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IRRADIATION INDUCED DISORDER IN LOW-DIMENSIONAL ORGANIC SEMICONDUCTORS - N-METHYL-DERIVATIVES OF PYRIDINIUM WITH TCNQ

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Abstract N-Methyl-derivatives of pyridinium with TCNQ are organic semiconductors with a gap of 0.6 eV approximately. In the pure materials the partially compensated semiconductor model explains very well the main features of the transport properties. But this model cannot explain the whole set of results especially the magnetism of these compounds. In this paper conductivity and thermopower data of pure and irradiated samples are presented and discussed together with the E.S.R. data.

INTRODUCTION

Recently we have shown [1,2] that in a relatively large homologous group of N-Methyl-derivatives of pyridinium with TCNQ, conductivity and thermopower data can be interpreted in terms of partially compensated semiconductor model. What is more surprising is fact that for small defect concentrations (introduced by irradiation) this model was fully confirmed [3,4].

The magnetic susceptibilities measured on these compounds [5] are typical of Heisenberg systems of localized spins interacting through exchange integrals of the order of 10 K what is in a total contradiction with extended single electron model of the conduction. The introduction of disorder by irradiation creates a large variety of new experimental situations in which both pictures can be compared and discussed.

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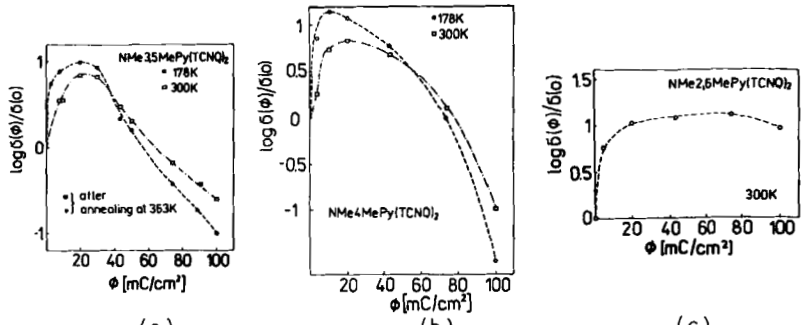
EXPERIMENTAL AND DISCUSSION

The samples were irradiated at 21 K with 2 MeV or 2.5 MeV electrons at selected doses from 0 to 100 mC/cm^2. Figs. 1a,b,c show the long axis conductivity of single crystals of each kind as a function of the irradiation dose. At low doses the conductivity increases as a function of the dose to a value about 10 times larger. Then, at about 20 mC/cm^2, it saturates and reaches maximum. After the dose of 20 mC/cm^2 the conductivity starts decreasing. This decrease is much faster in NMe 3.5 MePy(TCNQ)$_2$ which is most one-dimensional of our series than in NMe 2.6 MePy(TCNQ)$_2$ which is more tow-dimensional [1,2]. Figs. 2a,b show the typical temperature behaviour of the conductivity in the doping range (0-20 mC/cm^2) and in the localization range ($\phi \gg 20$ mC/cm^2). The thermoelectric powers of all compounds are negative after electron irradiation regardless of the sign of the initial thermopower (fig. 3a,b). For the low doses the activation energies for the conductivity and the S vs 1/T slope agree within 0.01 eV. At higher doses this agreement is worse than 0.13 - 0.2 eV due to almost temperature independent Seebeck coefficient.

