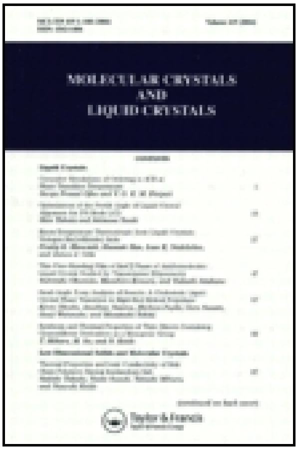

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# Chemical Principles of Designing Organometallic Ferromagnets

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# CHEMICAL PRINCIPLES OF DESIGNING ORGANOMETALLIC FERROMAGNETS

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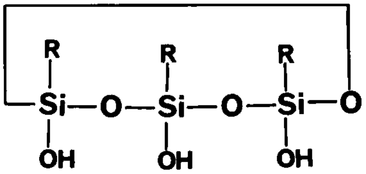
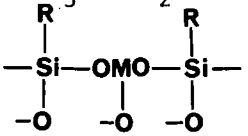
The idea of designing ferromagnets chemically boils down to uniting paramagnetic atoms by means of a chemical reaction and "turning on" positive exchange interaction between them, which aligns the atoms' electron spins into ferromagnetic order. This general idea can be tested using organometallic polymers with metal paramagnetic atoms in the polymer chain. The metal atoms are isolated by organic fragments and are not bound by exchange interaction. Two ways can be used to turn on the exchange. The first is to remove the isolating fragments between the metal atoms or to replace them by electron-conductive fragments which allow the exchange interaction. The second is to build new molecular bridges able to turn it on.

Among numerous organometallic polymers organo-polymetallic siloxanes are especially attractive. Obtained in nonaqueous solutions via condensation of the sodium salt of cyclosiloxane



with metal salts ($FeCl_3$, $CoCl_2$, etc), they contain fragments



$$-\overset{\displaystyle R}{\underset{\displaystyle -O}{Si}}-O\underset{\displaystyle -O}{M}O-\overset{\displaystyle R}{\underset{\displaystyle -O}{Si}}-$$

$R = Ph, CHCH_2$

$M = Fe, Co$

with alternating -Si-O-M- and -SiOSi- bridges. They can also contain six-member siloxane cycles, open chains, and cross-linked structures.

Through fractional separation one can isolate polymer fractions with M/Si ratio ranging from $10^{-3}$ - $10^{-2}$ to 1.5. In fractions with high M/Si ratio long molecular fragments -MO(SiOSiO)$_n$M- with high n are substituted by short fragments with n=1 and even n=0 (-MOM-). The exchange interaction between metal atoms through long bridges is low (which is implicitly suggested by NMR data on organic substituent R: the paramagnetic shiftsof these groups' protons do not exceed their measurement accuracy). However, in short fragments of -MOM- type with covalent bonds, the exchange interaction must be appreciable and it must align the atoms' electron spins into ferromagnetic order. Indeed, we have observed a dependence of an iron atom magnetic moment in polyferrosiloxanes on Fe/Si ratio. The magnetic moment of a metal atom depends not only on M/Si ratio but also on conversion in the dismutation reaction. The higher the metal content and conversion the larger the share of -MOM-fragments and their clusters. The effect manifests itself in the behaviour of magnetic moment but so far we have failed to establish certain regularities.

The nonequivalency of metal atom also clearly manifests itself in the Mössbauer spectroscopy (Figure 1). There are at least three types of iron atoms with the same isomer shift of 0.45 mm/s and different quadrupole splittings. The spectra bear no evidence of the pre-

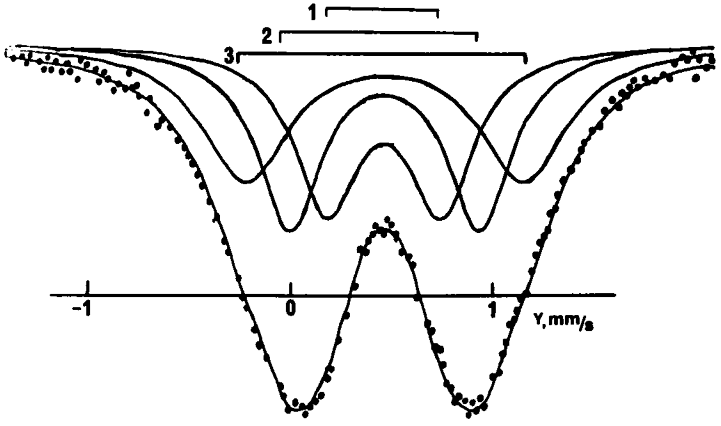


FIGURE 1. $^{57}$Fe Mössbauer spectra of polyferrosiloxane. Three doublets with different quadrupole splittings belong to three types of iron atoms.

