

## **Chapter 6: Introduction to Molecular Magnetism and Crystal Engineering**

## **6.1 Introduction**

The control of bulk magnetic properties has proven to be extremely difficult (Carlin, 1986; Kahn, 1993; Miller and Epstein, 1994; Turnbull et al., 1996). This is in part due to the many different types of magnetic behaviors that have been characterized. At least fourteen different magnetic behaviors have been identified in solids (Hurd, 1982). These different magnetic behaviors arise from the various spin-spin interactions observed in these materials. The complexity associated with controlling magnetic properties has arisen from difficulties in controlling the spatial arrangement of spin containing units. Here we provide an introduction to bulk magnetic behaviors, describe several strategies for controlling spin-spin organization, and expand on one of these strategies, crystal engineering. Later chapters and appendixes, in this section, provide examples of different magnetic materials that take advantage of the methods discussed here to control spin-spin interactions.

## **6.2 Magnetism**

Magnetic materials play critical roles in our daily lives. Magnetism was first discovered by the ancient Greeks and used by the Chinese to create a “south pointing” compass (Mattis, 1981). Since the invention of the compass, the number of devices that use magnetic components has skyrocketed. A small number of the applications of magnetic materials include frictionless bearings, medical devices, magnetic separators, loudspeakers, microphones, switches, sensors, data storage devices, motors, and generators (Miller and Epstein, 1994). The extensive commercial viability of magnetic materials has driven research in this area.

Traditional magnetic materials are two- and three-dimensional arrays of inorganic atoms, composed of transition metal or lanthanide metal containing spin units. These materials are typically produced at very high temperatures using metallurgical methodologies. In contrast to traditional magnetic materials, molecular magnets are organic or inorganic/organic hybrid materials, comprised of either metal containing spin units or organic radical containing spin units. It has been postulated that these materials will allow for the low temperature synthesis of magnetic materials, materials with better optical properties, the combination of magnetic properties with mechanical, electrical, and/or optical properties, better control over a material's magnetic characteristics, and materials that can be easily processed (Miller and Epstein, 1994).

In order to design materials with interesting bulk magnetic properties it is necessary to understand how bulk magnetism arises in samples. A complete understanding of magnetism has not yet been formulated, however many of the general principles of magnetic behavior are well established. Some of those principles are reported here.

### *6.2.1 Diamagnetism and Paramagnetism (Carlin, 1986; Kahn, 1993)*

On the atomic level there exist two fundamental types of magnetism: diamagnetism and paramagnetism. All of the more complex magnetic behaviors which are observed evolve from these basic magnetic phenomena.

Diamagnetic behavior is characterized by repulsion of a substance out of an applied magnetic field. This behavior arises from the interaction of the applied magnetic field with molecular or atomic orbitals containing paired electrons. With the exception of the hydrogen radical, all atomic or molecular materials exhibit some diamagnetic behavior. This magnetic behavior is temperature independent, and the strength of the interaction is roughly proportional to the molecular weight of the material.

Paramagnetism is characterized by the attraction of a substance into an applied magnetic field. This behavior arises as a result of an interaction between the applied magnetic field and unpaired electrons in atomic or molecular orbitals. Typically, paramagnetic materials contain one or more unpaired electrons, and the strength of paramagnetic interactions are temperature dependant. However, some substances exhibit temperature independent paramagnetism (TIP) that arises as a result of a coupling between the magnetic ground state and non-thermally populated excited states. TIP has been observed for materials with both paramagnetic and diamagnetic ground states, and it is usually associated with electrically conducting materials.

Classically, the term magnetism refers to substances that at the atomic level exhibit temperature dependant paramagnetic behavior and will thus be used in this context. The non-zero spin angular moment associated with an unpaired electron gives rises to a magnetic moment. Upon pairing, electrons within an orbital exhibit opposing magnetic moments, resulting in no net magnetic moment. In general, bulk magnetic properties arise as a result of long-range interactions between unpaired electrons.

### *6.2.2 Cooperative Magnetism*

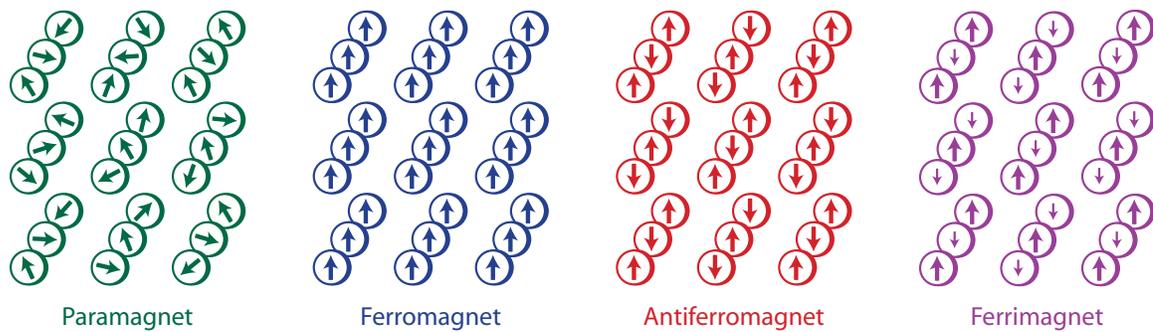
Bulk magnetic behavior arises from interactions between paramagnetic atoms or molecules. These interactions can create materials that are either magnetic or non-magnetic, depending on how adjacent magnetic spins align with each other. Over 14 different possible magnetic interactions have been described in the literature (Hurd, 1982). Several of the important types of magnetic interactions are presented below.

#### *6.2.2.1 Dimensionality*

Although magnetic interactions occur in three dimensions, the type and strength of these interactions can be different in each dimension. This gives rise to magnetic materials with one cooperative interaction type in one dimension and different cooperative interaction types in the other two dimensions. Typically in cases where different magnetic interactions are observed due to dimensionality, the material is characterized by the strongest interaction.

