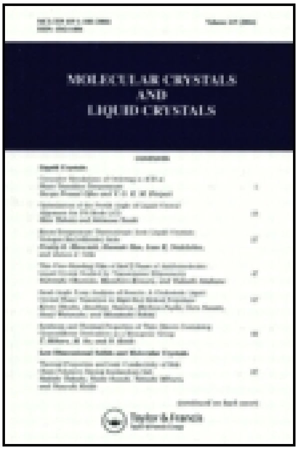

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FERROMAGNETIC INTERACTIONS ABOVE ROOM TEMPERATURE IN A SCHIFF-BASE METAL-ORGANIC POLYMER.

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Abstract The magnetic properties of an iron-bonded Schiff base polymer of general formula $\{[Fe(C_{13}H_{17}N_3)_2]SO_4{\cdot}6H_2O\}_n$ are reported. Mössbauer spectroscopy shows that the polymer contains about 20±8 % of Fe^{3+} ions, despite the fact that only Fe^{2+} is used in the synthesis. A large out-of-phase component of the a.c. magnetic susceptibility is observed at zero external magnetic field and temperatures as high as 350 K. This result is characteristic of the presence of net magnetic moments in the material. The saturation magnetization is estimated to correspond to a saturation magnetic moment of 0.10 μ_B per structural repeating unit of the polymer.

INTRODUCTION

The search for molecular ferromagnetic materials is important because of their potential industrial applications. Apart from some metals and alloys, intermetallic compounds, together with a not very extensive list of inorganic derivatives, have been traditional sources of ferromagnets. In the last few years, however, the possibility of preparing entirely organic-based ferromagnets has become a major challenge for organic chemists. In addition, the area between purely inorganic and purely organic compounds has not escaped attention. Indeed, it has proved to be a very exciting field where a large variety of magnetic ordering phenomena have been found.

Some years ago, the polymeric Schiff base $(C_{13}H_{17}N_3)_n$ (**P**), where n was supposed to be large, was reported to combine with iron (II) sulfate and to give rise to a metal-organic complex polymer of formula $[\{Fe(C_{13}H_{17}N_3)_2\}SO_4\cdot 6H_2O]_n$ [1]. The substance was considered ferromagnetic because of its unusually high magnetic susceptibility at room temperature. Recently, the magnetic properties of this material have been more extensively studied by T. Sugano et al.[2,3]. From magnetization measurements in the temperature range of 1.9 K to 300 K the authors conclude that the iron-bonded polymer exhibits a field-induced phase transition from an antiferro- to a ferromagnetic state characteristic of metamagnetic behavior. Critical fields, Hc, for the metamagnetic transition are reported to be weaker than 600 Oe and rather temperature dependent, Hc decreasing when T increases[2].

In order to have a better understanding of the unusual properties of this substance we have made extensive magnetic susceptibility measurements using an a.c. technique and studied the magnetization of the material as a function of magnetic field and temperature. A.c. susceptibility measurements at zero external field are relevant because they can contribute to elucidate whether the material is a meta- or a ferromagnet. In the present paper we report on the a.c. magnetic susceptibility and magnetization measurements as a function of field and temperature. The samples used in the experiments were also studied with Mössbauer spectroscopy and the results are also briefly discussed.

EXPERIMENTAL SECTION

The material was prepared following synthetic methods already described in the literature[1]. Condensation of 2,6–pyridine-dicarbaldehyde with 1,6–hexanediamine afforded polymer (**P**) as a white powder with correct spectral and microanalytical data. Reaction of (**P**) with a boiling aqueous solution of iron (II) sulfate readily led to a dark-violet precipitate. Elemental analyses are in good agreement with the formula

$[\{Fe(C_{13}H_{17}N_3)_2\}SO_4{\cdot}6H_2O]_n$. Deoxygenated solvents and nitrogen atmosphere were used along the whole process. The synthesis was repeated several times modifying the temperature of the reaction in the polycondensation step. Two samples, hereafter designed as I and II, corresponding to reactions at 158 °C and 78 °C respectively, were selected for the experiments.

