 320 K, with a shallow minimum at T_min ≈ 285 K. The quantum-quantum (Drillon model) curve was obtained by digitizing numerical results (for gs = gs = 2) presented in the literature [126], and setting J so that the minima coincide. Based on the numerical result that k_BT_m insensitive/J = 2.1 for the (2, 1/2) case, the intrachain coupling parameter for [MnTPP]-[TCNE] is J/k_B ≈ −135 K. However, this result assumes isotropic g-values both equal to 2. While this is expected of the organic spin unit [TCNE], the [MnTPP] spin may have g ≠ 2. Although the shape of the experimental data follow the quantum theory, the data are above the theoretical curve at high temperatures. The difference may arise from interchain coupling and/or a mixture of ferromagnetic and antiferromagnetic bonds, as well as variations in gs.

The quantum-classical model of Seiden et al. has three parameters (J, gs, and gs). Some trial fits for gs = 2 and minima at T_min, labeled “QC” for quantum-classical, are presented in Fig. 53. An expanded view of the systematic variation of gs from 0.5 to 3, keeping the minimum on T_min, is shown in Fig. 54. As the model curves have a minimum which cannot dip any lower than that of the curve for gs ≈ 0.4, where
the "minimum passes through a minimum," it is concluded that Seiden's model with $g_s = 2$ cannot account for observation in [MnTPP][TCNE]. Variation of $g_s$ is a possibility, but no obvious improvement results from small deviations away from 2 for any $g_s$. It is noted that the temperature of the minimum depends on $g_s$ and $g_s$ only through their ratio, for a given $J$. In the curve labeled $f(T - 50)$, the curve for a set of parameters which do not produce a minimum at $T_{min}$, but do reproduce the magnitude of the minimum, are shown. The actual position of this curve is 50 K lower in temperature; shifting the minimum to $T_{min}$ is an ad hoc accounting for 3D long-range ordering. The curve is observed to follow the data fairly well, indicating that some extension of Seiden's model may be able to account for the initial effects of interchain interactions.2

[MnTPP][TCNE] represents a new testing ground for these 1D models, in that (1) Mn has III oxidation, with spin 2, (2) [TCNE] is a small, organic, spin-carrying unit, rather than a second metal (d-based) site, and (3) $|J|$ and $T_{min}$ are much larger than previously known examples, and (4) the quantifiable disorder (in the [TCNE] orientation) may lead to suppression of even short-range effective moments through canting.

4.5.2 Critical Analysis and “Soft” Transition

Is there a transition to long-range magnetic order at low temperature? This question can be answered with a static scaling analysis of the d.c and a.c. data. However, it may be appropriate to comment first on the specific heat, which shows no anomaly.

2One first attempt, replacing (4.6) by an effective form with $\chi_0 \sim (T - \theta)^{-1}$, did not lead to improvements immediately significant enough to justify the additional parameter $\theta$ or the artificial merging with the Curie-Weiss law, which cannot rigorously be expected to apply near a minimum.
\(\chi T\) Minimum and Theoretical Models

(2,1/2) Ferrimagnetic Chain

Figure 53: \(\chi T\) minimum in [MnTPP][TCNE] and theoretical model fits. The quantum-quantum (2,1/2) ferrimagnetic model of Drillon et al. is shown for both \(g\)-values equal to 2. The quantum-classical (QC) curves correspond to (??) with varying \(g_s\), by \(J\) fixed by positioning the minimum at \(T_{\text{min}}\).
Figure 54: $\chi T$ minimum in [MnTPP][TCNE] and theoretical model fits. The quantum-quantum (2,1/2) ferrimagnetic model of Drillon et al. is shown for both $g$-values equal to 2. In the quantum-classical curves, $g_S$ is systematically varied to show the dependence of the minimum on $g_S$. 
Two methods may be used to extract the magnetic specific heat – subtraction of $C_p$ for a diamagnetic or paramagnetic isomorph, or functional modeling. The former is the most reliable – no assumptions other than that of equivalent states phonon states need be made. In the present case where a magnetic anomaly is not already visible above the lattice background, a very close structural match is desired. No such compound is available presently. The latter method presupposes a knowledge of the functional form of the various contributions to $C_p$ and uses extrapolation of this form through the critical region. The functional modeling of $C_p$ of [MnTPP][TCNE] was done with $C_p(T) = \beta T + \delta T^{3/2}$ and $C_p(T) = \beta T^3 + \delta T^{3/2}$, corresponding to one- and three- dimensional lattice vibrations, respectively, corrected by a 3D spin wave contribution. These fits are discussed further below; it suffices here to say that no obvious excess in the form of a peak was observed within experimental error (~ 5%) below 20 K. This null result would lead one to speculate that there is either no true continuous phase transition in [MnTPP][TCNE], or that the underlying 3D critical region is very narrow.

