

Electron-spin-resonance studies of pyrrole polymers: Evidence for bipolarons

J. C. Scott, P. Pfluger,* M. T. Krounbi, and G. B. Street

IBM Research Laboratory, 5600 Cottle Road, San Jose, California 95193

(Received 25 March 1983)

ESR measurements have been performed on samples of neutral polypyrrole, polypyrrole-perchlorate, oxygen-doped polypyrrole, and poly(β,β' -dimethylpyrrole perchlorate). A narrow Lorentzian line is observed in oxidized, highly conducting films, but no correlation between conductivity and either linewidth or intensity is found. Electrochemically cycled films, which remain highly conducting, show little or no detectable ESR absorption. It is deduced that the ESR signal seen in the as-prepared material does not arise from the current-carrying species, but rather from accidental neutral π -radical defects. The absence of paramagnetism in the metallic state is discussed within the framework of bipolaron formation.

I. INTRODUCTION

The electrical transport mechanism in conducting polypyrrole remains a central problem in the understanding of this material. From earlier studies of the physical properties of various pyrrole polymers, including conductivity,¹ thermoelectric power,¹ Hall effect,¹ infrared and visible spectroscopy,^{1,2} photoelectron spectroscopy,³ ¹³C NMR,² and electron diffraction,⁴ it has become clear that conventional metallic-band transport theory provides an inadequate description.⁵ Although the thermoelectric power is consistent with hole-type metallic conduction, the Hall coefficient is anomalously small and negative. The temperature dependence of the conductivity, $\sigma \sim \exp[-(T_0/T)^{1/4}]$, suggests a three-dimensional variable-range-hopping mechanism. Diffraction results show that, indeed, there is considerable structural disorder which is necessary in order to localize the electronic wave functions. In addition, it is apparent that the chemistry of polymerization and oxidation is very complicated.^{4,6} Although there is evidence from ir and NMR spectroscopies that the basic ring structure is retained in the polymer, recent x-ray photoemission spectroscopy (XPS) results⁶ show that there are several stages of oxidation affecting, particularly, the nitrogen atom. Moreover, electrochemical cycling is found to replace the anions originally obtained from the electrolyte solution with oxygen-containing anions (perhaps OH⁻).^{4,6}

It has previously been found² that polypyrrole, in both its neutral-insulating and oxidized-conducting states, exhibits a strong ESR signal. In order to obtain more information concerning the charge carrying species and the changes introduced by electrochemical cycling, we have performed a more comprehensive ESR study on a variety of neutral and oxidized polypyrrole films, examining the dependence of the g value, linewidth, and intensity on the concentration of various oxidants, on temperature, and on the electrochemical history of the sample. It is found that there is no correlation of the ESR spectrum with the transport properties, and that, moreover, it is possible by electrochemical cycling to reduce the spin concentration without affecting the conductivity. Hence we conclude that the paramagnetic species are predominantly neutral and, conversely, that the charge carriers are spinless. It is

suggested that these latter species are bipolarons, singlet-bound states of two positively charged polarons.

For the work which we present in this paper, ESR spectra were obtained, using a conventional X -band (9.3 GHz) spectrometer, on several different samples, all prepared in a continuously purified rare-gas atmosphere: neutral polypyrrole (PP⁰) prepared by electrochemical reduction of perchlorate films,² PP⁰ oxidized progressively with gaseous O₂, polypyrrole-perchlorate (PP⁺ClO₄⁻) as initially prepared by electrochemical polymerization of pyrrole in silver-perchlorate solution, and poly-3,4-dimethylpyrrole perchlorate (P β DMP⁺ClO₄⁻) synthesized in an analogous way. All samples were loaded into the quartz ESR tube in the dry box where they had been prepared, in order to avoid exposure to atmospheric oxygen. For some samples of the perchlorate, after spectra had been obtained on the original films, the effect of oxygen exposure was examined.

