PHOTOGENERATION OF SOLITONS IN TRANS-(CH)x: THE REVERSED SPIN-CHARGE RELATION OF THE PHOTOEXCITATIONS

J. Flood, A. Heeger

To cite this version:

HAL Id: jpa-00222818
https://hal.archives-ouvertes.fr/jpa-00222818
Submitted on 1 Jan 1983

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
PHOTOGENERATION OF SOLITONS IN TRANS-(CH)$_X$: THE REVERSED SPIN-CHARGE RELATION OF THE PHOTOEXCITATIONS

J.D. Flood and A.J. Heeger

Department of Physics, University of California, Santa Barbara, CA 93106, U.S.A.

Résumé - Des études de résonance paramagnétique électronique (EPR) de haute sensibilité ont été faites pendant illumination avec hω > Eg. Ces expériences ont établi la limite supérieure du rendement quantique de spins paramagnétiques produits par la photoexcitation. Nous avons conclu que les photoexcitations chargées sont sans spin et par conséquent elles ont la relation spin-charge inversée qui caractérise les solitons. Le rapport photoproducif des solitons chargés comparés aux solitons neutres est plus grand que 10$^2$.

Abstract - High sensitivity ESR studies of trans-(CH)$_X$ have been carried out during photoexcitation with hω > Eg. The results set an upper limit on the number of photoinduced spins and on the quantum efficiency for photoproduction of unpaired spins. We conclude that the charged photoexcitations are spinless and therefore have the reversed spin-charge relation of solitons. The photogeneration branching ratio, charged solitons to neutral solitons, is greater than 10$^2$.

Because of the electron-hole (e-h) symmetry of trans-(CH)$_X$, a bond-alternation domain-wall (soliton) causes the formation of a localized electronic state at mid-gap /1,2/. The soliton can be neutral with spin 1/2 (one electron in the mid-gap level) or charged + or − with spin zero (zero or two electrons, respectively, in the mid-gap level). The reversed spin-charge relationship for solitons is a direct manifestation of charge fractionalization discovered in the mathematical analysis of spinless fermion systems /3,4/. In trans-(CH)$_X$, the fractionalization and the associated reversed spin-charge relation arise since the localized mid-gap state derives from 1/2 a state from the occupied valence band and 1/2 a state from the empty conduction band, for each sign of spin.

Soliton-antisoliton (S-Ś) pairs can be generated in trans-(CH)$_X$ either by charge transfer doping or by photoexcitation. Dynamical calculations which follow the time evolution of a (CH)$_X$ chain after injection of an electron-hole (e-h) pair have been carried out by Su and Schrieffer /5/. They found that the photoinjected e-h pair evolves to S-Ś in a time of the order of $\sim 10^{-13}$ sec.

Initial confirmation of these ideas came from photoexcitation experiments /6,7/. The photoproduction of S-Ś pairs implies the photogeneration of states in the gap, as observed experimentally /8,9/. In an attempt to determine the spin-charge relation for the
photoinduced carriers, Flood et al /10/ studied the electron spin resonance (ESR) during photoexcitation. They were able to set limits on the quantum efficiency for photoproduction of spins (and for the absolute number of photogenerated spins). These limits were several orders of magnitude below the estimated QE for photoproduction of gap states and charge carriers. Thus, Flood et al /10/ concluded that the photogenerated charge carriers are spinless and identified them as charged S-S pairs.

Subsequently, Orenstein et al revised their earlier estimate /8/ of the QE for photoproduction of gap states. From a more detailed analysis of the data, they concluded that the QE was about \(10^{-2}\) (rather than of order unity) at low excitation levels /11,12/. Moreover, they found that the strength of the photoinduced absorption saturated with increasing laser pump power. For a continuous Ar laser, they found saturation at power levels above about 10 mW, corresponding to about \(3 \times 10^{12}\) excitations in the thin film sample /12/.

Because of the importance of establishing the spin-charge relation, we have extended the studies of ESR during photoexcitation. By using a spectrometer with higher sensitivity, we have been able to improve our signal-to-noise by more than two orders of magnitude. Consequently, at low temperatures (10 K) and with a laser power level of 10 mW on the sample, we find an upper limit for the number \(N_s\) of photogenerated spins, \(N_s \leq 3 \times 10^{10}\). Similar measurements at room temperature (100 mW laser power on the sample) set an upper limit of \(N_s < 6 \times 10^9\).

