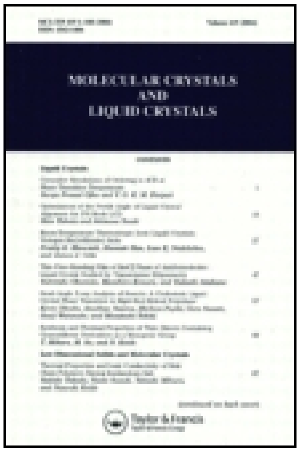

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# Inducing Spontaneous Magnetization in Antiferromagnets

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# INDUCING SPONTANEOUS MAGNETIZATION IN ANTIFERROMAGNETS

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Abstract. Spontaneous magnetization is a most important property in magnetism because of both practical and fundamental reasons. However, nature tends to favour antiferromagnetic alignment better than ferromagnetic one. This is particularly so in the case of molecular systems. This paper emphasizes the point that such tendency does not necessarily excludes the possibility of the presence of spontaneous magnetization in systems where antiferromagnetic interactions dominate and reviews several possibilities other than the well-known ferrimagnetism that permit inducing spontaneous magnetization in antiferromagnets. Examples include favouring non collinear antiparallel alignment of the magnetic moments, or the flipping of spins to parallel alignment by the action of a small magnetic field. The introduction of a certain degree of magnetic disorder in antiferromagnetic lattices can also produce a remnant magnetization in the material. Necessary conditions required for each strategy and some selected examples are discussed.

## INTRODUCTION

Spontaneous magnetization is a most important property in a magnetic material when its potential applicability is being considered. Without excluding the applied interest of certain paramagnets which magnetization is null (e.g., high-spin molecules and high-spin low-spin equilibrium systems), such importance also holds in the case of molecule-based materials. The reason stays in that spontaneous magnetization induces large anomalies in the magnetic susceptibility, particularly in the ac susceptibility, which are almost independent of the magnitude of the magnetic moment and depend more of the measuring conditions (applied field, exciting current, etc.) and of the crystal shape (demagnetizing field). Such sharp changes in $\chi$ can be used for magneto-optical applications, magnetic switching or for the development of magnetic sensors and actuators.

Spontaneous magnetization arises as the consequence of net (uncancelled) magnetic moments in an ordered magnetic structure. This statement summarizes two necessary conditions:[1]

1. The material must undergo a transition to a magnetically ordered state. Although in most cases the departure state will be a paramagnetic one, more complex possibilities

departing from an already ordered magnetic state, such as spin reorientations, are also valid.

2. Magnetic ordering should not completely cancel the magnetic moments.

The parallel alignment of the magnetic moments of the sample in a ferromagnetic structure is the most obvious choice of a material possessing spontaneous magnetization. From a practical point of view the choice is, however, not so obvious, since ferromagnetism is the exception rather than the rule in the list of magnetic materials. Magnetic interactions require strict conditions to be ferromagnetic and it is very difficult, particularly in the case of molecule-based materials, to arrive to a solid possessing extended, intermolecular, ferromagnetic interactions. Antiferromagnetism is, in general, more energetically favoured than ferromagnetism.

Such natural tendency to antiferromagnetism has forced to develop synthetic strategies to make full advantage of it and yet lead to new molecule-based magnets. Thus, the simultaneous crystallization of interacting radical molecules of different spin moment has been proposed for the preparation of organic ferrimagnets.[2] A rather similar approach has been successfully applied using bimetallic complex salts.[3] The assembling of ferrimagnetic chains or layers into a 3-dimensional magnetic lattice has been extensively explored leading to the preparation of a quite rich variety of molecular ferrimagnets.[4-10] Finally, three-dimensional networks of interacting magnetic moments of different magnitude have also been developed[11-13] yielding in some cases high $T_c$ molecule-based magnets.[14, 15]

