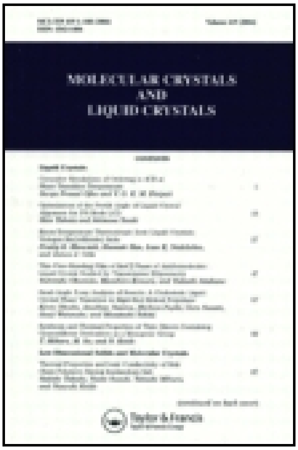

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Magnetic Phenomena in Molecular Solids: A Tutorial Approach

Fernando Palacio [a] , Francisco J. Lazaro [a] & A. J. Van Duyneveldt [a b]

[a] Instituto de Ciencia de Materiales de Aragón, C.S.I.C. y Universidad de Zaragoza, 50009, Zaragoza, Spain
[b] Kamerling Onnes Laboratorium, University of Leiden, 2300 RA, Leiden, The Netherlands

Version of record first published: 22 Sep 2006.

To cite this article: Fernando Palacio , Francisco J. Lazaro & A. J. Van Duyneveldt (1989): Magnetic Phenomena in Molecular Solids: A Tutorial Approach, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 176:1, 289-305

To link to this article: http://dx.doi.org/10.1080/00268948908037488

Mol. Cryst. Liq. Cryst., Vol. 176, pp. 289–306
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

MAGNETIC PHENOMENA IN MOLECULAR SOLIDS: A TUTORIAL APPROACH.

FERNANDO PALACIO*, FRANCISCO J. LAZARO AND A.J. VAN DUYNEVELDT†
Instituto de Ciencia de Materiales de Aragón, C.S.I.C. y Universidad de Zaragoza, 50009 Zaragoza (Spain).

Abstract. Some basic concepts in magnetism are discussed in the context of molecular solids. A brief outline about the experimental techniques useful to investigate these new magnetic materials is given, with special emphasis in the a.c. susceptibility technique. The basic idea that bulk magnetism can only be achieved by means of inter-molecular magnetic interactions is outlined after explaining the thermodynamic fundamentals of magnetic ordering. Some extension is devoted to account for the phenomena associated with superparamagnetism, since very high spin molecules may exhibit these magnetic properties in the absence of inter-molecular interactions. Finally, some fundamental properties of ferromagnetic materials are commented on discussing how they might affect to molecular ferromagnets.

INTRODUCTION

The study and applications of the magnetic properties of materials is a very long standing area of research and technological interest. A common characteristic in most magnetic materials is to have ion- (or atom-) based properties. Then, when magnetic cooperative phenomena appear, it is a consequence of the extended interactions between the magnetic moments of the ions (atoms) that comprise the material. However, not always the magnetic properties of a given material can be directly related to its component ions (atoms). A well known example is the Pauli magnetism of

---

† Permanent address: Kamerling Onnes Laboratorium, University of Leiden, 2300 RA Leiden, The Netherlands.

electrons delocalized in a conduction band; another one concerns to the rather restricted type of materials whose magnetic properties should be ascribed to the constituent molecules rather than to the ions. These materials are *molecular solids* which can be understood as composed by molecules, either neutral or ionic, held together in the solid by hydrogen bonds or van der Waals interactions. If magnetic ordering arises, it is now due to the extended interactions between the magnetic moments of the *molecules* in the solid. Examples of these, so called, *molecular magnetic materials* are inorganic magnetic clusters, most organic free radicals and a variety of organometallic compounds.

In regular ion-based magnetic materials, cooperative phenomena is a rather common feature. In contrast, not many molecular magnetic materials have been found to exhibit magnetic ordering. Indeed, the list is rather short if we restrict our attention (as we shall do it in this paper) to purely organic and organometallic materials. Some few free radicals presenting antiferromagnetic ordering have been found[1,2] and, very recently, the existence of an organometallic ferromagnet has been well established.[3] In addition, two more organic ferromagnets have been reported although these results have not been reproduced yet.[4-6]

Molecular solids present interesting peculiarities as potential magnetic materials. The possibility that organic molecules can be slightly modified may allow the modulation of the magnetic properties of the material. Organic magnets should possess very low density, both mass and magnetic, as compared to metal-based conventional ones. Moreover, they may consist of magnetically interacting molecules possessing a very high spin. A rather large number of molecular conductors are already known and the finding of a conducting molecular magnet, either organic or organometallic, is an exciting possibility. Nevertheless, the electrical conductivity of most molecular materials is extremely poor and that can be a very useful property for a potential magnet. An additional reason for the appealing interest of organic magnets lies in the natural abundance and non–strategic distribution of their constituent elements.

