

SYNTHETIC METALS: APPLICATIONS OF THE MÖSSBAUER EFFECT AND OTHER METHODS

G. WORTMANN

*Institut für Atom- und Festkörperphysik
Freie Universität Berlin, D-1000 Berlin 33, Germany*

A review is given about the current activities in the field of the "synthetic metals". This nomenclature is used for materials which consist basically of non-metallic components, but reach metallic conductivities by doping or intercalation reactions with additional components acting as donors or acceptors. Typical examples are conducting polymers like doped polyacetylene or graphite intercalation compounds. The contributions of Mössbauer studies in understanding the electronic, magnetic, and structural properties of such systems are outlined. Comparison with other spectroscopic methods is given in selected cases.

1. INTRODUCTION

The synthesis and characterization of novel materials with adjustable properties are the subject of current research activities. A large number of these materials are named "synthetic metals", since they are basically built up from organic, and not metallic components. Their common property is an electric conductivity comparable with that of normal metals. The activities in this field started by the investigation of the surprising transport properties in some graphite intercalation compounds /1-3/ and doped polyacetylene /4-7/. Nowadays, the term "synthetic metals" is used for a wider class of materials, including the organic superconductors, the transition metal dichalcogenides and one-dimensional systems with spin and charge density waves. The scope of synthetic metals is outlined in the editorial of a journal using this nomenclature as its name /8/. The scientific interest is based, on the one hand, on possible applications of these materials, e.g. as a substitute for normal metals, in batteries and accumulators, as solar cells, as catalyzers or in other fields /1,9/. On the other hand, basic research is stimulated by a variety of unusual properties of these systems, based in part on the reduced dimensionality of these materials: Conducting polymers are basically one-dimensional (1D) systems with strong impacts on the transport properties, which are theoretically described by solitons or polarons /10,4-7/. Intercalation compounds are two-dimensional (2D) systems exhibiting strongly anisotropic behavior in conductivity, magnetism and supraconductivity. In addition, the 2D intercalated layers may exhibit unusual structural phase transitions /1-3/.

This review will concentrate on two classes of synthetic metals, namely the graphite intercalation compounds (GIC) and conducting polymers (mostly doped polyacetylene) and their investigation by means of Mössbauer spectroscopy and related microscopic techniques. In the following chapter, a short outline of specific properties of graphite intercalation compounds and conducting polymers will be given. Chapter 3 contains examples of Mössbauer studies on donor and acceptor GICs. Chapter 4 deals with investigations of doped polymers. In the concluding chapter the possibilities and limitations of Mössbauer spectroscopy and other methods are summarized.

2. STRUCTURAL AND ELECTRONIC PROPERTIES OF GRAPHITE INTERCALATION COMPOUNDS AND CONDUCTING POLYMERS

2.1. Graphite Intercalation Compounds

The first synthesis of a GIC was reported more than a century ago /11/. Some of the peculiar properties of these compounds, e.g. the periodicity of the intercalated layers, called staging, were detected by the application of X-ray diffraction techniques. Systematic investigation of their physical properties started only a few decades ago, with a dramatic increase in activities initiated by the report on an electric conductivity in AsF_5 -GIC comparable with that of copper /12/. There exists a large number of excellent reviews /1-3,13,14/ about the properties of GICs, with the one of Dresselhaus &

Dresselhaus /1/ being still the most comprehensive. The current activities concerning GICs are contained in recent conference proceedings /15,16/.

A large number of atomic and molecular species can be intercalated into graphite /13,14/. These intercalants are classified as donors or acceptors, corresponding to the direction of the charge transfer between the graphite and the intercalant layers. The most common and widely studied donor GICs are those prepared with alkali metals like Li, K, Rb, and Cs. In Fig. 1 a schematic view of such a GIC is shown. The intercalate forms a well-defined commensurate structure in registry with the hexagonal graphite layers. A fascinating property of GICs is the staging phenomenon. According to the preparation conditions, the alkali atoms are inserted in a periodic way into the graphite host, where the number of carbon layers between the intercalant layers defines the *stage* of the GIC (see Fig. 1). Recently, ternary systems of donor GIC have gained strong interest because of the dynamical properties of the intercalate, e.g. in $K_{1-x}Cs_x$ -GICs /17/, or because of the superconducting properties of systems like $KHgC_{2n}$ /18/.