II. RESULTS

A. Neutral polypyrrole

The spectrum of PP⁰ consists of two distinct lines: a narrow component of width ~ 0.4 G peak-to-peak, Lorentzian in shape, with an intensity at room temperature corresponding to $\sim 2.10^{19}$ spins/g (1 spin per 600 monomers), and a wide component, intermediate between Gaussian and Lorentzian, ~ 2.8 G wide and accounting for 6.10^{19} spins/g. (Note that these values are only approximate due to the difficulty of analyzing the line shape which results from the superposition of the two components.) The temperature dependence of the intensities reveals that the narrow component is thermally activated with a characteristic temperature of ~ 220 K, while the wide line has Curie behavior indicating a fixed number of spins (1 per 200 rings). There is little dependence on temperature of the narrow linewidth, but the wide line broadens with cooling to about 4 G peak-to-peak at 5 K, its shape becoming more Gaussian.

B. PP⁰ oxidized chemically with gaseous O₂

A glass apparatus was constructed so that three pieces of PP film, under the same O₂ pressure, could be used to

monitor simultaneously weight uptake using a quartz oscillator, conductivity in a four-point contact device, and ESR. At each pressure the samples were allowed to come into equilibrium with the oxygen vapor before measurements were made. The results at room temperature are shown in Fig. 1 where several (overlapping) stages can be seen in the doping process.

(1) From zero to about 0.2% weight uptake, the conductivity rises by (at least) 4 orders of magnitude, but there is no change in the ESR linewidth. The intensity of the narrow line, however, increases during this stage by about a factor of 5, or roughly by one spin for three oxygen molecules.

(2) Above 0.3% O_2 , the conductivity saturates at a constant value of (typically) $10^{-2} \Omega^{-1} \text{cm}^{-1}$ and the ESR intensity starts to drop again.

(3) At roughly 0.5%, the narrow line has virtually disappeared and the underlying wide line remains. This broadens a little more (from about 3 to approximately 4 G) at saturating O_2 pressures, namely 600 Torr and 2% weight uptake. The intensity at this stage is quite similar to its initial value of 1 spin per 200 monomer units, in spite of the fact that assuming all the oxygen is in the form of O_2^{2-} species, the stoichiometry implies a charge transfer of 1 electron per 50 rings.

(4) Pumping at any stage above 0.5% weight uptake removes only a small amount ($<0.2\%$) of oxygen and does not alter the conductivity. By contrast, there is an enormous change in the linewidth, which drops back to 0.4 G. There is no longer any indication of a wide component, but the intensity is little altered.

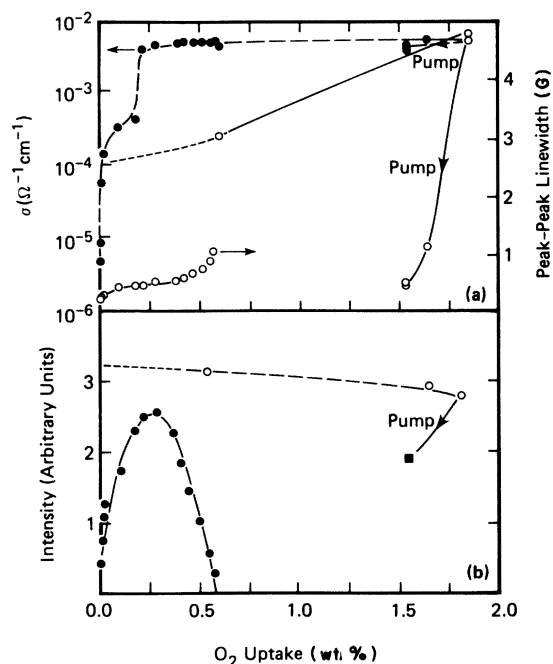


FIG. 1. (a) Conductivity (●) and ESR peak-to-peak linewidths (○) in polypyrrole as a function of oxygen weight uptake. (b) ESR intensity contributions from the narrow (●) and wide (○) components.

It should be emphasized that results have been obtained on several different samples and that all show similar stages of oxygen uptake.

For three of the ESR samples He exchange gas was mixed with the O_2 so that the sample could be cooled to He temperatures at various stages of oxidation. ESR spectra at low temperature on these samples permit observation of the wide component only and reveal that it is much less affected by the oxidation process than the narrow line which dominates the room-temperature spectrum. The low-temperature width of the wider line, which is 5 G in PP^0 , decreases to 3 G, and its intensity increases by a factor of 2 at 0.2% O_2 , the concentration at which the conductivity saturates. Additional oxygen then slowly brings both properties back towards their original values, again implying fewer spins than expected on the basis of simple charge-transfer considerations.