It is, therefore, not surprising that in the last few years the subject of molecular magnetism has captivated the interest of many chemists, most of them not previously familiarized with magnetic materials. The aim of this paper is to describe some basic aspects of magnetism related with molecular solids which could be useful for understanding the properties of molecular magnetic materials. For a more extended treatment of the magnetism of solids there are excellent books available to the non-specialist.[7-11]

In this paper we start summarizing the most important experimental techniques used to characterize magnetic materials. We pay special attention to ac magnetic susceptibility since it is an extremely useful technique when net magnetic moments are present. In a next section we briefly review the mechanisms which have been proposed to stabilize a high-spin ground-state in a molecular solid and inspect the concept of magnetic ordering. The presence of high-spin molecules in a material does not necessarily imply ferromagnetism although interesting phenomena may be present. Indeed, high-spin molecules may give rise to superparamagnetic behavior and we devote a section to account for this property. Finally, we describe some aspects of bulk ferromagnetism which we consider could be useful when they are applied to characterize a molecular ferromagnet.

EXPERIMENTAL METHODS

Magnetic properties of materials are mainly studied by magnetization as well as static and dynamic susceptibility measurements. The macroscopic magnetic behavior of a sample is mostly expressed by the volume density of its magnetic moments, i.e. its magnetization **M**. Classical methods to measure the magnetization are based on the force acting on the sample when it is placed into an inhomogeneous magnetic field (Faraday or Gouy methods) or on the total electromotive force induced in a pick-up coil when the sample is moved in a constant magnetic field (vibrating sample magnetometer). Modern magnetometers often incorporate SQUID detectors. The magnitude of the magnetization **M** usually depends on the value of the external magnetic field **H** applied to the sample. From these experimental methods one determines the *static* (or *dc*) magnetic susceptibility by dividing the measured magnetization by the applied magnetic field ($\chi_{dc} = \chi_o = M/H$). In the limit of weak external magnetic fields the static susceptibility coincides with the slope of the magnetization curve at the origin; then it is called *initial* susceptibility.

In practice, for real systems, the function M(H) is far from being linear, resulting in a χ_{dc} which is field dependent. Then, it is more useful the measurement of the so called *ac-susceptibility* ($\chi_{ac} = dM/dH$), which can also give some insight about the magnetic mechanisms involved in the sample.[9,12] The experimental technique to determine χ_{ac} is based upon the variation of the mutual inductance of a set of two coils when a magnetic material is inserted. The sample is placed into a coil (primary) which generates an a.c. magnetic field. The in-phase and the out-of-phase components of χ are determined by phase sensitive detection of the voltage induced in the secondary coil. This kind of set-up has proved to be very efficient.[13]

Let us briefly describe the kind of information which can be obtained from χ_{ac}. When an oscillating component is added to the external field, the total magnetic field acting on the sample will be, using complex notation,

$$H = H_0 + h \exp(i\omega t)$$

where h is the amplitude of the alternating field, ω the frequency andt the time. As a result, the magnetization will also show an oscillating part,

$$M = M_0 + m \exp[i(\omega t - \phi)]$$

M_0 and m being, respectively, the magnetization at the constant field H_0 and at the alternating field h. In general, due to relaxational processes, M is not able to follow the external field instantaneously resulting in a corresponding phase delay ϕ. The a.c. susceptibility is then

$$\chi_{ac} = |\chi| \exp(-i\phi) = \chi' - i\chi''$$

In the limit of low frequencies compared to the time constants of the relaxational processes, the real part χ' ("*in-phase*" susceptibility) coincides with the slope of the magnetization curve at $H = H_0$. When relaxation effects become appreciable, the imaginary component χ'' ("*out-of-phase*" susceptibility) starts to be nonzero.

The relaxation phenomena, responsible for the out-of-phase component χ'' as well as of a variation in χ', can be treated assuming a two level system with a characteristic relaxation time τ. Two well differentiated time effects, or relaxation processes, take place. One process depends on the interactions between the spins and affects the spin system only; it is called *spin-spin relaxation*, and it is a measure of the time taken for the spin system to reach internal equilibrium after a disturbance created by the alternating magnetic field.