The results of the static scaling analysis are presented in Fig. 55. The Kouvel-Fisher [127] scaling function $X_{KF}(T) = \chi'(d\chi'/dT)^{-1}$ (Fig. 55a, left axis), obtained from the real zero-field a.c. susceptibility $\chi'$, has the linear (scaling) form $X_{KF}(T) = (T - T_c)/\gamma$ only above ~ 16 K. The critical temperature $T_c \approx 12.5$ K and average susceptibility exponent $\gamma \approx 1.6$ are obtained from the $T$-intercept and inverse slope of $X_{KF}$, respectively. The fact that $\chi'$ does not obey a power law in $|t|$ within ~ 3 K above $T_c$ may reflect the presence of strong spatial anisotropy ($J_{\text{inter}}/J_{\text{intra}} \sim 10^{-2}$) – the build-up of long-range intrachain correlations is particularly sensitive to defects and disorder, possibly leading to the formation of quasi-1D “domains” well above $T_c$. Consequently, the “core” (3D) critical region is not probed in this measurement and

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3 An example of a desired isomorph would be [ZnTPP][TCNE].
the observed $\gamma$ is expected [127] to be enhanced over its true value. The effective exponent $\gamma(T) = (T - T_c)/X_{KF}$ (Fig. 55, right axis) elucidates the presence of a region ($T < 16$ K) where $\chi'$ does not scale, below an unusually wide range where $\gamma(T)$ is fairly constant, falling off slowly as $T$ increases.

The value $\gamma \approx 1.6$ is used to restrict the parameter space $(\beta, \delta)$ in the scaling of $M(T, H)$ (Fig. 55b) through the Griffiths-Rushbrooke relation [128] $\gamma = \beta(\delta - 1)$. The trial critical temperature $T_c^{tr}$ for which the $M(T)$ data appear to coalesce for the three smallest applied fields (over a limited reduced temperature range above $T_c^{tr}$) is independently found to be $T_c \sim 13 - 13.5$ K. It is estimated that $\beta \sim 0.5$ and $\delta \sim 4.2$, though the accuracy and precision are limited by the relative insensitivity of the analysis to the choice of $\beta$ and $\delta$, and that the (possibly enhanced) $\gamma$ is obtained from data above 16 K. The $T_c$ value obtained is significantly lower than that obtained by extrapolating the maximum slope [118, 120, 108] of the low-field $M(T)$ curve to $M = 0$, which gives $T_c \approx 18$ K.

Direct analysis of the isothermal $M(H)$ data near $H = 0$ for a range of temperatures above and below $T_c$ may be used as an independent check on the extracted $T_c$. The Arrott plot $M^2$ vs. $H/M$ is shown on a log-log scale in Fig. 56. In such a plot, the low-field data are supposed to form a set of straight lines passing through the origin at $T_c$. On a log scale, the increasing magnetization at the lowest field as $T \rightarrow T_c^+$ is evident in the slope of the bottom ends of the data curves. The temperature just before the point where the low-field slope turns back to negative values corresponds to $T_c$. From the figure, then, $T_c \approx 13$ K, in accord with the scaling analysis. Attempts to directly scale $M(H)$ with the Arrott-Noakes form suffered from a lack of the data over several decades of vanishingly small fields needed for such an analysis.

