

## Magnetic phase transition, aggregate formation, and electrical conductivity in FeCl<sub>3</sub>-doped polyacetylene

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Both Fe<sup>3+</sup> and Fe<sup>2+</sup> ions occur in FeCl<sub>3</sub>-doped polyacetylene. At low dopant levels (< 0.01 mole fraction) both Fe<sup>2+</sup> and Fe<sup>3+</sup> ions are paramagnetic down to 4.2 K. At dopant levels > 0.01 mole fraction, there is evidence from Mössbauer spectroscopy that Fe<sup>2+</sup> ions associate into aggregates which are magnetically ordered below 25 K. Aggregate formation appears to correlate with high electrical conductivity.

Polyacetylene can be doped with a variety of molecules including FeCl<sub>3</sub>, H<sub>2</sub>IrCl<sub>6</sub>, AsF<sub>5</sub>, and I<sub>2</sub>.<sup>1,2</sup> Charge transfer between dopant molecules and polyacetylene strongly affects the conductivity of the polymer. For dopant concentrations  $y \leq 0.01$  mole fraction, the polymers are semiconducting. For  $y \geq 0.01$  mole fraction, the polymers are metallic. In semiconducting IrCl<sub>6</sub>- and AsF<sub>5</sub>-doped polyacetylene,  $\ln \rho \propto T^{-1/2}$ , where  $\rho$  is the resistivity.<sup>2,3</sup> In the IrCl<sub>6</sub>-doped polymers, the characteristic temperature dependence has been shown to correlate with the formation of dopant aggregates.<sup>2</sup> In this paper we present temperature-dependent Mössbauer spectroscopic and resistivity data for FeCl<sub>3</sub>-doped polyacetylene that show: (1) transfer of electrons from polyacetylene to dopant, resulting in both Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in the lattice; (2) aggregate formation by Fe<sup>2+</sup> ions for  $y \geq 0.01$  mole fraction, but no aggregate formation by Fe<sup>3+</sup> ions; (3) magnetic ordering in the Fe<sup>2+</sup> aggregates below 25 K; and (4) conductivity at room temperature going from semiconducting behavior for  $y < 0.01$  mole fraction to nearly metallic behavior for  $y > 0.01$  mole fraction. This is the first report of magnetic cooperativity in doped polymers.

The preparation of the *cis*-polyacetylene and the details of the characterization of the resultant gel-like material have been described in previous publications.<sup>4,5</sup> The anhydrous FeCl<sub>3</sub> dopant was heated in a dynamic vacuum at 100°C for one hour prior to use. Doping was accomplished by immersing a polyacetylene pressed gel in a solution of 0.8 g of FeCl<sub>3</sub> dissolved in 100 ml of dry nitromethane. Doping time determined the weight uptake of dopant. After doping, all samples were thoroughly washed with fresh nitromethane to remove unreacted dopant. All manipulations were carried out in an inert atmosphere. For low dopant levels ( $y < 0.01$ ), a 4% <sup>57</sup>Fe-enriched FeCl<sub>3</sub> dopant was used to enhance the signal studied by Mössbauer spectroscopy. The natural abundance of <sup>57</sup>Fe, the isotope used in Mössbauer spectroscopy, is 2%.

Elemental analysis of a typical sample of polyacetylene doped by weight with 0.0135 mole fraction FeCl<sub>3</sub> was as follows: 77.14% C, 6.52% H, 3.95% Fe, and 8.1% Cl (total 95.71%). This corresponds to an empirical formula of CH(FeCl<sub>3.23</sub>)<sub>0.011</sub>. The high Cl/Fe ratio is consistent with results obtained by Pron *et al.*<sup>6</sup> who suggested the presence of a (FeCl<sub>4</sub>)<sup>2-</sup> ion on the basis of room-temperature Mössbauer data. Our elemental analysis and Mössbauer

spectroscopy results at cryogenic temperatures indicate that when polyacetylene is doped with FeCl<sub>3</sub>, the majority of the dopant present in the polymer is an Fe<sup>3+</sup> species, as Pron *et al.*<sup>7</sup> have also recently observed. Cyclic voltammetry studies on our FeCl<sub>3</sub>-nitromethane doping solution indicated only ferric ions (Fe<sup>3+</sup>), independent of whether the dopant solution was freshly made up or aged several days. This suggests that the small amount of Fe<sup>2+</sup> observed is created as a product of the charge-transfer reaction with the polyacetylene.

Mössbauer spectra for FeCl<sub>3</sub>-doped polyacetylene ( $y = 0.01$  mole fraction) at 40 and 4.2 K are shown in Fig. 1.

