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Spin glass behavior in complexes of iron doped coordinated polymers

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Abstract

Magnetization measurements were performed on metal polycarbosilazane complexes polymers doped with Fe(II) and Fe(III)-ions. Zero field cooled (ZFC) and field cooled (FC) magnetization for Fe(II) doped polymer were found to bifurcates at a freezing temperature T_g, showing typical spin glass behavior but at much higher fields (~kOe) than what is commonly observed in metallic spin glass(~Oe). However, the ZFC magnetization of Fe(III) doped polymer did not reveal any spin-glass behavior. The magnetization curves showed very little Hysteresis effects and saturate at about 40 kOe at 2 K then drops sharply at 20 K. The saturation magnetization continues to drop gradually up to room temperature ~300 K.

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1. Introduction

Understanding the nature of magnetic coupling between magnetic ions doped in various matrix is a key factor in the design of new magnetic materials. For example, ferromagnetic coupling units have been found in organic radicals with triplet ground state, which resulted in ferromagnetic behavior in organic material [1,2]. However, anti-ferromagnetic coupling could lead to frustrated interaction in the presence of certain degree of disorder. Ultimately this will lead to spin glass behavior [3].

Spin–glass behavior continues to fuel interest in disordered and ordered materials with random spin distribution as well. Diverse materials reveals spin glass behavior, the range of material includes but not limited to disorder and quazicrystalline material. The signature for this magnetic state has been observed concentrated transition metal alloys of Cu–Mn, Ag–Mn and Ni–Mn in the fifties and sixties of last century by Owen et al. [4] and Kouvel et al. [5]. In 1971 Cannella et al. observed sharp cusp-like peaks in the low field ac magnetic susceptibility of Au–Fe 'dilute' alloys [6]. Cannella and Mydosh attributed the observed peak in the susceptibility to long range antiferromagnetic ordering arising from RKKY interaction between magnetic Fe-impurities in an Au matrix [7]. However, neutron scattering measurements revealed no new lines at the cusp temperature; and the magnetic moments are essentially randomly oriented [8].

In this paper we present magnetic measurements that reveals spin glass behavior in macromolecular complexes of coordinated polymers (oligomer type) reacted with Fe(II) and Fe(III) magnetic ions. These results reveal for the first time, a non-typical spin glass like behavior in polymers doped with Fe-ions.

2. Experimental details

The samples used in this paper have been prepared by incorporation of $FeCl_2$ and $FeCl_3$ into poly-*N*, *N*-bis

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(dimethylsilyl) ehtylenediamine [–Si$(CH_3)_2$NHCH_2CH_2 NH–]$_n$ Matrix (PDMSEN). The iron ions are coordinated to the nitrogen of the PEDCSZ backbone. Although there is no detail information about the coordination environment of iron in these macromolecular complexes, it is reasonable to presume that they adopt the most common octahedral geometry with dimethylsilyldiamine, Cl^- and H_2O moieties in the coordination sphere [10,11]. The detailed preparation and inclusion of Fe(II) and Fe(III) magnetic ions in the complex matrix has been described in Refs. [10,11]. Fine powder of the sample has been molded in non-magnetic disc-shaped plastic and allowed to dry overnight in diluted varnish. Magnetization data (M versus H and M versus T) were recorded using a computer controlled PAR-4500/150A vibrating sample magnetometer (VSM) incorporating a 9 Tesla superconducting magnet. The temperature was measured in the range 2–300 K using a calibrated carbon glass resistor located near the specimen. The magnetic moment was calibrated using pure nickel standard. The overall accuracy in the temperature measurements is better than 1% throughout the range, while that of the magnetization measurements is estimated to be approximately 5%. The magnetic field was applied along the plane of the disc.

3. Results and discussion

The zero field cooled state (ZFC) was obtained by cooling the sample in zero magnetic field from room temperature down to 4.2 K. A 1 kOe magnetic field was applied parallel to disc-plane, and the magnetization was monitored while the temperature being swept between 4 and 300 K. The field cooled branch (FC) was obtained by cooling the sample from room temperature to 4 K in 1 kOe [9]. The changes in magnetization are shown in Figs. 1 and 2 for polymers doped with Fe(II). The corresponding results for polymers doped with Fe(III) are shown in Fig. 3 and 4.

