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High-pressure electron-spin dynamics in disordered conducting polymers

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We report a study of the electron-spin dynamics in disordered conducting polymers by high-pressure electron-spin-resonance (ESR) measurements. Our model system is a polypyrrole doped with long chains of polyanion. Applying pressure the ESR linewidth increases with a rate of 50%/kbar, the spin susceptibility decreases by 30%/kbar, while the resistivity is decreased only by 3%/kbar. We can quantitatively account for the observed behavior in a model where the magnetic properties are dominated by thermally excited triplet bipolarons.

Conjugated polymers such as polyacetylene, polyaniline, polypyrrole, etc., have attracted considerable interest in fundamental and applied research. Their common exciting feature is that the conductivity can be increased by a few orders of magnitude upon doping. Even when the polymers are disordered, their room-temperature conductivity easily reaches hundreds of S/cm. In order to make progress in the engineering of conducting polymers, it is important to understand the charge dynamics in these systems and to answer a few fundamental questions: which are the entities that carry the current, how are they formed, what limits their propagation, what is the role of the dopants, etc.?

In disordered conducting polymers, the charged species are coupled to lattice deformations, the conductivity is due to the hopping of these polaronic carriers. It is usually considered that the majority of the carriers are paired into diamagnetic bipolarons.[1] Besides the conventional Coulomb interaction and the electron-phonon coupling, it was shown recently[2,3] that a significant coupling persists between the counterion and the charge created on the polymer chain. Indeed this coupling influences strongly the electronic ground state of the conducting polymer. For example, it was shown that the coupling through the counterion stabilizes weakly bound bipolarons.[2] The triplet state of these weakly bound bipolarons is thermally accessible and, thus, contributes to the susceptibility. This analysis is supported by electron-spin-resonance (ESR) measurements on polypyrrole (PPY) samples[4] or polyanyline and derivative systems.[5]

The coupling of the charge carriers through the doping centers (counterions) depends strongly on the polymer-counterion distances which can be modified by applying hydrostatic pressure. Since ESR is a very sensitive probe for magnetic properties, we have performed pressure dependence study of the ESR properties of two disordered conducting polymer. We have completed these measurements by measuring the pressure dependence of the electrical resistivity. It will be shown that, in contrast to low-dimensional organic conductors, in disordered conducting polymers the spin susceptibility is much more sensitive to pressure than the conductivity. These observations are very well accounted for by the pressure dependence of the singlet-triplet energy separation of the bipolarons.

Two kinds of electrochemically doped polypyrrole films have been studied: PPY doped with sulfated ions of a long polyhydroxyether chain (sample No. 1) and PPY doped with benzene sulfonate ions (sample No. 2).[6] In both samples the PPY is fully oxidized with one charge per three pyrrole monomers. Their PPY volume fractions are 7% and 55% leading to an average separation $\bar{\delta}$ between the doping centers of 4 and 2.0 pyrrole monomer lengths for No. 1 and No. 2, respectively. The transport properties of these films are presented elsewhere.[7]

Helium gas is used as a pressure transmitting medium in the high-pressure ESR cell.[8] The pressure in the cell is measured with an InSb gauge. Pressures up to 2 kbar were applied at room temperature. We have used SiC fibers as a spin standard in order to avoid uncertainties due to the eventual changes in the cavity Q factor with pressure. The susceptibility of these fibers is pressure independent in this pressure range.

