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MÖSSBAUER STUDY OF SbF_5 -DOPED POLYACETYLENEF. Godler⁽¹⁾, B. Perscheid⁽¹⁾, G. Kaindl⁽¹⁾, K. Menke⁽²⁾ and S. Roth⁽²⁾*(1) Freie Universität Berlin, Berlin, F.R.G.**(2) Max-Planck-Institut für Festkörperforschung, Stuttgart, F.R.G.*

Résumé - Nous avons étudié la spectroscopie Mössbauer du ^{121}Sb du polyacétylène dopé au SbF_5 avec des concentrations de 0,1 à 8,4 % molaire. Les spectres révèlent la présence de molécules de SbF_3 , SbF_5 et SbF_6^- . A partir des intensités relatives des spectres, nous avons pu déterminer les fractions relatives des trois espèces en fonction de la concentration en dopant.

Abstract - SbF_5 -doped polyacetylene was studied on samples with dopant concentrations ranging from 0.1 to 8.4 mol%, using ^{121}Sb Mössbauer spectroscopy. The spectra reveal the presence of SbF_3 , SbF_5 , and SbF_6^- , respectively. From the relative intensities of the well-separated subspectra we could determine the relative fractions of the three molecular species as a function of dopant concentration.

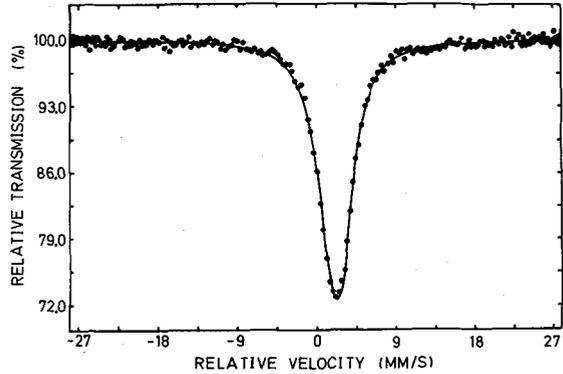
Introduction

The electrical conductivity of doped polymers can take up characteristic features of semiconductors and metals [1], dependent on the chemical reaction of the dopant with the polymer and the dopant concentration. The experimental problem of analyzing the reaction products in the highly conducting state of the polymer can be solved by means of Mössbauer spectroscopy in those cases where the dopant contains appropriate isotopes. We report here on Mössbauer experiments on SbF_5 -doped polyacetylene with dopant concentrations ranging from 0.1 to 8.4 mol% using the 37.1 keV resonance in ^{121}Sb . The transmission spectra were recorded at 4.2 K with a $\text{Ca}^{121\text{m}}\text{SnO}_3$ single line source by means of a large area intrinsic Ge-detector.

Sample preparation and characterization

Foils of polyacetylene were prepared using the Shirakawa-method [2] with a catalyst concentration of 0.2 mol/l of $\text{Ti}(\text{OnBu})_4 \cdot 4 \text{Al}(\text{C}_2\text{H}_5)_3$ in toluol. The foils were polymerized floating on the toluol. After the catalyst has been washed out in a Soxhlet-apparatus for 20 h at -70°C the foils were dried for 4 h in vacuum. The chemical analysis of a typical foil exhibited the following values: 91.33 w% C, 7.85 w% H, 0.27 w% Al, and 0.21 w% Ti, respectively, resulting in a molar H/C ratio of 1.024. The foils had a diameter of 50 mm and a thickness of 120-150 μm and were doped from both sides in a double-funnel device. Different dopant concentrations were obtained by variation of the temperature between -20°C and $+20^\circ\text{C}$ and the time of ex-

Fig. 1 - ^{121}Sb Mössbauer spectrum of the SbF_5 dopant at 4.2 K.



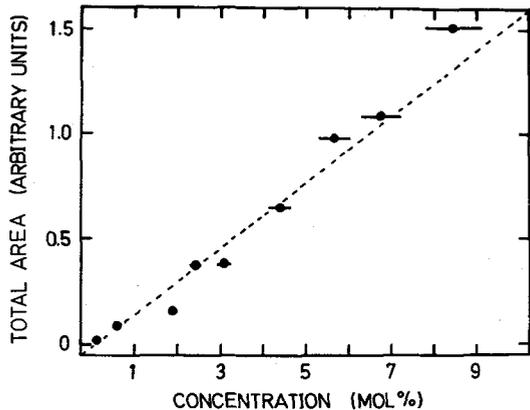
posure. The doped foils were pumped for 15 h in high vacuum and kept thereafter in inert atmosphere or vacuum throughout all following experiments.

In order to obtain a maximum purity of the dopant SbF_5 was distilled twice before doping the foils. The purity was checked by a Mössbauer spectrum (see Fig. 1) which showed a pure SbF_5 resonance.

Determination of dopant concentration

The dopant concentration of the whole foil was determined gravimetrically. For the Mössbauer studies circles of 12 mm diameter were cut out and used as absorbers. After the experiment the absorbers were chemically analysed using the ICP-method [3]. The concentrations of

Fig. 2 - Total resonance area of the ^{121}Sb Mössbauer spectra of SbF_5 -doped polyacetylene versus concentration. The resonance areas were normalized to the same areal thickness of undoped polyacetylene foils.



