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MAGNETIC STUDIES OF POLYMETALORGANOSILOXANES

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Abstract Iron (3+) and cobalt (2+) polyorganosiloxanes were synthesized and characterized magnetically. The cobalt containing polymers were found to have a ferromagnetic ground state with a mean value of J of about 10K. The iron containing polymers demonstrated both ferromagnetic coupling with a mean J value ranging from 10 to 50K (depending on Fe concentration) and antiferromagnetic interaction with an exchange constant having an absolute magnitude of about 10 times less. Several models were developed to fit the experimental data. For both systems the best model found was the following: ion-ion coupling (5/2+5/2 for Fe and 3/2+3/2 for Co) arising from interactions within the polymeric chain, complicated by inter-chain interactions which are positive and negative for Co and Fe, respectively. A molecular field approximation was used to calculate the contribution of this interaction.

INTRODUCTION

The objective of this paper is to present results of a detailed investigation of iron- and cobalt- containing polymetallicorganosiloxanes (PMOS) using magnetic susceptibility measurements and theoretical modeling. This study was undertaken

largely because of rapidly growing interest in modeling in molecular magnetic materials [1,2].

RESULTS AND DISCUSSION

The cobalt- and iron- containing PMOS samples were synthesized using a three step procedure as described by Levitsky [3]. Table 1 lists eleven samples investigated in the present study according to metal concentration and silicon/metal atomic ratio. General formula: $\{[RSi(OH)_x(O_{(3-x)/2})]_yMO_{n/2}\}_m$, where R ≡ Ph-, CH_2=CH-; M ≡ transition metal; n = valency of metal; y = variable determined by the ratio Si/M in a polymer.

Fig.1 shows the results of our magnetic susceptibility measurements as a function of temperature for the Fe-1 and Fe-5 samples. The results for the other iron-containing PMOS samples lie within these for Fe-1 and Fe-5. Since the results point to the presence of both ferromagnetic and antiferromagnetic interactions, we have applied a model which includes the molecular field expression (1).

TABLE 1 PMOS samples.

Code of sample	Metal conc.,%wt.	Si/Fe, at.
Fe-1	7.9	5.50
Fe-2	15.4	2.05
Fe-3	16.7	0.90
Fe-4	29.4	0.64
Fe-5	28.8	0.62
Co-1	5.1	7.3
Co-2	14.8	2.0
Co-3	18.9	1.7
Co-4	20.9	1.4
Co-5	21.0	1.4
Co-6	24.6	1.1

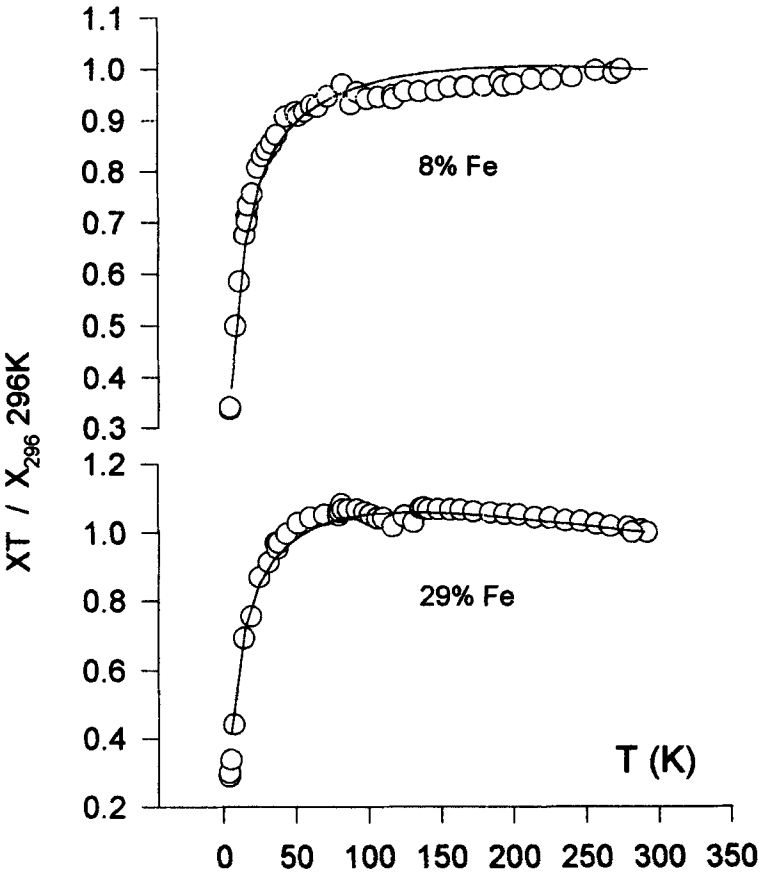

FIGURE 1 Iron containing PMOS. Experimental results with theoretical curves.