#### *6.2.2.2 Paramagnetism, Antiferromagnetism, Ferromagnetism, and Ferrimagnetism (Carlin, 1986; Kahn, 1993)*

Generally, the bulk magnetic behavior of a material can be described by one of the four major classes of magnetism. The major classes of magnetism are paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism. These classes of magnetic behavior describe how adjacent magnetic moments would interact with each other at absolute zero. The interactions are shown in Figure 6.1 and described below.



**Figure 6.1:** The alignment of magnetic moments at absolute zero for the four principle classes of magnetism. No alignment of adjacent magnetic moments is observed for paramagnets. Ferromagnets exhibit parallel alignment of adjacent magnetic moments. Antiferromagnets exhibit antiparallel of adjacent magnetic moments. Ferrimagnets are composed of two magnetic spins of different strength and exhibit antiparallel alignment.

*Paramagnetism.* In a paramagnetic material each individual electron spin is unaffected by its neighbors. The spins of a paramagnetic material can easily be aligned by an applied magnetic field. However the alignment is weak, and upon removal of the magnetic field the system relaxes back to a random distribution of magnetic moments. True paramagnetic materials are extremely rare, since most materials exhibit one of the other three principle classes of magnetism at very low temperatures.

*Ferromagnetism.* Ferromagnetism is characterized by parallel alignment of adjacent magnetic spins that results in a large net magnetic moment. Ferromagnetic alignment of adjacent magnetic spins is rare since it can only be achieved if there is zero quantum mechanical overlap between the spin-containing orbitals. In this case alignment of the spins, which correlates their motions and minimizes electron-electron repulsions, is the most stable state. Unlike paramagnets, ferromagnets exhibit a net magnetic moment in the absence of an applied magnetic field.

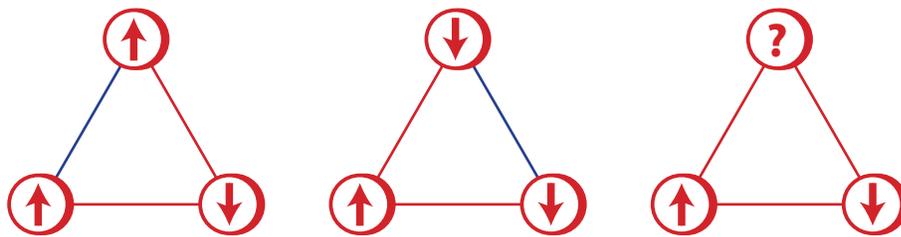
*Antiferromagnetism.* In an antiferromagnet, magnetic spins are aligned antiparallel, which results in a material with no net magnetic moment. At absolute zero, antiferromagnets exhibit a diamagnetic response to an applied magnetic field. The alignment of spins antiferromagnetically is analogous to the process of bonding and is thus favorable. Antiferromagnetism is the most commonly observed bulk magnetic behavior, and long-range antiferromagnetism is even exhibited by materials that order locally ferromagnetically.

*Ferrimagnetism.* Ferrimagnetism is a special case of antiferromagnetism, where the material consists of a lattice of rigidly alternating spins of different magnitudes. As in antiferromagnetism, the adjacent magnetic spins align antiparallel. However, since the adjacent spins are of different magnitudes, the resulting material exhibits a net magnetic moment in the absence of an applied magnetic field. Ferrimagnetism is responsible for the magnetism in magnetite, where Fe(III) ions,  $S=5/2$ , are observed to alternate with Fe(II) ions,  $S=2$ .

Although the four major class of magnetism account for the majority of observed magnetic behaviors, many other classes of magnetism exist. Many of these classes are subtle variations of the previously described major classes of magnetism. For example, a three dimensional metamagnet is a two dimensional ferromagnet that orders antiferromagnetically in the third dimension upon application of low magnetic fields and ferromagnetically upon application of high magnetic fields.

### 6.2.2.3 *Magnetic Frustration (Manson et al., 2000; Toulouse, 1977; Villain, 1977)*

Magnetic frustration is typically the result of an antiferromagnetically ordered triangular lattice. If there is quantum mechanical overlap between adjacent magnetic moments, the spins align antiparallel, however if the spins are on a triangular lattice this is unattainable. As illustrated in Figure 6.2 it is impossible to align a triangular arrangement of spins, such that all spins interact antiferromagnetically. This has been termed spin frustrations, since if two of the spins align antiferromagnetically a third spin cannot be aligned antiferromagnetically with both of the spins.

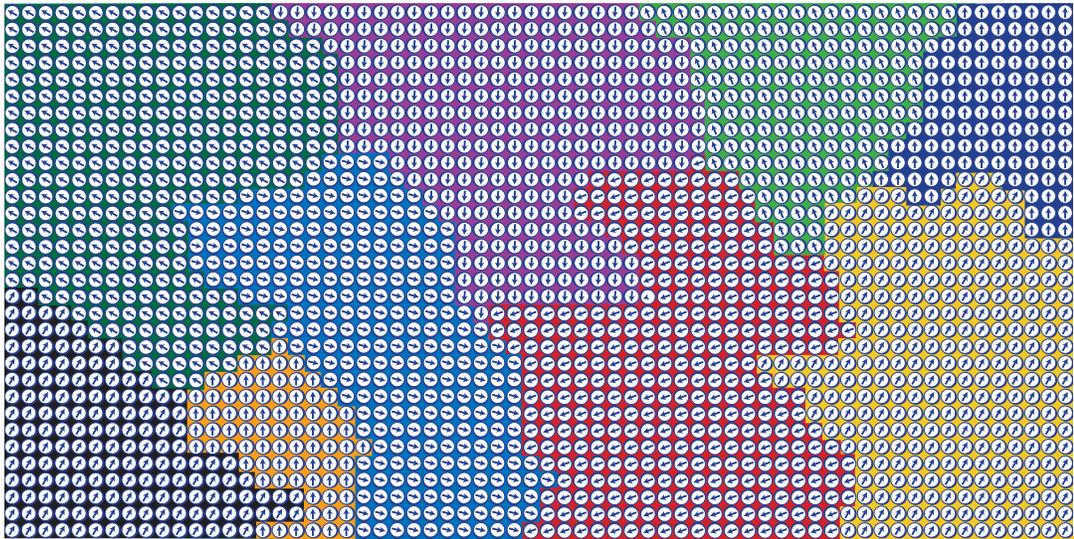


**Figure 6.2:** Magnetic frustration is illustrated. In the case of magnetically frustrated systems it is impossible for all spins to be align antiparallel.