The experimental observation of a "slow" transition to long-range ferrimagnetic
Figure 55: (a) Kouvel-Fisher scaling function $X_{KF} = -\chi'(d\chi'/dT)^{-1}$ (left axis) and temperature-dependent effective critical exponent $\gamma(T) = (T - T_c)/X_{KF}$ (right axis); (b) Scaling of d.c. magnetization $M(T, H)$ above $T_c^{tr}$ for $\beta = 0.5$ and $\delta = 4.2$, where $h = H/T$. See text for details.
Figure 56: Log-log Arrott Plot of $M(H)$ of [MnTPP][TCNE]. The low-field data are at the bottom ends of the curves for each temperature.
order in \([\text{MnTPP}]^{2+}:[\text{TCNE}]^{-}\cdot\text{2PhMe}\) reflects the quasi-one-dimensional (1D) magnetism in this system. In chain-like magnets, significant long-range longitudinal spin-spin correlations build up well before 3D order is established. For instance, specific heat studies reveal that a very high fraction of the magnetic entropy of quasi-1D magnets lies above \(T_c\) [49]. It is also noted that below \(H \sim 100\) Oe, the maximum-slope intercept definition of the critical temperature yields \(T_c \approx 18\) K, independent of field, while above 100 Oe, the \(T_c(H)\) intercept of \(M(T)\) increases rapidly with \(H\). This behavior is similar to that of quasi-one dimensional Heisenberg antiferromagnets with large anisotropy [129].

### 4.5.3 Origin of Long-Range Order

The origin of long-range order is of central interest to the design and understanding of molecule-based magnets. Because of the rather large spin-spin distances that can be involved in molecular systems, as well as the presence of p-based moments in unique chemical configurations, the sign of the magnetic coupling may be a delicate geometric balance between direct exchange, superexchange (CI), and dipole forces. In quasi-1D systems this may be especially true. Quasi-1D magnets eventually order at some low temperature when interactions from neighboring chains begin to become important. On a crude level, as a spin “sees” things, interchain distances effectively reduce as \(T\) diminishes. This increase in “proximity,” actually just thermal quietude, has a similar effect as increasing the magnitude of the spin-spin coupling.
Dipole Interactions in FI Chains

Many quasi-1D magnets possess fairly large interchain distances ($d > 6 \text{ Å}$), with correspondingly weak exchange pathways between interchain spin pairs. As was mentioned in the Introduction, superexchange relies on the spreading of a spatial wavefunction onto a ligand site. The combined overlap and ligand wavefunction is then the starting point for determining the overlap with the second-neighbor ligand, etc. A simple example of a method which determines the sign of an effective superexchange through a p-orbital-based path is Ovchinikov's “star”-rule [130]. Essentially, unambiguous pathways through alternant ligand structures leads to the sign of exchange being $(-1)^N$, where $N$ is the number of bonds in the path. Thus, one simply hops along connecting atoms, typically carbons and nitrogens, marking “up” and “down” alternately until one arrives at the second spin center. Such is the scheme for creating high-spin oligomers and eventually, one hopes, high-$T_c$ magnets, through the meta-carbenes [131].

If the superexchange path is very long, or is either not well-defined or has ambiguities, the exchange coupling is drastically reduced. All three detractions exist in [MnTPP][TCNE]: the interchain distances are on the order of 10 Å, and there is no direct bond between phenyl rings (Mn-Mn pathway), nor between phenyl rings and either form of [TCNE], (Mn-TCNE pathway). If the spatial overlap between ligands of closest approach is taken to be an antiferromagnetic bond, the eventual effect between interchain spin neighbors is ambiguous, as the overlap angles permit even- and odd-numbered paths to be defined [119]. Furthermore, as will be seen, the variation of $\theta$ and $T_c$ is not extremely sensitive to the substitution of different interchain ligands on the phenyl rings, as would be the case if the interchain interactions were mediated by an exchange of the type discussed in the Introduction. That is,
para and ortho substituted ligands should decrease \( \theta \) significantly if the interchain interaction is primarily due to wavefunction overlap. (This statement has a strong caveat - it holds strictly when the substitutions have only the effect of increasing the lengths of proposed exchange paths. Other factors such as the degree of disorder and the molecular chain registry are potentially of equal importance.)