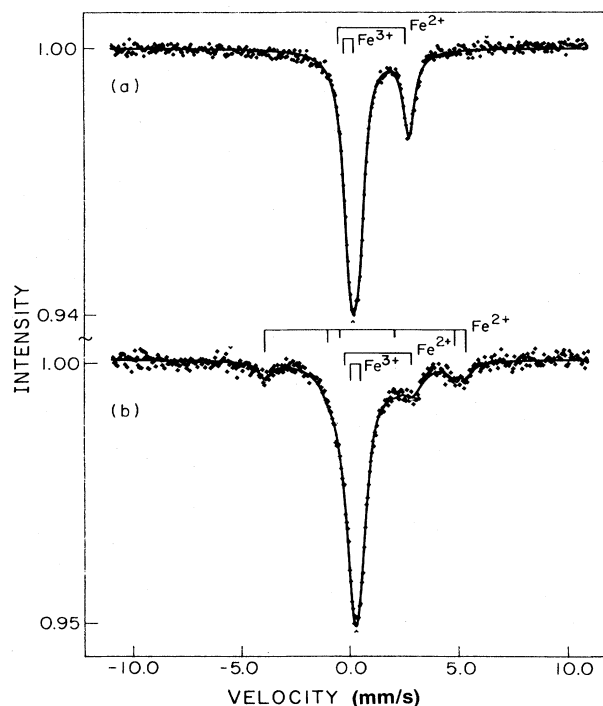


FIG. 1. Mössbauer spectra for CH(FeCl<sub>3</sub>)<sub>0.011</sub> at (a) 40 K and (b) 4.2 K. Parts of the Fe<sup>2+</sup> lines are split magnetically in the 4.2-K spectrum.

In general, the spectra above 25 K consist of a superposition of subspectra attributable to  $\text{Fe}^{2+}$  ( $\delta=1.37$  mm/s;  $\Delta E_Q=2.83$  mm/s at 40 K) and  $\text{Fe}^{3+}$  ( $\delta=0.33$  mm/s,  $\Delta E_Q=0.34$  mm/s at 40 K) with one of the  $\text{Fe}^{2+}$  lines overlapping the  $\text{Fe}^{3+}$  line. At 290 K the  $\text{Fe}^{3+}$  absorption is negligible and only the  $\text{Fe}^{2+}$  spectrum ( $\delta=1.20$  mm/s;  $\Delta E_Q=2.37$  mm/s) is observed in agreement with Pron, Kulszewicz, Billand, and Przyluski.<sup>6</sup> The  $\text{Fe}^{3+}$  absorption intensity increases with decreasing temperature so that below 100 K it is the dominant feature of the spectrum.

Below 25 K the  $\text{Fe}^{2+}$  spectrum shows magnetic hyperfine splitting ( $H_{\text{hf}}=260$  kOe), indicating magnetic ordering of the  $\text{Fe}^{2+}$  ions. Some unsplit  $\text{Fe}^{2+}$  intensity remains, which diminishes with decreasing temperature with the concomitant increase of the intensity of the magnetic subcomponent. Application of an external magnetic field up to 60 kOe at 4.2 K results in a magnetic hyperfine field of  $-440$  kOe at the  $\text{Fe}^{3+}$  sites, indicating that  $\text{Fe}^{3+}$  is present as paramagnetic ions with  $S=\frac{5}{2}$ . The hyperfine field is close to the magnetic hyperfine field in solid  $\text{FeCl}_3$  below its magnetic ordering temperature of  $\approx 16$  K,<sup>8</sup> suggesting that the  $\text{Fe}^{3+}$  ions have  $\text{Cl}^-$  ligands. The  $\text{Fe}^{2+}$  lines are obscured by the  $\text{Fe}^{3+}$  hyperfine lines in the applied field spectra, so we cannot ascertain whether the  $\text{Fe}^{2+}$  magnetic ordering is ferromagnetic or antiferromagnetic.

The Mössbauer data<sup>9,10</sup> favor identification of the  $\text{Fe}^{3+}$  species with  $(\text{FeCl}_4)^{1-}$  and the  $\text{Fe}^{2+}$  species with  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ . The presence of  $(\text{FeCl}_4)^{1-}$  is consistent with extended x-ray absorption fine-structure results.<sup>11</sup> The identification of  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  was unexpected,<sup>12</sup> but it is compelling due to the similarity of the observed spectra with those published for powdered  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ .<sup>13</sup> It assumes that the principal component of the electric field gradient is perpendicular to the direction of the magnetic field at the nucleus. Best-fit parameters for the magnetic subcomponent of Fig. 1 are  $\delta=1.30$  mm/s,  $\Delta E_Q=2.88$  mm/s, and  $H_n=260$  kOe.