Mössbauer spectra were measured on powder samples at liquid nitrogen and room temperatures. No differences were observed between the spectra corresponding to samples I and II. The spectra at 77 K present higher absorption intensity than at 300 K where reduction of the Mössbauer factor is observed.

Magnetic a.c. susceptibility measurements at zero external field, were made between 4.2 K and 350 K using a computer controlled susceptometer^4. The amplitude of the exciting field was 1 Oe and the frequency 122 Hz. Magnetization measurements between 2.4 K and 200 K were conducted using the same equipment, by integrating the voltage induced in the secondary coils when the sample was moved in the presence of an external magnetic field produced by a superconducting magnet.

RESULTS

Typical Mössbauer spectra are shown in Figure 1. A Lorentzian least-squares curve fitting analysis indicates that the spectra can be explained as the superposition of two spectra, A and B, the parameters of which agree

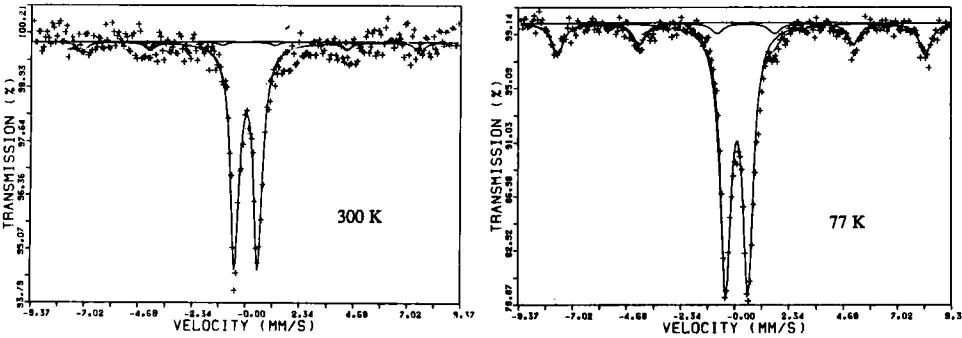

FIGURE 1. Mössbauer spectra of $[\{Fe(C_{13}H_{17}N_3)_2\}SO_4{\cdot}6H_2O]_n$ at 300 K and 77 K. The solid lines correspond a Lorentzian least-squares fit as explained in the text.

very well with previously reported ones[3]. The spectrum A presents six peaks consistent with hyperfine splitting due to an internal magnetic field while the spectrum B consists of two peaks of quadrupole splitting. Isomer shift δ, quadrupole splitting ΔE_q and internal field H_i are summarized in Table I for both samples and temperatures.The values indicate that spectrum A corresponds to the presence of high-spin (S = 5/2) Fe (III) in the samples and spectrum B to low-spin (S = 0) Fe (II) in full agreement with Sugano et al.[3] The proportion of Fe(III) in the samples, calculated from the ratio of the spectral areas, is 0.20±0.09 which agrees within the error bars with the value of 0.3 estimated from X-ray photoelectron spectroscopy[3]. Attempts to prepare an analogous derivative starting from iron (III) sulfate were unsuccessful.

TABLE I Isomer shift δ (relative to metallic α-Fe), quadrupole splitting ΔE_q and internal field H_i calculated from the Mössbauer spectra of samples I and II of $[\{Fe(C_{13}H_{17}N_3)_2\}SO_4{\cdot}6H_2O]_n$ at 77 and 300 K.

	T (K)	Spectrum A (Fe^{3+})			Spectrum B (Fe^{2+})	
		δ mms^{-1}	ΔE_q mms^{-1}	H_i T	δ mms^{-1}	ΔE_q mms^{-1}
Sample I	77	.51±.08	.10±.08	50	.233±.003	1.04±.06
	300	.26±.18	.05±.18	46	.17±.01	1.01±.02
Sample II	77	.50±.04	.11±.04	49	.26±.01	.97±.01
	300	-	-	-	-	.92±.04

Temperature dependence of the in-phase, χ', and out-of-phase, χ'', components of the magnetic susceptibility data corresponding to sample I are depicted in Figure 2. The χ' curve presents a broad maximum at about 250 K and then decreases monotonically down to 20 K, where it remains temperature independent. There are two interesting features in the measurements presented in Fig. 2. The first is the anomalous high values of χ'. At 250 K χ' = 4.5 emu/mol, a value about 100 times higher than the expected for a typical paramagnet with S = 5/2 and g = 2. The second is the presence of a rather high out-of-phase component of the susceptibility. The χ'' curve shows a maximum around 160 K and then slowly drops to almost zero at 4.2 K.