One is led, ironically (considering the dismissal at the beginning of Sec. 1.3), to the dipole interaction between chains as a real possibility to explain long-range order. In \([\text{MnTPP}][\text{TCNE}]\), the net spins of neighboring chains, presumably limited in length by disorder, may act coherently to couple with energies of order of a few K, even at 10 Å distance. In a simple calculation, a 1 K dipole potential at 10 Å would require the participation of net spins of size \( S \sim 20 - 30 \), neglecting next-nearest neighbor chains. In \([\text{MnTPP}][\text{TCNE}]\), this requirement corresponds to 10 to 20 unit cells along the chain. But wait a minute – doesn’t the dipole interaction favor a bulk state with low spin? It is responsible for the formation of domains, is it not?

The answer to the latter is yes – at mesoscopic length scales a system with bulk (ferro or ferri) magnetic order will tend to break into domains leading to zero net moment in the ZFC state. Of concern here is the formation of the individual domains. The case of ferrimagnetic chains is special. For a sufficiently large difference between spin values \((S_1 - S_2)\), there is always some inter- to intra-chain lattice distance ratio above which a net moment is favored in a chain pair. To see this, consider the model of ferrimagnetic chains depicted in Fig. 57. The model is consistent with the structure of \([\text{MnTPP}][\text{TCNE}]\) and is therefore labelled accordingly. Taking the \([\text{MnTPP}]-[\text{TCNE}]\) intrachain separation as \( a \), and the interchain distance as \( d \), the lattice can be treated, approximately, as fcc with a basis of 2 spins and intrachain repeat units of size \( 2a \) by \( d \). The dipole potential between a pair of Ising spins \((S_\alpha, S_\beta)\) separated
by $r$ is

$$V_{\alpha \beta} = \frac{S_\alpha S_\beta}{r_{\alpha \beta}^3}(1 - 3 \cos \theta_{\alpha \beta}), \quad (4.12)$$

where $\theta_{\alpha \beta}$ is the angle between $S_\alpha$ and $r_{\alpha \beta}$, if $S_\alpha$ is defined to point along $\hat{z}$. As Ising spin alignment is assumed, only coaxial, or longitudinal ($\theta = 0$) and transverse ($\theta = \pi/2$) configurations are considered:

$$V_{\alpha \beta}^L(\theta = 0) = -2 \frac{S_\alpha S_\beta}{r^3} \quad (4.13)$$

$$V_{\alpha \beta}^T(\theta = \pi/2) = \frac{S_\alpha S_\beta}{r^3} \quad (4.14)$$

**Isolated Chain: Longitudinal vs. Transverse** It is easily seen that the dipole interaction favors spins within one ferrimagnetic chain to align transverse to the chain axis. Writing $r = ja$ for spins separated by $j$ units along the chain, the total energy of an isolated F1 chain of length $n$ is

$$U_n = \sum_{j=1,3,5,...}^{n-1} (n - j)V_{12}(j) + \frac{1}{2} \sum_{j=2,4,6,...}^{n} (n - j)(1 + \gamma^2)V_{11}(j), \quad (4.15)$$

where $\gamma = S_2/S_1$. The factor $(n-j)$ is the number of ways of pairing spins separated by $j$ in a chain of $n$ spins. This sum was computed for $V = V_{\alpha \beta}^L$ and $V = V_{\alpha \beta}^T$. The results for $S_2 = -1/2$ are compared in Fig. 58. The preference for transverse alignment is further stabilized by increasing $S_1$.

The actual orientation of the spins depends of course on the particular balance between the dipolar field and the single-ion anisotropy for the system in question. The presence of an anisotropy of the form $-DS_\gamma^2$ favors longitudinal alignment for $D > 0$ and transverse alignment for $D < 0$. In [MnTPP][TCNE], the single-ion anisotropy of the Mn spin is likely positive and on the order of a few K [132], potentially putting it in direct competition with the dipole interaction. A compromise
Figure 57: Diagram of Ferrimagnetic Chains in [MnTPP][TCNE]
picture for \([\text{MnTPP}][\text{TCNE}]\) would then be a \textit{canted} spin system with longitudinal orientation dominating in smaller clusters and transverse orientation dominating in larger clusters.