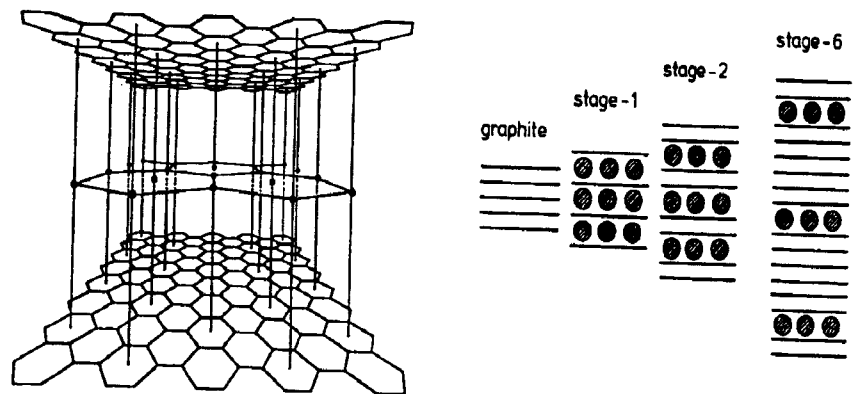


Fig. 1(a) Stereographic view of an idealized alkali metal GIC, where the intercalant forms a $(2 \times 2)R 0^\circ$ superlattice. (b) Schematic presentation of various stages of a GIC.

Acceptor GICs are formed by the insertion of molecular species into the Van-der-Waals gaps of the graphite host. Due to their polyatomic entities, the intercalant layers do not exhibit such simple commensurate structures as observed for donor GICs. The intercalated molecules form complex commensurate superstructures as observed in $SbCl_5$ -GICs, or exhibit commensurate-incommensurate phase-transitions like in Br_2 -GICs, or incommensurate intercalation like in $FeCl_3$ -GICs /1-3/. The intercalate itself forms a sandwich structure for acceptor molecules like $FeCl_3$ or $SbCl_5/SbCl_6^-$. In some cases, more than one molecular species is inserted, giving rise to complex structures, e.g. spatially separated intercalant structures, as discovered recently /19/.

2.2. Doped Polymers

In the last few years, a large number of polymers have been synthesized, which exhibit in their doped form the promising properties expected for a synthetic metal. The most investigated system is polyacetylene (PA), polymerized first by Shirakawa /20/. PA exhibits a tremendous increase in conductivity upon doping /21/. In the meantime, other polymers like polyphenylene, polypyrrole, polythiophene, and polyanilin are also intensively studied /5-7/.

These polymers have one feature in common - they possess conjugated double bonds (regular alternation of single and double bonds). Polyacetylene, $(CH)_x$, is the most simple prototype of a conjugated polymer (see Fig. 2). It would be an ideal one-dimensional metal in its trans-configuration, if the two π -electrons in the double bonds behaved like those in the benzole ring, namely delocalized and fluctuating. However, as we learn from solid-state physics textbooks, the Peierls theorem states that a one-dimensional metal with a half-filled band is unstable and undergoes

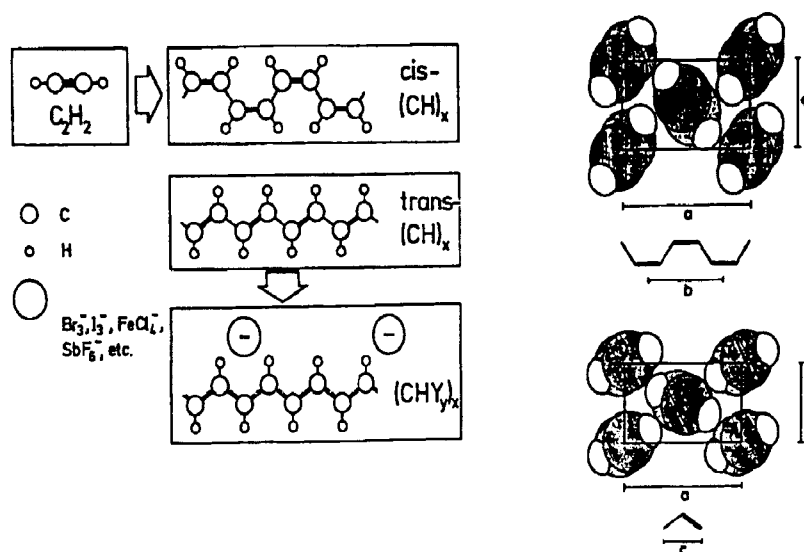


Fig. 2: Schematic presentation of preparation and doping of polyacetylene (left hand side). The acceptor counterions can have a linear shape when halogen polyanions are inserted. On the right hand side, the unit cell of $cis-(CH)_x$ and $trans-(CH)_x$ are shown (at the top and bottom, respectively).

