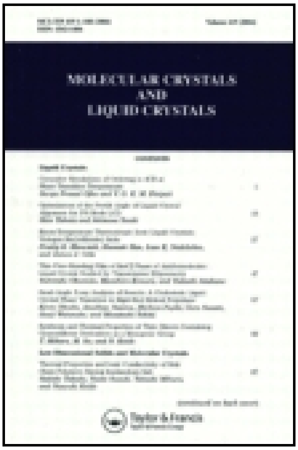

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Optical Properties of Heavily-Doped Polyacetylene

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OPTICAL PROPERTIES OF HEAVILY-DOPED POLYACETYLENE

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Abstract The optical properties of electrochemically-doped $[CH(ClO_4)_y]_x$ are discussed. The heavily-doped regime, best described as a gapless incommensurate Peierls insulator, is characterized by high dc conductivity, a large Pauli susceptibility and by the disappearance of the original interband transition of undoped $(CH)_x$. The optical spectrum shows a pseudogap at ~0.5 eV and vibrational modes which imply that the carbon-carbon bondlength is not uniform.

INTRODUCTION

In this paper we describe optical studies of electrochemically-doped polyacetylene, $[CH(ClO_4)_y]_x$, at doping levels of $0<y<0.07$. Beginning with the earliest studies[1], the electronic properties of heavily doped trans-$(CH)_x$ have been described as "metallic". The metallic state is thought to occur because the bond alternation of the undoped polymer is suppressed by doping, leading to closure of the semiconducting energy gap. This picture has been used to describe the results of transport,[1-3] magnetic susceptibility,[3,4] specific heat,[5] far-infared,[1] optical,[6] and electron energy-loss[7] studies. In this paper we show that the optical properties of heavily-doped $(CH)_x$ are not metallic but instead are those of a one-dimensional system stabilized by an incommensurate charge-density wave distortion. On account of the strong disorder in the material[8,9] and the consequent short relaxation time for the charge carriers, a large density of states exists in the Peierls gap.[10,11]

EXPERIMENTAL DETAILS

Polyacetylene was produced by the Shirakawa technique and doped electrochemically with ClO_4^- ions from a solution of $LiClO_4$ in acetonitrile using Pt as a counter electrode. Concentrations were determined by weight uptake. Each doped film was cut up and portions were distributed for the measurements. The magnetic susceptibility was measured with a high-field Faraday balance. Four-probe electrical conductivity and thermopower measurements were done simultaneously in a closed-cycle refrigerator over temperatures from 10 to 300 K. Reflectance measurements were done with a Michelson interferometer in the far infrared and a grating monochrometer in the infrared and visible; the frequency-dependent conductivity was determined by Kramers-Kronig analysis.

RESULTS

Fig. 1 shows the effect of doping on the room-temperature dc conductivity σ_{RT} and the normalized Fermi-energy density of states $N(E_F)/N_o$ (determined from the susceptibility). Here, N_o=0.14 states/(eV-C atom) is the expected[12] value of $N(E_F)$ for "metallic" $(CH)_x$. Three distinct regions may be identified in these data.[13] Region I, with $0 \leq y < 0.02$, has low values for both σ_{RT} and $N(E_F)$. In region II, where $0.02 < y < 0.04$, the conductivity is quite high yet $N(E_F)$ is low. Region III, with $0.04 < y < 0.08$ is the "heavily-doped" regime. Here, both σ_{RT} and $N(E_F)$ are high, although $N(E_F)$ saturates at only about 80% of the value expected for metallic $(CH)_x$.

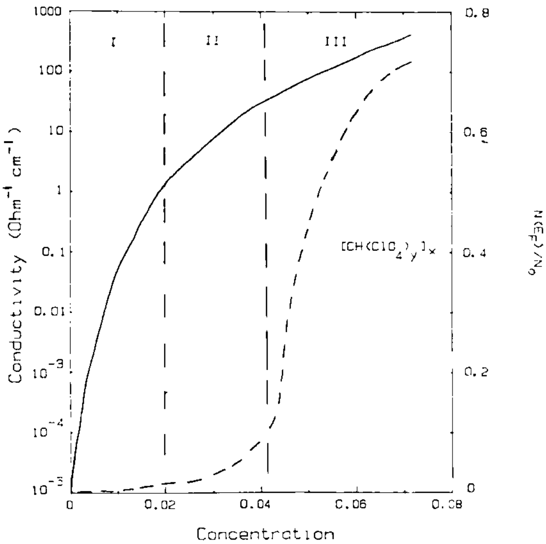

Fig. 1. Room-temperature dc conductivity (solid line and magnetic susceptibility (dashed line of $[CH(ClO_4)_y]_x$ versus dopant concentration.