### 6.2.2.4 *Domain Structure (Bertotti, 1998; Carlin, 1986; Kahn, 1993)*

Materials that exhibit a net magnetic moment, such as ferromagnets and ferrimagnets, often exist as a series of magnetic domains. Typically in the absence of an applied magnetic field, no magnetization is observed for ferromagnetic or ferrimagnetic materials. These materials generally consist of series of magnet domains with each magnetic domain having a net magnetization in the absence of an applied magnetic field. However, random orientation of the magnetic domains within a sample results in the apparent lack of magnetization in the absence of an applied magnetic field. Figure 6.3

illustrates a domain structure for a two dimensional ferromagnet. The domain structure of a sample is rearranged by application of an external magnetic field. The results of applied magnetic fields on materials that exhibit bulk magnetism is further discussed in section 6.2.3.2.



**Figure 6.3:** The random orientation of domains within a two dimensional ferromagnetic is shown. This random orientation gives rise to an apparent lack of magnetization for these samples in the absence of an applied magnetic field.

### 6.2.3 *Temperature and Field Dependence (Carlin, 1986; Kahn, 1993; Miller and Epstein, 1994; Turnbull et al., 1996)*

Magnetic interactions are typically characterized by their responses to variations in temperature and applied magnetic field. Each of the different types of magnetic interactions described above has a characteristic response to temperature and applied magnetic field. These responses are used to determine the specific type and strength of a

magnetic interaction. The temperature and field dependence of the general classes of magnetic interactions are reviewed here.

### 6.2.3.1 *Paramagnets*

The temperature and field dependent behavior of an ideal paramagnet is well described and is useful in magnetic characterization. Paramagnets are composed of many independently acting magnetic spins. In a sample, the magnitude of the magnetic spin ( $S$ ) is the molecular spin state of the paramagnetic molecule or atom. Temperature dependence in paramagnetic materials is described by the Curie law, and field dependence is described by the Brillouin function. A brief description of each of these functions is give below.

*Curie Law.* Before considering the temperature dependence of a paramagnetic material the concept of magnetic susceptibility ( $\chi$ ) must be defined. Magnetic susceptibility is the quantitative measure of the response of a material to an applied magnetic field. The definition of magnetic susceptibility is given in equation 6.1, where  $M$  is magnetization, and  $H$  is applied magnetic field.

$$\chi = \frac{M}{H} \quad (6.1)$$

The Curie law (6.2) describes the temperature dependence of an ideal paramagnet, where  $\chi_m$  is molar magnetic susceptibly,  $N$  is Avagadro's number,  $g$  is the "spectroscopic

splitting factor" (Lande  $g$  factor),  $\mu_\beta$  is the Bohr magneton, and  $k$  is the Boltzmann constant.

$$\chi_m = \frac{Ng^2\mu_\beta^2}{3kT} S(S+1) \quad (6.2)$$

This equation is usually reduced to the form in equation 6.3, where  $C$  is the Curie constant. It is important to note that the Curie law is only valid when  $H/kT$  is small.

$$\chi_m = \frac{C}{T} \quad (6.3)$$

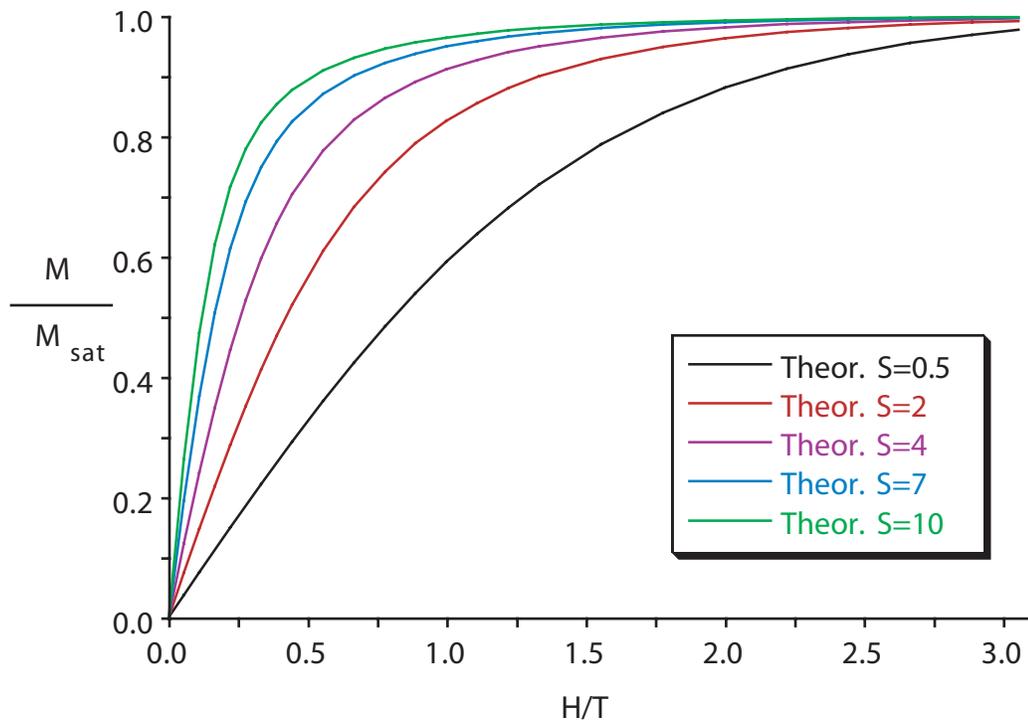
*Brillouin Function.* The Brillouin Function describes the magnetization of an ideal paramagnet without regard to the magnitude of  $H/kT$ . In practice this function is used to determine the spin state of a paramagnet by varying applied magnetic field at constant temperature. The function is given below, where the variables are as defined above or by the subsequent equations 6.5 and 6.6.

$$M = Ng\mu_\beta S \cdot B_s(y) \quad (6.4)$$

$$B_s(y) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S}y\right) - \frac{1}{2S} \coth\left(\frac{1}{2S}y\right) \quad (6.5)$$

$$y = \frac{g\mu_{\beta}SH}{kT} \quad (6.6)$$

Figure 6.4 shows a plot of the Brillouin function for various magnetic spin states. Using a Brillouin analysis the spin state of a material can be determined without knowing the exact chemical composition of the material, since it can be determined from the magnetization as a function of applied field and the saturation magnetization of the sample.