Raising the temperature above 300 K for films with O_2 concentrations in the 0.5% to 1.0% range, where the narrow line is no longer seen at room temperature, restores a signal of width 0.5 G or less. It is found that this is not due to oxygen desorption, as in the pumping experiments, but rather indicates that the disappearance of the narrow line is caused by an increase in its activation energy. Although, because of irreversible chemical changes, we were unable to reach sufficiently high temperature to obtain an accurate value of the activation energy, we estimate it to lie in the range 300–400 K for 1% oxygen concentration.

C. Perchlorates of polypyrrole and poly(β, β' -dimethylpyrrole)

As-synthesized films of polypyrrole-perchlorate exhibit a strong narrow ESR signal. The temperature dependence of the intensity is dominated by a Curie contribution corresponding to 1 spin per 50 monomers, which is considerably less than the degree of oxidation determined by analysis or electrochemically, namely, 1 electron per 3 monomers. We cannot yet conclusively rule out a Pauli term in the susceptibility of these films, but we can place an upper limit of $0.5 \times 10^{-5} \text{cm}^{-3}/\text{mole}$. The linewidth of the conducting polymers is 0.2 G, independent of temperature, and the shape is Lorentzian but slightly asymmetric. Since the sample thickness and conductivity are too small to give a Dysonian line, and since, moreover, the asymmetry persists to low temperature where the conductivity is less by several orders of magnitude, we believe that the shape is due to an anisotropy or an inhomogeneous distribution in the g tensor. Poly(β, β' -dimethylpyrrole perchlorate), as synthesized by electrochemical polymerization, yields an ESR signal similar to the unsubstituted polymer, except that the linewidth (0.11 G) is a factor of 2 smaller.

The ESR spectra of both $PPClO_4$ and $P\beta DMPClO_4$ are extremely sensitive to the presence of oxygen, and the above results are obtained only in rigorously clean, inert gas atmospheres. Admission of small amounts of O_2 or air results in a progressive increase in linewidth up to a factor of 100, and the change is entirely reversible on pumping. The integrated intensity and position of the line remain the same throughout such an exposure-pumping cycle. (See Table I.)

Electrochemical cycling of polypyrrole films has been

TABLE I. Room-temperature ESR experimental parameters for the materials discussed in this paper. Also given is the g factor of deuterated *trans*-polyacetylene. All g values are accurate to ± 0.00001 , except as noted.

Material	g value	Peak-to-peak linewidth G	Susceptibility (10^{-5} cm $^{-3}$ mole)
PP ⁰ narrow line	2.002 55	0.2–0.3	0.2–0.8
PP ⁰ wide line	2.002 61	2.5–3.0	0.6–2.0
PP ⁰ plus O ₂	2.002 80	1.3–1.7	1–3
PP ⁰ plus O ₂ , pumped	2.002 80	0.3–0.4	1–3
PPClO ₄	2.002 58	0.2–0.3	2.0±0.5
PPClO ₄ exposed to O ₂	~2.002 6	~30	~2
PPClO ₄ exposed to O ₂ and pumped	2.002 58	0.3–0.4	2–3
PβDMPClO ₄	2.002 61	0.11	1.4±0.5
PβDMPClO ₄ exposed to O ₂	2.002 6	12	~1.0
PβDMPClO ₄ exposed to O ₂ and pumped	2.002 61	0.12	~1.4
(CD) _x	2.002 68		

found to make radical changes to the chemistry,^{4,6} without affecting the conductivity of oxidized samples. The primary difference is that while the originally polymerized film contains the anion of the electrolyte from which it is prepared, cycled films are found to contain only oxygen (or OH⁻) species. To investigate further the properties of these cycled films, we obtained ESR spectra of polypyrrole films which had been electrochemically cycled up to five times in a cell containing Bu₄NClO₄ electrolyte, always ending in the oxidized-conducting state. In each case the ESR intensity dropped by an order of magnitude or more. For one sample in particular, although the conductivity was unaltered from that of the uncycled film (15 Ω⁻¹ cm⁻¹), there was no evidence of any ESR signal at all, even with the sensitivity of the instrument increased one thousandfold. The reduction in ESR signal seems to depend critically on the conditions under which the electrochemical cycling is performed, and further work is under way to optimize this effect.

