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ESR study of the temperature dependence of metallic complexes of alkali-metal-doped polyacetylene

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In this work, we have followed the evolution of the electron-spin-resonance (ESR) linewidth ($\Delta H_{\text{p.p.}}$) of highly-alkali-metal-doped polyacetylene, as a function of the nature of the dopant and the temperature in the range 4–300 K. The room-temperature linewidth increases with increasing atomic number (Z) of the dopant, suggesting a significant contribution to the width from the spin-orbit coupling of the unpaired electrons on the dopant site. This linewidth behavior versus Z follows a Z^α law, with $\alpha \simeq 2.3 \pm 0.7$. In the case of Li-, K-, and Rb-doped films, the linewidth decreases with decreasing temperature down to 100 K for Li-doped films and ~50 K for K- and Rb-doped ones where it starts to increase. This temperature behavior can be analyzed in terms of gradual transition from a high-temperature metallic state where interchain electron hopping plays a dominant role, to a low-temperature semiconducting state where electrons are mainly confined along the chains.

I. INTRODUCTION

Using ESR, we have investigated the magnetic properties of the metallic state of polyacetylene complexes with alkali-metal dopant atoms in order to obtain information about the origin and nature of the electronic magnetism in these systems. Highly doped polyacetylene with donors or acceptors exhibits a relatively high electrical conductivity and is commonly likened to a metal though the temperature dependence of the conductivity is not metallike. This behavior of the conductivity versus temperature has been verified by several authors[1–3] for both *p*- and *n*-type doped $(\mathrm{CH})_x$.

A complementary approach to the study of metallic polyacetylene has been to investigate its magnetic properties. The magnetic properties of undoped $(\mathrm{CH})_x$, which exhibits semiconducting behavior, have been investigated by different groups.[4–6] The ESR-linewidth temperature dependence has been studied and the observed increase of $\Delta H_{\text{p.p.}}$ with decreasing temperature has been analyzed in terms of thermally activated spin delocalization.

On the other hand, the magnetic properties of metals such as alkali metals have been for a long time the subject of extensive research and a lot of experimental data concerning the temperature dependence of the conduction-electron-spin-resonance (CESR) linewidth and the g factor has been reported.[7] Comparing these results, Beuneu and Monod[8] have been able to test Elliott's model which relies on the spin-orbit interaction in defining the CESR linewidth. We find it particularly interesting to make a similar comparison using the available data concerning the metallic complexes of $(\mathrm{CH})_x$ with alkali-metal dopant atoms, in an attempt to test the existing models[9,10] for metals and to gain a better understanding of these metallic systems.

II. EXPERIMENT

The polyacetylene $(\mathrm{CH})_x$ films were prepared according to the Shirakawa technique.[11] Chemical doping was carried out by immersing *cis*-rich $(\mathrm{CH})_x$ films of convenient sizes for ESR study in a $0.3M$ solution of alkali-metal–naphthalene complexes in tetrahydrofuran (THF). In all cases, doping was achieved up to saturation (> 15%) and the samples were washed with pure THF distilled from the solution and pumped for several hours by constant cryogenic pumping. The ESR tubes containing the samples were sealed under high vacuum, to avoid the possibility of atmospheric contamination.[12]

ESR spectra were recorded in the temperature range from 4 to 300 K, using an *X*-band (9.5 GHz) ER 200D Bruker spectrometer, provided with a ESR 900 Oxford instrument with a continuous-flow helium system.

III. RESULTS AND DISCUSSION

A. Room-temperature variation of $\Delta H_{\text{p.p.}}$ with the nature of the dopant

We present in Fig. 1, experimental data of the corrected[13] ESR-linewidth $\Delta H_{\text{p.p}}$ versus the dopant atomic number Z at room temperature for highly-alkali-metal-doped $(\mathrm{CH})_x$. These data include our values as well as values reported by various authors.[12,14–17] In any case, the observed ESR spectra consist of a characteristic Dysonian[18] asymmetric line whose shape is consistent with that for a metallic state. The large range of $\Delta H_{\text{p.p.}}$ values obtained for Li-doped $(\mathrm{CH})_x$ is related to the solvation effect which influences significantly the width as we have mentioned earlier.[19] For highly Na-doped samples $\Delta H_{\text{p.p.}}$ values from 6 to 10 G have been reported.[14,15] In the case of K-doped films a large range of $\Delta H_{\text{p.p.}}$ values was observed at room temperature, which was mainly due to the influence of the annealing on the line broadening. In agreement with the recent work of Forbes *et al.*,[16] we have observed that under thermal treatment (180 °C for $\frac{1}{2}$ hour) the K-doped linewidth significantly increases from ~5 to ~35 G. Highly Rb- and Cs-doped $(\mathrm{CH})_x$ have been less extensively investigated by ESR. In both cases, we have obtained ESR spectra which consist of a relatively large asymmetric line with $\Delta H_{\text{p.p.}} = 50 \pm 10$ G for Rb-doped films and $\Delta H_{\text{p.p.}} = 300 \pm 50$ G for Cs-doped ones and, contrary to the case of K-doped samples, there was no annealing effect on the linewidth.