**Pair of Chains: Coplanar vs. Normal**  The dipole potential for a pair of chains whose Ising spins are oriented perpendicular to the chain axes is now computed. Two geometric situations arise due to the presence of the second chain. When the transverse spins lie normal to the plane made by the chain pair, any two spins on different chains are also transverse to each other, and so the appropriate pair potential is \(V_{\alpha\beta}^{T}(\theta = 0)\). When the transverse spins lie in the plane made by the chain pair, the relative orientation of two spins ranges from longitudinal for nearest (interchain) neighbors to asymptotically transverse for increasingly separated pairs. Thus, the dipole interaction between two spins on neighboring chains, separated by interchain distance \(d\) and intrachain distance \(j\alpha\), is given by

\[
V_{\alpha\beta}^{\perp}(\mu, j) = V_{\alpha\beta}^{T}(\mu, j) = \frac{S_{\alpha}S_{\beta}}{d^{3}} \frac{1}{(1 + (j\mu)^{2})^{3/2}} \quad \text{normal} \tag{4.16}
\]

\[
V_{\alpha\beta}^{\parallel}(\mu, j) = \frac{S_{\alpha}S_{\beta}}{d^{3}} \frac{(j\mu)^{2} - 2}{(1 + (j\mu)^{2})^{5/2}} \quad \text{coplanar}, \tag{4.17}
\]

where the lattice ratio \(\mu = \alpha/d\) is introduced for convenience.

For neighboring chain interactions, the total energy sums are slightly rearranged because now even \(-j\) corresponds to different spins. The coplanar (\(\parallel\)) or normal (\(\perp\)) sums are

\[
U_{n}^{\parallel,\perp} = nV_{12}^{\parallel,\perp}(\mu, 0) + \sum_{j=1,3,5,...}^{n-1} (1 + \gamma^{2})(n - j)V_{11}^{\parallel,\perp}(\mu, j) + \sum_{j=2,4,6,...}^{n} 2(n - j)V_{12}^{\parallel,\perp}(\mu, j) \tag{4.18}
\]

The neighbor-chain ferrimagnetic coplanar dipole interaction energy is computed for the case where spins of the same species on different chains are aligned (the net
Figure 58: Dipole Energy for Single FI Chain
moment state) and shown in Figs. 59, 60, and 61, for \( \mu = 1, 1/2, \) and 1/3, respectively. The physical situation in [MnTPP][TCNE] corresponds most closely to \( \mu = 1/2 \). The stability of a net moment at \( S_1 = 2 \) in this case is clear. What is remarkable is that the situation is much less certain for \( S_1 < 2 \). In this simple model, a plane of antiferromagnetic chains \( (S_1 = 1/2) \) will prefer to align into stripes, so \( U_n > 0 \). Even for \( S_1 = 1 \), though, a minimum of 12 spin pairs is required before a net moment is favored. \( S_1 = 2 \) is the only case (for \( \mu = 1/2 \)) where a net moment is favored at all chain lengths. Further separation of the chains has the expected effect of stabilizing the case of net moment, as the chains begin to look more and more like longitudinal spins as they separate. The other direction, however, is quite interesting. For \( \mu = 1 \), an antiferromagnetic solid is favored. The reason is that if the chains are sufficiently close, the next-nearest interchain neighbors (same spin type) and further neighbors are outside the longitudinal ferromagnetic cone of the dipole interaction, and thus cannot contribute to overcoming the dipole-unfavored nearest neighbor interaction (see Fig. 57). From the form of the dipole energy, the opening angle of this cone is \( \phi = \cos^{-1}(1/3)^{1/2} = 0.955 \text{ rad} = 55 \text{ degrees} \). The critical lattice ratio above which a net moment is not supported for FI chains is therefore bounded from above by \( \mu_c^{\text{max}} = (a/d)_c^{\text{max}} = \tan \cos^{-1}(1/3)^{1/2} = 2^{1/2} \), which is as expected. The reason this is an upper bound is that it only considers the effect of a single spin and the three spins closest to it on the next chain. Further neighbors will tend to further destabilize a net moment because these are all outside the FM cone. That is, the net moment will actually be lost at lower values of \( \mu \) than \( 2^{1/2} \). In the present model, the true critical value is between 1 and 1/2. (The value \( \mu_c \approx 0.7 \) was obtained via bitonic search).