The ferrimagnetic route to develop molecular materials possessing spontaneous magnetization and yet having antiferromagnetic interactions is not the only possible one. In this paper three alternative approaches which can be particularly suitable for molecular systems will be explore. In particular, the conditions that favour metamagnetic transitions and weak ferromagnetism will be reviewed. In addition, it has recently been shown that a small degree of disorder in an antiferromagnetic lattice can also produce spontaneous magnetization.[16, 17] The general chemical complexity of molecular substances together with the weakness of the intermolecular forces that often are the only responsibles of the packing of the molecules into the crystal, make molecular materials particularly prone to develop small amounts of chemical and/or structural defects that may produce certain disturbances at low magnetic fields in the magnetic lattice. In the last part of the paper the nature of such disturbances and its likely origin will be discussed.

## METAMAGNETISM

Metamagnetism is the name given by Becquerel and van den Handel to the transition from antiferromagnetism to ferromagnetism cause by the application of a magnetic field or by a change in temperature.[18] Only field-induced metamagnetic transitions will be considered here. This type of field-induced phase transition should not be confused with the *spin-flop* (SF) one. Although both are of first order, the first generally consists in simple *reversals* of the local spin directions that tend to align the moments parallel to the magnetic field, while the second is a flopping of the spins that aligns them perpendicular to the field.[19, 20] The differences are clearly evidenced in the respective characteristic phase diagrams which are schematically represented in Figure 1 as a function of the internal field, $H_i$. (The internal field is the applied field corrected from the demagnetizing field). As the material is cooled in zero field it undergoes a second-order phase transition at the Néel temperature, $T_N$, from the paramagnetic (PM) into an antiferromagnetic (AF) state. On the application of a magnetic field below, although close to, $T_N$ there is again a second order phase transition from the antiferromagnetic to the paramagnetic state. This behavior persists for a range of temperatures below $T_N$. The line of critical points corresponding to the second order transitions is marked as a solid line in Fig. 1a. On the application of a field at low temperatures, however, the behavior changes dramatically. Although the phase transition from the antiferromagnetic to a field-induced ferromagnetic state is still present, it is now of first order. This behavior persists all the way down T = 0. The line of first order transition temperatures is shown as a dashed line in Fig. 1a. The line of critical points at high temperatures and the line of first order transitions meet at the *tricritical point,* $T_t$. It is important to note that anisotropy constrains the spins to lie parallel to the easy axis in both the antiferromagnetic and the field-induced ferromagnetic phases.

The spin-flop transition is also of first order (dashed line in Fig. 1b), since it is accompanied by a discontinuity in the magnetization, whereas the transition from the spin-flop phase to the paramagnetic one is of second order. In the Molecular Field treatment, the critical fields for the AF to SF phase transition, $H_{SF}$, and for the SF to PM phase transition, $H_c$, are given by

$$H_{SF} = (2H_E H_A - H_A^2)^{1/2} \tag{1}$$

$$H_c = 2H_E - H_A \tag{2}$$

where $H_E$ denotes the exchange field and $H_A$ the anisotropy field. From equations (1) and (2) follows that an increase in anisotropy increases $H_{SF}$ while it lowers $H_c$. For $H_A = H_E$ the two critical fields become equal and the flopped phase is no longer energetically favourable. Then, the moments go over directly from an antiferromagnetic alignment to a ferromagnetic alignment at $H_c$. Metamagnets are the subset of antiferromagnetic substances that not showing SF phase exhibit a first order transition in a certain temperature range at $H_c$.