The other process, called *spin-lattice relaxation*, involves the interactions between the spins and the lattice vibrations of the crystal; it is several orders of magnitude slower than the spin-spin process and temperature dependent. In a typical ac susceptibility determination, where a.c. frequencies are below 10^5 Hz, one can neglect spin-spin relaxation effects. In this case the spin system may be considered in thermodynamic equilibrium and may be treated as a separated system with its own temperature. At low frequencies this system will always be at equal temperature to that of the system of lattice vibrations and the susceptibility of the substance will have its static or *isothermal* value, $\chi_0 = \chi_T$. On the other extreme, the period of the oscillating field is much shorter than the time it takes for the magnetic moments to reorientate. In that case, the heat exchange between the spin and the lattice systems is almost zero and the substance will show its *adiabatic* value, χ_S. Following Casimir and Du Pré,[14] at any intermediate frequency ω, the susceptibility components can be written:

$$\chi' = \chi_S + \frac{\chi_T - \chi_S}{1 + \omega^2\tau^2} \qquad \chi'' = \frac{\chi_T - \chi_S}{1 + \omega^2\tau^2}\,\omega\tau$$

For the outcome of ac susceptibility measurements this means that $\chi_{ac} = \chi_T$ if low frequencies ($\omega << \tau^{-1}$) are used, and $\chi_{ac} = \chi_S$ in the case of measurements made at high frequencies ($\omega >> \tau^{-1}$).

Another useful relation between adiabatic and isothermal susceptibilities comes from strict thermodynamic considerations. If C_M and C_H are the specific heats at constant magnetization and constant magnetic field, respectively, then one can prove,[9]

$$\frac{\chi_S}{\chi_T} = \frac{C_M}{C_H}$$

For a paramagnetic substance $C_M = C_H$ at zero external magnetic field and therefore, $\chi_T = \chi_S$.

The out-of-phase component is proportional to the energy absorbed by the substance from the oscillating excitation field. The work made on the sample by the field is given by dW = -HdM, therefore the energy absorbed per cycle and unit volume is given by

$$E = \frac{\omega}{2\pi} \int_{\mathrm{cycle}} H\,dM = \frac{\omega}{2\pi} \chi'' h^2$$

In the absence of net magnetic moments in the substance there will essentially not be energy absorption at zero external magnetic field, $\chi'' = 0$, and M and H will be in phase. If, on the contrary, net magnetic moments, either bulk or local, are present in the sample, they will be forced to execute small hysteresis cycles by the alternating magnetic field, the area of these cycles being given by the above integral. As a consequence, M will lag H and $\chi'' \neq 0$. This feature makes the ac susceptibility technique very useful for tackling unknown magnetic systems.

MAGNETIC INTERACTIONS AND MAGNETIC ORDERING

Since the subject of ferromagnetic interactions in molecular solids have been extensively reviewed recently,[15] we shall only summarize here the different mechanisms of exchange interaction that can occur in a molecular material and discuss some simple thermodynamic fundamentals that support the concept of magnetic ordering. Firstly, intra-molecular magnetic interactions should be distinguished from inter-molecular ones. Intra-molecular interactions can originate high-spin molecules if they are ferromagnetic, the size of the total spin magnetic moment depending on the number of unpaired electrons in the molecule. Several mechanisms have been proposed for stabilizing parallel spin alignment in a molecule.[16,17] An approach is to obtain a molecular orbital configuration possessing a degenerate ground state then, because of the Hund's rule, spin moments will align parallel occupying half of the degenerated states. This is the molecular equivalent of high spin configuration in inorganic ions. Degeneracy may involve nonbonding orbitals,[18,19] as in the case of the polycarbenes prepared by Iwamura and coworkers,[20-22] or it may be originate because of high molecular symmetry.[23] In this second case the maximum number of unpaired spins is obviously very limited although, as we discuss below, the possibility of extended ferromagnetic interactions between neighbor molecules has been proposed based on McConnell's model.[24,25] However, there seems to be no limit to the spin multiplicity that is possible to achieve *via* nonbonding orbitals and, probably because of it, many synthetic efforts are focused to the preparation of very high spin molecules.

A ferromagnetic material cannot be obtained just by increasing the magnetic moment of a molecule. Ferromagnetism is a bulk property of the solid and therefore, it requires (ferro)-magnetic interactions extended throughout the material. In consequence, a material consisting of non-interacting magnetic molecules, as it is shown below, is not a ferromagnet since no magnetic order is present. Instead, such material can be considered a superparamagnet if it consists of very high-spin molecules.

