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NMR evidence for the metallic nature of highly conducting polyaniline

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Polyaniline doped with camphor sulphonic acid (PANI-CSA) has been shown to yield a material that, after casting from solution in *meta*-cresol, exhibits a temperature-independent magnetic susceptibility [Y. Cao, P. Smith, and A. J. Heeger, Synth. Met. **48**, 91 (1992); N. S. Sariciftci, A. J. Heeger, and Y. Cao, Phys. Rev. B **49**, 5988 (1994)]. We report recent ^{13}C NMR experiments on uniformly ^{13}C-enriched PANI-CSA in which the ^{13}C spin-lattice relaxation rates are shown to obey a modified Korringa relation for relaxation via the hyperfine coupling to conduction electrons. This observation of Korringa relaxation in polyaniline provides strong evidence for a metallic state in this material. An estimate is made of the Korringa enhancement factor that provides a measure of the degree of electron-electron correlations present. Two-dimensional spin-exchange experiments are also reported, which show that the ^{13}C NMR signal results from a heterogeneity in the sample over at least a 30-Å distance scale. These results are discussed in terms of the spatial extent of the doping-induced defect.

INTRODUCTION

Conducting polymers have been the focus of a great deal of research in the past two decades, as much for fundamental scientific reasons as for the development of new materials for modern technology.[1] Despite this attention, certain basic questions concerning their electronic structure remain unsolved. Notably, issues such as the nature of the carrier particles, whether polarons or spinless bipolarons,[2] and the dimensionality of the electrical conduction are still under debate.

Solid-state nuclear magnetic resonance (NMR) is very sensitive to the microscopic details of charge and spin distributions and dynamics, through Knight shifts[3] and relaxation behavior.[4] However, all attempts to date to observe a Knight shift in the ^{13}C NMR spectrum of a conducting polymer, due to the hyperfine interaction of the nuclei with the polarons, have failed.[5–12] The slight shifts that have occasionally been observed, of the doped state relative to the undoped state, can be accounted for by the removal of charge from the conjugated π system by oxidative doping.[13] The spin-lattice relaxation behavior is a more sensitive indicator of the hyperfine interaction of the nuclei with conduction electrons than the Knight shift. Nuclear spin-lattice relaxation in metals occurs via the hyperfine interaction with electrons within kT of the Fermi surface. As a result, a linear relation between the spin-lattice relaxation rate and temperature is observed, as shown by Korringa.[14] Unfortunately, spin-lattice relaxation in conducting polymers is generally dominated by spin diffusion to fixed paramagnetic centers, the presence of which are confirmed by a substantial Curie term in the magnetic susceptibility. In polyacetylene doped with Br_2, Kume *et al.*[15] reported Korringa relaxation of the protons, though this has not been observed in other conducting polymers. The lack of either an observable Knight shift or Korringa relaxation has tended to carry substantial weight for the bipolaronic theory of conduction in nondegenerate–ground-state conducting polymers. Further support is provided by electron-spin resonance studies, which show a dramatic increase of the paramagnetic susceptibility with increasing oxidation, at

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low doping levels, followed by a decrease in spin susceptibility with higher levels of doping. This was viewed as evidence for a polaron to bipolaron conversion in the high doping regime.[16] The same observation can be accounted for, however, by the conversion of localized spin-$\frac{1}{2}$ defects into a metallic structure, which would decrease the susceptibility by T/T_F, T_F being the Fermi temperature.[17]

In this paper we report an observation of Korringa relaxation in polyaniline, specifically, films of uniformly ^{13}C enriched polyaniline doped with camphor-sulphonic acid (PANI-CSA). We have further performed one- and two-dimensional ^{13}C NMR experiments on PANI-CSA performed with the aim of characterizing the NMR line shape. These results give an indication of the spatial extent of the doping-induced defect. PANI-CSA was chosen for this study as it has been shown to exhibit high electrical conductivities [100–400 S/cm Ref. (18)] as well as a temperature-independent (Pauli) magnetic susceptibility down to temperatures as low as 50 K.[17,19]