The pressure dependence of the spin susceptibilities (χ_s) and of the linewidths (ΔH) of Nos. 1 and 2 are shown in Figs. 1 and 2. The susceptibilities are decreasing while the linewidths are increasing with pressure. The first pressure cycle is associated with an irreversible change of the line-

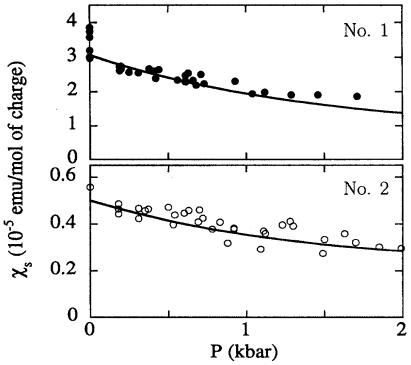

FIG. 1. Variation of the spin susceptibility with pressure for Nos. 1 and 2: $\partial \ln \chi/\partial p = -23$ and -18 %/kbar, respectively. The solid lines correspond to the pressure dependence of the spin susceptibility in the singlet-triplet model discussed in the text.

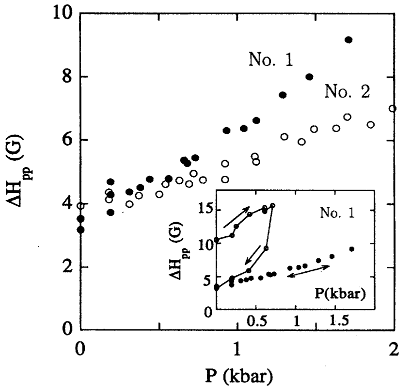

FIG. 2. Reversible variation of the ESR linewidth with pressure at 300 K for Nos. 1 and 2: $\partial \ln \Delta H/\partial p=74$ and 37.5 %/kbar, respectively. In the inset the first pressure cycle is shown which leads to irreversible changes of the linewidth due to oxygen absorption/desorption.

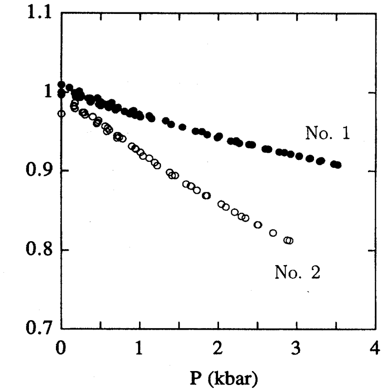

FIG. 3. Pressure dependence of the resistivity normalized to ambient pressure value at 300 K for Nos. 1 and 2: $\partial \ln \rho/\partial p=-2.7$ and -6.2 %/kbar, respectively. The ambient pressure resistivity values are 0.33 and 0.06 Ωcm, respectively.

width due to the adsorbed oxygen. (This behavior is shown in the inset of Fig. 2 for No. 1 where the solid lines are related to the first pressure cycle.) It is well known that the linewidth of conducting polymers may be dramatically increased in the presence of oxygen because of a magnetic contact between the spins of the polymer and the triplet states of the oxygen molecule. Recent works[9] suggest that oxygen is diffusing into the material before being adsorbed in some traps where they are in contact with the spin system. No special precaution regarding a possible air contamination has been taken before the first pressure cycle. Before starting the experiments, the linewidths of Nos. 1 and 2 were 10 and 7 G, respectively. (It has been checked in an independent experiment that the "intrinsic" linewidth obtained by dynamic pumping of the sample space is ~3 G for both samples and it is obtained in a typical time scale of 4 h.) After the first pressure cycle, the ambient pressure linewidth is almost the same as the "intrinsic" one. This suggests that the irreversible reduction of the linewidth observed after this cycle is due to the expulsion of oxygen during depressurization. The exact mechanism of oxygen expulsion is unknown but may involve the replacement of the adsorbed oxygen molecules by helium.[9] Six months after the experiments, the linewidth of Nos. 1 and 2 is still the "intrinsic" linewidth. Note that this irreversibility does not affect neither the susceptibility nor the conductivity as can be seen in Figs. 1 and 3. It suggests that the interaction between the oxygen molecule and the polaronic carriers is of pure magnetic origin and is not associated with trapping of carriers. The change of the ESR linewidth on following pressure cycles are fully reproducible.

