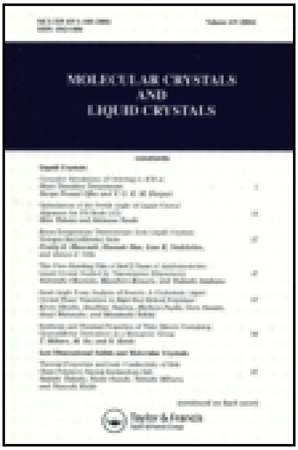

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Magnetoresistance Studies of $(CH)_x$

H. Isotalo [a], P. Kuivalainen [b], H. Stubb [a] & J.-E. Österholm [c]

[a] Semiconductor Laboratory, Technical Research Centre of Finland, Otakaari 5A, SF-02150, Espoo, Finland

[b] Electron Physics Laboratory, Department of Electrical Engineering, Helsinki University of Technology, Otakaari 5A, SF-02150, Espoo, Finland

[c] Neste Oy Research Centre, SF-06850, Kulloo, Finland

Version of record first published: 17 Oct 2011.

To cite this article: H. Isotalo, P. Kuivalainen, H. Stubb & J.-E. Österholm (1985): Magnetoresistance Studies of $(CH)_x$, Molecular Crystals and Liquid Crystals, 117:1, 177-180

To link to this article: http://dx.doi.org/10.1080/00268948508074619

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 177-180
0026-8941/85/1174-0177/$10.00/0

MAGNETORESISTANCE STUDIES OF $(CH)_x$

H. ISOTALO[1], P. KUIVALAINEN[2], H. STUBB[1] AND J.-E. ÖSTERHOLM[3]
1. Semiconductor Laboratory, Technical Research Centre of Finland, Otakaari 5A, SF-02150 Espoo, Finland
2. Electron Physics Laboratory, Department of Electrical Engineering, Helsinki University of Technology, Otakaari 5A SF-02150 Espoo, Finland
3. Neste Oy Research Centre, SF-06850 Kulloo, Finland

Abstract The magnetoresistance of lightly and heavily $CuCl_2$-doped trans-polyacetylene (PA) has been studied. In lightly doped PA an anomalous magnetoresistance typical of inorganic covalent amorphous semiconductors such as α-Si was found. This observation strongly supports the idea of a dominating hopping conduction in deep gap states near the Fermi level.

INTRODUCTION

Although much experimental data on the electrical transport properties of polyacetylene (PA) have been obtained during the last few years, a consistent picture of the transport mechanism has not yet been established. The difficulties arise e.g. due to the fibrillar morphology of PA and the disorder caused by the large dopant concentrations. In organic semiconductors magnetoresistance (MR) studies have given much valuable information about the electrical transport processes even in the case of amorphous materials[1]. In this paper we present the results of MR measurements on both lightly and heavily $CuCl_2$-doped PA.

EXPERIMENTAL RESULTS

PA thin films were synthesized using the Shirakawa method, for details on sample preparation see ref 2. The results of dc MR measurements vs applied magnetic field at various temperatures for heavily $CuCl_2$-doped PA samples are shown in figure 1. At low temperatures MR typically is negative at low magnetic fields, passes through a minimum and becomes positive at higher magnetic fields. This behaviour is similar to the one observed in heavily I_2 or AsF_5-doped PA[3-6] and also in heavily doped silicon[7].

In lightly $CuCl_2$-doped PA even small magnetic fields cause

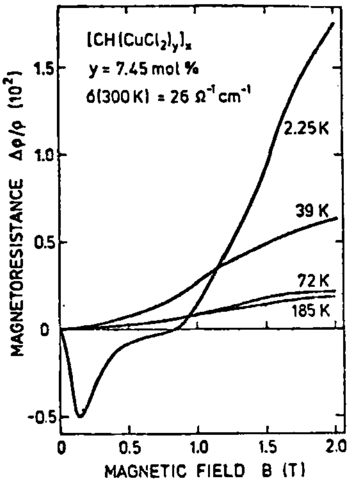

FIGURE 1 MR vs applied magnetic field at various temperatures in PA heavily doped with $CuCl_2$

