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Polaronic ferromagnetism in conducting polymers

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Abstract

Ferromagnetic behavior at room temperature is reported in metal-free-conducting polymer samples of poly(3-methylthiophene) doped with ClO_4^-. Magnetic moments associated with spin $\frac{1}{2}$ positive polarons are possibly interacting through a Dzialoshinski–Moriya anisotropic superexchange via the dopant anions, giving rise to weak ferromagnetism. © 2001 Elsevier Science B.V. All rights reserved.

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Research into conducting polymers has been stimulated not only by the potential applications of these materials [1–3] but also by the very interesting basic phenomena that appear upon doping [4,5]. Among the conducting-polymers, polythiophene and its derivatives, such as poly(3-methylthiophene), have been extensively studied as model compounds due to their simple mechanism of oxidation/reduction. During the oxidation process of poly(3-methylthiophene), in the first stage polarons are formed. Polarons are stable defects that carry charge and have spin $\frac{1}{2}$. As the number of polarons increases, they are converted into bipolarons, which are double charged and have zero spin.

In this work we report the occurrence of room temperature ferromagnetic behavior in pellets of metal-free partially doped poly(3-methylthiophene) with ClO_4^-. For doping the sample studied in this work we have used a $(H_5C_2)_4NClO_4$ salt, but similar results are also obtained using $LiClO_4$. We made measurements using a different cation to elucidate the role of the cations in the ferromagnetic behavior. We believe that the observed behavior is intrinsic, due to the polarons formed in the polymeric chains. The superexchange interaction occurs via the dopant anions. The symmetry of the system is very low and weak ferromagnetism arises due to a Dzialoshinski–Moriya [6] interaction between canted spins.

Sample studied here was electrochemically prepared at 25°C by applying to the cell a constant potential of 1.48 V (referred to a quasi-reference silver electrode) in an acetonitrile solution with 0.2 M methylthiophene and 0.1 M $(H_5C_2)_4NClO_4$. Electrochemical deposition with the total charge fixed in 100 C, resulted in a powdered sample on the Pt electrode. After the synthesis, the open circuit potential of the cell, V_{oc}, was 0.80 V, indicating that the polymer was in the oxidized state. The solution was changed twice to remove the soluble oligomers and the polymer was then partially reduced in a 0.2 M $(H_5C_2)_4NClO_4$ acetonitrile solution, the amount of reduction being controlled by measuring V_{oc} at the end of each reduction step. Samples for which $V_{oc} = 0.35$ V, have the highest values of remanence. After reduction, the polymeric sample was scrapped with a glass spatula, and a powdered sample resulted. The powder was uniaxially pressed (23 kbar) in an aluminium die to make pellets. Contamination with magnetic metallic nanoparticles was ruled out by atomic absorption analysis. The levels of contamination determined were below 10 ppb for Fe, and Ni and Co were absent. Magnetic

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measurements were performed using a quantum design SQUID magnetometer, model MPMS-5S.

Fig. 1a shows the magnetization versus field for this sample at three different temperatures: 300 K (triangles), 50 K (squares) and 5 K (crosses). The remanent magnetization (M_R) at 300 K and 5 K are 4.4×10^{-4} and 8.54×10^{-4} emu/g, respectively. The coercive field (H_c) at those temperatures are 85 and 170 Oe, respectively. Fig. 1b shows the details of the hysteresis curve at 300 K. From the data in Fig. 1a we observe that besides ferromagnetic behavior (clearly observed in Fig. 1b), the sample also shows diamagnetism (observed at room temperature) and paramagnetism (observed at low temperatures). This means that only a fraction of the sample shows ferromagnetic behavior, which excludes the possibility of observing a classical ferromagnetic magnetization versus temperature curve.

Fig. 2 gives an evidence of the possible origin of this ferromagnetism. It is shown there that the magnetization versus temperature behavior, measured with a field of 50 Oe. Full circles show the zero-field cooling (ZFC) warming from 1.8 to 300 K. Open circles show the magnetization data taken by cooling the sample with a same field (FC). The same curves measured with a field of 5000 Oe are shown in the inset. Above 50 K the magnetic susceptibility shows a diamagnetic behavior, which is also observed in Fig. 1a. The data in Fig. 2 show evidence of antiferromagnetism as a first order mechanism observed in the 50 Oe ZFC curve because the paramagnetic contribution is not so important as in the FC curve. For the high field data shown in the inset both ZFC and FC coincide, showing that high order effects in the magnetic field do not allow to observe the antiferromagnetic behavior.

We have also performed magnetic relaxations experiments at 2 K to study the possibility of spin glass ordering. No relaxation was observed within the data acquisition time of 10 min.

Our assumption for this ferromagnetic behavior is that the polarons formed in the monomeric units are interacting via the perclorate dopant. The direct superexchange interaction will give rise to antiferromagnetic coupling as can be guessed from Fig. 2. But in this semicrystalline material, the spins are canted and the anisotropic superexchange Dzialoshinski–Moriya interaction acting on the canted spins will allow weak ferromagnetism to take place.

The unstable sample of poly(3-methylthiophene) loses charges if it is stored in air. Fig. 3 shows the room temperature magnetization as a function of magnetic field curve taken just after synthesis (squares) and measured 5 months later (circle). The sample was stored in air at room temperature. As can be observed the nice ferromagnetic behavior disappeared leaving only a diamagnetic contribution. The ferromagnetic behavior has disappeared as the charges, and consequently the spins. These results confirm the polaronic characteristic of this weak ferromagnetism.