III. DISCUSSION

A. g factors

In addition to the linewidth and intensity measurements which have been described above, careful g -factor determinations were made on each of the polymers under investigation. Absolute field and frequency measurements were made for PPClO₄, which was then used as a reference sample for the remaining materials. The results are given in Table I. The g factors all lie in the range of 2.0025 to 2.0028, typical of the values for radicals in the π system of polyenes and aromatics. In the same sequence of experiments, the g factor of *trans*-polyperdeuterioacetylene was compared to that of PPClO₄ and found to differ by only 1 part in 10⁴. Note that any radical localized on or near a heteroatom, such as oxygen in carboxylic species or nitrogen in pyridines, has a g -value shift⁷ of at least 10⁻³. Hence we conclude that the radical defects in all the polypyrroles which we have studied are π based and do not involve much nitrogen-centered, or in the case of the

oxidized film, oxygen-centered character.

The two lines in PP⁰ differ by a small but detectable amount, the wide component having a g -value shift which is $6 \pm 2 \times 10^{-5}$ larger than that of the narrow component. The implication is that the two contributions to the ESR signal arise from two distinct types of electronic states.

B. Linewidths

The linewidths are rather small compared to those in other π -radical systems where the dominant broadening mechanism is the hyperfine interaction (typically 20–25 G) with adjacent protons. This leads to the conclusion that hyperfine broadening is reduced by delocalization, by motion, and/or by exchange. In the case of PP⁰, the broader component is clearly decoupled from the species giving rise to the narrow component, indicating that there are (at least) two different types of defects. This, in addition to other evidence from x-ray and electron diffraction⁴ and XPS,³ implies a system which has a considerable amount of disorder leading to the possibility of inhomogeneous broadening through a distribution of g values.

The narrower linewidth in PβDMPClO₄ compared to unsubstituted PPClO₄ can be attributed to two causes: First, since there are no hydrogen atoms bonded to the conjugated carbons, the hyperfine broadening is considerably less; second, the degree of structural disorder is known to be less,⁴ leading to a reduced inhomogeneous linewidth. In spite of the fact that the conductivity of the substituted material is less by an order of magnitude, the line remains Lorentzian in shape and has a similar intensity to that of the unsubstituted pyrrole polymer.

C. Relationship of ESR to conductivity

Many of the results which we have outlined above are contrary to the assumption that the ESR signal arises from the same species which carry the electric current. In this section we shall enumerate the items of evidence which lead to the unavoidable conclusion that the paramagnetic centers do not contribute to the conductivity.

(1) The spin concentrations in PPClO_4 , PP^0 , and PPO_2 are of comparable magnitude. This should be contrasted with the differences in conductivity (10^2 , $<10^{-6}$, and $10^{-2} \Omega^{-1} \text{cm}^{-1}$, respectively) and in formal degree of oxidation (0.3, 0, and 0.02). Clearly the number of electrons removed from the polymer chain is not the same as the number of spins. Oxidation must proceed by transfer of (roughly) equal numbers of up-spin and down-spin carriers, as from a degenerate band. Such a mechanism implies a Pauli temperature-independent contribution to the susceptibility, which has not been observed, perhaps because it is overwhelmed by the much larger Curie term.

(2) There is no correlation between the linewidth in PPClO_4 , which increases by at most a factor of 2 between 4 and 300 K, and its conductivity, which obeys a three-dimensional variable-range-hopping relation. If the ESR signal was due to electrons hopping among localized states, then the inhomogeneous and hyperfine widths would be averaged by the motion whose rate can be estimated from the conductivity to be faster than the Larmor frequency at room temperature, and the line would broaden as the hopping rate decreases at low temperature. If the conductivity were due to motion of free carriers (which we believe not to be the case), then the linewidth would be due to spin-flip scattering from phonons and would decrease considerably below the Debye temperature.

(3) The doping experiment of PP^0 with O_2 shows no change in linewidth and relatively minor changes in intensity in the range of concentration where the conductivity is changing by 3 orders of magnitude. Thus the concentration of carriers is unrelated to the ESR intensity and the carrier mobility is unrelated to the linewidth.

(4) Little or no ESR signal can be observed in highly conducting electrochemically cycled films.