A molecular-based magnetic solid can be understood, from a thermodynamical point of view, very much like an ion-based solid just considering the total spin magnetic moment of each molecule. At temperatures much higher than a critical temperature T_c, the orientation of a molecular spin does not depend on the orientations of neighbor spins. As a consequence, the correlation length for a pair of spins, ξ, that is, the length along which a pair of spins are magnetically correlated, is zero or very small. In the absence of inter-molecular magnetic interactions the correlation length is negligible and temperature independent. If, on the contrary, magnetic interactions between neighbor molecules are present the situation becomes different. To simplify the discussion, let us consider a ferromagnetic interaction without the existence of any anisotropy. Now, the spin pair correlation length will increase as the temperature decreases. At temperatures near, but still above, T_c the orientation of molecular spins will be almost parallel to each other over a distance of the order of the correlation length ξ. The solid itself is still a paramagnet, since the magnetization of a macroscopic volume much bigger than ξ^3 and the time average spin value are equal to zero. At $T = T_c$ the correlation length tends to infinite and below that temperature a *spontaneous magnetization*, M_s, arises which can be considered the order parameter of the transition.

The divergence of the correlation length at T_c is important because it guarantees the magnetic system to be volume independent at $T \leq T_c$. As a consequence, a high spin molecule is not a ferromagnet independently of its size and total spin moment, since the size of the molecule establishes an upper limit for the correlation length ξ. Only when magnetic interactions between molecular spin moments are present one expects magnetic ordering in the material below a temperature T_c. In general, T_c is higher the stronger are the magnetic interactions. If, in addition, the dominant effect of the interactions aligns the molecular moments parallel, the material becomes a ferromagnet.

The presence of intermolecular magnetic interactions is therefore of fundamental importance to achieve a magnetically ordered solid. McConnell was the first to suggest theoretical mechanisms to stabilize ferromagnetic coupling between molecules. A model, further extended by Breslow, considers configuration mixing along a $...D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}...$ chain where either the cation D (donor) or the anion A (acceptor) possesses a virtual triplet excited state. Although a solid consisting of ideal magnetic linear chains does not order at finite temperature, the presence of small inter-chain interactions causes magnetic order to appear at $T_c > 0K$. In fact, the only existing well identified example of a molecular ferromagnetic solid shows this type of interaction.[3,26] It consists of stacks formed by $[Fe^{III}(C_5Me_5)_2]^{\bullet+}$ cation donors alternated with $[TCNE]^{\bullet-}$ anion acceptors. The difficulty in this type of materials is that the inter-stack interactions are much weaker than the intra-stack ones.[27] As a consequence, the ferromagnetic ordering is triggered by the weak inter-stack interactions and has to be expected to occur at low temperature ($T_c = 4.8K$ for the above mentioned ferromagnet).

In addition, we should consider another model, also proposed by McConnell,[16] based on spin exchange, throughout a Heisenberg-Dirac type of interaction, between positive and negative spin densities of neighbor molecular orbitals. So far this mechanism has only been explored for intramolecular interactions.[28,29] However, it is good to realize that Heisenberg-Dirac exchange interaction is the predominant type of mechanism in the magnetism of ordered inorganic solids where interaction pathways throughout non–covalently bonded entities are common.[30,31] In our opinion, the possibilities of this mechanism to originate bulk ferromagnetism in molecular systems remain unexplored.

HIGH SPIN MOLECULES: SUPERPARAMAGNETISM

Systems with no long range magnetic order, but nevertheless possessing large magnetic moments, may present characteristic magnetic properties typified as superparamagnetism.[32] This behavior is typical of non–crystalline materials.

Consider a cluster composed by entities (ions, molecules, radicals, or a very high spin molecule) having magnetic moments relatively close together and suppose that, by some means (e.g., superexchange), there is a positive (ferromagnetic) interaction between them. One can imagine a material formed by an assembly of such clusters. If these clusters have enough size as to be macroscopic, an internal ordering may be established below a critical temperature T_c. If T_c is high enough the magnetic moments within the cluster may be completely aligned at the experimental temperatures, while the intercluster interaction within the material may remain very low, hampering long range order.

The magnetic behavior of such an ensemble of clusters is similar to that of a paramagnet. Each cluster behaves like a large magnetic moment $\mu = M_s V$ where M_s is the saturation magnetization within the cluster and V its volume. Assuming that all the clusters are equal and are single domain, the sample magnetization can be written with the classical Langevin function, $\mathbb{L}$:

$$M = N \mu \, \mathbb{L} \, (\mu H / k_B T)$$

where N is the number of clusters per unit volume, k_B the Boltzmann constant and H the external applied field. As can be easily seen, and like a normal paramagnet, magnetization curves taken at different temperatures should coincide if plotted versus (H/T). Moreover, there should be no hysteresis in the magnetization plots, just as in the case of a normal paramagnet.