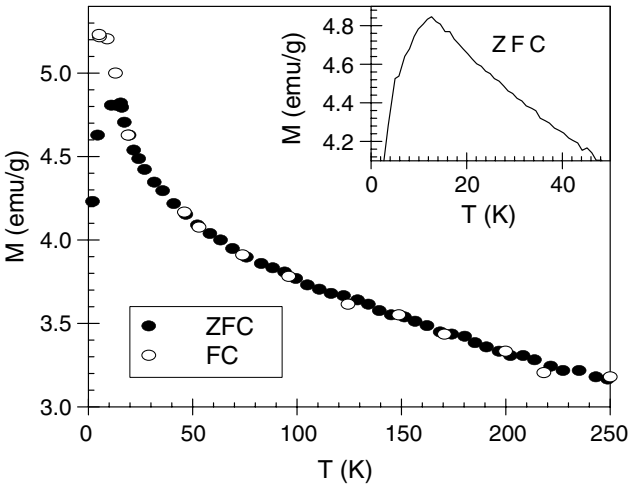

Fig. 1. Fe(II) doped polymer: irreversibility in ZFC and FC magnetization measured in 1 kOe. The inset figure shows the peak position in ZFC magnetization.

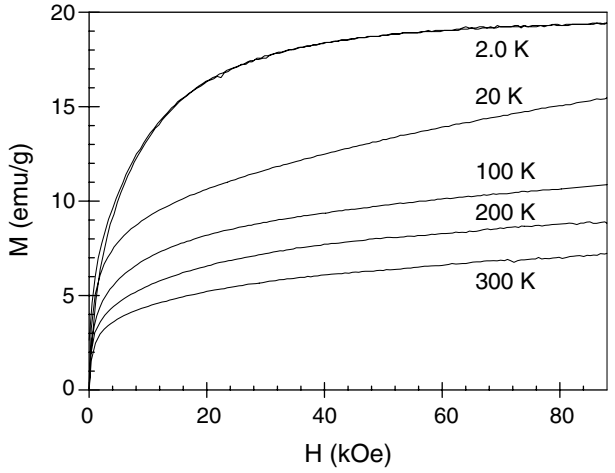

Fig. 2. Variations of the magnetization with applied field at various temperatures for Fe(II)-polymer.

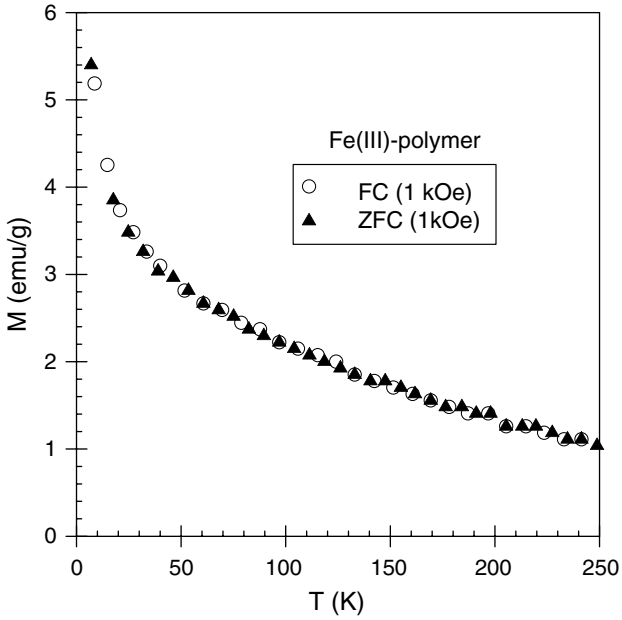

Fig. 3. Variations of the ZFC and FC magnetization with temperature measured in 1 kOe for Fe(III)-polymer.

