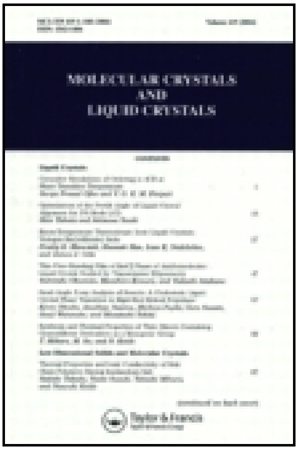

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Molecular Ferromagnetics

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MOLECULAR FERROMAGNETICS

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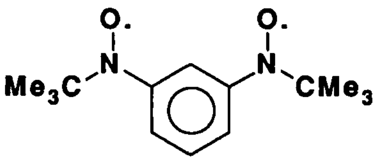
Abstract Possible ways to obtaining organic and molecular ferromagnets are considered and the principles of their molecular design are critically reviewed. Theoretical predictions are compared to experimental data and some conclusions are made concerning the feasibility of the various ways. Particular emphasis is placed on the description of ferromagnetic coupling observed in various systems by McConnell's Heitler-London model.

INTRODUCTION

Much attention is now being paid to a fascinating problem of organic and molecular ferromagnetism. In order to make organic or molecular ferromagnets one should meet three requirements: first, one needs a building material - high spin organic molecules; second, one should know how to organize this material into a molecular system with the ferromagnetic spin alignment; and third, the spin density should be sufficiently high to ensure substantial magnetization, high Curie temperature, and dipole interaction required to develop a domain magnetic structure

The first requirement is easier to satisfy than the latter two. There exists a vast number of known stable radicals (S = 1/2) and biradicals with positive intramolecular exchange interaction (S = 1),[1] for example



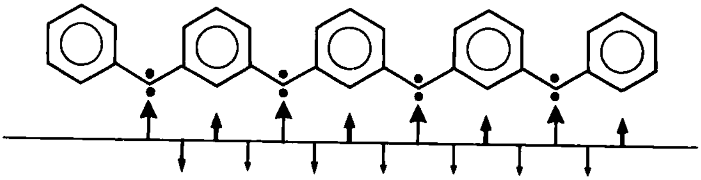
High spin polycarbenes have been synthesized;[2,3] hypothetical structures of linear, potentially high spin molecules[4-6] and two-dimensional cross-linked high spin structures have been proposed;[7] and mixed organometallic high spin molecules have been synthesized.[8-10] In other words we either have at our disposal various building materials for ferromagnets or we know how to obtain them. However, the main problem, the second one, lies in ensuring the ferromagnetic order of spin molecules. The fact is that in organic spin molecules a unpaired electron occupies upper molecular orbitals, being localized mainly on the "surface" of the electron shells. That is why the intermolecular exchange interaction responsible for spin orientation is negative, arranging the spins of neighboring, even high spin molecules, opposite to each other, so that the total macroscopic spin is zero. For this reason radicals and polyradicals[11], high spin polycarbenes,[2] and organometallic high spin molecules[8] in solid phase are antiferromagnetic and even solid oxygen is diamagnetic.

Another piece of evidence of the negative intermolecular exchange is provided by chemically induced dynamic polarization of electrons of radical pairs in liquids. The sign of polarization indicates unambiguously that in such pairs the exchange interaction between radicals-partners, averaged by molecular motion with respect to orientations and interspin distances, is negative.[12]

Several suggestions have been made on how to overcome this barrier on the way to molecular ferromagnets. The first one was formulated as early as 1963 by McConnell[13] who appealed to spin distribution. The leading role in spin propagation along a spin molecule belongs to two mechanisms - spin delocalization and spin polarization. The latter induces negative spin densities at some points of the molecule. The interplay of the two mechanisms results in the spin distribution with alternating areas of positive and negative spin densities. Suppose that spin molecules in a crystal or glass are arranged in such a remarkable manner that one molecule's positive spin density regions face another molecule's negative spin density regions and this alternation of spin density signs holds for the whole bulk. The negative interspin exchange aligns two spin subsystems - the positive spin densities oriented in one direction and the negative ones in the opposite, as in a ferrimagnetic structure. The positive spin densities, however, are considerably higher than the negative ones, which is why the macroscopic spin corresponds to the ferromagnetic alignment.