In the limit of low H/T, the initial susceptibility can be written in a Curie–like way as:

$$\chi = N\mu \, / \, 3k_B T$$

A clear result is that one observes a Curie constant *n* times greater than for a paramagnet, where *n* is the number of single magnetic entities per cluster. When some inter-cluster interaction (e.g., dipolar) is included a molecular field appears leading to a Curie-Weiss like behavior.[33]

In the original theory of Néel, the magnetization changes in the non–interacting single-domain clusters are only due to moment rotations and not to domain wall displacements. Those clusters experience magnetocrystalline and shape anisotropy. In the most simple case of one grain with uniaxial anisotropy the magnetization can take two possible opposite easy directions, separated by an energy barrier $W = KV$, where K is the anisotropy constant and V the sample volume. Thus, the system can be studied in a similar way as paramagnetic relaxation. A relaxation time, τ, can be defined as

$$\tau = \tau_o \exp(W/k_B T)$$

where τ_o is a characteristic time of the system. The existence of different cluster sizes and shapes leads to a distribution of relaxation times, with an average value τ_{av}, that in general is also temperature dependent. The time τ is then the average time needed for a given kind of cluster to reverse its magnetization after removing the external applied field. The practical consequence is that when the measuring time, τ_m, is greater than τ one observes a behavior similar to a paramagnet. However, for $\tau_m < \tau$ the complete reorientation of the magnetic moments of the cluster cannot take place during the measuring time. Thus, below a blocking temperature T_B, given by the condition $\tau_{av}(T_B) = \tau_m$, the system appears "blocked" and its behavior is strongly dependent on τ_m.

In general, the relaxation times increase with decreasing temperature. Thus, when one measures magnetization at low temperature ($T<T_B$), apparent hysteresis may be found due to the slow response of the system. Therefore, in the process of characterizing the magnetic behavior of a new substance the mere existence of hysteresis cannot be indicative of ferromagnetism by itself.[34] In Figure 1 it is shown the field dependence of the magnetization of a superparamagnet at a temperature well below T_B. It is a common feature in superparamagnets to exhibit remanent magnetization below a certain temperature.[32] The remanence depends on the way of cooling the sample, whether field cooled or zero field cooled, and serves as an additional evidence of how large time effects influence the observed magnetic behavior of these materials.

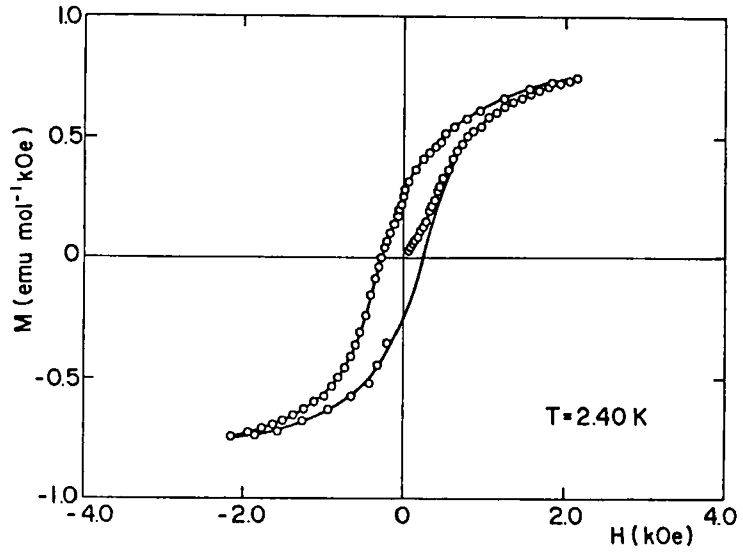

FIGURE 1. Hysteretic behavior of the field dependence of the magnetization in a superparamagnetic material below the blocking temperature.