4. Fe(II)-polymer

Fig. 1 displays typical spin glass magnetic behavior: the temperature dependence of both magnetization curves ZFC and FC in 1 kOe applied magnetic field. The ZFC branch exhibit a sharp peak at $T_g \sim 13$ K, which is about 2° below the temperature where the ZFC and FC curves bifurcate. In typical spin glass material, the peak in the ZFC magnetization versus temperature is commonly seen in very low ac-susceptibility [6], or magnetization measurements at low dc-magnetic field ~50 Oe [9]. The FC curve continue to increase as T is lowered below T_g, indicating that the FC-remanent magnetization also continue to increase below T_g. This would suggest a sort of mixed spin

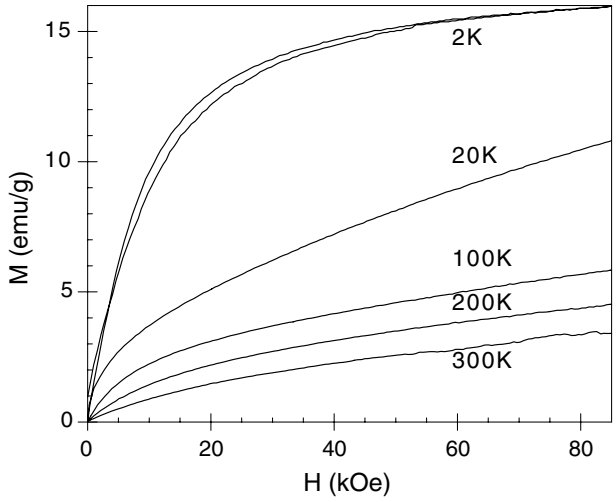

Fig. 4. Variations of the magnetization with applied field at various temperatures for Fe(III)-polymer.

glass super-paramagnetic behavior at temperature lower than T_g.

The magnetization curve measured at various temperatures (2–300 K) as a function of field, $M(H)$ is presented in Fig. 2. The initial magnetization rises sharply, reaching half the saturated value at about 5 kOe, and the saturation (18.4 emu/g) at about 40 kOe. Moreover, the magnetization curve shows very little Hysteresis and its high field susceptibility is $1.17*10^{-5}$ emu/(Oe g). The saturation magnetization (M_s) initially drops rapidly, reaching at 20 K to almost half its value at 2 K. This behavior is followed by a much slower reduction at higher temperatures, reaching at 300 K to about one third of its initial value at 2 K. The sharp increase in the magnetization is commonly seen in ferromagnetic material, however the susceptibility measurements did not show any plateau often observed in ferro-spin-glass state at low fields [9].

5. Fe(III)-polymer

Similar sets of magnetization measurements have been performed on polymer doped with Fe(III). The results are shown in Figs. 3 and 4. The variations of the ZFC and FC magnetization measured in 1 kOe applied field are shown in Fig. 3. Figure shows that both curves overlaps on top of each other and no maximum has been observed in either case. The spin glass behavior is not clearly discriminated in Fe(III) doped polymers. In this regard the low field ac-susceptibility will be the preferred experimental technique for further investigation.

Fig. 4 shows the variations of the magnetization with the applied magnetic field for Fe(III)-polymer. The behavior is similar to Fe(II)-polymer's results shown in Fig. 2, however, with different saturation magnetization (M_s) and high field susceptibility. However, the reduction in M_s values in Fe(II)-polymer is faster than what we have seen in M_s values of Fe(III)-polymer.

XRD analysis revealed that the polycabosilazne chain-chain distances have increased from 6.94 Å to 7.29 Å in Fe(II)-polymer and Fe(III)-polymer respectively. Ultimately, the shorter chain-chain separation in Fe(II)-polymer will lead to higher degree of disorder and more frustrated spin-spin interaction and the observed spin-glass behavior.

In conclusion, the variation of the ZFC and FC magnetization reveals a spin glass behavior in Fe(II)–doped polymer. No such behavior has been seen in Fe(III) doped polymer. The sharp initial rise in M versus H curves of both materials are similar to the ferromagnetic behavior, however, the M versus T curves did not show any plateau often observed in ferro-spin-glass state at low fields [9].

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