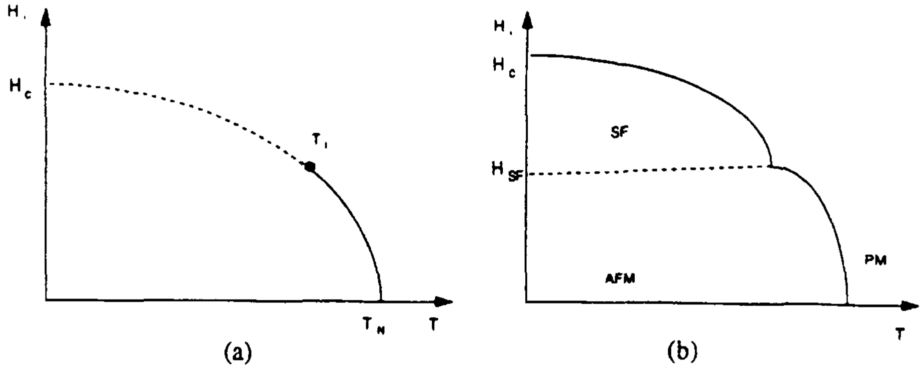


FIGURE 1. Magnetic phase diagrams for antiferromagnets: a) simple metamagnet; b) low anisotropy antiferromagnet

The Molecular Field theory prediction[21] for magnetic behavior of a metamagnet is schematically shown in Figure 2a and 2b, where the dependence with the internal field of the magnetization, M, are represented at two different temperatures. In the temperature range between $T_N$ and $T_t$, the magnetization displays a change in the slope which is finite and discontinuous at the transition (Fig. 2a). For $T < T_t$, M exhibits a discontinuity and the transition is of first order (Fig. 2b). At temperatures below the tricritical point the isothermal susceptibility shows a rather peculiar dependence with the applied field which is exemplified in Figure 2c. Such form of the susceptibility curve is consequence of the coexistence of the two phases, antiferromagnetic and field-induced ferromagnetic, that occurs below $T_t$.

For the purpose of this paper, the important point to emphasize here is the conditions required for a metamagnetic transition to occur. There are two important ones:

1. There must be a certain degree of magnetic anisotropy in the system, large enough to prevent the occurrence of a spin-flop phase.
2. There must be competing interactions that force the low temperature phase transition to be of first order at $T > 0$.

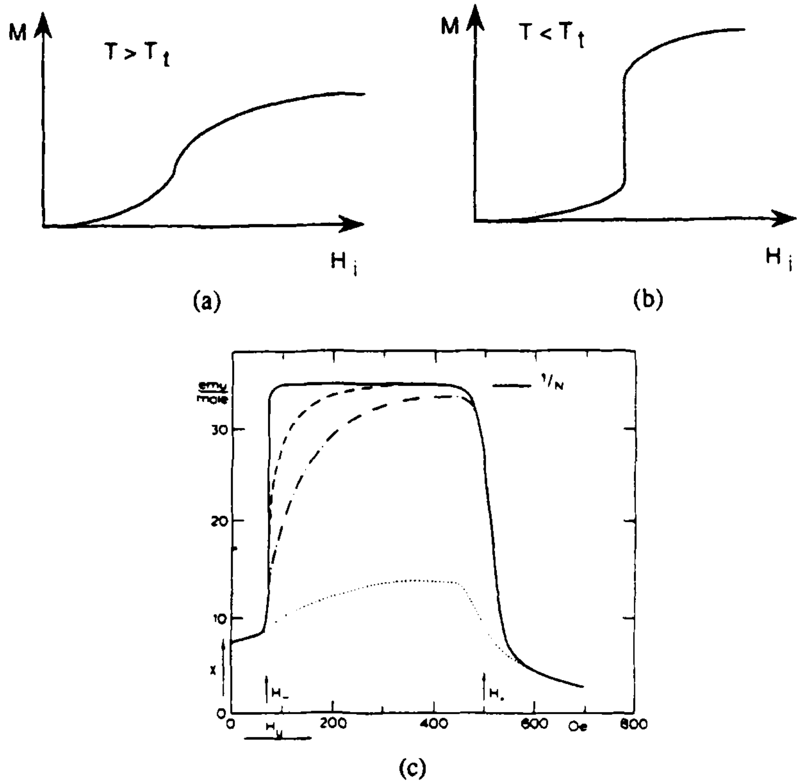


FIGURE 2. a) and b) schematic behavior of M as a function of the internal field and at temperatures above and below the tricritical point for a simple metamagnet; c) isothermal susceptibility (solid line) of $Co[(CH_3)_3NH]Cl_3.2H_2O$ as a function of the applied field. The crystal has been oriented with the easy axis (*c* axis) parallel to the field direction. The in-phase components of the ac susceptibility measured at 20.8 Hz (-----); 82 Hz (-.-.-) and 2.6 kHz (.....) have been included (after ref. 22).