THE ^{13}C MR LINE SHAPE IN POLYANILINE

Figure 1(a) illustrates the ^{13}C NMR spectrum of the powdered emeraldine base (insulting form) of polyaniline, acquired under conditions of cross polarization and magic angle spinning with ^{1}H decoupling during acquisition. The position of the lines as well as their relative intensities is in good agreement with previously published work.[8,10] Figure 1(b) is the spectrum of camphor-sulphonic acid doped ^{13}C labeled polyaniline. The PANI-CSA films were cast from *meta*-cresol, which yields a material with high conductivities as well as a temperature-independent susceptibility.[17,19] Inasmuch as metallic transport is observed, this investigation was begun with the hope of observing microscopic metallic behavior in polyaniline with a probe possessing atomic site resolution. Unfortunately, the pronounced broadening often observed in the doped state of conducting polymers[5–12] was present for PANI-CSA as well. Figure 1(b) shows a 60-ppm unresolved resonance with no shift in the first moment. Any Knight shift, if present, would likely be obscured by the broadening. As the magnetic susceptibility is quite low, $\chi_x = 3\times10^{-5}$ emu/mole (two rings), such shifts might be on the order of 10–15 ppm, which would not be resolved in the spectrum of Fig. 1(b). The origin of this broadening has never convincingly been determined. It has been suggested that it is due to the inhomogeneous distribution of charge over the polymer backbone.[10] This mechanism seems to be approximately the correct size to lead to the observed effect. Fully doped PANI has one charge distributed over two aromatic rings. As one charge gives rise to a 160-ppm shift in the ^{13}C NMR spectrum,[13] each resonance could be broadened by ~13 ppm due to an incommensurate charge distribution; however, there could also be incommensurate spin-density distributions contributing to the observed broadening. This situation is further complicated by the possibility that spin-density shifts (Knight shifts) and charge-density shifts are expected to be on the same order of magnitude and may be in opposite directions.[20]

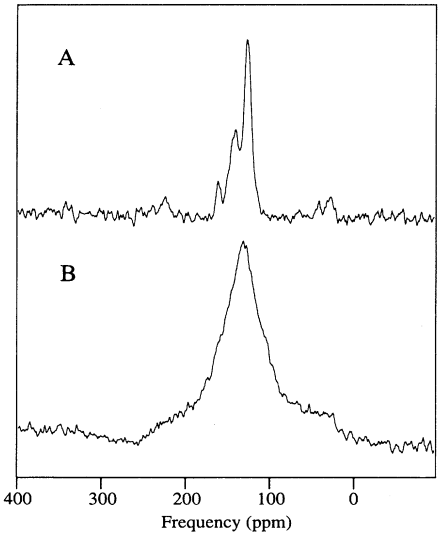

FIG. 1. ^{13}C cross-polarized MAS spectra of polyaniline. (a) Undoped emeraldine base polyaniline. Resolved center bands are at 123.5, 136.5, and 157.9 ppm from TMS. The spinning speed was $\omega_r/2\pi = 10.000$ kHz, the cross-polarization time was 2.5 ms, and 1048 scans were added. (b) Camphor-sulphonic acid doped uniformly ^{13}C enriched polyaniline. The spinning speed was $\omega_r/2\pi = 10.000$ kHz, the cross-polarization time was 2.5 ms, and 512 scans were added.

METALLIC RELAXATION IN POLYANILINE

Even when no Knight shifts are resolved, an effect of the conduction electrons on the spin-lattice relaxation may be observed. However, this effect is often masked by the contribution due to the interaction with fixed paramagnetic impurities. Relaxation measurements on powders of PANI, doped in the solid state, which display a strong Curie contribution to χ_s exhibit a 173-ms T_1 at 300 K, which changes only slightly with temperature, as one would expect for relaxation via spin diffusion to fixed paramagnetic centers. In these samples, the more rapid relaxation due to this mechanism tends to mask the conduction electron contribution.