Hence we conclude that *the paramagnetic species are not the current carriers*.

D. Nature of the paramagnetic centers

If the spins are not associated with free carriers, then what is their origin and, conversely, why do the carriers not contribute appreciably to the magnetism? Since the concentration of spins is, to a first approximation, unaffected by electrochemical reduction of the original film and by subsequent gas-phase reoxidation, and since the spins do not carry current, we conclude that the paramagnetism arises from neutral defects. The g values imply that these defects are in the π system. Figure 2 shows some of the ways in which a neutral radical defect can arise in the idealized polypyrrole structure. Note, in particular, the possibility of defects associated with the addition of hydrogen to the conjugated carbons, which is appealing in view of the excess hydrogen found consistently in elemental analysis.² There may also be solitonlike defects,⁸ although the structures on each side of them are not degenerate, and hence their mobility is limited. In addition, it is to be expected that there are some paramagnetic centers due to a few residual anions left by incomplete reduction. It is found in optical studies⁹ that the 1 eV absorption characteristic of the oxidized polymer is present to a small extent in all electrochemically reduced films and vanishes only in *in situ* experiments in the presence of

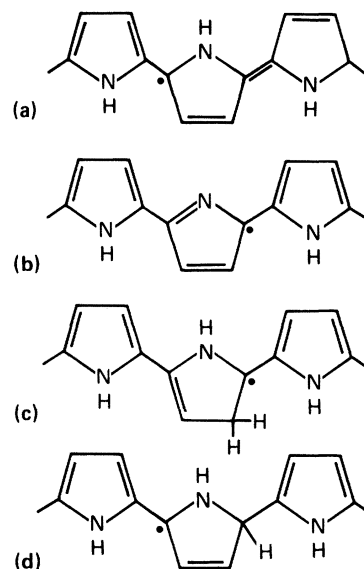


FIG. 2. Several possible mechanisms for the formation of a radical defect in the π system. (a) A bond-alternation domain wall analogous to the soliton which has been discussed for polyacetylene (Ref. 8). However, in this case the bond structure to the right is energetically less favorable than that to the left. (b) A radical induced by the removal of the N proton. (c) and (d) Radicals induced by the addition of protons at the β and α positions, respectively. Note that defects (b), (c), and (d) may delocalize and propagate away from their origin by the formation of an intervening structure like that of the right side of (a).

strong reducing agents. We shall return to the "very light doping" regime below.

In the conducting films (and in the absence of oxygen) the ESR line is narrowed and has a Lorentzian form. Recall that the effect of physisorbed oxygen is to broaden the line by a factor of 100 while retaining its Lorentzian shape, implying an increase in the relaxation rate due to spin-flip scattering from paramagnetic oxygen molecules. This phenomenon could arise in the case of both translational motion of the defect and spin diffusion mediated by exchange. However, the fact that the line remains narrow to helium temperatures strongly suggests an exchange-narrowing mechanism arising from the relatively strong overlap of extended molecular wave functions, or perhaps mediated by the relatively small concentration of more mobile carriers. This latter exchange mechanism would explain why one of the lines in insulating PP^0 , namely, the 3–4 G line of constant spin concentration, is so much broader than in the conducting forms. By contrast, the thermal activation of the narrow line suggests motional narrowing due to delocalization of the excited state.

Hence we are led to a picture of singly occupied, but neutral, molecular defect states in both neutral-insulating polypyrrole and the heavily oxidized conducting form. Since the spin concentration is not radically altered by oxidation, these states cannot lie at the Fermi energy. However, they are only singly occupied and, therefore, there must be a Coulomb correlation energy U for double occupancy and spin pairing. The situation is illustrated schematically in Fig. 3 where disorder-induced bandtailing