Both conditions can be satisfied in the case of molecular materials. In fact, metamagnetism has been observed in a short variety of compounds, both organic and inorganic. Table I summarizes characteristic magnetic data of a list of them. It is interesting to notice that, in contrast with some theoretical predictions requiring a rather strong magnetic anisotropy for the occurrence of metamagnetism, there are molecular materials where this anomaly has been observed and yet they possess quite low anisotropy. A common characteristic of such low anisotropy materials is that the metamagnetic transition occurs at quite low magnetic fields, of the order of some Oesterds, while field transitions in typical metamagnets are in the kOe range. Some few representative examples are described below.

TABLE I Molecular materials with metamagnetic behavior

| Compound | $T_N$ (K) | $T_t$ (K) | $H_c$ (Oe) | Refs. |
|---|---|---|---|---|
| $Mn(CH_3COO)_2.4H_2O$ | 3.18 | --- | 6 at 1.4K | 23, 24 |
| $(C_{14}H_{22}N_2O_2)Mn(hfac)_2$ | 5.5 | --- | 200 at 1.8K | 25 |
| $[Mn(C_5Me_5)_2][DDQ]$ | 8.5 | 7.5 | $H_{c1}$ = 650 at 4K<br>$H_{c2}$ = 900 at 4K | 26 |
| $[Fe(C_5Me_5)_2][TCNQ]$ | 2.55 | $1.87<T_t<2.34$ | 1500 at 1.87K | 27 |
| $Fe(py)_2.(NCS)_2$ | 6.0 | --- | 1100 at 4.2K | 28 |
| $Fe_4Cl_8(THF)$ | ≈15 | --- | 13700 at ? | 29 |
| $Co[(CH_3)_3NH]Cl_3.2H_2O$ | 4.14 | 4.13 | 60 at 2.3K | 22, 30 |
| $Ni(NO_3)_2.2H_2O$ | 4.19 | 3.85 | 3400 at 1.5K | 31 |
| $(C_6H_{22}N_4)CuCl_6$ | 8.9 | 8.86 | 50 at 4.2K | 32 |
| $(NpO_2)_2C_2O_4.4H_2O$ | 11.6 | 9.0 | 1000 at 8K | 33 |
| TANOL suberate | 0.38 | 0.3 | 100 at 0.07K | 34 |
| MOTMP | 0.14 | --- | 330 at 0.07K | 35 |

hfac = hexafluoroacetyl-acetonate
DDQ= 2,3-dichlro-5,6-dicyanobenzoquinoneide
TCNQ= 7,7,8,8-tetracyano-p-quinodimethanide
py = pyridine
THF = tetrahydrofurane
TANOL = 2,2,6,6-tetramethyl-piperidine-4-yl-1-oxyl
MOTMP = acryloyloxy-2,2,6,6-tetramethyl-piperidine-1-oxyl

$Mn(CH_3COO)_2.4H_2O$ seems to be the first molecular material for which a metamagnetic transition has been reported. In this compound, which orders at 3.18K, the $Mn^{2+}$ ions are located in planes separated by layers of $H_2O$ molecules. Neutron diffraction experiments show that inter-plane interactions are antiferromagnetic while within the planes there are competing ferro- and antiferromagnetic interactions.[36] Magnetization measurements on single crystals indicate that a metamagnetic transition occurs when a magnetic field of 6 Oe is applied parallel to the *a* crystallographic axis.[23, 24]