As PANI-CSA film cast from *meta*-cresol have a temperature-independent susceptibility, the relaxation rates are not determined by the presence of fixed paramagnetic centers. The PANI-CSA films exhibited exponential spin-lattice relaxation rates with T_1 at 300 K = 283 ms and the value of T_1 being independent of frequency between 75 MHz (283 ms) and 100 MHz (265 ms) to within experimental error (±15–20 ms). This is to be compared with highly nonexponential relaxation rates observed for the emeraldine base form of PANI in which a distribution of T_1 values was observed ranging from 100 ms to 10 s, with the peak around 3 s.[8] For the insulating forms of PANI, ^{13}C relaxation is most likely to result from a distributions of motions in the megahertz range as measured by Kaplan *et al.*[10]

Figure 2 shows the spin-lattice relaxation rates $(1/T_1)$

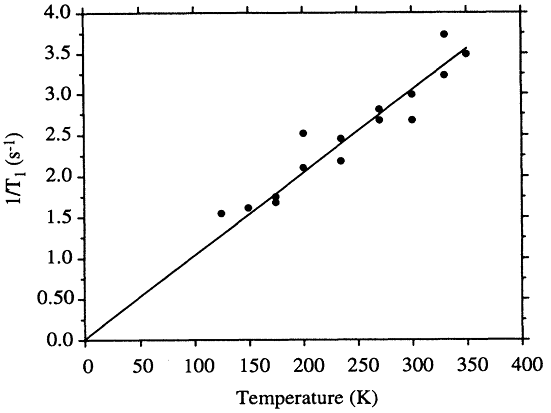

FIG. 2. ^{13}C spin-lattice relaxation rates versus temperature for uniformly ^{13}C labeled PANI-CSA. Rates were determined from exponential fits of eight to twelve delays in an inversion recovery experiment. Points at the same temperature were fits to decays acquired from different positions on the line and give an indication of the precision of the rates. The line is the best linear fit to the data, with the constraint that it goes through $T=0$, $1/T_1=0$.

versus temperature for PANI-CSA. The linear dependence of $1/T_1$ with temperature is suggestive of the Korringa relation for spin-lattice relaxation in classical metals. In organic conductors, a modified relaxation is used,[21-23]

$$1/T_1=K^2(1+\tfrac{1}{2}\varepsilon)C_0S_KT\ , \tag{1}$$

in which K is the Knight shift,[3] $C_0=(4\pi k/\hbar)(\gamma_n/\gamma_e)^2$, and $\varepsilon=d^2/a^2$ is the ratio of the anisotropic and isotropic contributions to the hyperfine interaction, respectively. S_K is the Korringa scaling factor which takes into account the low dimensionality of the charge transport and the electron correlations.[21,23] For classical metals, $\varepsilon=0$ and $S_K=1$, and the Korringa relation is recovered. In organic conductors, however, the anisotropic part is often important ($0<\varepsilon<4$) and the system is often highly correlated leading to scaling factors of 50–500 in, for example, the organic conductor fluoranthene$_2$(PF$_6$).[20] From the slope of the line in Fig. 2, assuming a maximum of 10–15 ppm for any Knight shift present, one obtains a minimum value of S_K ranging from 50 to 150. The Korringa enhancement factor may be enhanced by as much as an order of magnitude due to the presence of disorder, as recently discussed by Shastry and Abrahams.[24] The largest disorder-induced enhancement factors occur in the regime $k_F\lambda_i=1$, in which k_F is the Fermi wave vector and λ_i is the inelastic mean free path. In PANI-CSA, $k_F=\pi/2c$, in which c is the unit cell length of 7.2 Å as determined by x-ray diffraction,[25] and λ_i was estimated to be approximately 7 Å,[26] which yields a value for $k_F\lambda_i\cong\pi/2$. This accounts for a large part of the Korringa enhancement in this disordered metal in the critical regime near the metal-insulator transition. The presence of the high external magnetic field of 9.4 T will also lead to weak localization of the electrons,[18] further reducing λ_i and increasing the enhancement factor. Even so, the positive Korringa enhancement, which is substantially larger than unity, points to the importance of antiferromagnetic correlations among the electrons.[27] The presence of hyperfine induced relaxation shows clear evidence for mobile polarons; however, the coexistence of mobile bipolarons cannot be ruled out.