sence of $FeCl_3$ and iron hydroxides, while doublets 1 and 2, judging by isomeric shifts and quadrupole splittings, correspond to supermagnetic iron oxide, $Fe_2O_3$, but differ significantly in dynamic parameter f' (0.63 for $Fe_2O_3$ and 0.22-0.25 for polyferrosiloxane). It can be that the doublets belong to metal atoms in different ligand ( -MOSiOM-, -MOM-, and -MOM- clusters) and intermolecular coordination surroundings. ESR spectra of polyferrosiloxanes correspond to $Fe^{+3}$ ion spectra (high spin $d^5$ configuration) in a weak crystalline field (singlet with $g \approx 2.003 - 2.006$).

Shortening of interatomic bridges, which gives rise to exchange interaction, is an effective way to ferromagnets. This way is far from being exhasted and we shall follow this direction further.

Another way is to remove the organic fragments and to unite the paramagnetic atoms into clusters. Thus, thermodegradation of polymetallosiloxanes at 300-800°C yields ferromagnetic compounds with magnetization of 10 to 50 G/g (depending on metal content in the starting polymers and degradation temperature), while the polymer disposes of 50 to 90 % of phenyl groups in the form of benzene and diphenyl, the vinyl groups being isolated in the form of ethylene. The remaining organic groups are transformed into polyaromatic compounds, amorphous carbon, the metal's carbide, and FeSiC. X-ray phase analysis reveals that solid ferromagnetic product contains FeSiC phases with low crystallinity, iron carbide and metallic $\alpha$-Fe with the size of clusters of about 350 Å. The whole amount of oxygen is concentrated in the amorphous $SiO_2$ phase.

The Mössbauer spectra of ferromagnetic products (Figure 2) exhibits a weak doublet similar in its parameters (isomeric shift and quadrupole splitting) to one of the doublets of the starting polymer's spectra (it appears to belong to -MOM- fragments). Besides, there is a doublet from reduced high spin $Fe^{+2}$, a doublet from iron carbide (about 30%) and a sextet of $\alpha$-Fe (about 45-50%).

Thermolysis of mixed iron-cobalt polymetallosiloxanes presents one interesting feature: the yield of $\alpha$-Fe reaches to 90%, i.e. cobalt induces formation of iron clusters. The static magnetization of mixed iron-cobalt ferromagnets reaches 70 G/g.

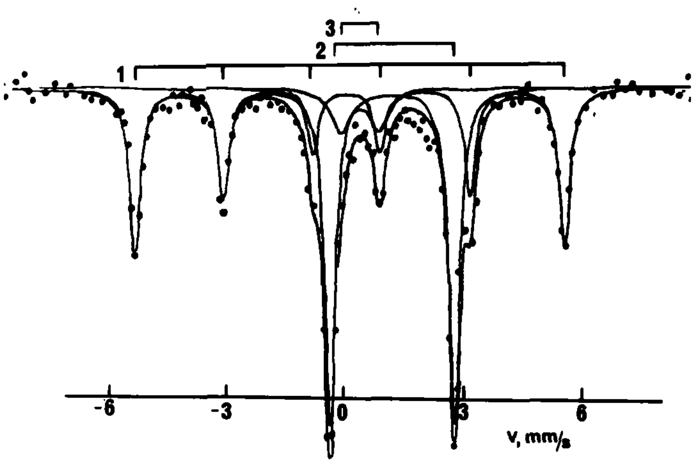


FIGURE 2. $^{57}$Fe Mössbauer spectra of polyferrosiloxane-based ferromagnetic. Sextet 1 belongs to $\alpha$-Fe, doublet 2 - to $Fe^{+2}$, doublet 4 - to $Fe^{+3}$.

Clearly, thermodegradation is the simplest, most primitive way of turning on exchange interaction and transforming a paramagnetics into ferromagnets. Such ferromagnets are composite materials with small high frequency magnetic losses, yet with considerable static magnetizations.

The next problem is to turn on exchange interaction by means of building conductive bridges between metal atoms. This work is in progress.