The observed pressure dependencies are very strong: the spin susceptibilities decrease by $\partial \ln \chi/\partial p=-23$ and -18 %/kbar, while the linewidths increase by $\partial \ln \Delta H/\partial p=74$ and 37.5 %/kbar for Nos. 1 and 2, respectively. These effects are huge with respect to the small variations reported for the pressure dependence of the dc conductivity and the optical absorption of PPY.[10,11] We have also measured the pressure dependence of the resistivity of our films at room temperature in the same pressure cell in a four probe configuration. The normalized resistivities (ratio of the resistivity at pressure P to the resistivity at ambient pressure) are plotted in Fig. 3. The resistances decrease by $\partial \ln \rho/\partial p=-2.7$ and -6.2 %/kbar for Nos. 1 and 2, respectively, in agreement with Ref. 10. The decrease of the resistivity with pressure is related to the decrease of the hopping distances.

Qualitatively these results very much resemble the pressure dependence of the ESR and transport properties of quasi-one-dimensional organic conductors. In these systems the spin susceptibility and resistivity vary due to the increased screening of the on-site Coulomb correlations, and the ESR linewidth increases with increased interchain hoppings with pressure. One can say that conducting polymers are also quasi-one-dimensional conductors, just disordered ones. However, comparing the numbers it turns out that there are some essential differences: $\partial \ln \chi/\partial p$ is usually in the range of $-(4-8)$%/kbar and $\partial \ln \rho/\partial p\sim-30$ %/kbar in the case of organic conductors[12,13] compared to $-(20-30)$ and $-(2-7)$%/kbar in the present case. So for disordered conducting polymers the spin susceptibility has a stronger pressure dependence than the resistivity while in the case of the quasi-one-dimensional organic conductors it is just the opposite suggesting that the underlying physics is different in the two families.

In order to describe the observed pressure dependence of the magnetic properties of our conducting polymers we have to take into account the coupling between the charge and the counterions. It was shown by Bussac and Zuppiroli[2] that the exchange energy J between the singlet and the triplet states of a bipolaron depends exponentially on the separation ℓ between the two counterions. For ℓ of $\ell^{\text{crit}}>\ell>\ell^{\text{min}}$ weakly bound bipolarons are stabilized for which J is comparable to k_BT and the triplet state is thermally accessible giving χ_t spin susceptibility. For $\ell>\ell^{\text{crit}}$ the two charges behave like a pair of independent polarons giving Curie susceptibility χ_C. Finally, for small separations $\ell<\ell^{\text{min}}$, conventional ESR silent bipolarons are formed for which the triplet states are thermally inaccessible. The total susceptibility is thus composed of two terms: χ_C of unpaired polarons and χ_t coming from the triplet excitations of bipolarons.

The temperature dependence at ambient pressure of the susceptibility of Nos. 1 and 2 permits determination of χ_C and χ_t at each temperature. At room temperature it leads to $N_C = 0.6\%$ isolated polarons/charge and $N_t = 1.8\%$ equivalent spins/charge for No. 1. The comparable numbers are smaller for No. 2 (0.17 and 0.22 %, respectively) since the average dopant separation is smaller.

When studying the pressure dependence of the spin susceptibility one does not have to worry about the Curie component because in this dilute polaron system, at least at these low applied pressures, the spins remain uncorrelated. This was checked on No. 1 at 200 K where χ_C did not show any pressure dependence. On the other hand when pressure is applied at high temperatures, where an appreciable number of triplet states is present, the separation between the counterions is reduced and the exchange energy of the bipolarons is increased, making the triplet state higher in energy. The amount of thermally excited triplet bipolarons is thus decreased leading to a decrease of the susceptibility. A quantitative estimation of this effect is given below.