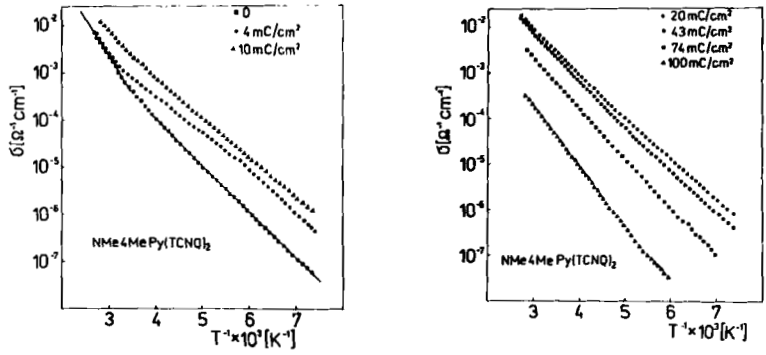
Not singlet-triplet structure was visible on the ESR spectra of pure and irradiated NMe4MePy(TCNQ)$_2$ confirming the Heisenberg character of the system. The low temperature Curie-tail grows linearly with the irradiation dose [4]. From 0 to 50 mC/cm^2 irradiation was found to introduce $6 \cdot 10^{18}$ spins/cm^3 per mC/cm^2.

For the low defect concentrations the σ vs 1/T and S vs 1/T behaviours can be explained with single one-electron semiconductor model with deep lying localized impurity states. In this scheme irradiation produces electrically active centers acting as normal dopants. The number of defects calculated on the base of this model is 0.3% for NMe3.5MePy(TCNQ)$_2$ irradiated at 20 mC/cm^2. However there is a lot of details in transport properties which are difficult to understand in terms of this model. But the main objection arises from the magnetic properties displaying correlated character of spins. In addition the number of localized spins is about 30 times



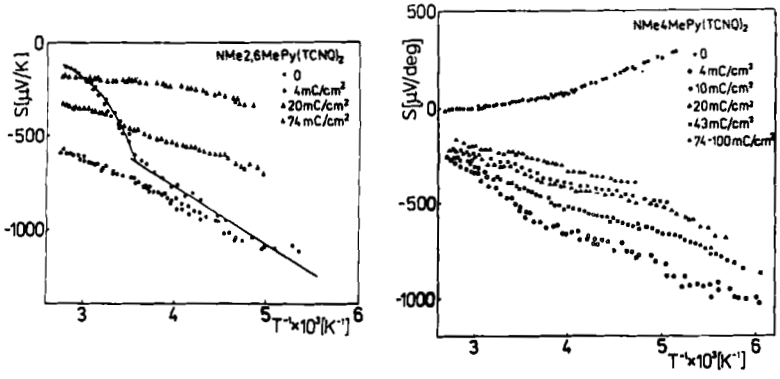
(a) (b) (c)

Fig. 1 Normalized conductivity as a function of irradiated dose



(a) (b)

Fig. 2 Temperature variation of conductivity in the doping (a) and localization (b) range



(a) (b)

Fig 3 Temperature dependence of the Seebeck coefficient of pure and irradiated crystals

larger than number of dopants calculated from the transport properties. Moreover the recent optical studies on irradiated samples confirm the magnetic estimation of detect concentration [6]. In the localization range the increasing difference between the Peltier coefficient and the activation energy can be explained by Mott and Davies picture [7] i.e. introducing "the mobility edges" in the conduction and the valence band. Then the activation energies for σ and S differ by the hopping energy W [4,7].

Due to low mobilities in these systems ($\sim 1\,cm^2\,V{\cdot}S$) it is also reasonable to consider the presence of polaronic states [2,4]. The low disorder to high disorder cross-over observed in the transport properties could be viewed as a large polaron to small polaron transition [4]. Nevertheless the recent microwave experiments on $NMe4MePy(TCNQ)_2$ [8] indicate that some transport details are inconsistent with the small polaron-model.

Substantial coulomb interaction are needed to explain the semiconducting properties of these compounds. In the limit of $U = \infty$ one can expect the creation of soliton-antisoliton pairs with charges $\pm \frac{e}{2}$ [4]. The formation energy of these pairs $2\Delta/\pi$ is almost identical to our experimental values (~ 0.19 eV). On the other hand one can assume that the main interaction is within the diade ($4t' << U << 4t$). This can lead to a Mot-insulator of correlated electrons on dimer pairs. The magnetic properties are those of a Heisenberg chain with low exchange between sites. In the present experimental state we give some advantage to the Mot-insulator-model.

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