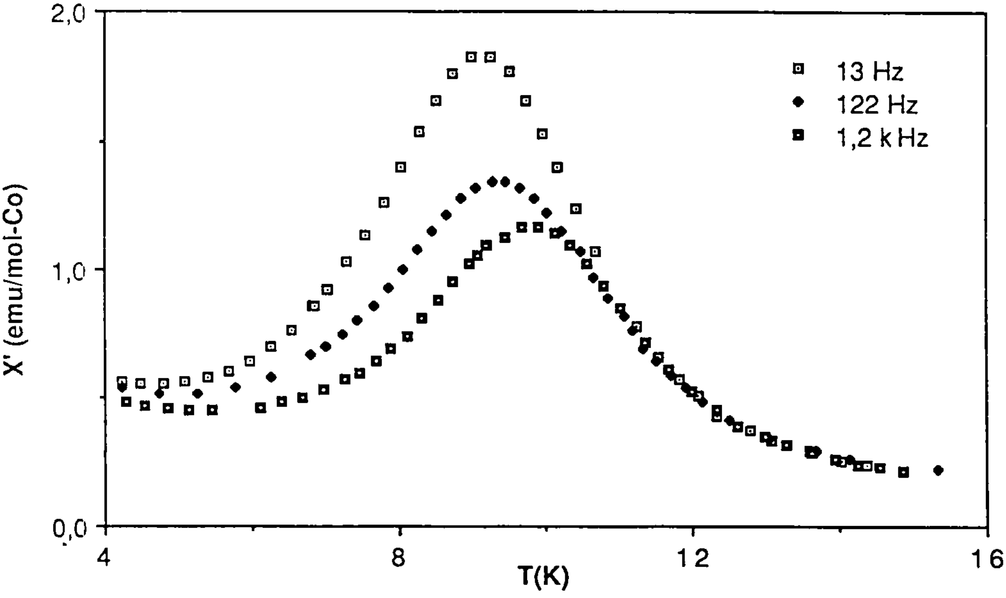

FIGURE.2. Characteristic frequency dependence of a superparamagnet. It clearly shows how an increasing of the measuring time, $\tau_m = 1/\nu$, reduces the blocking temperature, T_B.

A category of systems that exhibit similar effects are the so called spin glasses, where randomness and frustration are the origin of their particular behavior.[35] It is far beyond the scope of this paper to discuss these classes of systems in any detail. For that purpose, there exists clarifying articles in the literature comparing the experimental behavior of superparamagnets and spin-glasses.[36,37]

In many cases superparamagnets as well as spin glasses are characterized using ac susceptibility measurements. This is an adequate technique for these systems since an additional external magnetic field is not required and permits the study of the characteristic frequency dependence. The outcome of this relatively easy experiment usually shows a cusp in χ' at the temperature recognized as the blocking temperature T_B (for superparamagnets), or the freezing temperature T_f (for spin glasses). Near the maximum of the χ' versus T curve, χ'' starts to be non-zero. An example of the typical behavior for the ac susceptibility of a superparamagnet is given in Figure 2.[38]

MOLECULAR FERROMAGNETISM

As discussed above, a material may be called a ferromagnet if the interactions among the individual magnetic moments tend to align the moments parallel. For the experimentalist this effect becomes obvious below a finite transition temperature T_c where the correlation lenght becomes infinite. Therefore, for $T<T_c$, the material exhibits spontaneous magnetization, giving rise to a rapid increase of the magnetic susceptibility. This applies to the static susceptibility as well as to the in-phase component of χ_{ac}. In addition, the existence of correlation of moments at $H = 0$ yields, in an ac susceptibility experiment, a non-zero signal in the out-of-phase component χ'' due to the effective field created at the site of each magnetic moment. However, as it has been shown in the previous section, the existence of a χ'' signal should not be considered as conclusive for the existence of long range magnetic ordering.

The same features should hold for a molecular ferromagnet, where one should expect cooperative phenomena below a transition temperature. Ferromagnetic alignment is a bulk property present within the whole volume of the sample, but reality is again more complex. In practice a ferromagnetic material may not show a net magnetic moment in the absence of a magnetic field. This effect arises since one has to consider the material as possibly broken in domains, each with a net magnetic moment. The equilibrium state of the sample magnetization is determined by the minimum of the magnetic free energy F. For our purposes, the most relevant contributions to F are the sample energy under the external field and those coming from the demagnetizing field, the magnetic anisotropy and the exchange interaction.[9]

When the material orders ferromagnetically there appears uncompensated moments on its surface (magnetic pole density). This originates an extra magnetic field, opposite to the sample magnetization, called demagnetizing field, resulting in an increase of the free energy of the sample. To minimize F, a structure of domains with their net moments essentially antiparallel may appear in the sample. This reduction of the total free energy takes place at the expense of the exchange energy in the domain walls where the magnetic moments do not fulfil the requirement of parallelism with all their neighbors. Consequently, the total magnetization of the sample may be zero even below T_C.

On the other hand, if an external magnetic field is applied, the balance between the different magnetic free energy contributions must be modified. The magnetic system develops a new energy minimum and a new domain structure is formed. As a result, the net magnetic moment can be reached only by domain wall displacements. This effect on the magnetization M upon increasing H from zero cannot be mistaken with the usual alignment induced in a paramagnet by an external magnetic field, for the effect is orders of magnitude larger.