$(C_6H_{22}N_4)CuCl_6$ is another layered compound with a structure consisting of ferromagnetic planes coupled antiferromagnetically. Antiferromagnetic ordering arises at 8.9K. Metamagnetic transitions have been reported to occur in this compound at temperatures below the tricritical temperature, $T_t$ = 8.86K, induced by the action of small magnetic fields. At 4.2K the transition field is 50 Oe.[32]

TANOL suberate was considered to be for some time an organic ferromagnet. However, magnetic measurements at low field revealed that this compound is, in fact, an antiferromagnet with a metamagnetic transition at about 100 Oe, as shown in Figure 4a.[34] Neutron diffraction experiments have confirmed the antiferromagnetic ordering of this compound in the absence of any applied magnetic field. The structure consists of layers of symmetrically related NO groups parallel to the *ac*-plane. Adjacent layers are 10.8 Å apart from each other. The two magnetic moments of every molecule, each corresponding to a TANOL group, are located in two adjacent layers. The antiferromagnetic structure consists on an array of antiferromagnetically coupled ferromagnetic layers, as shown in Figure 11b.[37]

MOTMP is another organic substance presenting antiferromagnetic ordering in the absence of an applied magnetic field. Susceptibility measurements show a maximum at 0.16K with $T_N = (d\chi/dT)_{max}$ = 0.14K Specific heat measurements present a lambda anomaly at 0.14K indicative of antiferromagnetic ordering and a broad maximum centered at around 0.4K which fits well with the theoretical prediction for the contribution of S = 1/2 Heisenberg chains. The intra-chain interaction has been determined as $J/k_B$ = 0.45K. Magnetization measurements below 0.14K exhibit the characteristic s-shape of metamagnets.[35] The source of competing interactions can be speculated as coming from the antiferromagnetic interaction of ferromagnetic chains.

## WEAK FERROMAGNETISM

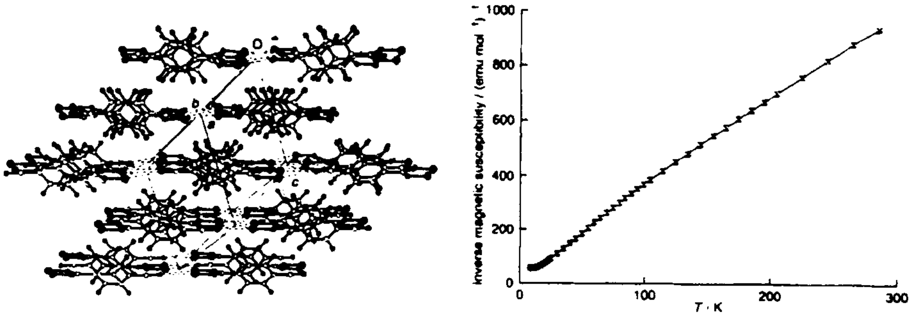
Antiferromagnetic substances whose moments are not exactly collinear can exhibit spontaneous magnetization at the ordering temperature. These substances are known as *weak ferromagnets*. Their interest in the design of molecule-based compounds exhibiting spontaneous magnetization has already been emphasized.[8] Since the magnetic properties of weak ferromagnets have been recently reviewed,[38] only the conditions which permit the occurrence of a canting in the magnetic moments will be considered here.

A general expression for the magnetic energy in terms of the sublattices magnetization must include a term of the form

$$\mathbf{d} \cdot [S_i \times S_j] \qquad (3)$$

where **d** is a constant vector, in order to account for the antisymmetrical part of the spin coupling. It is clear that this term will tend to cant the spins because the coupling energy is minimized when the two spins are perpendicular to each other. It can be proved[39] that **d** cancels when a center of inversion is located at the point half way between two interacting molecules, each belonging to a different antiferromagnetic sublattice.