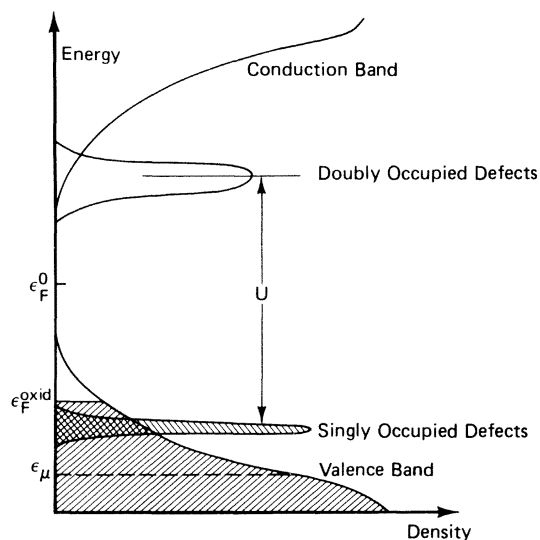


FIG. 3. Hypothetical band structure of oxidized polypyrrole. Disorder induces considerable bandtailing into the gap and introduces a mobility edge ϵ_μ . The Fermi energy, which would lie at ϵ_F^0 in the neutral material, is lowered upon oxidation, but the density of paramagnetic defects is not much affected. The correlation energy U precludes the double occupancy of defect states.

has been invoked to account for a nonzero-state density above the defect levels. There is evidence for disorder in both structural studies⁴ and in the temperature dependence of the conductivity.¹ Coulomb correlation occurs in the dangling-bond states of amorphous inorganic semiconductors¹⁰ and accounts for the behavior of the Fermi level and spin concentration as a function of p - and n -type doping. We believe that polypyrrole is the first example of a conducting polymer in which there is experimental evidence that correlation energies have an important effect on defect states. It is probable that a similar picture applies to other conducting polymers, e.g., polyparaphenylene and polyphenylene sulphide. The radical centers in polypyrrole are relatively stable to gas-phase oxidation, but can be progressively removed by electrochemical cycling.

The absence of paramagnetism associated with the current carrier can be explained in terms of bipolarons.¹¹ For certain classes of model-conjugated polymers it has been shown^{12,13} that two positive paramagnetic species (polarons) can become bound to form a nonmagnetic bipolaron. The structure of the resulting object is shown schematically in Fig. 4. Although we cannot yet say conclusively that bipolarons are the current carriers in oxidized polypyrrole, the available evidence is highly suggestive: The initial rise in the ESR intensity as neutral polypyrrole is oxidized with oxygen is consistent with the

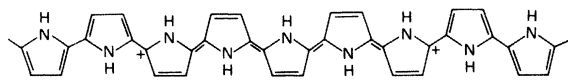


FIG. 4. Schematic structure of a bipolaron in polypyrrole. The positive charges are expected to be spread out to a much greater extent than shown here.

formation, predominantly at first, of polarons; further reaction leads more and more to double charging of the same chain segments so that bipolarons are formed and the ESR intensity falls; the independence of magnetic and transport properties, and especially the possibility of conductivity without any paramagnetism, implies a diamagnetic character of the mobile charges. The neutral radical defects which seem to be present in all electrochemically synthesized films are then to be viewed merely as reactive chemical centers which mask the intrinsic properties of the polymer and which can be removed by appropriate chemical processing, e.g., electrochemical switching.

The succession from neutral polymer through light doping to moderate and heavy doping may then be viewed as follows. In nominally neutral PP there are a few paramagnetic species that can be thermally activated out of the traps formed by residual anions. The concentration of these bound polarons can be estimated at about 0.1% in the most carefully reduced films. The thermally activated species is a mobile polaron which exhibits the narrow ESR line of "neutral" and lightly doped PP. Additional oxidative doping initially injects further positive polarons, but as the charge transfer increases, the polaron density reaches a point where it is more favorable for the polarons to pair up as bipolarons.

The energetics of such a description are shown schematically in Fig. 5. In this picture, which we emphasize is hypothetical at the moment, the neutral defects D^0 lie at a lower energy than the positive polaron states P^+ which are introduced at doping levels such that a given conjugated chain segment carries only one charge. A second charge can be introduced at an energy which includes not only the polaron binding energy ($E_p - E_V$), but also the binding energy of two polarons into a bipolaron. We note that for the bipolaron structure to exist, it is necessary that Coulomb repulsion in this case be smaller than the elastic- and electronic-bonding energies. The formation of bipolaron states in the gap of oxidized polypyrrole is con-