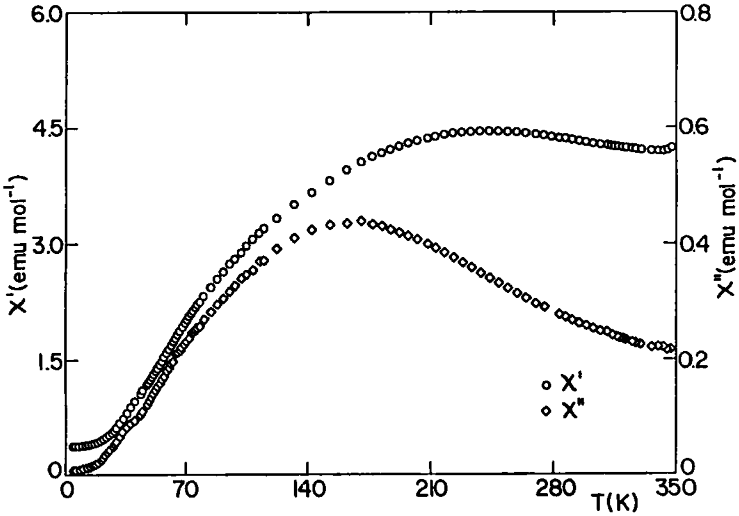

FIGURE 2. Temperature dependence of the a.c. magnetic susceptibility of $[\{Fe(C_{13}H_{17}N_3)_2\}SO_4{\cdot}6H_2O]_n$ at zero external magnetic field.

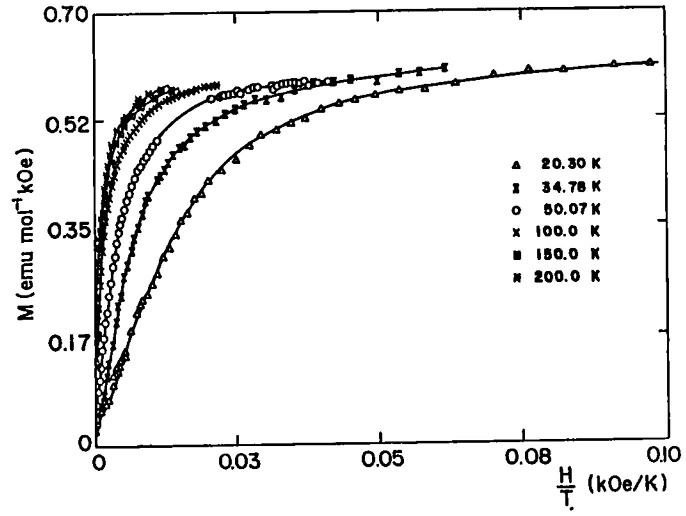

FIGURE 3. Magnetization isotherms of $[\{Fe(C_{13}H_{17}N_3)_2\}SO_4{\cdot}6H_2O]_n$ at various temperatures as a function of H/T.

Measurements corresponding to sample II (not shown) exhibit the same general behavior; however, values of the susceptibility corresponding to sample II are smaller by a factor of 3 with respect to those corresponding to sample I, the maxima being shifted towards lower temperatures.

Initial magnetization measurements are shown in Figure 3 for a variety of temperatures. The curves increase rapidly until at about 2 kOe they reach a value nearly temperature independent; this is in agreement with curves previously published[2]. On the basis of these measurements, the saturation magnetization is estimated to be Ms(0) = 0.58 emu·kOe/mol. What is in contradiction with previous results is the existence of magnetic hysteresis. Figure 4 exhibits an isothermal magnetization loop showing magnetic hysteretical effects. The curve was made at 2.40 K, a temperature which corresponds in the reported magnetic phase diagram to the region where metamagnetic transitions appear at the highest magnetic fields (at about 500 Oe at 2.40 K). Similar curves were obtained at every temperature measured. The existence of magnetic hysteresis is consistent with the observed χ'' component in the susceptibility measurements.