For simplicity, we will assume that all bipolarons have the same exchange energy J separating the singlet-triplet states. The equivalent spin density due to excited triplet is

$$N_t = 8/[3 + \exp(J/k_B T)]. \tag{1}$$

From the value of N_t quoted above we found $J_0/k_B \sim 1800$ K (2400 K) for No. 1 (No. 2) at ambient pressure. The relation between the exchange integral J and the dopant separation $\bar{\delta}$ is[2,14]

$$J = A \exp[-2.8(\bar{\delta} - \delta_{\min})]. \tag{2}$$

By applying an hydrostatic pressure P, $\bar{\delta}$ is slightly decreased and $J(P)$ is related to the elongation (assuming small variations) by

$$J(P) = [1 - 2.8 e(P) \bar{\delta}] J_0, \tag{3}$$

where $e(P)$ is the elongation ($e < 0$), $\bar{\delta}$ and J_0 are the ambient pressure values. Using the Young's modulus and the Poisson ratio[15] we found a contraction of $|e| = 1$ and 1.6 % for Nos. 1 and 2 at 1 kbar which leads to $J(1\ \text{kbar})/k_B \sim 2000$ and 2600 K, respectively.

Inserting $J(P)$ in formula (1) one obtains the pressure dependence of $N_t(P)$, that is of the total spin susceptibility:

$$\chi_s(P) = (g^2 \mu_B^2 / 4 k_B T)[N_C + N_t(P)]. \tag{4}$$

It is plotted as solid lines in Fig. 1. The agreement with the experimental data is very good. Note that no adjustable parameter has been introduced.

The strong increase of the linewidth ΔH with pressure can be explained using the same model. In Ref. 4, we have suggested that the spin lattice relaxation of the excited triplet bipolarons is dominated by an Orbach relaxation through the singlet state. It leads to a relaxation rate $1/T_1$ related to the χ_t susceptibility by $\chi_t / T_1 \sim 1/T$ and, thus, to $\Delta H(P) \chi_t(P) = C^{\text{st}}$ at room temperature for a pure triplet system.

In No. 1 at low pressure the main contribution to the ESR line is coming from excited triplet bipolarons (75% of the spins at ambient pressure, 60% at 1 kbar). The product $\Delta H \chi_t$ is $\sim 7 \times 10^{-5}$ G emu/mol while it is $\sim 8 \times 10^{-5}$ G emu/mol at 1 kbar which shows good agreement with the preceding discussion despite the presence of extra Curie spins.

The contraction of the distances with pressure which leads to strong modifications of the ESR characteristics, affects the conductivity to a lesser extent, since the conductivity of these materials is due to hopping. A detailed discussion of the hopping mechanism is given in Ref. 16. Let us recall the main elements in order to give an estimate for the pressure effect. At constant temperature and within the critical path scheme, the conductivity is proportional to the hopping rate:

$$\sigma \sim \exp(-2\alpha R_c),$$

where α is the localization rate and R_c is the critical hopping distance over which the hopping probability is negligible. In these materials, $1/\alpha \sim 4$ in PPY units and R_c is equal to some intercharge distances (namely to some $\bar{\delta}$). With an applied hydrostatic pressure and for small variations:

$$\Delta\sigma/\sigma = -2\alpha R_c e(P).$$

At 1 kbar, a typical 1% contraction leads to a resistivity decrease of the order of a few percent, depending on the ratio $R_c/\bar{\delta}$. This is in agreement with the observations.

It is interesting to compare the order of magnitude of the pressure effect on the conductivity and on the susceptibility. Roughly speaking, a 1% contraction leads to an increase of 1% of the typical transfer integral t which leads to an increase of 2% of the conductivity since the conductivity is proportional to the square of the transfer integral. Within a band picture, the same increase of t leads to a broadening of the band of 1% and thus to a decrease of the density of state of the same order of magnitude: the optical absorption spectrum does not show any significant change up to 10 kbar.[11] In the same way, a 1% contraction increases the attraction through the doping center by 1% leading to an effect on the susceptibility of the same magnitude: this effect is neglected. Since the room-temperature susceptibility is dominated by thermally excited species (triplet states), the decrease of the susceptibility is not proportional to the transfer integral, it decreases exponentially and a typical 10% effect is observed.