In Fig. 2 we plot the temperature dependence of  $-\ln A$

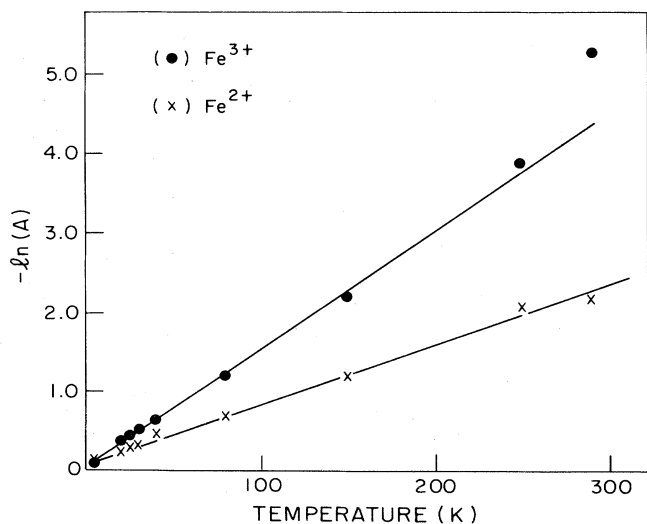


FIG. 2. Normalized relative absorption intensities  $A$  of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in  $\text{CH}(\text{FeCl}_3)_{0.011}$  plotted as  $-\ln A$  as a function of temperature.

for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , where  $A$  is a normalized Mössbauer absorption intensity. In the harmonic approximation,  $-\ln A$  is proportional to  $\langle x^2 \rangle$ , the mean-squared displacement of iron atoms on a particular site.<sup>14</sup> Different temperature dependences of  $-\ln A$  for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  reflect different local vibrational energy spectra, with  $\text{Fe}^{3+}$  ions more loosely bound than  $\text{Fe}^{2+}$ . The temperature dependence of  $-\ln A$  for  $\text{Fe}^{2+}$  is similar to that for Fe in solid  $\text{FeCl}_3$ .

For dopant concentrations  $y < 0.01$  mole fraction, the  $\text{Fe}^{3+}$  spectra are unchanged. The  $\text{Fe}^{2+}$  spectra are different in two ways compared with  $\text{Fe}^{2+}$  at the higher dopant concentrations. First, the dependence of the absorption intensity on temperature is now more pronounced and rather similar to that of  $\text{Fe}^{3+}$ . Second, the  $\text{Fe}^{2+}$  lines do not show magnetic hyperfine splitting down to 4.2 K.

We interpret these results as follows: Although iron is present as  $\text{Fe}^{3+}$  in the  $\text{FeCl}_3$  dopant, approximately 30% of the iron atoms are reduced to  $\text{Fe}^{2+}$  in the polymer. Paramagnetic  $\text{Fe}^{3+}$  ions are dispersed along the polymer chain, in loosely bound sites. At low dopant concentrations ( $y \leq 0.01$  mole fraction)  $\text{Fe}^{2+}$  ions are also dispersed along the polymer chain and remain paramagnetic down to 4.2 K. For  $y > 0.01$  mole fraction, most of the  $\text{Fe}^{2+}$  ions form aggregates with binding comparable with that of solid  $\text{FeCl}_3$ . A magnetic phase transition occurs in these  $\text{Fe}^{2+}$  aggregates at about 23 K. This ordering temperature is comparable with those in various  $\text{Fe}^{2+}$  halides,<sup>8</sup> and is the same as that of  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ .<sup>13,15</sup> We have not been able to repeat the experiments of Przyluski *et al.*<sup>16</sup> who reported only  $(\text{FeCl}_4)^{1-}$  anions (no  $\text{Fe}^{2+}$  species) present in electrochemically doped polyacetylene. We found that polyacetylene doped chemically with no applied voltage from our solution of  $\text{LiClFeCl}_3$ -nitromethane.

The formation of dopant aggregates appears to be related to a semiconductor-to-metal transition as a function of dopant concentration in  $\text{FeCl}_3$ -doped polyacetylene. The room-temperature resistivity as a function of dopant concentration  $y$  is shown in Fig. 3. Note the change in activation energy, shown in the inset, at  $y \approx 0.01$ . It is at this concentration that both the magnetic and electrical properties of  $\text{CH}(\text{FeCl}_3)_y$  change character. Although the magnitude of the conductivity of  $\text{FeCl}_3$ -doped polyacetylene is never high enough to be truly metallic, the thermopower  $S$  is positive, linear in  $T$ , and for  $y > 0.03$  extrapolates linearly to  $S=0$  at  $T=0$ , indicating metallic electron behavior.<sup>17</sup> For lower concentrations of  $y$ ,  $S$  is a linear function of  $T$  but does not extrapolate to  $S=0$  at  $T=0$ . Free-electron behavior in the thermopower has previously been observed in heavily doped  $\text{AsF}_5$ -doped polyacetylene.<sup>1</sup> The thermopower is a zero current measurement and is insensitive to interfibril contacts<sup>1</sup> or gaps between metallic regions. Thus a material like doped polyacetylene may have thermally activated electrical conductivity and at the same time a characteristically metallic thermopower.