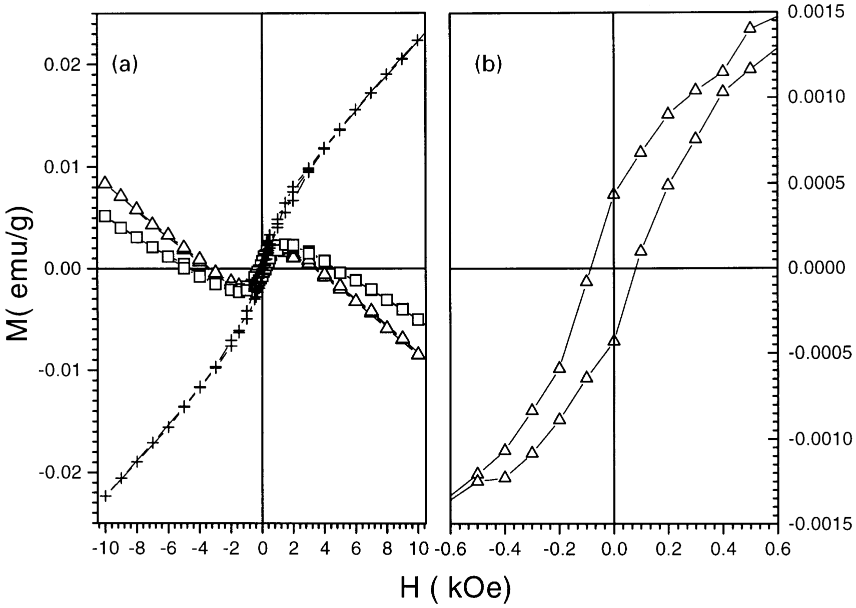

Fig. 1. (a) Magnetization versus field curves at 300 K (triangles), 50 K (squares) and 5 K (crosses). (b) Amplification of the central portion M versus H curve at 300 K showing the hysteresis.

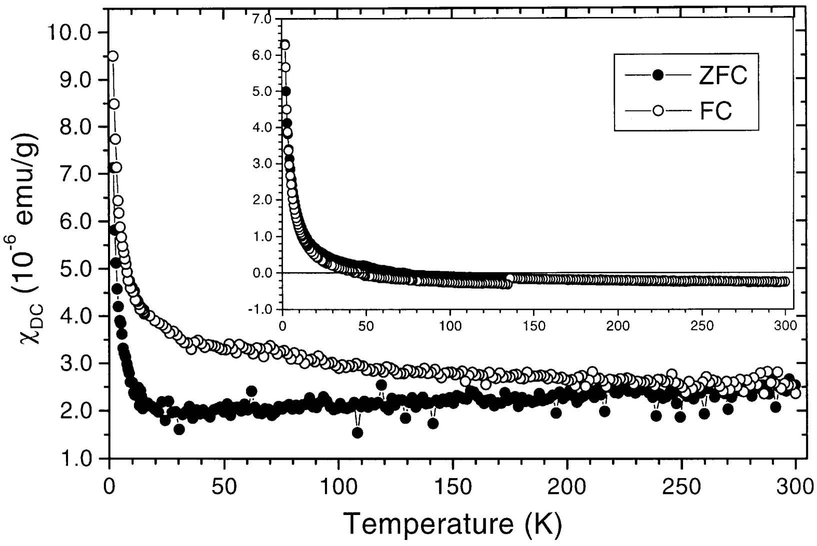

Fig. 2. Magnetic susceptibility (M/H) versus temperature measurements for the zero field cooling (●) and field cooling (○); $H = 50$ Oe. The inset shows the same measurements with $H = 5000$ Oe.

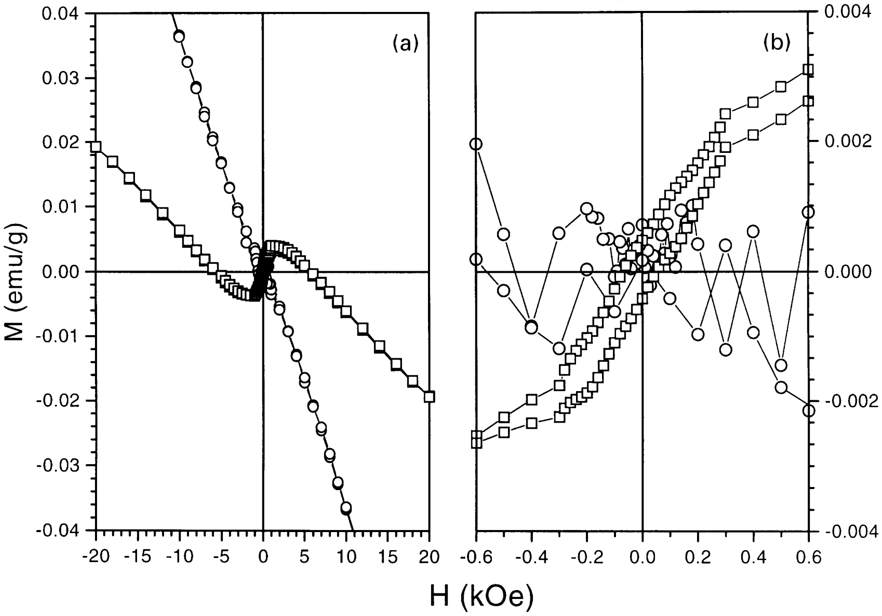

Fig. 3. (a) Magnetization versus field at 300 K for sample taken just after synthesis (□) and the same sample measured 150 days later, stored in air (○). (b) Amplification of central portion.

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