**Figure 6.4:** Brillouin curves for ideal paramagnets with various S values are shown. Magnetization normalized to the saturation magnetization is plotted against H/T. Systems with large S values saturate more quickly in response to increasing magnetic field than those with low values of S.

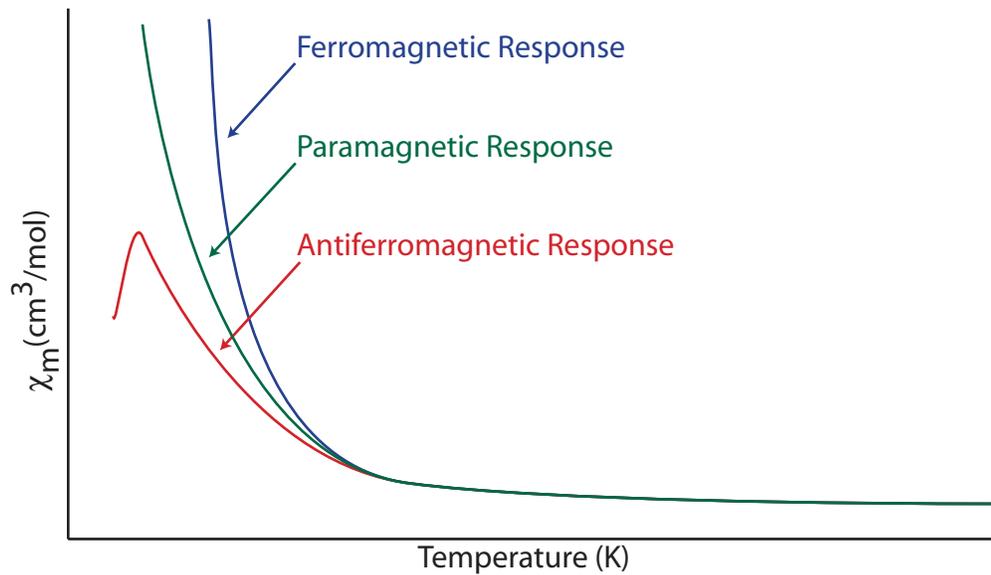
### 6.2.3.2 *Temperature Dependence of Cooperative Magnetic Effects.*

All magnetic materials behave as paramagnets at high temperatures, because thermal energy over comes the alignment and tosses the spins about randomly. The critical temperature of a material is the onset temperature for magnetic order. For a particular material the high and low temperature regimes are defined relative to the critical temperature, with the high temperature region lying above the critical temperature and the low temperature region lying below the critical temperature. A material does not exhibit bulk magnetism until well below its critical point.

Typically, temperature dependant magnetism is observed by examining the susceptibility of a material as a function of temperature. Analysis of the properties of a particular material is carried out by examining the temperature dependence as a function of susceptibility, a function of the susceptibility temperature product, and a function of the inverse susceptibility. Each of these analyses provides slightly different information about the bulk magnetism of the material.

*Susceptibility vs. Temperature.* Typical plots for magnetic susceptibility as a function of temperature for ferromagnetic, paramagnetic, and antiferromagnetic materials are shown in Figure 6.5. In general, it is difficult to determine the type of magnetic interactions occurring in a sample from the plot of susceptibility as a function of temperature. The most useful information can be obtained for antiferromagnetic materials, which exhibit a maximum at low temperature. The temperature at which the maximum is observed provides information on the strength of the magnetic interactions, with stronger

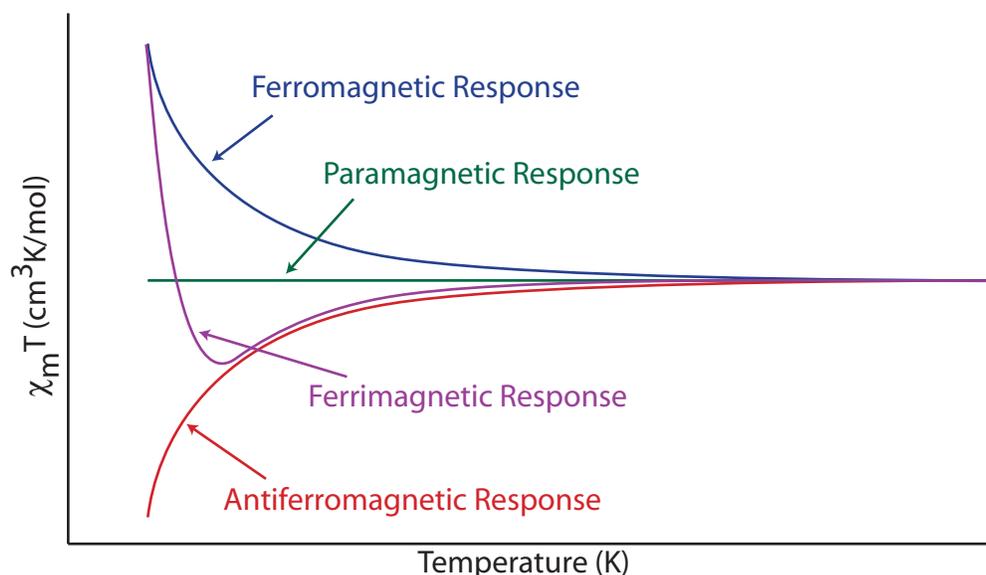
antiferromagnetic interactions occurring at higher temperatures. The shape of the maximum suggests the dimensionality of interactions, with one and two dimensional antiferromagnets marked by a rounded maximum and three dimensional antiferromagnets marked by a sharp peak.