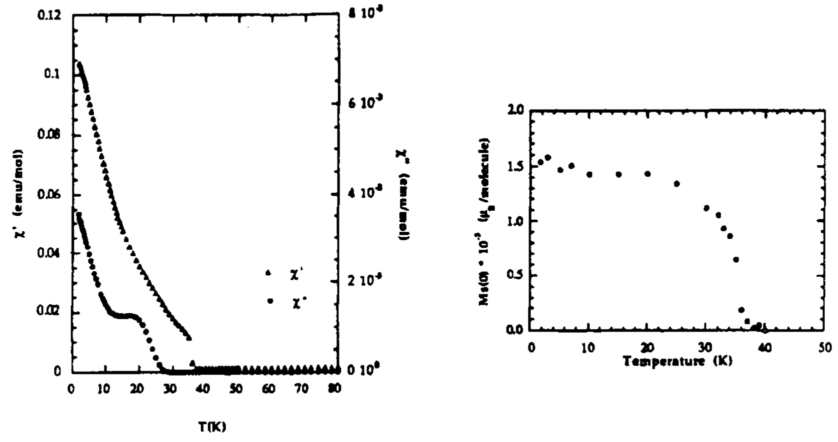
The magnetic properties of α- and β- polymorph phases of the dithiadiazolyl radical *p*-$NCC_6F_4CNSSN^{\bullet}$ exemplifies beautifully the symmetry requirements for weak ferromagnetism. The α-phase crystallizes in the triclinic P-1 space group with two molecules per unit cell. The molecules are related through an inversion center (see Figure 3a) and the magnetic behavior of the substance corresponds to that of a collinear antiferromagnet (see Figure 3b).[40]



3a) 3b)

FIGURE 3. Structural and magnetic characteristics of the α-phase of the dithiadiazolyl radical. (From ref 40)

The β-phase, on the other hand, crystallizes in the orthorhombic Fdd2 space group with Z = 8. As in the case of the α-phase, the structure consists of infinite chains of monomeric dithiadiazolyl radicals. The key structural difference between the two phases is that the chains of the β-phase are all aligned in the same direction, whereas alternate chains of the α-phase are arranged antiparallel to one another. The important implication is that no inversion center relates any two interacting molecules in the β-phase and, consequently, antisymmetric interaction constant **d** does not cancel. Since **d** is proportional to Δg/g, the very small anisotropy of this molecule is enough to move the spins away from collinearity.[41] The magnetic characteristics of the β-phase are shown in Figure 4. It is worth to remark two important features



(a) (b)

FIGURE 4. Magnetic properties of β- dithiadiazolyl radical. a) Ac susceptibility, where the insert shows the raising of the out-of-phase component at $T_N$. b) Temperature dependence of the spontaneous magnetization as determined from the M *vs*. H curves. (From ref. 41)

1. The very small magnetization resulting from the canting of the magnetic moments. Its value at saturation is estimated to be of the order of 1.5x10-3 μB.[41]
2. The huge raising of the susceptibility below 36K.

This underlines the point raised in the introduction that no matter how small the magnetization of a substance can be, its effects in the susceptibility are very large.

## DISORDER IN ANTIFERROMAGNETS

The observation of spontaneous magnetization at very low magnetic fields in disordered easy axis antiferromagnets has been reported recently.[16, 42-44] The anomaly has been found in quite diverse compounds all bearing in common low magnetic anisotropy. Thus, $Mn_{1-x}$ $Zn_xF_2$ is a typical inorganic compound that crystallizes with the rutile structure whereas $K_2Fe_{1-x}$ $In_xCl_5H_2O$ and $Rb_2Fe_{1-x}In_xCl_5.H_2O$ are two isomorphous compounds that crystallize in the Pnma space group. The iron compounds are formed by discrete $[FeCl_5(H_5O)]^{2-}$ octahedra which are hydrogen-bonded together.[45] For the undiluted compounds the ordering temperature,$T_N$, and the ratio between the anisotropy field and the exchange field, $\alpha = H_A/H_E$, are, respectively, 67.33K and 1.6x10-2 for $MnF_2$, 14.06K and $8.5x10^{-3}$ for $K_2FeCl_5.H_2O$, and 10.00K and $3.4x10^{-3}$ for $Rb_2FeCl_5.H_2O$.[46-48]