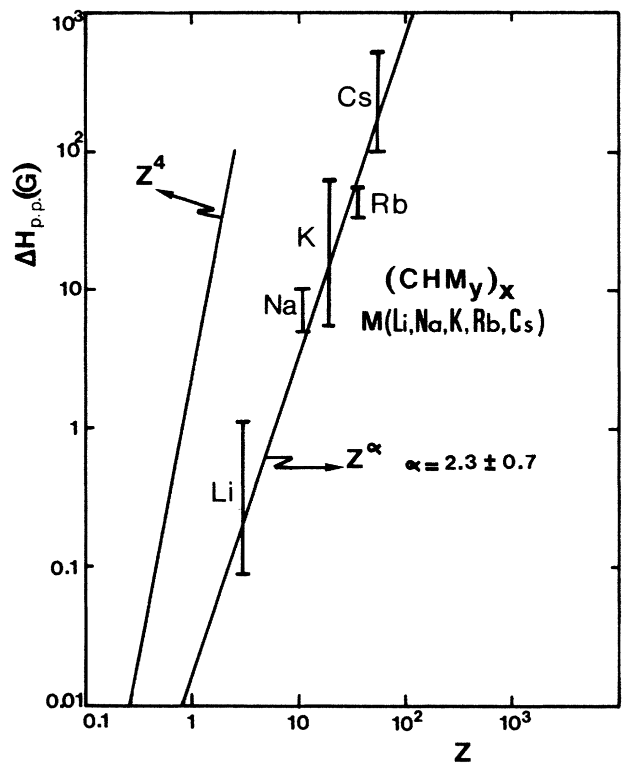

FIG. 1. Room-temperature variation of the CESR linewidth of highly-alkali-metal-doped $(CH)_x$ vs the atomic number Z of the dopant (dopant concentration y—14% to 16%).

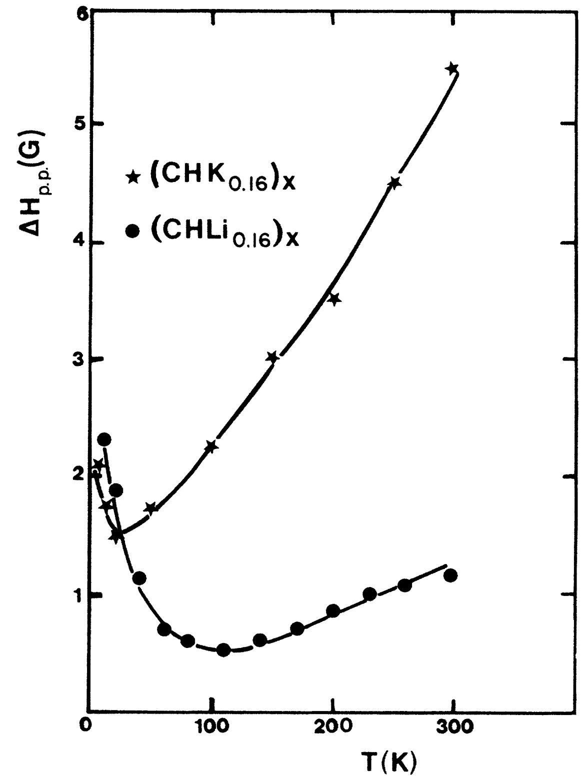

FIG. 2. ESR linewidth of highly Li- and K-doped *cis*-$(CH)_x$ as a function of temperature. Solid lines are guides to the eye.

The room-temperature ESR linewidth $\Delta H_{p.p.}$ tends to increase with increasing atomic number of the alkali-metal dopant (Fig. 1), as already observed in the case of alkali-metal-doped polyphenylene[20] and graphite.[21] By analogy with these two cases, we expect that one important contribution to the line broadening comes from the spin-orbit interaction in the alkali-metal dopant atoms. According to the theory of Elliott[9] and Yafet[10] showing the importance of spin-orbit coupling in the spin relaxation process in simple metals and semiconductors, the extended dependence of the ESR linewidth on the dopant atomic number should follow a Z^4 law. However, as plotted in Fig. 1, using the experimental data obtained at room temperature, $\Delta H_{p.p.}$ seems to follow a Z^α law, with $\alpha \simeq 2.3 \pm 0.7$. A similar behavior could be observed in the room-temperature ESR-linewidth dependence or intercalant atomic number of graphite lamellar compounds with alkali metals.[21] We thus suggest that phonon-modulated spin-orbit coupling is probably the predominant relaxation process in which the dopant plays the dominant role. However, the discrepancy with the Z^4 law (see Fig. 1) could be due to the contribution to the width of other relaxation mechanisms also depending on the nature of the dopant (solvation of Li^+ and Na^+, for instance).