The value for \(N_s\) is two orders of magnitude below the number of gap states determined at the same temperature and laser power level by Orenstein et al /11,12/. Denoting \(\gamma_{ch}\) as the QE for photoproduction of charge carriers (and charged gap states) and \(\gamma_s\) the QE for photoproduction of spins, our results place a lower limit on the branching ratio, \(\gamma_{ch}/\gamma_s \geq 10^2\). The conclusions from these data are the following:

1) The photogenerated charge carriers are spinless. This reversed spin-charge relation indicates that the photogenerated excitations are solitons.

2) The branching ratio (photogeneration of charged solitons compared to neutral solitons) is at least \(10^2\).

For these measurements, an IBM Instruments (Bruker) ESR spectrometer (equipped with optical access cavity) was used. Additional improvement in signal-to-noise was obtained through signal averaging with a Nicolet 1270. The sample temperature was controlled by a variable temperature Helitran system. For illumination, we used the 2.41 eV line from an Ar ion laser. The samples were semi-transparent films (~0.1 um thick) of trans-(CH)\(_x\) which absorbed most of the incident visible light. The films were polymerized directly on the inner wall of an ESR tube as cis-(CH)\(_x\) and isomerized to trans-(CH)\(_x\) by heating to 180°C for about five minutes. The dark signal corresponded to \(3 \times 10^{13}\) spins with a line width at 300 K of about 1 G. The dark signal was calibrated by comparison to a ruby standard. Subsequent values for \(N_s\) used the dark signal as a secondary standard. The sensitivity of the apparatus to photoinduced spins was verified through the observation of unpaired spins in spinach leaf in response to the green laser light. Experiments were carried out at room temperature and at about 10 K. In order to minimize possible sample heating, helium gas was diffused into the sealed ESR tube with the sample polymerized on the inner wall.
The spin resonance was studied during illumination using both standard ESR with continuous illumination and double modulation with chopped light. For the higher sensitivity double modulation measurements, the laser light was chopped at 87 Hz. Since this period (~11 msec) is long compared with the decay times of the photo-induced absorption /8,11,12,13/, any photogenerated ESR signal would follow the light intensity and be amplitude modulated by the chopped light. The standard derivative signal was detected with a lock-in amplifier at 100 kHz (output time constant of 1 msec), and the output was fed into a second lock-in set to detect the chopping frequency. The resulting signal was then stored in the Nicolet 1270 for signal averaging.

At room temperature, the double modulation technique with signal averaging set an upper limit for the number of photogenerated spins (10 gauss sweep at \(g = 2\)): \(N_s < 6 \times 10^9\). These measurements were carried out with 100 mW laser power on the sample. A series of broader sweeps (60 gauss above or below \(g = 2\)) were carried out to search for triplets. Because of the broader sweep, there is less sensitivity for a given signal averaging time. We were, however, able to set an upper limit on the number of triplets at less than \(2 \times 10^{10}\).

At 10 K, the double modulation technique with signal averaging set an upper limit of \(3 \times 10^{10}\) for \(N_s\) at \(g = 2\). Broader sweeps (60 gauss above or below \(g = 2\)) also placed the limit for the number of photogenerated triplets at \(3 \times 10^{10}\). The above value for \(N_s\) (\(g = 2\)) at 10 K was not limited by the sensitivity of the spectrometer, but rather by sample heating. Under the conditions described above (10 mW chopped light incident on the sample), a weak signal was observed with magnitude \(10^3\) smaller than the dark signal. Although this weak signal could result from photogenerated spins, the corresponding temperature change (due to sample heating by the absorbed laser light) needed to produce such a signal would be only about \(10^{-2}\) K! Nevertheless, the observed signal set an upper limit of \(3 \times 10^{10}\) on the number of photogenerated spins.

For the continuous and double modulation techniques

\[
N_s = \gamma_s \phi \tau
\]

where \(\phi\) is the photon flux and \(\tau\) is the lifetime of the photoinduced excited state. In their low temperature photoinduced absorption studies, Orenstein and Baker /8,11,12/ have shown that the decay is non-exponential (a power law) with the signal falling off by a factor of two in a few milliseconds. Thus, the limit on \(N_s\) can be re-expressed as a quantum efficiency, \(\gamma_s\), defined as the number of spins generated per photon.