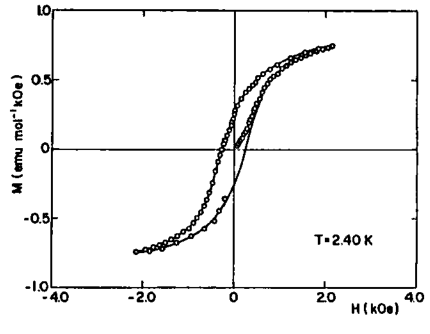

FIGURE 4. Hysteresis loop of $[\{Fe(C_{13}H_{17}N_3)_2\}SO_4{\cdot}6H_2O]_n$ at 2.40 K

DISCUSSION

From the synthetic conditions one should expect a polymeric complex consisting of tridentate Schiff bases and hexacoordinated Fe(II) ions. As it is typical in related coordination compounds the iron would exhibit a low-spin S = 0 configuration[5] and the material would be diamagnetic. However, the observed χ'' component in the susceptibility and the magnetic hysteretical effects suggest the existence of net magnetic moments in the material. Since these moments are present even above room temperature, the ferromagnetic interactions are expected to be strong. In addition, the Mössbauer spectrum corresponding to the Fe(III) ions indicates the existence of an internal magnetic field which may be interpreted as a consequence of magnetic interactions in the polymer.

The existence of net moments when no magnetic field is present[6] excludes the possibility of metamagnetism since in that case the material would have been antiferromagnetic. As a consequence no out-of-phase component of the susceptibility would have been observed and χ' would tend at T = 0 to 2/3 of its maximum value.

To consider the material as a ferromagnet seems, on the other hand, rather plausible. Such a possibility would also be in agreement with the magnetization results and with the existence of magnetic hysteresis. The estimated value of the saturation magnetization Ms(0) = 0.58 emu·kOe/mol corresponds to 0.10 μ_B per repetitive structural unit of the polymer, or to 0.52 μ_B/Fe(III)-at. if every Fe(III) present in the material is considered to contribute to the ferromagnetic behavior. This is about ten times smaller than the expected Ms for a S = 5/2 and g = 2 system, suggesting partial contribution of the iron (III) ions to the ferromagnetic ordering. The presence of Fe (III) ions in paramagnetic state in the material might be in contradiction with Mössbauer results. However, the fraction of paramagnetic Fe(III) would give a small quadrupolar splitting in the spectra which could be hidden by the large quadrupolar splitting corresponding to the iron (II) ions. In order to verify this possibility, new measurements at lower velocity range are in progress.

The descent observed in χ' at low temperature can be related with an increase of the relaxation times in the magnetic system. The magnetic moments would be unable to follow the oscillations of the exciting field and in the limit they would be decoupled from the lattice phonons, χ' would decrease tending to its adiabatic value and χ'' would tend to zero since no magnetic hysteresis losses would be present. These phenomena are frequently observed in systems with small net magnetic moments.[7]

Besides the above arguments one has to be cautious before accepting magnetic long range ordering in the material, whichever it could be. Mössbauer results indicate that the magnetism in the material has to be associated with the presence of iron (III) ions. In that case the polymer is a diluted magnetic system. The concentration of the magnetic centers in the material would be about x = 0.20. This value is just in the percolation limit, x_p, for an f.c.c. crystalline system[8]. However, the polymer is an amorphous material and estimations for x_p should be higher. Thus, considering the high values of the susceptibility, superparamagnetism should not be disregarded. In fact, superparamagnetic behavior would be in agreement with the results here reported. The a.c. susceptibility should present an out-of-phase component and both χ' and χ'' would show a maximum, χ''_{max} appearing at lower temperature[9]. The Mössbauer spectra corresponding to Fe (III) ions would as well exhibit a sextet, providing relaxation time of the atomic spins is smaller than Mössbauer measuring time.

In order to determine whether the system has long range order or it consists in weakly interacting clusters formed by a number of magnetic sites linked by strong ferromagnetic interactions, more experiments are required. In particular the frequency response and high temperature field dependence of the a.c. susceptibility are in progress.

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