Fig. 2 shows the frequency-dependent conductivity $\sigma_1(\omega)$ of a sample in each region, with region I represented by y=0.016, region II by y=0.034, and region III by y=0.061. The optical transition between the valence band and conduction band of the undoped polymer, which occurs[6] at 11000 cm^{-1} (1.4 eV), is seen as the dominant feature in region I. It is weaker in region II. And, it is essentially not observed in region III. This transition is absent in all of our samples with $y \geq 0.045$. The doping-related midgap absorption[6,14] is a shoulder at 6000 cm^{-1} (0.75 eV) in region I samples. In region II, the strength of this absorption increases and the center frequency is lower. Finally, in region III, it appears at 4000 cm^{-1} (0.5 eV) and is the only strong electronic absorption in the entire frequency region below 25000 cm^{-1} (3 eV).

The low frequency structure is shown more clearly in Fig. 3, where we plot for the three samples of Fig. 2 the frequency-

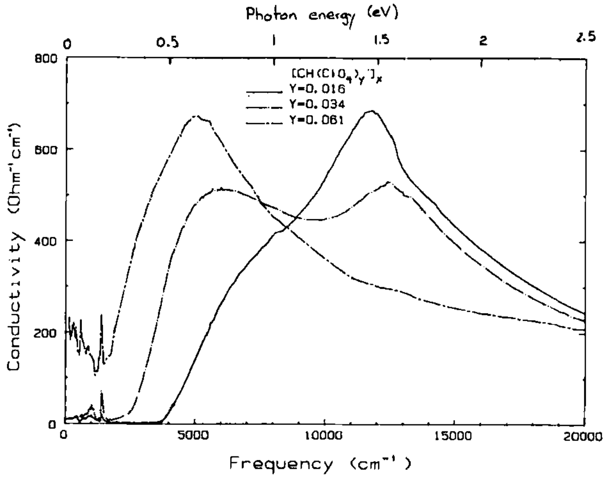

Fig. 2. Frequency-dependent conductivity of three samples of doped polyacetylene.

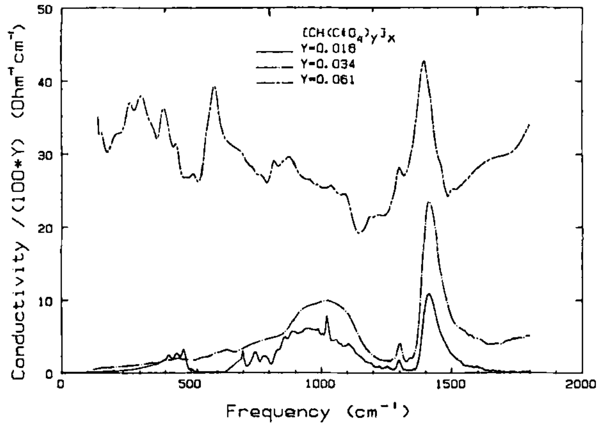

Fig. 3. Ratio of frequency-dependent conductivity to dopant concentration.

dependent conductivity divided by the dopant concentration, y, expressed as a percentage. In region I samples, narrow lines[15] at 1290 cm^{-1} and 1400 cm^{-1} are associated with internal vibrations of charged solitons whereas the broad maximum occuring between 500 and 900 cm^{-1} is the "pinning" mode of the soliton.[16,17] Note that these features are present in all three regions. Further, the area under the peaks and above the broad background increases linearly with concentration (allowing for the accuracy of the concentration determination and of the reflectance measurement) as the dopant concentration nearly quadruples. That region III samples have these vibrational features in their spectra[18] is evidence against the notion that heavily-doped polyacetylene is metallic. If the bond lengths were uniform and the gap closed, then these vibrations would not be infrared active.

DISCUSSION

To reconcile the conclusion that the gap has not closed with the absence of the interband transition at 1.4 eV in the data of Figs. 2 and 3, we propose[19] that heavily-doped polyacetylene is best described as a gapless incommensurate Peierls insulator. According to this model, the bond alternation or charge density wave which causes the gap in the first place still exists at high doping levels but is incommensurate with the lattice. This Peierls distortion ordinarily would render the polymer an insulator but in the case of strong disorder the gapless state exists with finite but reduced Fermi-surface density of states and dc conductivity.[10,11] The gapless Peierls state is analogous to the gapless state in superconductors except that in the latter case it is induced by scattering from magnetic impurities whereas in the former it results from ordinary impurity scattering. Because the gap occurs at an incommensurate wavevector, only a single optical transition is allowed — from the valence band to a new conduction band, occupying the midgap energy range.[20] Note that we see no evidence for a percolation transition involving metallic and insulating regions.[3] A mixed phase of small bandgap and large bandgap semiconductors would show a simultaneous decrease of the intraband transition and increase of the "midgap" transition; however, the sudden turn-on of the susceptibility (Fig. 1) is inconsistent with such a picture.

In summary, heavily-doped $(CH)_x$ is not metallic as generally believed. There is no closed-gap, uniform-bond state; instead, the bond length distortion becomes incommensurate at dopant levels above about 0.04. The signature of this transition is a rise of the density of states at the Fermi surface (induced by disorder) and a disappearance of the 2Δ interband transition.