**Figure 6.5:** Magnetic susceptibility as a function of temperature for paramagnetic, ferromagnetic, and antiferromagnetic materials.

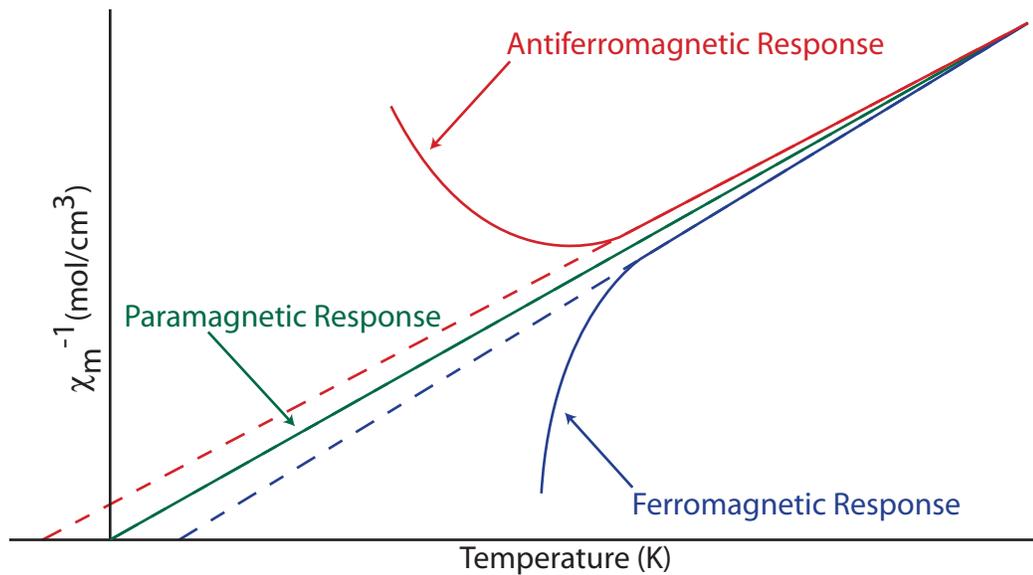
*Susceptibility Temperature Product vs. Temperature.* Analysis of the susceptibility temperature product as a function of temperature provides information about the basic interactions occurring in magnetic materials. A typical plot of susceptibility temperature product as a function of temperature is shown for an ideal paramagnet, ferromagnet, antiferromagnet, and ferrimagnet in Figure 6.6.

The temperature susceptibility product of a true paramagnetic material does not vary with temperature, while variations are observed for other types of magnetism. The invariant portion of the temperature susceptibility product at high temperatures for all types of cooperative magnetism is due to the effective paramagnetic behavior of magnetic materials above their critical temperatures. Ferromagnetic materials display an upward deviation from the curve for an ideal paramagnet as the ferromagnetic interaction energy overcomes thermal energy. Conversely, antiferromagnetic interactions display downward curvature with decreasing temperature as the magnetic moment for the sample goes to zero. For ferrimagnetic materials a slight downward curvature is first observed, due to interactions between adjacent magnetic moments. Ferrimagnetic materials then display upward curvature due to an increasing correlation length within the system.



**Figure 6.6:** A typical plot for the susceptibility temperature product as a function of temperature is shown for paramagnetic, ferromagnetic, antiferromagnetic and ferrimagnetic materials.

*Inverse Susceptibility vs. Temperature.* An ideal paramagnet has a linear relationship between inverse susceptibility and temperature that intersects at zero as defined by the Curie law. Deviation from this linear relationship and the Curie law is observed for materials that exhibit cooperative magnetic effects. As seen in Figure 6.7, a ferromagnetic material exhibits a downward deviation, while an antiferromagnetic materials exhibits a upward deviations. In all cases the data at high temperature are linear, since thermal energy is greater than the energy of the magnetic interations.



**Figure 6.7:** A plot of inverse susceptibility as a function of temperature is shown for a paramagnet, a ferromagnet, and an antiferromagnet. The dotted lines indicate deviation of the high temperature data from the paramagnetic case.

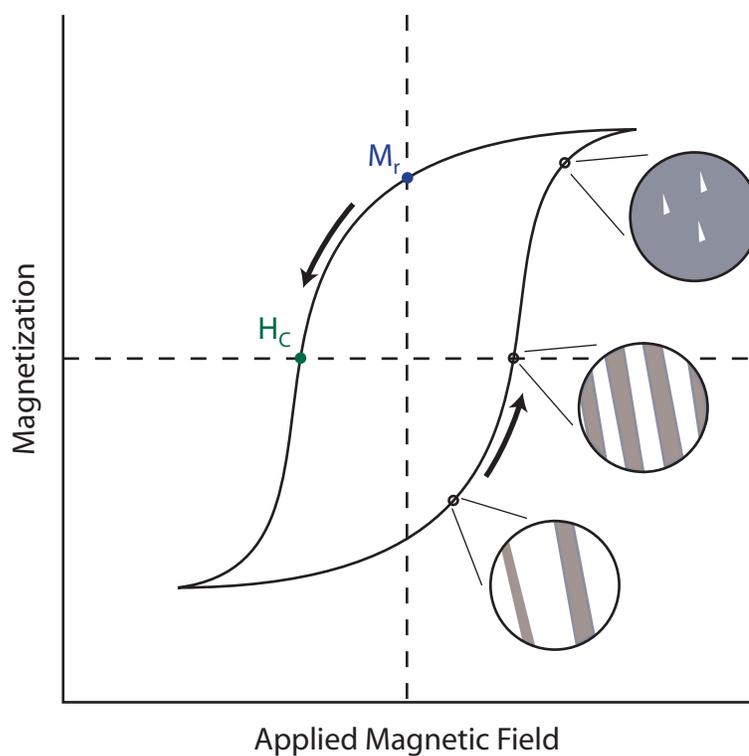
A modification of the Curie law (1.3), known as the Curie-Weiss law (1.7), describes this deviation. The Weiss constant ( $\Theta$ ) is proportional to the strength of the magnetic interactions observed. Positive Weiss constants indicate ferromagnetic interactions, while negative Weiss constants indicate antiferromagnetic interactions. This framework

is useful for looking at the predominate interaction in the material and the strength of that interaction.

$$\chi_m = \frac{C}{T - \Theta} \quad (6.7)$$

*Hysteresis (Bertotti, 1998).* One of the most distinctive features of materials with bulk magnetism is hysteresis. Hysteresis is observed for ferromagnetic and ferrimagnetic materials below their critical point and arises from rearrangement of domain walls within the material. The hysteresis of a sample is determined by looking at magnetization as a function of an applied magnetic field. A typical hysteresis curve for a bulk magnetic material is shown in Figure 6.8.