The domain structure is also dependent on the magnetic anisotropies of the material and the domain wall mobility is affected by the impurities in the sample. It is therefore not simple to foresee how domains will be formed in a molecular ferromagnet. It has already been mentioned that in comparison with classical magnets the density of the magnetic moments is expected to be considerably lower; although the size of the individual moment itself may be large. As explained above, a lower magnetic density leads to a weaker demagnetizing field. In that case, one can imagine that the size of the domains formed in a molecular magnet may be much larger than in a classical one. In fact, a comparison with weak ferromagnets seems adequate since these substances also exhibit low magnetization. In such systems the net magnetization arises due to canting of the antiferromagnetic sublattices by a few degrees, the net magnetic moments being therefore very small. In the case of $(C_3H_7NH_3)_2MnCl_4$ the domains were shown to be approximately 10^{-5} cm wide.[39]

Other important factor determining the magnetic microstructure of the ordered state is the magnetic anisotropy which gives rise to a prefered orientation of the magnetic moments. The question that arises now is: could one expect magnetic anisotropy to occur in a molecular ferromagnet? An important source of such anisotropy in classical magnets is the crystalline electrostatic field around the magnetic ion *via* spin-orbit coupling. The same origin can be present in molecular ferromagnets when they consist of organometallic substances or inorganic clusters, except that now the ligand field has a markedly covalent character. In these two substances one can imagine the possibility of changing the anisotropy by changing the transition metal. The strategy is similar to the followed in the case of classical magnets although it may be far more involved from a chemical point of view. It is less obvious how anisotropy should occur in purely organic ferromagnets. In such systems the molecular orbitals consist of s- and p- electrons only, and the effect of spin-orbit coupling should be rather small; this has indeed been observed in the EPR of free radicals. It is not clear, however, whether the same situation applies to complicated molecules posessing a large electron delocalization.

Three important contributions, namely, domain wall motion, magnetic anisotropy and spin relaxation, give rise to the phenomenon called remanence. It consists on the existence of a net magnetization in a sample after a previous externally applied field is switched off. In the case of a regular paramagnet, the net magnetization disappears due to thermal fluctuations. The process takes place in the time given by the spin-lattice relaxation time constant, which is of the order of milliseconds even at liquid helium temperatures. In a ferromagnetic material, the magnetization usually relaxes on a much larger time scale. The thermal fluctuation of the moments per domain is a lot less effective since the energy needed is much larger than in the case of a paramagnet. As a consequence, the ordering direction of a magnetic domain gets a preferential orientation and loss of information about this preference after the external field is switched off takes more time. In ferromagnets, typical remanences exist for hours or even for years, as in the case of permanent magnets, where very large anisotropy is present.

From the experimental viewpoint it is important to realize that at T_c the susceptibility should reach infinite. Nevertheless, in practice χ cannot exceed an upper limit due to the demagnetizing field. In fact this maximum value of

χ is 1/N, where N is the demagnetizing factor, determined only by the sample geometry.[9] This consideration holds for the static and for the isothermal susceptibility χ_T. In an ac susceptibility experiment this situation occurs when the entire magnetic system is able to orientate its magnetic moments at the requirement of the ac external magnetic field. In other words, the ac susceptibility has to be measured at low frequencies compared to the reciprocal time constants of the reorientational processes. In the case of ferromagnets, because of their comparatively slow magnetic changes, this situation seldom occurs, thus one observes a χ' which is lower than χ_T accompained by a χ'' signal. In molecular ferromagnets, if the above supposition about the domain size is correct and these systems can be compared to weak ferromagnets, the domain wall mobility is almost impossible and χ' should drop rapidly from a maximum immediately below the transition temperature.[40] Nevertheless strong confirmation whether ferromagnetism occurs in a specific molecular solid comes, in ac susceptibility measurements, from the determination of χ_T near the transition temperature T_c, keeping in mind that 1/N can be at least roughly estimated from the sample shape.

ACKNOWLEDGEMENTS

This work has been supported by the CICYT, under Grant No. MAT88–0174.

REFERENCES

1. A. Benoit, J. Flouquet, B. Gillon and J. Schweizer, J. Magn. Magn. Mat., 31-34, 1155 (1983).
2. C. Coulon, in "Organic and Inorganic Low-Dimensional Crystalline Materials", Ed. by P. Delhaes and M. Drillon, Plenum Press, New York, 1987, B168, p. 201.
3. S.R. Chittapeddi, K.R. Cromack, J.S. Miller and A.J. Epstein, Phys. Rev. Lett., 22, 2695 (1987).
4. Yu. V. Korshak, A.A. Ovchinnikov, A.M. Shapiro, T.V. Medvedeva and V.N. Spektor, JETP Lett., 43, 399 (1986).
5. Yu. V. Korshak, T.V. Medvedeva, A.A. Ovchinnikov and V.N. Spektor, Nature, 326, 370 (1987).