We will call this mechanism of spin alignment McConnell's Mechanism I and the regions of intermolecular contacts, where positive spin densities of one molecule are combined with negative densities of the neighboring molecules, are McConnell's 'Islands'. In these regions the spin alignment is ferromagnetic or strictly speaking ferrimagnetic.

Note that it is precisely this type of intramolecular spin interaction that has been proposed for high spin molecules,[40] causing molecular ferromagnetism. Thus, with polycarbene the spin distribution in the π-system is accompanied by alternating spin density, shown schematically below:



Here the thick arrows stand for positively oriented spins, while the thin arrows stand for negative ones. The total spin of the illustrated π-system is 2. The intramolecular exchange interaction of π- and α-electrons is positive and therefore the α-electron spins are aligned similar to total π-electron spin, thus making the total spin of the molecule of 4. Similar spin alignment is realized in other high spin organic molecules (including biradical **1**). Ovchinnikov[7] has convincingly demonstrated that this spin exchange mechanism leads to ferromagnetism and he also extended McConnell concept on the case of high spin macromolecules (one- and two-dimensional).

The second concept of intermolecular ferromagnetic spin arrangement was also advanced by McConnell (McConnell's Mechanism II). The concept involves linear $D^{+\cdot}A^{-\cdot}$ chains, where $D^{+\cdot}$ and $A^{-\cdot}$ are a cation-radical of donor D and an anion-radical of acceptor A. McConnell predicted[17] that under certain conditions quasi-one-dimensional ion-radical salts can also be ferromagnetic.

The concept was then further developed by Breslow[15,16] and generalized by Miller and Epstein.[17,18] The idea was to fulfill the conditions when the virtual charge transfer from one partner of the $D^{+\cdot}A^{-\cdot}$ pair to another stabilizes the high spin (triplet) state of the pair. However, it is not easy to fulfill these conditions. First, it is necessary that one of the partners, but not both, should have a degenerate and partly filled molecular orbitals. Second, the contribution of charge transfer into the high spin excited state should be rather large to ensure stabilization of the triplet (ferromagnetic) state of the pair with respect to the singlet (antiferromagnetic) state. Third, there should be no structural or electronic distortions (of the Jahn-Teller effect type) which decreases the symmetry and lifts the degeneracy of the partly filled orbital of one of the partners. Finally, one should bear in mind the Peierls instability of one-dimensional (linear) spin chains and the spin waves with antiferromagnetic interaction.

There is no direct evidence in support of Mechanism II nor is there a way to predict unambiguously what charge transfer and what spin state - singlet or triplet - are stabilized, and what interaction - ferromagnetic or antiferromagnetic - dominates. There is, however, direct experimental evidence in favor of Mechanism I. Triplet phenylcarbenes were introduced into different positions of spatially fixed by chemical bonds phenyl rings of paracyclophanes (pseudo-ortho, Fig. 1a, pseudo-meta, Fig. 1b, and pseudo-para, Fig. 1c).[28]

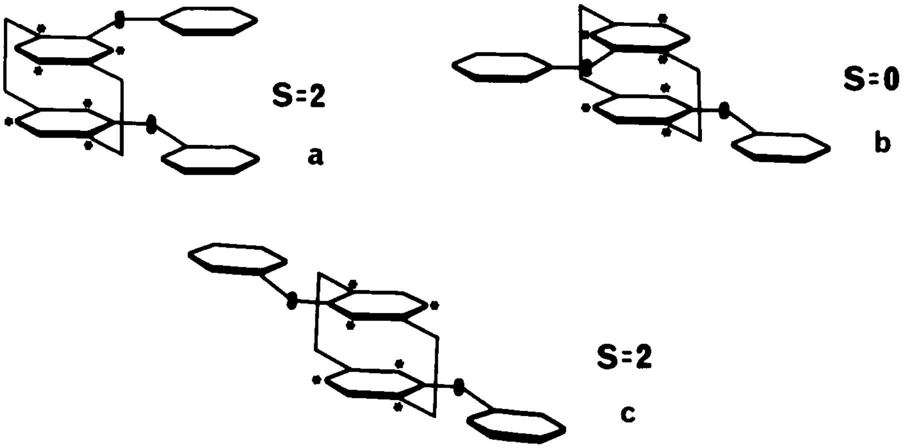


FIGURE 1. Paracyclophane carbenes. The positions with positive spin densities indicated by stars.