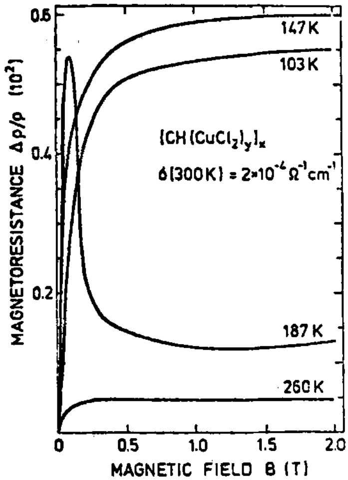

FIGURE 2 MR vs applied magnetic field at various temperatures in lightly $CuCl_2$-doped PA.

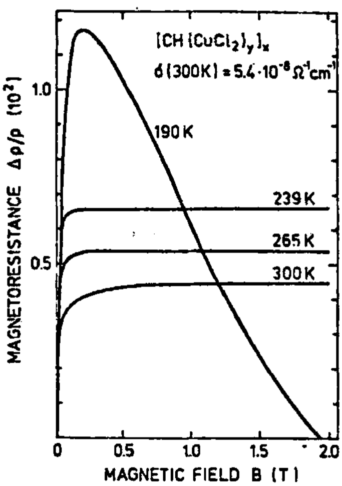

FIGURE 3 MR vs applied magnetic field at various temperatures in lightly $CuCl_2$-doped PA

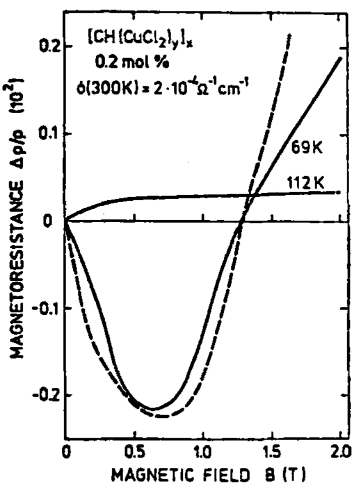

FIGURE 4 Magnetic field dependence of MR in $CuCl_2$-doped PA. The solid curve has been calculated using the Hedgcock-Raudorf model with μ=750 cm^2/Vs

a large decrease in the conductivity, figures 2 and 3. At higher fields the value of MR typically becomes only weakly dependent on magnetic field. This is the behaviour found in many covalent inorganic amorphous semiconductors such as silicon or germanium (for a review see ref. 1). Similar results have recently been obtained by Frankewich et al.[14] in undoped and lightly I_2-doped PA.

DISCUSSION

Most of the observed MR behaviour in heavily doped PA can be explained - at least qualitatively - by the two band model of Hedgcock and Rauford[8] for heavily doped semiconductors. In this model the existence of a band with high carrier mobility is assumed above an impurity band with low mobility separated by a sharp mobility edge between the two bands. On the application of a magnetic field the carriers are raised into the high mogility band from the low mobility band resulting in a negative MR. The ordinary decrease in the carrier mobility results in a positive contribution. The model has been fitted to the measured MR in figure 4 and a value μ = 750 cm^2/Vs for the mobility was found. However this value of μ should be used with caution, since the macroscopic dc-conductivity may not be an intrinsic value of PA but it may be limited by potential barriers between the fibrils.