6. J.B. Torrance, S. Oostra and A. Nazzal, Synth. Met., 19, 708 (1987).
7. R.L. Carlin, "Magnetochemistry", Springer, Berlin Heidelberg, (1986).
8. R.L. Carlin and A.J. van Duyneveldt, "Magnetic Properties of Transition Metal Compounds", Springer, Berlin Heidelberg, (1977).
9. A.H. Morrish, "The Physical Principles of Magnetism", R.E. Krieger Publ. Co., New York, (1980).
10. D.H. Martin, "Magnetism in Solids", M.I.T.Press, Cambridge (1967).
11. A. Herpin, "Théorie du Magnétisme", Press. Univ. France, Paris (1968).
12. A.J. van Duyneveldt, "A.c. susceptibility studies in solid state magnetism", Proc. Letnia Szkola Magnetyzmu, Bialowieza (1988).
13. Rillo, C. Ph. D. Thesis, I.C.M.A., University of Zaragoza (1986). Copies of this thesis are available upon request.
14. H.B.G. Casimir and F.K. du Pré, Physica, 5, 507 (1938).
15. J.S. Miller and A.J. Epstein, in "Organic and Inorganic Low-Dimensional Crystalline Materials", Ed. by P. Delhaes and M. Drillon, Plenum Press, New York, 1987, B168, p. 159.
16. H.M. McConnell, J. Chem. Phys., 39, 1910 (1963).
17. C.A. Coulson and G.S. Rushbrooke, Proc. Cambridge Phil. Soc., 36, 193 (1940).
18. N. Mataga, Theor. Chim. Acta, 10, 372 (1968).
19. A.A. Ovchinnikov, Theor. Chim. Acta, 47, 297 (1978).
20. H. Iwamura, Pure &Applied Chem., 58, 187 (1986).
21. T. Sugawara, S. Bandow, K. Kimura, H. Iwamura and K. Itoh, J. Am. Chem. Soc., 108, 368 (1986).
22. S. Marata, T. Sugawara and H. Iwamura, J. Am. Chem. Soc., 109, 66 (1987).
23. R. Breslow, Pure Appl. Chem., 54, 927 (1982).
24. H.M. McConnell, Proc. R.A. Welch Found. Chem. Res., 11, 144 (1967).
25. R. Breslow, Mol. Cryst. Liq. Cryst., 125, 261 (1985).
26. J.S. Miller, A.J. Epstein and W.M. Reiff, Acc. Chem. Res., 21, 114 (1988).
27. J.S. Miller, A.J. Epstein and W.M. Reiff, Chem. Rev., 88, 201 (1988).
28. K. Ito and K. Takai, Mol. Cryst. Liq. Cryst., 125, 251, (1985).
29. A. Izoka, S. Murata, J. Sugawara and H. Iwamura, J. Am. Chem. Soc., 107, 1786 (1985).
30. J.A. Puertolas, R.Navarro, F. Palacio, J. Bartolome, D. Gonzalez and R.L. Carlin, Phys. Rev.B, 31, 516 (1985).
31. F. Palacio, M.C. Morón, J. Pons, J. Casabó, K.E. Merabet and R.L. Carlin, Phys. Lett. A, 135, 231 (1989).
32. L. Néel, Ann. Géophys. 5,99, (1949).
33. K. O'Grady, A. Bradbury, S.W. Charles, S. Menear, J. Popplewell,

R.W. Chantrell, J. Mag. Mag. Mat. 31-34, 958 (1983).

34. F. Palacio, M.C. Morón, J. Garín, J. Reyes and J. Fontcuberta, Mol. Cryst. and Liq. Cryst., this volume (1989).
35. K. Binder, A.P. Young, Rev. Mod. Phys. 58,801 (1986).
36. J.M.D. Coey, J.Appl. Phys 49, 1646 (1978).
37. J.L. Tholence, Physica 126B, 157 (1984).
38. F. Palacio, F.J. Lázaro, J. Garín and J. Reyes, results to be published.
39. H.A. Groenendijk, A.J. van Duyneveldt and R.D. Willett, Physica 101B, 320, (1980)
40. F. Palacio and M. Andrés, in "Organic and Inorganic Low-Dimensional Crystalline Materials", Ed. by P. Delhaes and M. Drillon, Plenum Press, New York, 1987, B168, p. 425