Figure 5 shows typical magnetization results for a diluted crystal of $Rb_2Fe_{1-x}In_xCl_5.H_2O$ with x = 0.15.[17] Similar curves have been reported for crystals of the two other diluted systems.[43, 44] The rise of M below $T_N$ implies that a remanent magnetization, $M_r$, develops as the crystal orders antiferromagnetically. It is important to note that the data correspond to the longitudinal magnetization, e.g., the crystal mounted with the easy axis parallel to **H**. Experiments with crystals mounted with the easy axis perpendicular to the direction of **H** gave magnetization values orders of magnitude smaller below $T_N$.

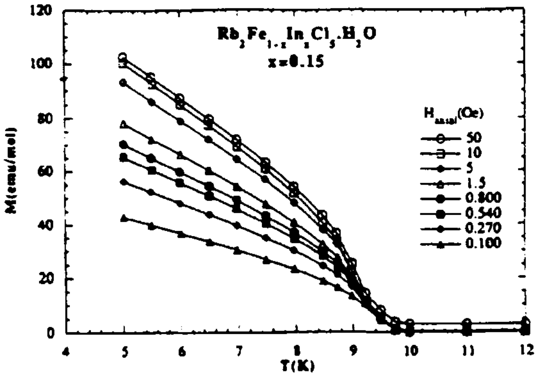


FIGURE 5. Temperature dependence of the magnetization for a sample of $Rb_2Fe_{1-x}In_xCl_5.H_2O$ with x = 0.15 at several axial magnetic fields. (After ref. 17).

The longitudinal magnetization below $T_N$ can be represented as the sum of two contributions:

$$M = M_r + \chi_{||}H_{axial} \qquad (4)$$

where $\chi_{||}$ is the *parallel* susceptibility along the easy axis. The relative size of the two terms of Eq. (4) differs for the three compounds. However, $M_r$ saturates always at low magnetic fields, in most cases lower than 1Oe. The remanent magnetization curves are found to differ only by a scale factor. In other words, if the values of $M_r$ on each curve are normalized to unity at one fixed temperature below $T_N$ then the normalized curves for all $H_{axial}$ *collapse* into a single one. In addition, by using instead of T the reduced temperature, $t = T/T_N$, data sets for different x in the same system can be collapsed into a single curve. Furthermore, if all the curves of $M_r$ vs. $t$ obtained for all the x values and $H_{axial}$ fields for the three compounds are normalized to unity at one fixed value of $t$, then all such a *renormalized* data collapse into a single *universal* curve. This universal data collapse is illustrated in Figure 6, where a value of $t = 0.5387$ has been used in the normalizing process. The figure compares three data sets for each compound. Since all normalize curves in each compound collapse into a single curve, the curve of Fig. 6 is representative of a large set of data sets so far available for the three compounds.[17] Residual magnetization observed at high magnetic fields in the high anisotropy $Fe_{1-x}$ $Zn_xF_2$ does not collapse into the same *universal* curve.[49]

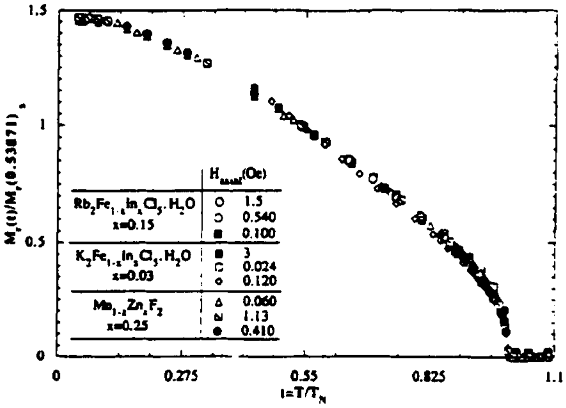


FIGURE 6. Normalized magnetization $M_T(t)/M_T(t=0.53871)$ as a function of the reduced temperature $t = T/T_N$ for a variety of diluted samples of $Mn_{1-x}$ $Zn_xF_2$, $K_2Fe_{1-x}In_xCl_5.H_2O$ and $Rb_2Fe_{1-x}In_xCl_5.H_2O$. (After ref. [17]).