The hysteresis of a material is typically defined by two distinctive points; the remnant magnetization ( $M_r$ ) and the coercive field ( $H_c$ ). Remnant magnetization is obtained by applying and removing a large magnetic field and represents the extent to which a bulk magnetic material exhibits spontaneous magnetism. The coercive field of a sample is the magnetic field required to bring the magnetization of a sample to zero. Coercive fields from 0.01 G to 15,000 G have been observed for different materials. In general materials with low coercive fields (< 1 G) have been termed “soft” magnets, while materials with high coercive field (>500 G) have been termed “hard” magnets.



**Figure 6.8:** A typical hysteresis curve for a material with a bulk magnetic moment is shown. The domain structure for the material is indicated at several points along the curve, where the gray domains are aligned with each other and with the magnetic field and the white domains are aligned randomly.

#### 6.2.4 Summary

In high-spin materials magnetic interactions are diverse and bulk magnetism is a complicated phenomenon. Materials composed of paramagnetic species exhibit a variety of responses to temperature and applied magnetic field. From these responses the interactions between adjacent magnetic spins can be determined and understood. Only a small number of the different types of magnetism and possible magnetic responses to either temperature or applied magnetic field have been explored here.

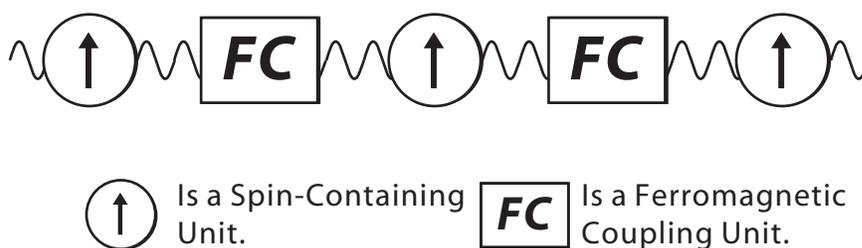
### **6.3 Design of Novel Magnetic Materials**

The design of novel magnetic materials has focused on the development of ferromagnetic and ferrimagnetic materials, since these materials are useful for device design. Various antiferromagnetic materials have received limited attention over the years, principally as model systems for testing physical theories. In general, the design of novel magnetic materials can be broken into two broad classes, the design of organic ferromagnetic materials and the design of organic-inorganic hybrid ferromagnetic and ferrimagnetic materials.

Several different approaches have been applied in attempts to build both organic and organic-inorganic hybrid materials. These approaches include high-spin organic polymers, bimetallic ferrimagnets, and crystal packing. Application of each approach will be described in the remaining chapters and appendices of this section.

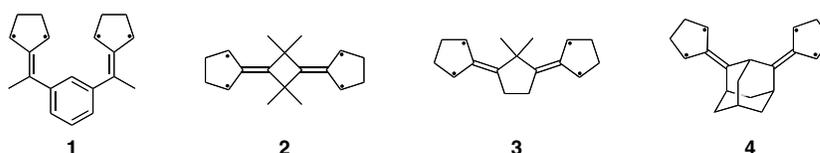
#### *6.3.1 High-spin Organic Polymers*

Our group has had a long-standing interest in understanding and applying the rules for ferromagnetic coupling of high-spin organic molecules (Anderson and Dougherty, 1998; Anderson et al., 1997; Dougherty, 1991; Jacobs et al., 1993; Kaisaki et al., 1991; Kearney et al., 1993; Murray et al., 1994; Silverman and Dougherty, 1993). Understanding these rules should allow for the creation of interesting magnetic organic materials. Figure 6.9 illustrates a useful model to generate a one-dimensional ferromagnet, where a ferromagnetic coupling unit enforces high-spin interactions between spin-containing units.



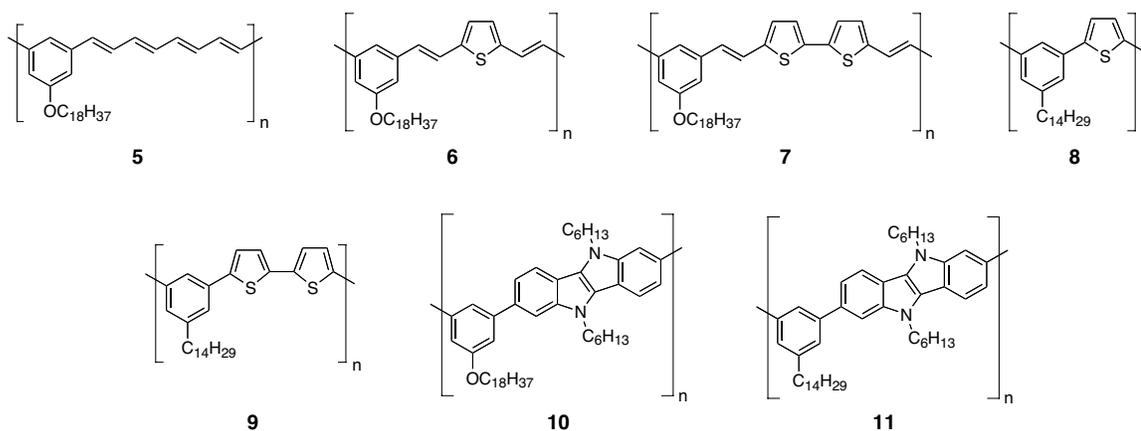
**Figure 6.9:** A schematic model for the design of high-spin organic molecules.