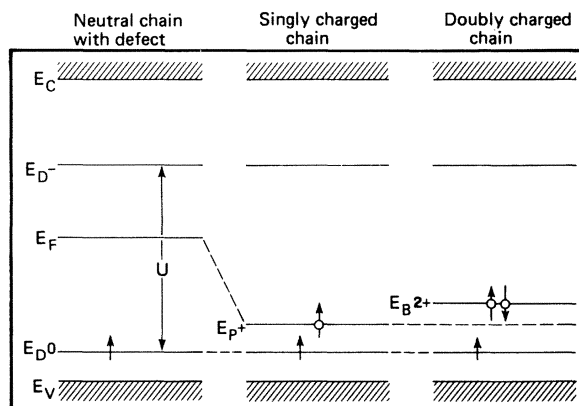


FIG. 5. Energy-level scheme for neutral defects (E_{D^0}), negatively charged (diamagnetic) defects (E_{D^-}), positive polarons (E_{P^+}), and bipolarons ($E_{B^{2+}}$) for various levels of doping of the molecular chain. E_V and E_C label the valence- and conduction-band mobility edges, respectively. For the purposes of simple illustration, the effects of disorder shown in Fig. 3 have been omitted from this diagram.

sistent with the onset of absorption observed at 1 eV in optical studies.^{6,9}

IV. CONCLUSION

ESR on pyrrole polymers exhibits a wealth of phenomena. We have shown that there is a distinction between the species which contribute to the magnetism and those which carry current, and it seems that much of the behavior which we have observed is "irrelevant" in the sense that it is due to extrinsic species and tells little about the intrinsic processes of conduction. The data allow the identification of the defect paramagnetic centers as neutral π radicals with energies somewhat below the Fermi level. We have suggested that the absence of any ESR signal which can be correlated with the conductivity is due to the formation of bipolarons. These are expected to be localized species which can carry current by hopping, in much the same way as polarons, except that they are doubly

charged and diamagnetic. The narrowing of the defect-induced ESR line in conducting forms of PP is intriguing since it implies that the static species are rapidly interchanging with the mobile carriers; in other words, the bipolarons are mediating an indirect exchange interaction. Finally, it has been shown that electrochemical cycling can remove the defects of the static radicals without affecting the conductivity. It will be interesting to explore the conditions favorable for complete removal of paramagnetic centers and to examine in more detail the properties of films so prepared.

ACKNOWLEDGMENTS

This work was supported in part by a grant from the U.S. Office of Naval Research. One of us (P.P.) is grateful for financial support from the Swiss National Science Foundation.

*Present address: Brown Boveri Research Center, CH-5405 Baden, Switzerland.

¹K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, G. P. Gardini, and J. F. Kwak, *Synth. Met.* **1**, 329 (1980).

²G. B. Street, T. C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott, and G. Weiser, *Mol. Cryst. Liq. Cryst.* **83**, 253 (1982).

³P. Pfluger and G. B. Street, *J. Chem. Phys.* (in press); P. Pfluger, U. Gubler, and G. B. Street (unpublished).

⁴G. B. Street, T. C. Clarke, R. H. Geiss, V. Y. Lee, A. Nazzal, P. Pfluger, and J. C. Scott, *J. Phys. (Paris) Colloq.* (in press).

⁵P. Pfluger, J. C. Scott, G. Weiser, and G. B. Street, *J. Phys. (Paris) Colloq.* (in press).

⁶P. Pfluger, M. T. Krounbi, G. B. Street, and G. Weiser, *J.*

Chem. Phys. **76**, 3212 (1983).

⁷See, for example, A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance* (Chapman and Hall, London, 1967).

⁸W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. B* **22**, 2099 (1980).

⁹K. Yakushi and L. Lauchlan (unpublished).

¹⁰R. A. Street, *Adv. Phys.* **25**, 397 (1976).

¹¹S. A. Brasovskii and N. N. Kirova, *Zh. Eksp. Teor. Fiz. Pis'ma Red.* **33**, 6 (1981) [*JETP Lett.* **33**, 4 (1981)].

¹²J. L. Brédas, R. R. Chance, and R. Silbey, *Mol. Cryst. Liq. Cryst.* **77**, 319 (1981); *Phys. Rev. B* **26**, 5851 (1982).

¹³J. L. Brédas, B. Themans, J. M. Andre, R. R. Chance, D. S. Boudreaux, and R. Silbey, *J. Phys. (Paris) Colloq.* (in press).