More recently, remanent magnetization has also been observed in metal-organic diluted compound of general formula $(CH_3NH_3)$ $_3Mn_{1-x}Cd_xCl_3{\cdot}2H_2O$.[50] The observation of the anomaly also in this linear chain antiferromagnet is consistent with the *universal* character manifested by the collapsing curve shown in Fig. 6 and indicates that the appearing of remanent magnetization in diluted low anisotropy antiferromagnets does not depend of the crystal structure and of the dimensionality of the compound. The magnitude of $M_r$, however, seems to be strongly compound-dependent. Data from three different compounds are compared in Figure 7 where also the low magnetic fields at which $M_r$ saturates is evidenced. Notice that solid solutions of $Rb_2FeCl_5.H_2O$ seems to act as $M_r$ *amplifiers* since they rise the value of $M_r$ up to four orders of magnitud with respect to the other compounds.

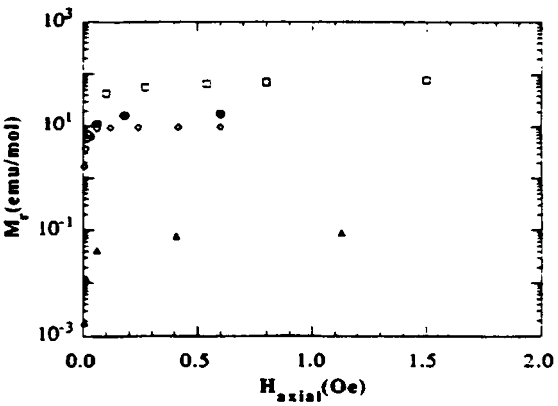


FIGURE 7. Field dependence of $M_r$ for the following representative samples: ☐ $Rb_2Fe_{1-x}In_xCl_5.H_5O$, $x = 0.15$; ◊, ● $K_2Fe_{1-x}In_xCl_5.H_5O$, $x = 0.03$ and 0.14, respectively; ▲ $Mn_{1-x}Zn_xF_2$, $x = 0.25$. Data taken at $t = 0.53871$. (After ref.17).

The origin for $M_r$ is not completely clear yet. Suggestions include the occurrence of domain wall magnetization as a consequence of pinning from the impurities [44] and also a piezomagnetic effect induced by random stress.[51] The recent determination of the magnetic structures of $Rb_2FeCl_5.D_2O$ and $K_2FeCl_5.D_2O$ excludes the piezomagnetic origin, sine the magnetic point group (*m'm'm'* ) is not consistent with piezomagnetism.[52] Therefore, surface magnetization in antiferromagnetic domain walls seems to be the most likely origin for $M_r$. Site-disorder should facilitate the formation of domains at low fields, because of the lower cost in exchange energy for walls passing through non-magnetic cations.

## CONCLUSIONS

The possibilities of antiferromagnets as potentially interesting magnetic materials have been emphasized exploring three different mechanisms that permit the appearing of induced magnetization. An essential feature for practical applications would be the relatively large change in the magnetization or in the magnetic susceptibility. Molecular compounds seem to be particularly adequated to taylor materials which exhibit one or more of the properties here described. Metamagnets could be used to construct bi-stable (multi-stable in the case of complex metamagnets) memory devices. The interest of molecular metamagnets is that their critical field tend to be considerably lower than that of inorganic metamagnets. However, before metamagnets and weak ferromagnets find any application it will be necessry to develop materials with high transition temperature. The possibility of inducing spontaneous magnetization by slightly disturbing the order in the antiferromagnetic lattice opens the door to virtually any low anisotropy antiferromagnet and does not seem to impose restrictions to high $T_N$ ones.

## ACKNOWLEDGMENTS

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