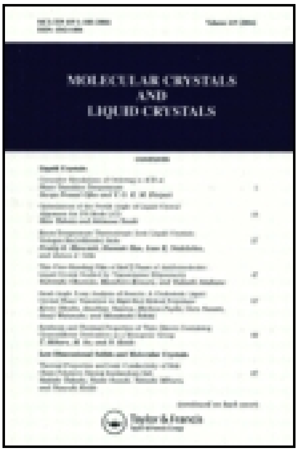

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FRACTAL FERROMAGNETIC EXCHANGE INTERACTIONS IN METAL-CONTAINING (NANOSIZE CLUSTERS) POLY-CONJUGATED SYSTEMS

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Abstract Polymers of acrylonitrile, Mtilon (Mt) - cyanoethylated cellulose hydrate $[(C_6H_7O_2)_{3-x}(OCH_2CH_2CN)_x]$ and Nitron (Nt) - commercial acrylic fiber containing 10-60% carboxylic groups have been specially prepared and modified by various metals (Fe, Co, Ni). Subsequent special thermal treatment yielded polymers containing metal nanosize clusters (40-200 Å) dispersed in the polymer matrix whose ferromagnetic properties has been thoroughly studied. The chief reasons hindering the creation of high-T_c molecular/polymer-based ferromagnets are determined and analyzed. The concept of fractal ferromagnetic exchange interaction between magnetic moments of neighboring nanosize metal clusters via polyconjugated system is proposed. A new effect of an increase in the specific saturation magnetization μ_s of metal atoms in clusters is reported. The effect is explained by the spin polarization of the polyconjugated matrix coating the metal clusters, somewhat similar to the chemical polarization of spins of electrons in a fractal geometry of clusters.

INTRODUCTION

A strong interest in organic and molecular ferromagnets aroused soon after sensational Russian discovery of high-T_c purely organic ferromagnet[1] has revived some of the old theoretical ideas and subsequently produced a number of excellent experimental results[2–4]. Much of the work has been devoted to the study of metal-organic and carbon-based organic ferromagnets. However, the former of them being quasi-1-D substances obviously revealed very low T_c, whereas the latter often contained hardly controllable amount of ferromagnetic impurities which made the organic origin of the ferromagnetism in them questionable. At the same time it was noticed that ferromagnetic behavior was always observed in the polymers containing metal clusters. This observation has given birth to the idea of metalopolymeric ferromagnets: small metal clusters evenly dispersed in polymer matrix and ferromagnetically coupled via π-electron system of the polymer. This was the approach employed in our study.

This contribution discusses the results of our experiments, their interpretation, a new concept of ferromagnetic interaction, and all together, perhaps, a new avenue to the creation of high-T_c ferromagnets.

EXPERIMENT

As it was mentioned earlier low T_c are inherent of all known organic/molecular ferromagnets. Embarking our own study we tried to understand the reasons for this and formulate necessary criteria to be met for creation of high-T_c molecular ferromagnet.

First of all, we noticed that the majority of ferromagnets are in fact quasi-1-D compounds with a large anisotropy of exchange interaction $\delta = \frac{A_{intra}}{A_{inter}} \gg 1$, where A_{inter} and A_{intra} are intermolecular and intramolecular exchange interactions, respectively. In addition, the distances between the spins are much bigger than in metals, thus leading to much weaker exchange interaction. We also would like to note that in organic substances electron density at the Fermi level is much lower and the symmetry of electron wave functions often favors an overall antiferromagnetic ordering.