One can easily see that when an unpaired π-electron travels from carbene to the phenyl ring of cyclophane, its spin density distribution in pseudo-ortho and pseudo-para structures forms McConnell's 'Islands', that is one phenyl ring's spin densities face another ring's spin densities of the opposite sign. McConnell's 'Islands' are not formed in pseudo-meta structures. In full accordance with this property the spin alignment in pseudo-ortho and pseudo-para structures is ferromagnetic (the ground state is the quintet) and antiferromagnetic in pseudo-meta structures (the ground state is the singlet).

In the next section both McConnell's mechanisms and their validity will be compared on the basis of experimental examples.

The third concept was advanced by Buchachenko.[11,20] The concept deals with cocrystallization of low spin and high spin molecules, such as mono and biradicals with spins of 1/2 and 1, respectively. In case their chemical structure is almost identical, one can expect that in a crystal both types of the molecules will alternate in a regular manner. The negative intermolecular exchange aligns the spins of neighbors in opposition, building two spin sublattices with the spins of one type of molecules being oriented to one side and the other type's spin being oriented to the opposite direction. The resulting ferromagnetic spin arrangement is represented schematically in Figure 2. Although yet to be tested in purely organic systems, O. Kahn and coworkers have designed metal based compounds which are described in the proceedings of this conference.

The experimental search for molecular and organic ferromagnetics is being carried out along three main directions: molecular crystals, purely organic polymers, and organometallic polymers.

MOLECULAR CRYSTALS

The Coppinger radical (galvinoxyl, **2**) should be regarded as the first organic system exhibiting ferromagnetic coupling. In its high temperature crystalline phase ($T \geq 85$ K) **2** is paramagnetic, yet showing signs of ferromagnetic order (positive Curie-Weiss temperature of 19 K, $J > 0$[21]). Below 85 K there occurs phase transition into antiferromagnetic phase. But in mixed phenol-radical crystals (phenol is the radical's precursor) the phase transition is suppressed with ferromagnetic coupling being preserved down to 2 K and positive exchange interaction, $J = 56.5\ \text{cm}^{-1}$.[22-24]

This anomalous magnetic behavior of galvinoxyl makes it different from all the other known radicals. Its crystalline structure is shown in Figure 3.[25] It is of interest to examine the first McConnell's concept: the areas of high positive spin density (oxygen atoms and phenyl rings) of one radical are faced

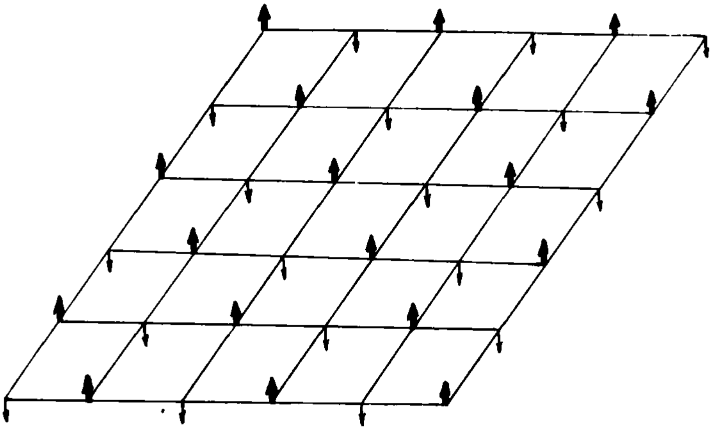
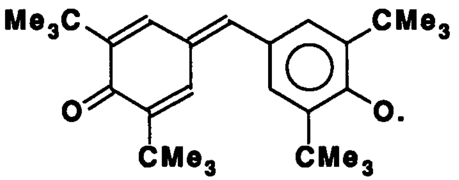


FIGURE 2. Two-dimensional scheme of spin organization.



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to another radical's low negative spin density areas (-CH=groups). The intermolecular exchange in these overlapping areas of spin densities with opposite signs - McConnell's 'Islands' - is negative and it arranges positive and negative spins into a lattice similar to that shown in Figure 2. As a result the total spin magnetization of the ferromagnetic type.