$$\chi'(T,J_f,J_{af}) = \frac{\chi_{ecp}(T,J_f)}{1-(2zJ_{af}/N\mu_B^2g^2)\chi_{ecp}(T,J_f)} \quad (1)$$

with

$$\chi(T) = \int_0^{J_{0f}} \chi'(T,J_f)\, P(J_f)\, dJ_f \quad (2)$$

and $\chi_{ecp}(T,J_f)$ as that corresponding to an exchange coupled pair of spin 5/2. $P(J_f)$ is a distribution function for the different ferromagnetic J_f couplings such that $\int P(J_f)\, dJ_f = N/2$ where N is the number of spins per unit volume. The precise form

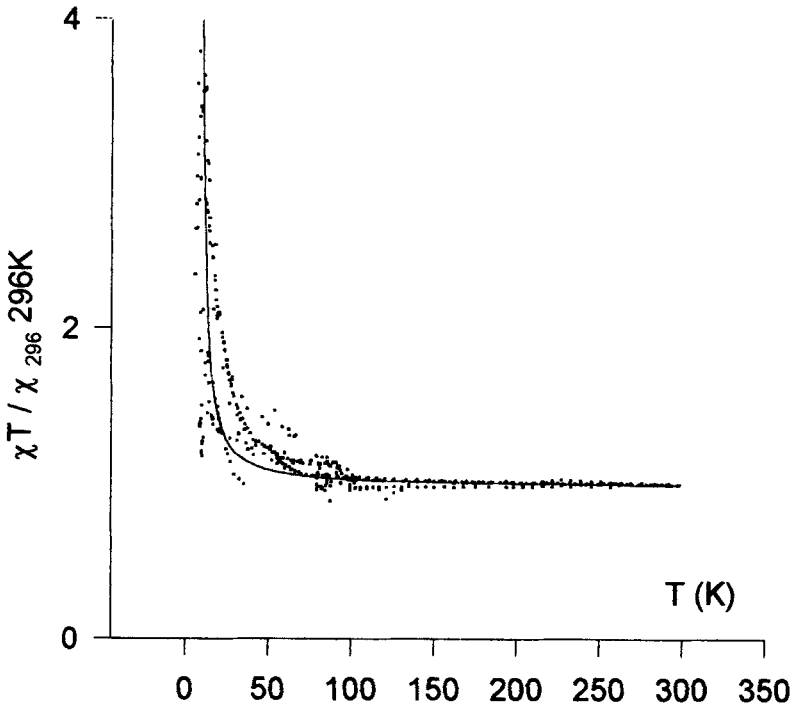

FIGURE 2 Cobalt containing PMOS. Experimental results and theoretical $\chi T(T)$ curve

of $P(J_f)$ is taken from Kahol and Mehring [4]. The result of such calculations, the details of which will be published later, are also plotted in Fig.1, which show satisfactory agreement with the experimental results. The distribution function $P(J_f)$ shows a maximum at $J_{fm} \approx 70K$ for the Fe-1 and at $J_{fm} \approx 28K$ for the Fe-5 samples. The J_{fm} value for samples Fe-2, Fe-3 and Fe-4 are 65, 33 and 31K, respectively. This trend shows that the magnitude of the ferromagnetic interactions decreases with an increase in the iron content in PMOS.

Fig.2 shows experimental results of magnetic susceptibility as a function of temperature for all the six cobalt- containing samples. Unlike PMOS-Fe, χ in PMOS-Co shows virtually no dependence on the cobalt content. Equation (1) and

(2) were also applied to fit the data with two modifications. First, the expression for χ_{ecp} corresponded to an exchange coupled pair of spin 3/2, and, second, J_{am} appearing in eq.(1) turned out to be of the ferromagnetic type. The value of J_{fm} was found to be around 2K for both the Co-1 and Co-6 samples.

In summary, samples of iron- and cobalt- containing polymetallicorganosiloxanes have been synthesized and their magnetic susceptibilities measured as a function of temperature. A simple model which involves pair spin correlation of order two has been used to analyze the magnetic susceptibility data. It is found that the dominant interactions in both the Fe- and Co- containing samples are ferromagnetic.

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