According to the above arguments, a plane of ferrimagnetic chains with coplanar transverse spins will sustain a net moment under certain spin and geometrical conditions due solely to dipole forces. By similar arguments, a plane of ferrimag-
netic chains with normal transverse spins will order as an antiferromagnet (no net moment) below some critical lattice ratio, larger than the $\mu_c$ in the coplanar case. The resulting spin ordering for a 3D collection of chains must then depend sensitively on the relative lattice ratios in both direction transverse to the chain axes. As the intrachain ordering in [MnTPP][TCNE] is likely non-Ising, the lowest energy state of the interchain dipolar interactions is more complex than ferromagnetic planes with antiferromagnetic interplanar coupling. Canting within and out of the ferromagnetic planes can lead to a complicated dipole energy landscape, many metastable minima of which may support a net bulk moment.

4.5.4 Reentrance and the Low Temperature Spin State

Isothermal Magnetization

The low-temperature isothermal magnetization $M(H)$ and the appearance of the "reentrant" transition may be interpreted as resulting from the behavior of interacting, anisotropic superparamagnetic clusters. Superparamagnetism (SPM) describes the behavior of well separated, classical (large $S$) spin clusters which behave paramagnetically at high temperatures, but due to internal shape or dipolar anisotropy energy barriers are "blocked" from undergoing global spin flips below a characteristic temperature $T_b$. SPM leads to broad maxima around $T_b$ in $M(T)$ and $\chi_{ac}$, with the latter following an Arrhenius frequency dependence $\omega = \omega_0 \exp(-E_a/k_B T)$, where $E_a$ is a characteristic anisotropy energy. In contrast, [MnTPP][TCNE] is a magnetically concentrated system, so intercluster interactions are likely very important, and may be responsible for the spin-glass-like behavior.

The 'S'-shaped crossover in $M(H)$ from low-$M$ to saturation occurs in a range
Figure 59: Dipole Energy for FI Chain Pair with $\mu = 1$
Figure 60: Dipole Energy for FI Chain Pair with $\mu = 1/2$
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**Frequency Dependence and Harmonics of \( \chi_{ac} \)**

The appearance of a second, lower temperature peak in \( \chi_{ac} \) is similar to that seen in "reentrant" spin-glass (RSG) alloys [133]. However, the frequency dependence of both lower \( (T_1) \) and upper \( (T_2) \) peak temperatures is quite strong, suggesting that [MnTPP][TCNE] lies somewhere between traditional RSGs and pure SPM. The fractional shifts in peak temperature per decade of frequency are \( (\Delta T_1/T_1)/(\Delta \log \omega) \approx 0.23 \) and \( (\Delta T_2/T_2)/(\Delta \log \omega) \approx 0.14 \). Fits to pure Arrhenius behavior give \( E_{a1}/k_B \approx 112 \) K and \( \omega_01/2\pi \approx 940 \) MHz \( (\tau_01 \approx 10^{-9} \) s) for \( T_1(\omega) \) and \( E_{a2}/k_B \approx 247 \) K and \( \omega_02/2\pi \approx 420 \) GHz \( (\tau_02 \approx 2.4 \times 10^{-12} \) s) for \( T_2(\omega) \). \( (\tau_0 = 2\pi/\omega_0 \) is the characteristic limiting relaxation time for a given frequency prefactor \( \omega_0 \). The peak positions are relatively close to the "typical" blocking temperatures obtained using \( T_b \approx E_a/25k_B \) [56]. The applicability of the model of tranverse spin freezing [133] to [MnTPP][TCNE] is a current direction of investigation.

It should be pointed out in this context that Eiselt et al. [134] have used a model employing interacting superparamagnetic clusters to reproduce the double-peaked susceptibility in very dilute \( (\text{Eu}_x\text{Sr}_{1-x})\text{S} \). In their model, the upper peak arises from ordinary SPM of small Eu clusters blocked by dipolar anisotropy, while the lower
peak is due to mean-field intercluster dipole interactions. Although [MnTPP][TCNE] is not dilute, its large anisotropy and tenuous long-range ferrimagnetism parallels the physics of such interacting SPM clusters, albeit on larger length and energy scales.
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