The anomalous magnetoresistance (AMR), shown in figures 2 and 3, is a typical phenomenon in e.g. amorphous silicon α-Si[1]. However, it remained unexplained for several years after the first observation of the effect in 1970 by Mell and Stuke[9]. In 1978 Movaghar and Schweizer[10] succesfully proposed a hopping model for AMR which was later improved by Osaka[11]. In the model it is assumed that anomalous hops with spin-flip contribute to the hopping conduction in the deep gap states near E_F. The spin-flip is needed if the final state is already occupied and the two electrons in the initial and final states have parallel spins. MR results from the magnetic field dependence of the spin lattice relaxation time. Quite recently Kurobe[12] proposed an alternative model for AMR, in which no spin-flip processes are involved. Also in this model electron hopping in the deep singly or doubly occupied gap states is assumed. The negative contribution to MR arises from a Zeeman shift of the electron energies and the non constant density of states, whereas the positive one results from the shrinkage of the electron wavefunction in the douply occupied gap states. Kurobe's model works well in α-Si explaining also the temperature dependence of AMR.

The above ideas can be applied to low conductivity PA if the conduction is assumed to be dominated by hopping processes in the deep gap states near E_F. This is the case e.g. in Kivelson's intersoliton hopping model[13]. Thus if in a small fraction of intersoliton hops the final state is douply occupied (e.g. when an electron jumps from one neutral soliton to another) the processes mentioned above should be possible also in trans-PA provided the positive correlation energy U for a doubly occupied state is reasonable. In α-Si U is estimated to be 0.2 - 0.5 eV[1,12].

In PA doped with magnetic dopants such as $FeCl_3$ the spin of a neutral soliton can be exchange coupled to the magnetic moments of the dopants. In this case the soliton has a binding energy of purely magnetic origin, which depends on temperature and the applied magnetic field. Recently Sichel et al.[15] have found that in $FeCl_3$-doped PA (y>1.5%) Fe^{2+} ions become magnetically ordered at low temperatures. Further they interpret their negative MR results as an indication of the coupling of charge carriers to the magnetic moments of Fe^{2+} ions. The neutral solitons exchange coupled to the magnetic moments are analogous to magnetic polarons[16] in magnetic or semimagnetic semiconductors and hence we could call it a "neutral magnetic soliton".

Finally we would like to point out that the observed AMR gives a new "boundary condition" for the models of the electrical transport in lightly doped PA.

REFERENCES

1. P.Kuivalainen, J.Heleskivi, M.Leppihalme, U.Gyllenberg-Gästrin and H.Isotalo, Phys.Rev. B26 2041(1982).
2. J.-E.Österholm, H.Isotalo and H.Stubb these proceedings.
3. F.J. Kwak, T.C. Clarke, R.L. Greene and G.B. Street, Solid State Commun. 31 355(1979).
4. G.M. Gould, D.M.Bates, H.M.Botzer, A.J.Heeger, M.A.Druy and A.G.MacDiarmid, Phys. Rev. B23 6820 (1981)
5. W.Ross, A.Philipp, K.Seeger, K.Ehinger, K.Menke and S.Roth, Solid State Commun. 45 933 (1983)
6. E.Ettlinger, W.Schoepe, M.Monkenbusch and G.Wieners, Solid State Commun. 49 107 (1984)
7. M.Balkanski and A,Geismara, J.Phys. Soc.Japan Suppl. 21 554 (1966).
8. F.T. Hedgcock and T.W.Raudorf, Solid State Commun. 8 1819 (1970)
9. H.Mell and J.Stuke, J. Non-cryst. Solids 4 304 (1970)
10. B.Movaghar and L.Schweitzer, J.Phys.C 11 125 (178)
11. Y.Osaka, J.Phys.Soc.Jpn 47 729 (1979)
12. A.Kurobe, Thesis, University of Tokyo, 1983, A.Kurobe and H.Kamimura, J.Non-cryst. Solids 59&60 41 (1983)
13. S.Kivelson, Phys.Rev. B25 3798 (1982)
14. E.L.Frankevich, I.A.Kadyrov and V.M.Kabryanskii JETP Letters 36 401 (1982)
15. E.K. Sichel, M.F.Rubner, J. Georger Jr., G.C. Papaefthymion, S.Ofer and R.B.Frankel, Phys.Rev. B28 6589 (1983)
16. P.Kuivalainen, J.Sinkkonen, K.Kaski and T.Stubb, Phys.Stat. Sol.(b) 94 181 (1979)