In conclusion, we have reported a high-pressure ESR study of a disordered conducting polymer. The strongly increasing linewidth and decreasing susceptibility with pressure are interpreted in a model where the high-temperature magnetic properties are governed by triplet excitations of the bipolarons. With pressure the exchange energy determining the singlet-triplet separation of the bipolarons is modified. For an increasing pressure, the exchange energy is increased leading to a decrease in the contribution of thermally excited triplet bipolarons to the susceptibility and to an increase of the linewidth. In fact, both the linewidth and the susceptibility variations are qualitatively (and quantitatively) similar to what is observed in triplet-exciton crystals such as the TCNQ salts.[17] For these compounds, it was shown that the pressure modifies the exchange integral between the singlet and the triplet states of the excitons, changing the ESR properties in the same way as observed above for disordered conducting polymers.

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[1] F. Genoud, M. Guglielmi, M. Nechstein, E. Genies, and M. Salmon, Phys. Rev. Lett. **55**, 118 (1985).

[2] M. N. Bussac and L. Zuppiroli, Phys. Rev. B **47**, 5493 (1993).

[3] F. Rachdi and P. Bernier, Phys. Rev. B **33**, 7817 (1986); S. Stafström, *ibid.* **47**, 12 437 (1993).

[4] O. Chauvet, S. Paschen, M. N. Bussac, and L. Zuppiroli, Europhys. Lett. **26**, 619 (1994).

[5] P. K. Kahol, W. R. Spencer, N. J. Pinto, and B. J. McCormick, Phys. Rev. B **50**, 18 647 (1994).

[6] W. Wernett, Synth. Met. **41-43**, 843 (1991).

[7] O. Chauvet, S. Paschen, L. Forro, L. Zuppiroli, P. Bujard, K. Kai, and W. Wernet, Synth. Met. **63**, 115 (1994).

[8] A. Sienkiewicz and M. Jaworski, High Pressure Res. **5**, 877 (1990).

[9] M. Nechstein and F. Genoud, Solid State Commun. **91**, 471 (1994); K. Aasmundveit, F. Genoud, E. Houze, and M. Nechstein, Synth. Met. **69**, 193 (1995); A. Bartl, L. Dunsch, D. Schmeisser, W. Gopel, and H. Naarmann, *ibid.* **69**, 389 (1995).

[10] D. S. Maddison and T. L. Tansley, J. Appl. Phys. **71**, 1831 (1992); A. Lundin, B. Lundberg, W. Sauerer, P. Nandery, and D. Naegele, Synth. Met. **39**, 233 (1990).

[11] K. Yakushi, L. J. Lauchlan, T. C. Clarke, and G. B. Street, J. Chem. Phys. **79**, 4774 (1983).

[12] For pressure effects in one-dimensional (1D) organic conductors, see D. Jerome and H. J. Schulz, Adv. Phys. **31**, 299 (1982).

[13] L. Forro, G. Sekretarczyk, M. Krupski, D. Schweitzer, and H. Keller, Phys. Rev. B **35**, 2501 (1987); L. Forro, J. R. Cooper, G. Sekretarczyk, M. Krupski, and K. Kamaras, J. Phys. (Paris) **48**, 413 (1987).

[14] In Ref. 2, the distances are 1D distances in polaron half-width units. The formula (2) has been modified to take into account the present situation: 3D distances in pyrrole monomer length units.

[15] The Young modulus E and the Poisson ratio ν are $E = 2.4$ and 1.5 GPa for Nos. 1 and 2, respectively, while $\nu = 0.38$ for both.

[16] L. Zuppiroli, M. N. Bussac, S. Paschen, O. Chauvet, and L. Forro, Phys. Rev. B **50**, 5196 (1994).

[17] A. W. Merkl, R. C. Hughes, L. J. Berliner, and H. H. McConnell, J. Chem. Phys. **43**, 953 (1965).