Another remarkable organic ferromagnet is quasi-one-dimensional crystals of decamethylferrocenium cation, $Fe[C_5(CH_3)_5]_2{\cdot}^{+}$, and tetracyanoethylenide anion salts.[26-28] This is a true ferromagnet which exhibits even spontaneous magnetization of 8 x 10^3 emuG/mol below 4 K. The origin of ferromagnetic exchange in the ion-radical salts of decamethylferrocene with tetracyanoethylene, 7,7,8,8-tetracyano-*p*-quinodimethane, and *n*-hexacyanobutadiene is explained[26,27] in terms of McConnell's Mechanism II, although Mechanism I appears to be an alternate. Figure 4 shows schematically the arrangement of cations and anions into a regular

linear (one-dimensional) chain and a diagram of spin distribution in a cation known from the contact paramagnetic NMR shifts of this cation.[28] The π-electron spin density in the cation's ring is positive, while the spin density in

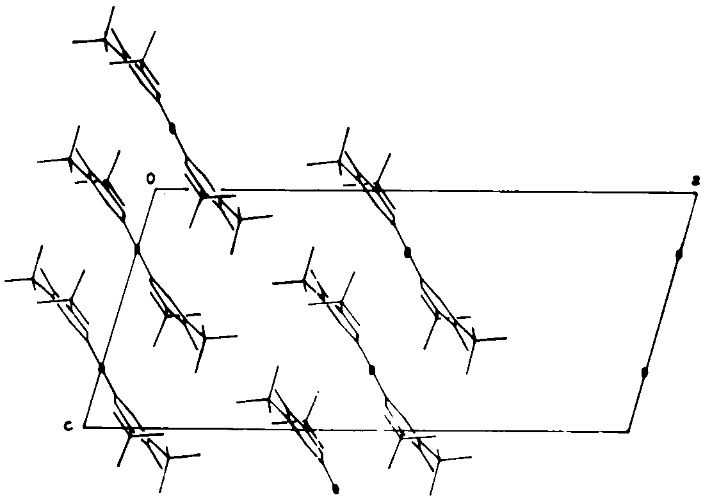


FIGURE 3. Crystalline structure of galvinoxyl, **2**, from ref. 25.

the methyl groups localized along the ring's perimeter is negative. McConnell's 'Islands' can be formed between the methyl groups of the cation's ring (negative spin density) and the anion's CN groups where the positive spin density is localized. These islands are responsible for the alternating pattern of negative and positive spin densities shown in Figure 4, which result in the ferromagnetic spin alignment and ferromagnetism.

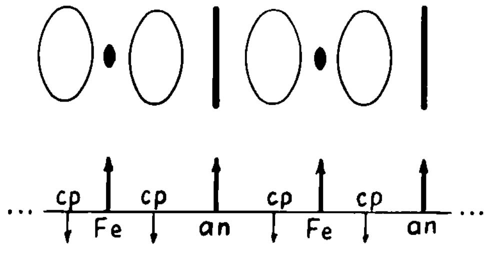
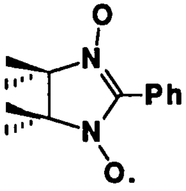


FIGURE 4. One-dimensional scheme of $[Fe(C_5Me_5)_2][TCNE]$.

Substituting the $C_5(CH_3)$ ligand in the ferrocenium cation by the C_5H_5 ligand should destroy McConnell's 'Islands' though it should not produce any substantial changes in the electron structure of the $D^{+}\cdot A^{-}\cdot$ pair. Therefore, the disappearance of ferromagnetism in $Fe(C_5H_5)_2{}^{+}\cdot$ salts is predicted by Mechanism II, but unfortunately suitable compounds have not been prepared to test this idea. Besides, the spin alignment in Ni^{III} and Cr^{III} salts is antiferromagnetic[28] and, although the data on the contact paramagnetic NMR shifts in $[Ni(C_5H_5)_2]^{\cdot+}$ and $[Cr(C_5H_5)_2]^{\cdot+}$ is ambiguous,[29] it is predicted that the spin distribution in these cations is different from what is observed for $[Fe(C_5H_5)_2]^{\cdot+}$and it looks like there are no McConnell's 'Islands' in the ion-radical salts of Ni^{III} and Cr^{III}. Thus, McConnell's Mechanism I is apparently more general as compared to Mechanism II for predicting organic ferromagnetism.