B. Linewidth temperature dependence for heavily Li-, K-, and Rb-doped $(CH)_x$

As shown in Figs. 2 and 3, increasing the temperature from 100 to 300 K for Li-doped films and from 50 to 300 K

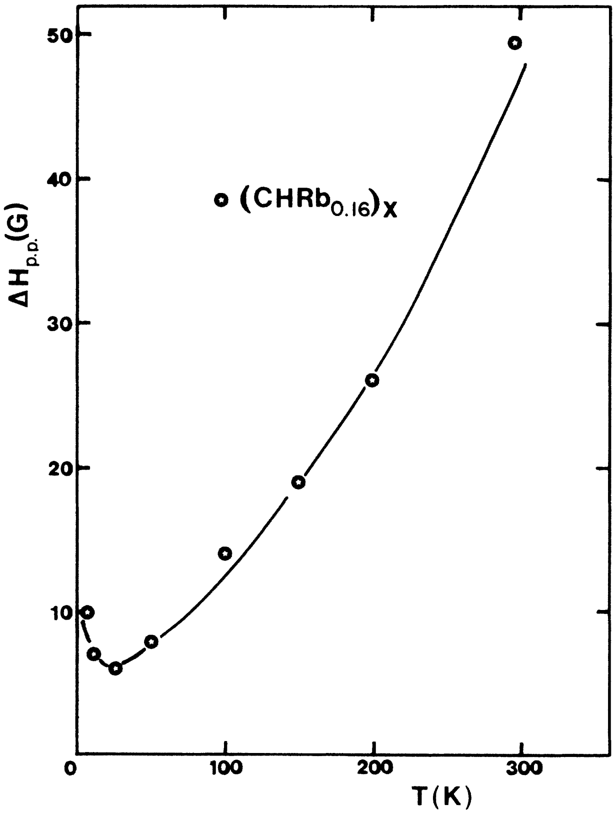

FIG. 3. ESR linewidth of highly Rb-doped *cis*-$(CH)_x$ as a function of temperature. Solid line is a guide to the eye.

for K- and Rb-doped ones, results in an increase of the linewidth which is nearly proportional to temperature. A similar behavior has been observed in the case of highly Na-doped $(CH)_x$.[22] Such a temperature dependence will be interpreted using the structural model developed by Baughman, Murthy, and Miller[23] concerning metallic complexes of polyacetylene with alkali-metal dopant atoms which predicts that the $(CH)_x$ chains form a host lattice in which the alkali-metal ions are present in channels. We expect such a structure to result in a spin-orbit coupling on the alkali-metal ions which is more efficient for electronic motion normal to the chains than along the chain. With increasing temperature above 50 K, the electron-activated transverse hopping becomes more and more efficient. Then spin-lattice relaxation via the spin-orbit coupling becomes the dominant relaxation process in defining the linewidth, yielding the observed $\Delta H_{\mathrm{p.p.}}$ increase with temperature.

On the other hand, for metallic systems in which the electronic longitudinal and transverse relaxation time, respectively, T_{1e} and T_{2e} are similar, the theory of Elliott[9] and Yafet[10] predicts that $T_{1e}^{-1} \simeq T_{2e}^{-1} \propto T$ for temperature T above the Debye temperature. Thus, according to the latter relation, the observed linewidth behavior as a function of temperature seems to follow a metallic T law, in agreement with the fact that the origin of the obtained ESR signal can be attributed to the delocalized electrons (see paragraph above).

Contrary to the preceding case, for low temperatures between 4 and 100 K for Li-doped $(CH)_x$ and between 4 and 50 K for K- and Rb-doped $(CH)_x$, the linewidth increases when the temperature decreases (see Figs. 2 and 3). Such a behavior could be interpreted as a consequence of electron localization on the chains, following a process similar to the one existing in the case of undoped $(CH)_x$. Therefore, when the temperature decreases the electron spends more and more time on a given chain and the hopping time between chains ($\tau_\perp$) becomes very large compared to the longitudinal scattering time ($\tau_\parallel$). Consequently, spin-lattice relaxation via the spin-orbit coupling is overcome by other relaxation mechanisms. The exchange between quasilocalized spins and the hyperfine interaction with the nuclear spins could explain the observed broadening of the line with decreasing temperature.

Further work is required in order to estimate the expected deviation of the electronic g factor from the free-electron g value, resulting from the spin-orbit coupling on the alkali-metal ions; the one predicted by Elliott[9] $(\Delta g)^2 = \tau \Delta H$ with τ the electron-phonon scattering time. It is also necessary to analyze in more detail the temperature dependence of the susceptibility of the alkali-metal–$(CH)_x$ complexes in order to gain further information about the nature of the spins in the metallic state, at low temperature. Such studies are now in progress.

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