A conduction model for charging-energy limited tunneling<sup>18</sup> has been applied to semiconducting  $\text{AsF}_5$ - and  $\text{IrCl}_6$ -doped polyacetylene<sup>2,3</sup> in which the charge carrier must tunnel from one conducting aggregate to another, giving rise to a characteristic temperature dependence  $\ln \rho \propto T^{-1/2}$  instead of the  $\ln \rho \propto T^{-1/4}$  behavior characteristic of variable range hopping<sup>19</sup> of carriers between dispersed atomic sites which has been observed in  $\text{I}_2$ - and  $\text{Br}_2$ -doped polyacetylene.<sup>20</sup> We find that for  $y < 0.014$  the characteristic temperature depen-

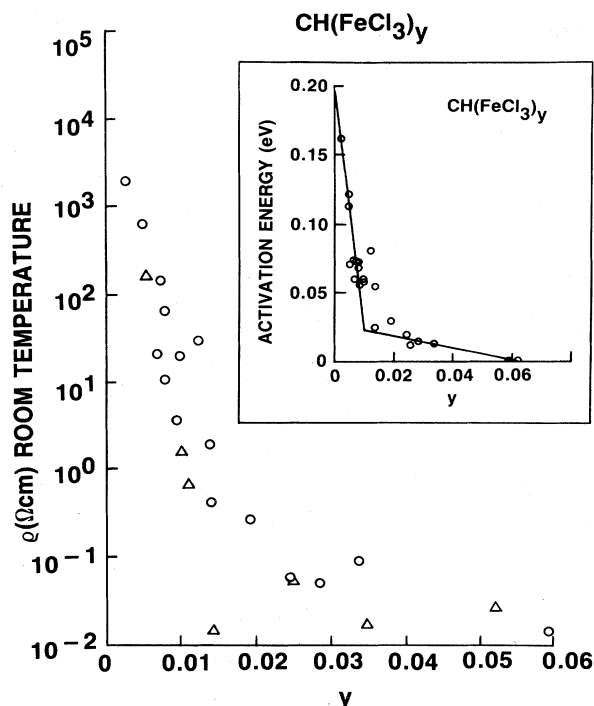


FIG. 3. Room-temperature resistivity of  $\text{CH}(\text{FeCl}_3)_y$  as a function of dopant level  $y$ . Inset shows the activation energy, determined from an Arrhenius plot of the resistivity between 300 and 100 K, as a function of dopant concentration  $y$ .

dence of the resistivity does not reliably fit either  $\ln \rho \propto T^{-1/4}$  or  $\ln \rho \propto T^{-1/2}$ . This suggests to us that the conduction mechanism is influenced by the presence of the  $\text{Fe}^{2+}$  aggregates. Furthermore, in several samples with  $\text{FeCl}_3$  doping level near  $y \approx 0.01$  we have observed a small peak or plateau near 24 K in the  $\rho(T)$  curves. For several samples with  $y > 0.015$ , we have observed a small negative magnetoresistance at 4.2 K. These two observations again suggest that the magnetic ordering in the  $\text{Fe}^{2+}$  aggregates affects the conduction process.

In conclusion, we have demonstrated that magnetic ordering occurs in  $\text{Fe}^{2+}$  aggregates when polyacetylene is doped with  $\text{FeCl}_3$ . The ordering occurs when the dopant concentration  $y \geq 0.01$ . At  $y \approx 0.01$ , the activation energy also changes. We propose that at this critical concentration the dopant molecules are close enough together that formation of aggregates of  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  becomes energetically favorable. In addition, at  $y \approx 0.01$ , the density of dopant molecules is sufficient for conduction to occur.

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<sup>12</sup>If this identification is correct, the means of introduction of  $\text{H}_2\text{O}$  in the system is not clear at present. However, it explains the contradictory results previously obtained by Pron *et al.* (Refs. 6 and 7) and indicates that samples are extremely sensitive to hydration.

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<sup>18</sup>The charging-energy limited tunneling model, developed by P. Sheng, B. Abeles, and Y. Arie [*Phys. Rev. Lett.* **31**, 44 (1973)] for conduction in granular metals has been modified by E. Simanek [*Solid State Commun.* **40**, 1021 (1981)] to relax some of the constraints on grain size. It is unlikely that the dopant aggregates in polyacetylene have a broad distribution of grain sizes.

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