The absence of McConnell's 'Islands' (i. e., antiferromagnetic behavior) is clearly seen in the ionic paramagnetic salts synthesized by Breslow et al.,[30,31] although structural information is unknown.

Finally, one should mention mixed organometallic molecular crystals of the type of metal hexafluoracetylacetonates complexes with paramagnetic ligands - nitroxyl radicals.[32,33] For instance, 3 $Cu[O_2C_2(CF_3)_2CH]_2 \cdot 2L$, where L are nitroxyls with two functional groups (one of which is paramagnetic) able to coordinate to metal ions. There are no real ferromagnets among such mixed organometallic crystals, but there are indications of ferrimagnetic order. Thus, both the intra- and intermolecular exchange interaction in the above mentioned complex are positive ($J_{intra} \approx 12$ cm^{-1}, $J_{inter} \approx 0.046$ cm^{-1}).[33] However, for a similar complex where L is Ullmann radical, **3**, the question of the sign of intramolecular **3** interaction is yet to be clarified.[33] In principle, this is a promising and attractive way to organometallic molecular ferromagnets.



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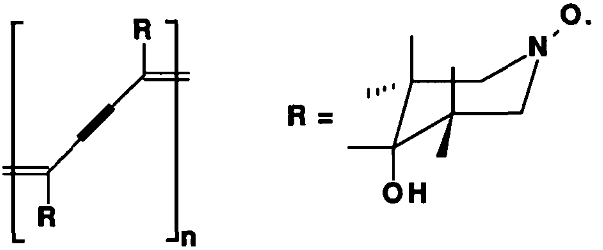
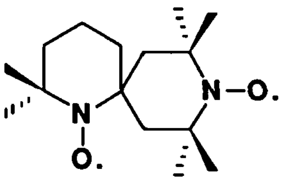
ORGANIC POLYMERS

Initial results in this area were achieved by Ovchinnikov and coworkers[34,35] The polymerization of a diacetylene substituted by two nitroxyl radicals R yields a species with ferromagnetic behavior amounting to 0.1 - 0.3% of the total mass. After magnetic separation the species exhibited magnetization of ~1 G. The Curie Temperature was 420 - 460 K and higher, i. e., ferromagnetism was preserved up to anomalously high temperatures.

The crystalline structure of the monomer - the ferromagnetic polymer's precursor[36] - excludes topochemical polymerization typical for several diacetylenes. However, one can assume that the polymer may contain the following type of blocks (units)



The two spin systems - one belonging to the main polyene chain and the other to the nitroxyl fragments, are independent; that is the exchange interaction between them is negligibly small. This stems from the fact that the paramagnetic fragments are independent even in the initial monomer (the ESR spectrum of the biradical is a triplet typical for the nitroxyl radicals) and there is no exchange between the unpaired electrons via the σ-system. Even in case of a biradical with closer paramagnetic centers, e. g.,



the exchange energy $J \ll 15$ G (i. e., $J \ll a$, where a is the hyperfine electron-nuclear interaction with the nucleus of ^{14}N).[37] The low J value is due to σ-bonds barrier which separates the two spin systems.

The substantially weak exchange interaction of the two spin systems ($J \ll 10^{-3}$ cm^{-1}) fails to agree with high temperature ferromagnetism and this means that the latter is not caused by the former. It is possible that the structure of Ovchinnikov's ferromagnetic polymer contains McConnell's 'Islands', but in this case one must conclude that the 'Island'-containing structures are so rigid that they are not destroyed by molecular motion and that they are preserved even at 450 - 500 K when the polymer itself undergoes chemical degradation. This, of course, is a strong assertion which is yet to be proved. In any case the origin of ferromagnetism in spin-labelled polydiacetylene remains a mystery.

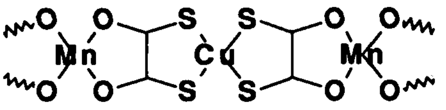
Flexible-chain polymers spin-labelled by nitroxyls (copolymer of styrene and maleic acid, polyglycidyl methacrylate, polyfulvene, etc.) also show the presence of 3 to 5% of ferromagnetic fraction.[38] Ferromagnetic grains after a magnetic separation where they are divided into two components; one with ferromagnetic behavior while the second without. Annihilation of nitroxyl radicals (under the action of acids or thermolysis) fails to destroy ferromagnetism, i. e., there is no direct relation between paramagnetism and ferromagnetism.