Obviously, it is not easy to avoid these difficulties. However, having thoroughly studied para- and ferromagnetism in numerous polyconjugated systems for a long time, we knew that metal clusters as well as the conditions under which the polyconjugated system had been formed could drastically change various properties of the polymer including magnetic. Thus, based on our knowledge of the properties of the polyconjugated polymers we can propose the following model of ferromagnet. If we have evenly distributed small metal clusters (we imply ferromagnetic metals) in the polyconjugated matrix, then it might be possible to "switch on" indirect exchange interaction between metal clusters via π-electrons of the polymer similar to $4f$-metals (RKKY interaction). Metal clusters must be small, i.e. they should not form the bulk phase, and hence show only superparamagnetic or slightly ferromagnetic behavior. How small can be metal clusters? 10 - 20 Å seems to be a pretty good estimate, because as studies show clusters bigger than 50 Å are already ferromagnetic. Besides, the clusters should not be large due to the fact that big clusters introduce rather strong anisotropy in the interactions (weak polymer-metal, strong intracluster), the thing we are trying to avoid. The metal concentration ought to be small too (less than 5 %, i.e. below percolation threshold) in order not to form bulk metal phase. On the other hand, the polymer matrix should resemble the structure of metal clusters, i.e. it should exist in a form of nanosize polyconjugated layers or "polyconjugated clusters". This means that any metal cluster has to be "dressed" in polyconjugated cluster forming cluster-inside-cluster structure, so that the interactions between electrons (spins) of metal and polymer are maximized. We also would like to note that both polyconjugated polymers and nanosize metal clusters have soft lattices and large constants of electron-phonon and spin-phonon interactions which stabilize various quasiparticles (e.g. solitons, polarons) in their structure and enhance intermolecular and exchange interactions between polymer molecules and metal clusters. This, in turn, may lead to the induced spin polarization of π-electrons, and therefore to higher saturation magnetization per metal atom in the composite. This last one can be experimentally observed.

First, we studied[6] specially prepared pure thermolized polymers (polyacrylonitrile (PAN), Mtilon (Mt), Nitron (Nt) and their derivatives) and found no ferromagnetic behaviour in them. Then these polymers were modified by ferromagnetic metals (Co, Ni, Fe) in a number of different ways. The main methods of metal introduction were placing the polymer into the water solution of metal salts, preparation of the joint solution of the polymer with metal salts in dimethylformamide, and mixing the solution of the polymer in dimethylformamide with specially prepared metal-containing epoxy. After that the polymers were thermolized in the inert atmosphere (N_2, Ar) to create the desired structure. Certainly, we varied the conditions of pyrolysis, so that to cut the growth of big metal clusters and thus, to be able to obtain reasonably good agreement with our estimate (20 $\AA$). We paid special attention to magnetic and structural properties of the composites as the most important ones. Specifically, we were interested in saturation magnetization of the sample, metal concentration in the polymer matrix and size distribution of metal clusters. Saturation magnetization and coercive force were measured using Faraday's balance with 5% accuracy, metal concentration was measured by two different methods (neutron activation and atomic emission analysis) with both of them giving consistent results and cluster sizes by X-ray small angle scattering with 10% accuracy.

According to the model proposed, indirect exchange interaction between neighboring metal clusters via π-conjugated electron system of the polymer might result in an increase of the specific saturation magnetization of metal atoms in clusters. However, this can be achieved only for small clusters ($d \leq 20\mathring{A}$) and low metal concentrations (less than 5%). As we can see from the Table I, we have succeeded in preparing composites with desired metal concentration. However, the cluster sizes were much bigger than we wanted them to be. Nevertheless, we still managed to observe the increase in saturation magnetization per metal atom (last column in Table I) which amounted up to 50% in some systems. It is clearly seen that we discovered the effect in those samples prepared with the epoxy (compounds containing E symbol in their name). This indicates that the usage of the epoxy leads to smaller metal clusters and their more uniform distribution in the polymer matrix, and overall better composite structure. Considering the accuracy of our measurements, we see that the uncertainty in the experimental value of saturation magnetization is about 10% which is less than the estimated magnitude of the effect. Thus, we managed to observe and extract the theoretically expected effect as being of the order of 40-50%. It should be noted that metal atoms can be either in low- or high-spin state which are analytically indistinguishable for the majority of ferromagnetic metals, and in our calculation of the theoretical value of the saturation magnetization we considered all metal to be in its high-spin state. This means that the value of the effect we obtained is underestimated. We also would like to note that no effect was observed for large metal clusters (i.e. high pyrolysis temperature), and for small metal clusters and poor polyconjugated structure (low pyrolysis temperatures). This implies that the effect is essentially of intrinsic origin (i.e. supplied by both metal clusters and polymer matrix) and is very sensitive to the structural changes in the composite.

DISCUSSION

Our experiment revealed that the utilized techniques of synthesis were not very well applicable to the systems in question. As we know, both polyconjugated polymers and nanosize metal clusters represent non-equilibrium systems, so that our composites are essentially non-equilibrium, whereas the methods used are aimed at producing more-or-less equilibrium structures.