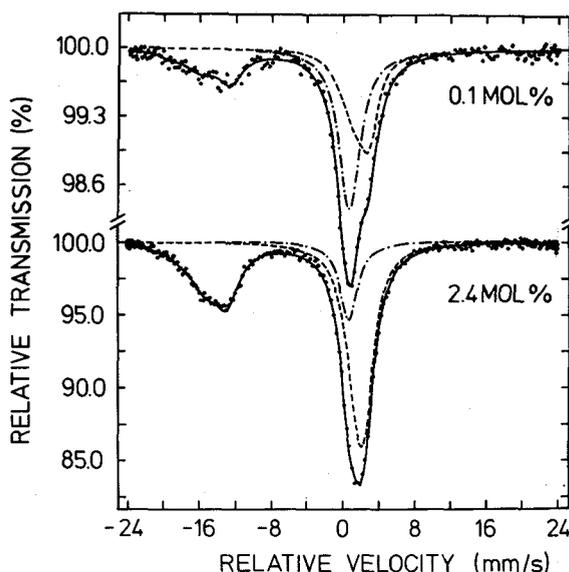
the cut-out circles differ considerably from the concentration of the whole foil, e.g. values of 1.6 mol%, 2.2 mol%, and 3.2 mol%, respectively, were determined for parts of the same foil. This finding proves that the doping is not homogeneous although a double-funnel device was used for doping. A detailed study of the spatial inhomogeneity using microscopic as well as macroscopic methods is in progress in our laboratories.

The Mössbauer spectra themselves allow an estimate of the dopant concentration. For relatively thin absorbers and at a given temperature the area under the resonance absorption curve is proportional to the areal thickness of resonating ^{121}Sb atoms. From this and the thickness of the polyacetylene absorber prior to doping a proportionality to the Sb concentration can be calculated. Fig. 2 shows the total resonance area normalized to the same areal thickness of undoped polyacetylene versus the concentration as determined with the ICP-method [3]. With this calibration one has a non-destructive method for estimating the concentration of SbF_5 -doped polyacetylene.

Results and discussion

Fig. 3 shows two typical Mössbauer spectra of SbF_5 -doped polyacetylene. The spectra reveal two resonances which can be identified from their isomer shifts as due to Sb^{3+} - and Sb^{5+} -ions [4]. The Sb^{3+} -resonance is supposed to originate from SbF_3 -molecules. The negative electric field gradient and the isomer shift are nearly the same as for pure SbF_3 . The Sb^{5+} -resonance can be fitted unambiguously by

Fig. 3 - ^{121}Sb Mössbauer spectra of SbF_5 -doped polyacetylene at 4.2 K (7 foils of 0.1 mol%, 3 foils of 2.4 mol%). Identified molecular species: SbF_3 (resonance at negative velocity), SbF_5 (dashed curve), and SbF_6^- (dash-dotted curve).



two subspectra: a single line and a quadrupole-split subspectrum. The single line is supposed to originate from SbF_6^- anions because here the antimony has a highly symmetric octahedral surrounding of fluorines which cannot cause an electric field gradient at the central atom. The quadrupole split spectrum is supposed to originate from SbF_5 -molecules. Again the electric field gradient is nearly the same as in pure SbF_5 .

With the above identification of the three molecular species of SbF_3 , SbF_5 , and SbF_6^- in polyacetylene their relative concentration can be determined from the fractional areas of the separate resonances relative to the total area.

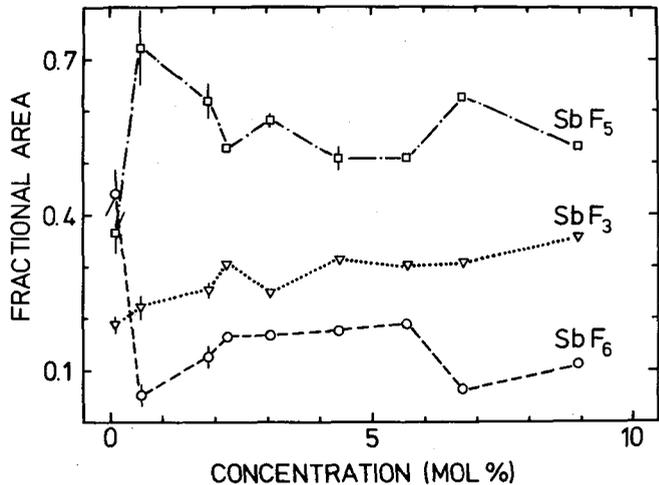
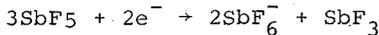
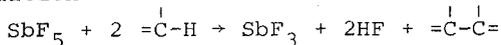


Fig. 4 - Fractional resonance areas of the ^{121}Sb Mössbauer spectra of SbF_5 -doped polyacetylene versus concentration.

Fig. 4 shows this fractional areas versus concentration. At low concentrations the major fraction of SbF_5 is converted to SbF_6^- during the doping reaction. This can be described by a formal oxidation of polyacetylene in analogy to the equation proposed by Bartlett et al. [5] for AsF_5 :



Indeed the ratio of SbF_6^- to SbF_3 is 2 within experimental accuracy. In addition a certain amount of SbF_5 is taken up by the polyacetylene without reaction. At high concentrations the SbF_6^- fraction decreases to a roughly constant value whereas the SbF_3 fraction increases. This finding can be explained by introducing a second reaction converting SbF_5 into SbF_3 . It may be hydrogen abstraction from the polymer according to the equation



This hydrogen abstraction may lead to additional C-C-bonds and a concatenation of the polyacetylene fibrils. The above interpretation of

the equations for the chemical reactions is based on the assumption that the dopant did not contain any SbF_3 . This has been proved experimentally by the Mössbauer spectrum of the dopant (see Fig. 1).

Isomer shifts and electric field gradients show only a weak dependence on concentration. A full account of all experimental results will be published elsewhere.

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