Ferromagnetic coupling units are structures that ferromagnetically couple any two spin containing units regardless of the structural details of the spin-containing unit. Potential ferromagnetic coupling units have been identified by considering organic radicals with triplet ground states and evaluated using triplet biradicals as spin containing units (Dougherty, 1991; Jacobs et al., 1993). Tetradicals **1-4** represent four potential spin containing units, which were evaluated by Dougherty and co-workers. Of these spin containing units only *m*-phenylene (**1**) and 1,3-cyclobutane (**2**) were effective ferromagnetic coupling units.



The smallest spin containing units for organic magnetic materials are charged or uncharged monoradicals. Although some monoradicals are stable, typically simple organic radicals are only stable at very low temperatures in solid matrices. Results from conducting polymers have shown that polarons, delocalized radical cations or radical anions, can be easily generated and are relatively stable at room temperature. A number

of prototypical one-dimensional polaronic ferromagnets were studied using oxidatively doped spin containing units to give poly radical cations (**8-11**) (Murray et al., 1994). The resulting materials did not exhibit unmistakable ferromagnetic interactions, however the results were encouraging.

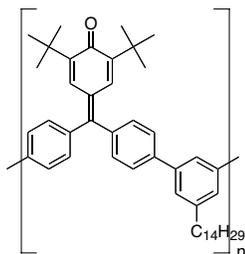


At low levels of doping, the materials displayed  $S$  values greater than one half. However at high levels of doping, these materials exhibited  $S$  values near one half, indicating no ferromagnetic interactions within the sample. Possible explanations for the lack of high-spin materials at high levels of doping include: intermolecular antiferromagnetic interactions, crosslinking, and bipolaron (spinless dication) formation from over oxidation.

To address these problems, a system based on the fuchone radical anion was designed (Anderson and Dougherty, 1998). This material, poly-*meta*-phenylene-fuchone (**12**), showed superior magnetic behavior to the oxidatively doped polymers. The material exhibited temperature dependant ferromagnetism with interactions beginning at about 40

K and an S value of 2 at a spin concentration of 60% of the theoretical maximum.

Appendix II describes attempts to improve upon poly-meta-phenylene-fusphone.



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### 6.3.2 Bimetallic Ferrimagnets

A common approach to the development of molecular magnetic materials has been the creation of bimetallic ferrimagnetic materials. In these materials ridged alternation of metal atoms containing different spin states leads to a material with a bulk magnetic moment independent of how the spins are coupled. If adjacent magnetic spins couple antiferromagnetically than a ferrimagnet results, while if the spins couple ferromagnetically than a ferromagnet results. The popularity of this approach arises from the ability to develop high-spin materials without needing to control ferromagnetic coupling.

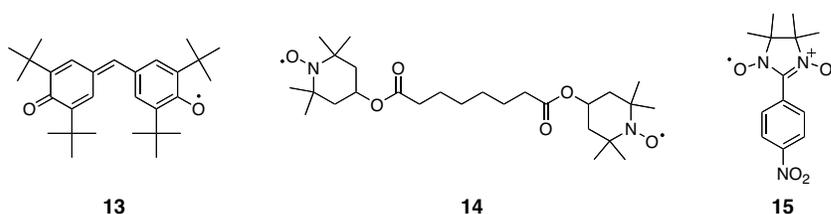
Classic examples of this strategy include Kahn's MnCu(pbaOH) ferromagnetic chains where pbaOH is 2-hydroxyl-1,3-propylenebis(oxamato) (Kahn et al., 1988; Pei et al., 1987), Caneschi and Gatteschi's metal-nitronyl nitroxide ferromagnetic chains (Caneschi et al., 1989a; Caneschi et al., 1989b; Caneschi et al., 1989c; Caneschi et al., 1988), and

Girolami's  $\text{Cs}_2\text{Mn}[\text{V}(\text{CN})_6]$  Prussian blue analog (Entley and Girolami, 1995). These materials all feature rigidly alternating magnetic spins of different magnitudes and all give rise to materials that exhibit bulk magnetic behavior. The ferrimagnetic critical temperature for  $\text{Cs}_2\text{Mn}[\text{V}(\text{CN})_6]$  is 230 K.

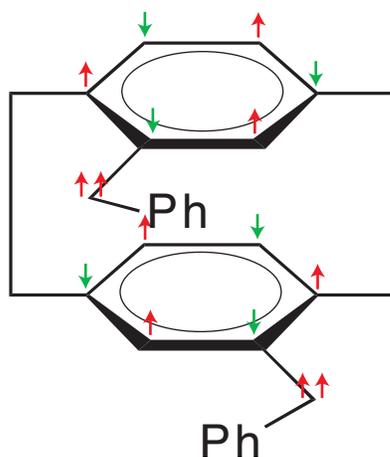
Attempts to design ferrimagnetic materials has created a host of interesting magnetic compounds. A series of novel bimetallic materials will be presented in Chapter 7.

### 6.3.3 *Crystal Packing*

A handful of stable crystalline organic radicals exhibit ferromagnetic behavior. Ferromagnetism in these materials arises from crystal packing. Galvinoxyl (**13**) shows ferromagnetic behavior between 300 K and 85 K, which arises due to parallel stacking between planar galvinoxyl radicals. Below 85 K galvinoxyl undergoes a phase transition, which results in antiferromagnetic behavior (Awaga et al., 1989; Awaga et al., 1987). Tanol radicals (**14**) exhibit two-dimensional ferromagnetism and order antiferromagnetically in the third dimension (Chouteau and Veyretjeandey, 1981). *p*-Nitrophenyl nitronyl nitroxide (**15**) is the first three dimensional organic ferromagnet and was discovered in 1991 (Tamura et al., 1991). This molecule orders ferromagnetically with a critical temperature of 0.60 K.



The ferromagnetic behavior observed for all these materials results from crystal packing. In these cases, the observed ferromagnetic behavior arose by chance. Strategies for designing ferromagnetic behavior into organic radicals have been proposed. The Cyclophane shown in Figure 6.10 represents one strategy that has been employed to design ferromagnetic packing (Izuoka et al., 1987). In this strategy two organic radicals are made to stack face-to-face, with regions of spin  $\alpha$  on one molecule most closely positioned to regions of spin  $\beta$  on another, the antiferromagnetic interaction between those regions result in alignment of the spins on the two molecules.