As it is well known, non-equilibrium structures and processes occuring in such

TABLE I. Characteristics of some polymer metal-containing ferromagnets

Compound	Pyrolysis Temperature, °C	C_{metal}, %	Cluster sizes, Å	Specific magnetization[a]
PAN-Co	700	2.1	60-100	0.8
PAN-E-Co	700	2.5	40-60	1.43
PAN-Co	800	2.6	100-150	0.88
PAN-E-Co	800	3.1	80-100	1.4
PAN-Co	900	1.3	200-300	0.92
PAN-E-Co	900	1.5	100-200	1.2
Nt-Co	700	2.1	60-90	0.82
Nt-E-Co	700	2.8	40-60	1.25
Nt-Co	800	3.2	100-150	0.92
Nt-E-Co	800	3.7	80-100	1.35
Mt-Co	700	1.9	60-80	0.86
Mt-E-Co	700	2.8	40-60	1.15
Mt-Co	800	2.7	100-150	0.91
Mt-E-Co	800	3.5	80-100	1.44

[a] the ratio of experimental to theoretically expected saturation magnetization

structures can be described by fractal physics[5,7], so we tried to explain the observed effect in terms of fractal physics. The main distinctions of fractal system are a long-range memory, i.e. the state of some atom is determined not only by its nearest neighbors, but also to a large extent by some other atoms and the history of the structure formation, and different from topological(d) dimensionality of fractal structure (D). As a result, these long-range correlations lead to a substantial change in relaxation patterns of the substance slowing down some of the relaxation processes and giving rise to their hierarchy[5], i.e. processes may occur only in a strict order determined by respective relaxation times τ and energy barriers Q. This picture in turn favors the formation of metastable non-equilibrium states, with some of them being able to exist for quite a long time. Physically, these metastable states reflect the coherent interrelation of energy states corresponding to different types of motion (e.g. spins, electrons, atoms, group of atoms etc.) and correlated with them synchronously occuring changes of electron and spin densities, elastic constants of individual bonds and can be called fractal excitations. Obviously, some processes (and some types of motion) take place in topological space, whereas other happen in fractal. Because of the different dimensionality these two types of processes will be only slightly linked, i.e. processes occuring in d-space will barely effect the processes in D-space. By saying this we mean that the actual structure and properties of the composite are determined by its fractal structure, and hence all relevant characteristics should be considered in D-space.

Now let us apply this picture to our system. Intermolecular and exchange interactions are strengthened in the fractal structure of the clusters which in turn leads to higher electron density at the Fermi level, lower anisotropy of exchange interactions ($\delta \approx 1$) and eventually to higher T_c. In addition, thanks to non-compact (porous) nature of the fractal structure, long-range correlations dominate in the fractal structure leading to the greatly diminished role played by pair potential (parabolic) and short-range interactions. As a result, ferromagnetic ordering becomes somewhat more favorable than antiferromagnetic and will allow us to obtain a fractal ferromagnet. Clearly, the exchange interactions in such composites would differ from known for conventional systems, and can be referred to as "fractal exchange interactions" implying that in this case they involve some complex exchange with linked different-scale excitations such as electron-phonon, electron-spin-phonon, electron-conformational ones. We would also like to note that the cluster structure of the polymer matrix makes it possible to achieve the spin polarization of π-system, so that it may have a non-zero net magnetization. Thus, polyconjugated matrix could make an additional enormous contribution to the total magnetization of the composite showing significant increase in the specific saturation magnetization (i.e. saturation magnetization per metal atom), and thus revealing the fractal nature of the magnet. In fact, as we have already discussed, the net effect has amounted up to 50% for some samples, and was far less than we had expected. The main reason is that we could not really create the desired fractal structure of the composite since pyrolysis was found to be inappropriate for this purpose, for its usage leads to the formation of bulk metal phase and poor polyconjugated structure (stochastic memory).

In conclusion, we would like to note that our study has experimentally confirmed the proposed theoretical model of the high-T_c ferromagnet, and exhibited the predicted effect of the increase in the specific saturation magnetization. It has also showed that some new methods of synthesis had to be invented, or some existing had to be considerably modified in order to obtain the desired ferromagnets. This facet of the problem being perhaps one of the most important is currently under way.

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