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ELECTRICAL TRANSPORT PROPERTIES OF IODINE DOPED POLYACETYLENE

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Résumé - Nous présentons des résultats expérimentaux sur la conductivité à courant continu et aux microondes de polyacétylene cis et trans, dopé à l'iode (gamme de température 4,2 K à 300 K). A la température ambiante nous n'avons trouvé aucune dépendance avec la température, mais aux basses températures la conductivité à 10 GHz est nettement plus élevée que pour un courant continu. A partir de la magnétorésistance à 4,2 K nous avons calculé une mobilité de Hall de l'ordre de 10^2 cm^2/Vsec.

Abstract - Measurements of the DC conductivity and the 10 GHz microwave conductivity of iodine doped cis and trans polyacetylene in the temperature range from 4.2 K to 300 K are reported. At room temperature no sample shows a frequency dependence; at low temperatures, however, the microwave conductivity of moderately doped samples is considerably higher than the DC value. From the magnetoresistance at liquid helium temperature an "effective" Hall mobility in the order of magnitude of 10^2 cm^2/Vsec is estimated for samples with various iodine concentrations.

Introduction

Polyacetylene has attracted considerable interest both in fundamental research and in industrial application /1/ since it is known that its conductivity can be varied more than 12 orders of magnitude upon doping /2/. A complete understanding of the transport mechanism, however, is still missing. To enlighten this situation we performed low frequency and microwave conductivity measurements of iodine doped (CH) in a wide temperature range. To estimate the carrier mobility at 4.2 K we measured the magnetoresistance in fields up to 7 T.

Experimental

Polyacetylene was synthesized by the standard procedure at -80°C described by Ito et al /3/. Raman studies show that over 90% of the as-grown sample is in the cis configuration /4/. Conversion to trans was done by thermal treatment at 190°C for 45 minutes in an argon atmosphere. Doping by iodine was carried out by exposing the sample at room temperature to iodine vapour for severeral hours depending on the doping level. To get a stable iodine content the sample has been pumped in vacuum for 15 hours. Afterwards the doping level has been determined by weight uptake.

The low frequency conductivity was measured by a conventional four point technique and 30 Hz lock-in detection. To measure the microwave conductivity we applied the cavity perturbation method /5/. Our experimental system has been described in detail elsewhere /6/. For variable temperature measurements between 10 K and 300 K we have used an evaporation type helium cryostat.

DC Conductivity

Fig. 1 and 2 show the temperature dependence of the low frequency conductivity of cis and trans polyacetylene, respectively, doped with various concentrations of iodine. There is no simple analytical behaviour for all doping concentrations but a continuous transition between at least three regions.
In the case of cis samples we find at high doping concentrations (above 15 at%) a power law
\[ \sigma = \sigma_0 T^{\nu} \]
as often is observed in dirty metals /7/; the exponent \( \nu \) is e.g. 0.8 for the 15.4 at% and 0.7 for the 18.7 at%. At medium concentrations
\[ \sigma = \sigma_0 \exp\left[-A/T\right]^{1/4} \]
holds as in three dimensional variable range hopping /8/. The value of \( A \) decreases from \( 5 \times 10^2 \) K to \( 1 \times 10^1 \) K for doping levels between 6 at% and 11 at% iodine. Below 5 at%
\[ \sigma = \sigma_0 \exp\left[-B/T\right]^{1/2} \]
is valid reminiscent of one dimensional variable range hopping /9/. The value of \( B \) varies from \( 1 \times 10^3 \) K to \( 2 \times 10^3 \) K in the concentration range 2.2 at% to 5 at%.

In highly doped trans samples the power law is less pronounced than in the cis samples, but in the other doping regimes the characteristics of the trans samples are similar to the cis samples with similar values of \( A \) and \( B \). At high doping levels the cis samples are the better conductors, whereas in the low doping regime the conductivity of the trans is higher. Further details will be published elsewhere /10/.

Microwave Conductivity
In Fig. 3 and 4 we compare the 30 Hz conductivity and the microwave conductivity of cis and trans samples at various iodine content for two different temperatures. At room temperature our samples showed no frequency dependence in both cases. At 120 K the cis samples show an enhanced microwave conductivity for doping concentrations below 4 at%, the frequency dependence being stronger for lower iodine content. In the case of the trans samples the conductivity is still frequency independent at 120 K even for doping levels below 2 at%. On cooling further down, however, an increased microwave conductivity can be observed for both isomeric modifications (Fig. 5).
Fig. 3, 4: Comparison between 30 Hz conductivity and 10 GHz conductivity at room temperature and at 120 K for iodine doped cis and trans (CH)$_x$

Fig. 5: Temperature dependence at 30 Hz conductivity and 9 GHz conductivity for iodine doped (CH)$_x$

Fig. 6: Magnetoresistance of iodine doped cis-(CH)$_x$ at 4.2 K (for the 7.2 at% iodine doped (CH)$_x$ the Corbino resistance is included). Insert: Resistance change of the filamentary samples at 7 T and at 4.2 K (from the Vienna group).
Our room temperature results are consistent with the data of Epstein et al. /11/ for iodine doped samples and of Grant and Kroumbi /12/ for AsF₅ doped samples who measured up to 500 MHz and 10 MHz, respectively. In contrast, Mihaly et al. /13/ have found at room temperature a strong frequency dependence of the conductivity between DC and 9 GHz for doping levels below 3 at% iodine.

Magnetoresistance
Fig. 6 shows the magnetoresistance of different iodine doped cis samples at helium temperature as a function of the magnetic field. The magnetoresistance decreases with increasing iodine content and becomes even negative for concentrations above 15 at%. To calculate the Hall mobility we measured the magnetoresistance in two different geometries, the conventional filamentary and the soriino geometry /14/.

We find a surprisingly high mobility in the range of 100 cm²/Vsec decreasing with increasing iodine concentration (e.g. 180 cm²/Vsec for 7.2 at% and 85 cm²/Vsec for 15.4 at%) A more detailed analysis of these data and this "effective" mobility will be published /15/.

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