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REFERENCES

1 C.K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, and A.G. MacDiarmid, Phys. Rev. Lett. 39, 1098 (1977).

2. K. Seeger, W.D. Gill, T.C. Clarke, and G.B. Street, Solid State Commun. 28, 873 (1978); J.F. Kwak, T.C. Clarke, R.L. Greene, and G.B. Street, Solid State Commun. 31, 355 (1979); Y.-W. Park, A.J. Heeger, M.A. Druy, and A.G. MacDiarmid, J. Chem. Phys. 73, 946 (1980); K. Mortensen, M.L.W. Thewalt, Y. Tomkiewicz, T.C. Clarke, and G.B. Street, Phys. Rev. Lett. 45, 490 (1980); E.K. Sichel, M.F. Rubner, J. Georger, Jr., G.C. Papaefthymiou. S. Ofer, and

R.B. Frankel, Phys. Rev. B 28, 6589 (1983).

3. Y. Tomkiewicz, T.D. Schultz, H.B. Brom, T.C. Clarke, and G.B. Street, Phys. Rev. Lett. 43, 1532 (1979); Y. Tomkiewicz, T.D. Schultz, H.B. Broom, A.R. Taranko, T.C. Clarke, and G.B. Street, Phys. Rev. B 24, 4348 (1981).
4. S. Ikehata, J. Kaufer, T. Woerner, A. Pron, M.A. Druy, A. Sivak, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. Lett. 45, 1123 (1980); A.J. Epstein, H. Rommelmann, M.A. Druy, A.J. Heeger, and A.G. MacDiarmid, Solid State Commun. 38, 683 (1981).
5. D. Moses, A. Dennenstein, A. Pron, A.J. Heeger, and A.G. MacDiarmid, Solid State Commun. 36, 219 (1980).
6. C.R. Fincher, Jr., M. Ozaki, M. Tanaka, D. Peebles, L. Lauchlan, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. B 20, 1589 (1979); M. Tanaka, A. Watanabe, and J. Tanaka, Bull. Chem. Soc. Jap. 53, 3430 (1980); A. Feldblum, J.H. Kaufman, S. Etemad, A.J. Heeger, T.-C. Chung, and A.G. MacDiarmid, Phys. Rev. B 26, 815 (1982).
7. J.J. Ritsko, E.J. Mele, A.J. Heeger, A.G. MacDiarmid, and M. Ozaki, Phys. Rev. Lett. 44, 1351 (1980); J.J. Ritsko, Phys. Rev. Lett. 46, 849 (1981).
8. A.J. Epstein, R.W. Bigelow, H. Rommelmann, H.W. Gibson, A. Feldblum, and D.B. Tanner, these proceedings.
9. P. Robin, J.P. Pouget, R. Comes, H.W. Gibson, and A.J. Epstein, Polymer 24, 1558 (1983).
10. M.J. Rice and E.J. Mele, Chemica Scripta 17, 121 (1981); E.J. Mele and M.J. Rice, Phys. Rev. B 23, 5397 (1981).
11. M.J. Rice, S. Strassler, and W.R. Schneider, Lect. Notes in Physics. 34, 282 (1975).
12. Assuming a 10 eV wide band and a tight-binding density of states.
13. We note that there exists also a fourth region, y>0.08. Our samples at these doping levels show clear signs of degredation: whereas some portions behave as do samples in region III, others have very low conductivity, are black in color, show a reemergence of the semiconducting interband transition, and are extremely brittle.
14. N. Suzuki, M. Ozaki, S. Etemad, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. Lett. 45, 1209 (1980); D.M. Hoffman, H.W. Gibson, A.J. Epstein, and D.B.Tanner, Phys. Rev. B 27, 3582 (1982).
15. C.R. Fincher, Jr., M. Ozaki, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. B 19, 4140 (1979).
16. E.J. Mele and M.J. Rice, Phys. Rev. Lett. 45, 926 (1980); M.J. Rice and E.J. Mele, Solid State Commun. 35, 487 (1980).
17. B. Horowitz, Phys. Rev. Lett. 47, 1491 (1981); Solid State Commun. 41, 593 (1982); 41, 729 (1982).

18. J.F. Rabolt, T.C. Clarke, and G.B. Street, J. Chem. Phys. 71. 4614 (1979); C. Benoit, O. Bernard, M. Palpacuer, M. Rolland, and M.J.M. Abadie, J. de Physique 44, 1307 (1983).

19. X.Q. Yang, D.B. Tanner, M.J. Rice, H.W. Gibson, A. Feldblum, and A.J. Epstein, to be published.

20. In principal, a reduced zone scheme should be used in the incommensurate case, which would allow transitions from anywhere in the valence band to anywhere in either conduction band. However, the matrix elements governing these transitions are significant only for those which are vertical in an extended zone scheme. [See M. Jestin, M. Kabbaj, J.P. Albert, and C. Jouanin, J. de Physique 44, Colloq. C3, 499 (1983).]