We find the following:

\[
\begin{align*}
N_s & \leq 3 \times 10^{10} & \text{10 K; 10 mW incident} \\
\gamma_s & \leq 3 \times 10^{-4}
\end{align*}
\]

The corresponding QE (\(\gamma_{\text{eh}}\)) for photoproduction of charged excitations with energy deep in the gap has been estimated by Orenstein to be somewhat greater than \(10^{-2}\) /11,12/. Picosecond spectroscopy /14,15/ shows an initial rapid time dependence (\(t < 100\) ps) followed by the slow decay which extends out all the way into the millisecond regime. In the photoinduced bleaching studies, Vardeny et al /14/ find \(\Delta \alpha(1500\) ps)/\(\Delta \alpha(1\) ps) to be \(6 \times 10^{-2}\) at 80 K where \(\Delta \alpha\) is the change
(< 0) in the absorption at 2 eV following a pump pulse. The implied QE (after the initial transient) of the long-lived charged excitations is therefore $\gamma_{ch} \sim 3-5 \times 10^{-2}$. We conclude that $N_{ch}/N_S = \gamma_{ch}/\gamma_S \geq 10^2$ at 10 K (10 mW laser power incident); the photogenerated charged excitations are spinless.

Two principal assumptions were made in the analysis:

i) That the spin lattice time ($T_1$) is sufficiently short for the photoinduced spins to come to thermal equilibrium before they decay,

ii) that the line width for the light induced ESR would be comparable to that of the dark signal.

$T_1$ measurements based on both saturation /16/ and on electron spin echo decay /17/ have been reported. The saturation method yields an estimate at 77 K of $T_1 \approx 70 \mu$sec. The values for $T_1$ obtained by spin echo increased from about 5 usec at 300 K to about 10 usec at 100 K. The transient measurements described earlier /10/ provide a direct estimate of $T_1$ under the precise conditions of the experiment. We found that the rise time (~ 100 usec) of transient heating signal was limited by instrumental resolution, so that $T_1 < 100 \mu$sec at 10 K, consistent with the above measurements. Thus $T_1 << \tau$ for the 0.5 eV photo-induced absorption which has been identified as resulting from a charged excitation /12/.

Extensive studies of the dark ESR have demonstrated that the line width is due to the hyperfine interaction narrowed by the delocalized nature of the spatial wavefunction and by the motion of the neutral soliton /18,19/. Since the neutral solitons are quasi-static at low temperatures (Solid State Effect in dynamic nuclear polarization studies), the line width of light induced spin resonance would result from the same intrinsic hyperfine interaction and be no greater than the 5 G width of the dark signal.

In summary, we have carried out a series of ESR experiments on samples illuminated with light at photon energies $\hbar \omega > E_g$. From these studies, we have been able to set an upper limit on the number of photoinduced spins and the corresponding quantum efficiency for photogeneration of unpaired spins. Since $N_{ch}/N_S = \gamma_{ch}/\gamma_S \geq 10^2$, the charged excitations are spinless. Independent experiments carried out in the time domain have demonstrated that pumping with photons at $\hbar \omega > E_g$ leads to charged localized excitations which diffuse over substantial distances before recombination and that these excitations are generated instantaneously (< $10^{-13}$ sec). Moreover, photoinduced absorption spectroscopy /8,12,13/ has demonstrated that these excitations have both the infrared signature /13/ and the mid-gap absorption /8,13/ expected for charged solitons. These data, together with the reversed spin-charge relation demonstrated by the ESR studies, provide detailed experimental evidence of the rapid generation of S-S pairs after injection of e-h pairs, are predicted by Su and Schrieffer /5/ and by Mele /20/. Furthermore, the conclusion that $\gamma_{ch}/\gamma_S \geq 10^2$ yields important additional information; the branching ratio (photoproduction of charged solitons compared to photoproduction of neutral solitons) is at least $10^2$. Schrieffer et al /21/ have recently shown that this large branching ratio is a fundamental aspect of the soliton photoproduction process and can be understood from basic parity considerations. Finally, we note that the experimental demonstration that charged solitons are spinless is particularly interesting in a broader context. The reversed spin-charge relation
is a direct manifestation of fermion charge fractionalization through soliton formation (charge 1/2 for each sign of spin), a phenomenon first predicted in the mathematical physics of field theory /3,4/.

References

11. ORENSTEIN, J., private communication.