ESTIMATE OF THE EXTENT OF THE DOPING-INDUCED DEFECT

As it seems clear that the broad spectrum of Fig. 1(b) is due to some sort of incommensurate distribution of an excitation, whether spin density or charge density or a combination, an important issue is the length scale over

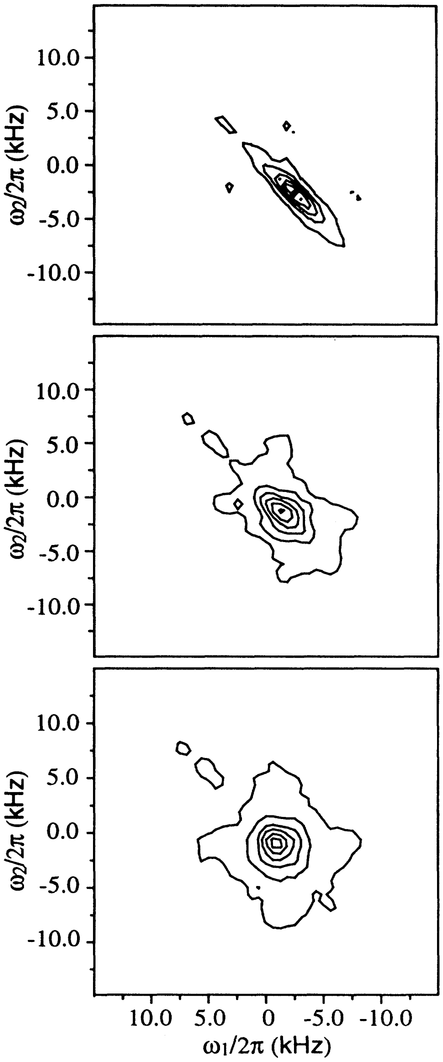

FIG. 3. Two-dimensional spin-exchange spectra of uniformly ^{13}C labeled polyaniline-CSA film. The spinning speed was $\omega_r/2\pi=5.3$ kHz, the cross-polarization time = 3 ms, the dwell time in both dimensions was 12.5 μs, and 64 t_1 increments were used with 512 scans per point. Mixing times for spin exchange are 300 μs (top), 5 ms (middle), and 15 ms (bottom).

which the excitation is delocalized. This can be estimated, with a two-dimensional spin-exchange experiment, by monitoring the time over which the magnetization diffuses over the entire line shape via the dipole-dipole interaction.[28] The experiment involves an evolution period and a detection period both in which the ^{13}C magnetization precesses freely. A mixing period is present between evolution and detection in which parts of the ^{13}C line with different frequencies exchange magnetization. This experiment is illustrated by the spectra of Fig. 3. The top spectrum is for a mixing time of 300 μs. For such a short mixing time, no frequency in the line is correlated with any frequency other than itself. The extension along the diagonal is a clear indication that the broadening is inhomogeneous in nature, just as one would expect for an incommensurate distribution. The homogeneous linewidth, measured perpendicular to the diagonal, is 880 Hz (12 ppm), and is likely to be due to ^{13}C-^{13}C dipolar couplings. In contrast, the same experiment performed on the natural abundance emeraldine base (not shown), with a 6-ppm inhomogeneous linewidth, yields a homogeneous linewidth of 85 Hz (1.1 ppm). For 5-ms mixing (middle) the presence of an off-diagonal intensity indicates some magnetization exchange and by 15 ms (bottom) the characteristic pattern of an isotropic distribution of magnetization, circular contours, has evolved.