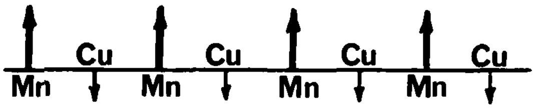
The magnetization of flexible-chain ferromagnetic polymers is 0.1 - 0.01 G/g and the Curie temperature 350 - 400 K. The metal ions content was measured (0.1 - 0.01%) and on this basis it was shown that experimentally measured magnetizations did not normally exceed the magnetizations calculated under the assumption that Fe ions were united into clusters of metallic α-Fe.[38] This, however, does not make it possible to conclude that Fe ions are reduced to metallic iron that ensured ferromagnetism. It may well be that metal ions organize paramagnetic macromolecular fragments into ferromagnetic organometallic structures (due to metal-ligand type of interaction).

Weak ferromagnetic behavior is often observed in degraded or carbonized polymers (including cellulose) and in polymers subjected to intense shear deformation at high pressure. It has a number of strange features (nonreproducibility, irreversible disappearance in time, etc) and therefore provokes strong skepticism. Its origin remains obscure. It may be caused by reduction of metal ions traces via chemical reactions induced by degradation or mechanical treatment, but one should not neglect the possibility of structural clusters formation with McConnell's 'Islands'. In any case it is not yet absolutely clear whether it is possible to obtain purely organic ferromagnetic polymers with no metal traces or admixtures. This direction is worthy of being further developed.

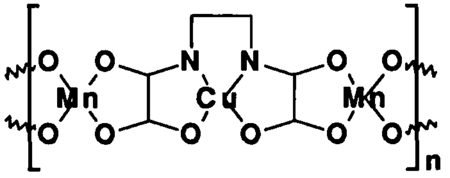
ORGANOMETALLIC POLYMERS

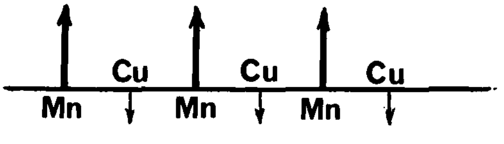
This way to ferromagnets is based on high spin macromolecules where paramagnetic metal ions alternate with organic bridges, forming linear (one-dimensional) spin chains. For example, in the polymer chain[8,10] the exchange interaction between Cu and Mn ions is carried on via the chemical bonds of organic bridges and is negative. Therefore, the ions form an alternating chain with Mn^{II} spins ($S = 5/2$) being oriented to one direction and the Cu^{II} spins ($S = 1/2$) to the opposite one. As a whole the molecule is found to be ferromagnetic.





A similar arrangement of spins is shown by another organometallic one-dimensional chain:[9]





Unfortunately, both polymers with ferromagnetic macromolecules turn to be antiferromagnetic at 5 - 8 K. This is due to the negative exchange interaction between polymer chains which aligns large magnetic moments of ferromagnetic molecules opposite to another. To avoid this intermolecular pairing one should induce structural changes to shift macromolecules with respect to each other so as to form McConnell's 'Islands' and ensure the ferromagnetic spin alignment.

One more area of investigations is organometallic ferromagnetic polymers based on chemical reactions of polymetallosiloxanes. These are covered in reference 39 and will not be discussed in the present paper.

CONCLUSIONS

Molecular ferromagnets is a highly intellectual area of scientific endeavor where there is plenty of room for a creative mind. The main difficulty lies in providing the molecular arrangement of molecules that ensures ferromagnetic alignment of spin. Another difficulty is a low spin density in molecular ferromagnets, an immense excess of "dead rock", i. e., spinless molecular groups. At spin densities of about 1 spin per 10^3 $Å^3$ the magnetization is of the order of 10 G/g. This means that molecular ferromagnets can hardly compete with classical metallic ferromagnets as far as the static magnetization is concerned. Still they can possess unusual dynamic magnetic properties - losses or their frequency dependence. In any case further development of this area will worth the trouble.

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