**Figure 6.10:** Spin interactions in a bis(diphenylcarbene)[2,2]paracyclophane system.

Previous work in our group has attempted to design ferromagnetic materials using the benzene-hexafluorobenzene crystal-engineering motif (Miller, 1998). Although interesting results were obtained using this motif, ferromagnetic packing was not achieved. Chapters 7 and Appendix III explore using the guanidinium sulfonate crystal engineering motif to design novel high-spin magnetic materials.

## **6.4 Crystal Engineering**

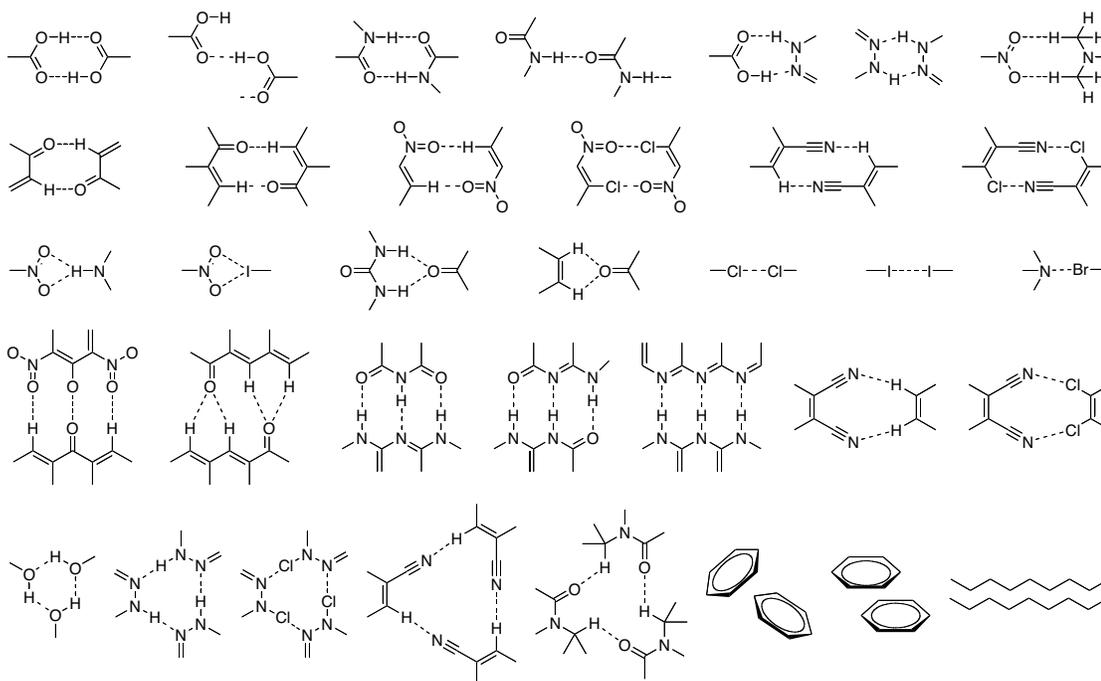
Crystal engineering is the process of designing the three dimensional structure of solids, using non-covalent interactions. Most of the work in this area has focused on the design of organic materials. It is hoped that crystal engineering will produce materials with useful physical properties, such as non-linear optics, catalysis, and magnetism.

### *6.4.1 Macromolecular Synthons*

In crystal engineering, as in conventional organic synthesis, conceptually a target structure can be broken down into smaller building blocks or synthons. The usefulness of a particular synthon depends on its generality. A large number of synthons for crystal engineering have been identified by searching small molecule structural databases and by rational design. Figure 6.11 shows 35 different molecular synthons that have been employed in crystal engineering (Desiraju, 1995).

One of the most robust synthons from Figure 6.11 is the carboxylic acid dimer. Of the small molecules examined by Desiraju, 85% of carboxylic acid groups dimerized (Desiraju, 1995). The robustness of a particular synthon for directing a molecule to

crystallize with a given pattern is a measure of its utility, in the same way that product yield is a measure of the utility of a particular synthon in conventional organic synthesis.



**Figure 6.11:** Molecular synthons that have been employed for crystal engineering.

#### 6.4.2 Rules for Crystal Packing

In general the packing of small organic molecules is difficult to predict. The synthons described in section 6.4.1 provide one approach to controlling crystal packing, however these synthons only control packing in onedimension (Dunitz and Bernstein, 1995), while useful materials typically require a defined three-dimensional molecular structure. Three of the critical forces in three dimensional crystal packing are reviewed below.

*Kitaigorodskii's principle of close packing (Kitaigorodskii, 1973).* Small molecules tend to pack so as to minimize void volume in their three-dimensional structure. Typically, for an organic molecule the van der Waals radii of its component molecules encompass 60-77% of the total volume. This high density is a result of van der Waals forces accounting for most of the crystal packing enthalpy.

*Satisfy hydrogen bond donors and acceptors (Kitaigorodskii, 1973).* Hydrogen bonds tend to be a dominant force in crystal packing because they are highly directional and sensitive to small geometric perturbations. The need to satisfy hydrogen bond donors and acceptors can result in less dense packing of a molecular solid than of the same molecular liquid. This is observed when comparing ice with liquid water.

*Minimize electrostatic energy (Kitaigorodskii, 1973).* Weak electrostatic interactions, such as bond dipoles, can play important roles in crystal packing. Crystals pack so as to minimize the overall electrostatic energy of the three-dimensional crystal structure.

Using these principles and some of the molecular synthons shown in Figure 6.1 progress has been made towards being able to design three-dimensional molecular structure (Nangia and Desiraju, 1998; Sarma and Desiraju, 2002). However crystal engineering remains extremely difficult and very few motifs have been developed that provide three-dimensional molecular control. A three-dimensional crystal engineering motif based on guanidinium disulfonates (Russell et al., 1997). developed by Ward and co-worker, is

described in Chapter 7 and Appendix III along with its application for the development of novel molecular magnetic materials.

## 6.5 Literature Cited

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