From this rate of spin diffusion under the dipole-dipole interaction, we can make an estimate of the distance involved. The spin-diffusion constant $D \propto b_{\mathrm{II}} r^2$, in which b_{II} is the dipolar coupling between like spins and is proportional to γ^2/r^3 and r is the average distance between spins. We can thereby estimate the spin-diffusion constant for ^{13}C from the known spin-diffusion constant for ^1H ($D_{\mathrm{HH}} = 0.8\ \mathrm{nm}^2/\mathrm{ms}$),[29]

$$D_{\mathrm{CC}} = D_{\mathrm{HH}} \left[\frac{\gamma_C}{\gamma_{\mathrm{H}}} \right]^2 \left[\overline{\frac{r_{\mathrm{HH}}}{r_{\mathrm{CC}}}} \right] = 0.084\ \mathrm{nm}^2/\mathrm{ms}\ , \qquad (2)$$

in which the difference in both the average distance between nuclei and the dipolar coupling strength between them have been rescaled for ^{13}C.[29] The average minimum distance between carbons has been taken to be 1.5 Å, the minimum distance between carbons within a ring. The spin-diffusion constant between rings, based upon an average minimum distance of 3 Å, is 0.042 nm^2/ms. An effective spin-diffusion constant, accounting for the "bottleneck" effect of a slow interring rate combined with a more rapid intraring rate, is given by[29]

$$\sqrt{D_{\mathrm{eff}}} = \frac{\sqrt{D_{\mathrm{inter}} D_{\mathrm{intra}}}}{(\sqrt{D_{\mathrm{inter}}} + \sqrt{D_{\mathrm{intra}}})/2}\ . \qquad (3)$$

The effective spin-diffusion rate for the polyaniline structure is $D_{\mathrm{eff}} = 0.058\ \mathrm{nm}^2/\mathrm{ms}$. Based upon this rate, the "lattice period" relevant for the spin diffusion, the distance between the centers of the nearest inhomogeneous charge distributions, assuming a one-dimensional spin-diffusion model, is given by

$$d = \sqrt{20.3 D_{\mathrm{eff}} t_m} \qquad (4)$$

and may be calculated to be $d = 34$ Å, in which t_m is the equilibration time from the initial rate approximation[29] and is taken to be 10 ms. The extent of the inhomogeneous distribution of charge itself must be somewhat shorter than this, but quantifying this distance would require assuming a specific model for the lattice of distributions present. As the answer would be strongly model dependent, we shall not do this. The distance scale measured here is on the order of estimates of excitation distributions in polyacetylene, 27 Å,[30–32] and poly(paraphenylene vinylene), 35 Å.[33] The possibility still exists, however, that the inhomogeneous broadening is due to an incommensurate bipolaron distribution, even though the spin-lattice relaxation is due to interaction with the polarons.

It should be noted that as polyaniline is in the critical regime at the metal-insulator transition, the effects of localization of the states may be quite strong here. Notably, the fact that a magnetic field tends to decrease the localization length in this regime[18] may lead to an underestimate of the length scale of the distribution.

EXPERIMENT

Spin-lattice relaxation measurements were performed on a Bruker MSL-400 spectrometer (9.4 T) equipped with a variable temperature probe. The temperature was controlled to 2 K with a Bruker temperature controller. Two-dimensional spin-exchange experiments were performed on a 300-MHz (7.1 T) homebuilt spectrometer. The magic angle spinning (MAS) probe was also homebuilt and incorporated commercial MAS equipment (Doty Scientific, South Carolina). Two-dimensional hypercomplex data sets were acquired and processed as in Ref. 34 to achieve pure-phase two-dimensional spectra.

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