a lattice distortion (dimerization), which is equivalent to the localization of the single and double bonds. The unit cell of $trans-(CH)_x$ contains two π -electrons (the double bond) and has therefore a filled band with a bandgap of about 1.4 eV, a value typical for a semiconductor. The "doping" of the $(CH)_x$ chain, shown schematically in Fig. 2, can be understood in a simplified approach as an oxidation of the double bonds. The defect electrons (holes) become mobile and delocalized, leading thereby to an enhanced conductivity within the chain. The actual mechanisms relevant for the transport properties in doped polyacetylene are much more complex and must consider also the poor long-range order within the $(CH)_x$ chains and the complex fibrillar morphology of the samples (at least as long PA produced by the Shirakawa method is concerned) /4-7/. An important aspect of the doping process of polymers is the considerable structural change induced in the polymer matrix by the insertion of the relative large counterions (e.g. SbF_6^- , $FeCl_4^-$, I_3^- or alkali metals) /22,23/. Structural investigations were hampered by the poor quality of the samples, especially of PA. The recent progress in the structure determination is based on the preparation of highly oriented $trans-(CH)_x$ by the method of Edwards and Feast /24/. A recent work on SbF_6^- -PA revealed a detailed structure analysis with an incommensurate sublattice of the SbF_6^- counterions /22,25/.

3. MÖSSBAUER STUDIES OF GRAPHITE INTERCALATION COMPOUNDS

3.1. Donator GICs: CsC_8 , CsC_{24} , and EuC_6

There are two useful Mössbauer resonances for the investigation of donator GICs, namely ^{133}Cs (81 keV) and ^{151}Eu (22 keV). Campbell, Montet and Perlow /26/ demonstrated in their study of stage-1 and stage-2 Cs-graphite the possibilities of Mössbauer spectroscopy to investigate the charge transfer and lattice dynamics in GICs. The analysis of the isomer shifts revealed that the intercalated Cs atoms are approximately 50% ionized in the stage-1 CsC_8 , but fully ionized in the stage-2 CsC_{24} . The Mössbauer results agree with NMR and optical studies. The question about the amount of charge transfer is still highly controversial for that class of GICs /3,16/. A further important outcome of this Mössbauer study was the striking demonstration of the anisotropic bonding of the Cs atoms in the intercalant layer. Using highly-oriented pyrolytic graphite (HOPG), the angular dependence of the f -factor with respect to the graphite c -axis was determined: $f_{||}$ as found = 20 times larger than f_{\perp} . The corresponding Debye temperatures were calculated as $\theta_{||} = 145$ K and $\theta_{\perp} = 76.5$ K.

Eu forms a stage-1 GIC with the formula EuC_6 . From the analogy with SrC_6 , Eu was expected to be in the divalent state. A Mössbauer study by Kaindl et al. /27/ confirmed this point. The ^{151}Eu isomer shift ($S = -11.7 \text{ mm/s}$) indicates that an appreciable amount of s-electron density has been transferred from the Eu^{2+} ions to the graphite layers. The magnetic interactions in EuC_6 are highly interesting because of their anisotropic behavior. The $S = 7/2$ spins form a quasi-2D Heisenberg magnet. The observed hyperfine fields below the antiferromagnetic ordering temperature at 40 K show an in-plane alignment of the Eu moments. The temperature dependence of the hyperfine fields follows roughly a $S = 7/2$ Brillouin function, which indicates for the stage-1 compound anisotropic, but still 3D exchange. Higher stages would be interesting for studying a truly 2D Heisenberg system but they are difficult to prepare. Recent magnetization measurements /28/ exhibit a series of spin-flop transitions, which can be explained only by a 4-spin interaction scheme.

In both Mössbauer studies on Cs- and Eu-GICs a pronounced electric-quadrupole interaction on the donor atoms was observed, with axially-symmetric negative electric-field gradients (EFG) parallel to the graphite c-axis: $V_{zz}(\text{Eu}) = -1.4 \cdot 10^{18} \text{ V/cm}^2$ and $V_{zz}(\text{Cs}) = -2.0 \cdot 10^{18} \text{ V/cm}^2$ /26,27./. In both cases the magnitude of the EFG can be reproduced satisfactorily by point-charge calculations. This gives additional support to the amount of charge transfer derived from the isomer shift data.

3.2. Acceptor-GICs: FeCl_3 -Graphite

The intercalant structure in FeCl_3 -GICs is similar to that of anhydrous FeCl_3 , which forms also a hexagonal layer compound. Anhydrous FeCl_3 can be regarded therefore as "stage-0" and reference system to the other FeCl_3 -GICs. The FeCl_3 sandwich layer (Cl-Fe-Cl) is incommensurate with the graphite layers (see Fig. 3a). It is now established that the FeCl_3 intercalant forms islands; their size (50 - 500 Å diameter) depends on the preparation conditions. This means that the intercalant density can vary considerably for differently prepared samples of the same stage. In addition, Fe vacancies and Cl-C bonds agitate against a homogeneous intercalant structure.

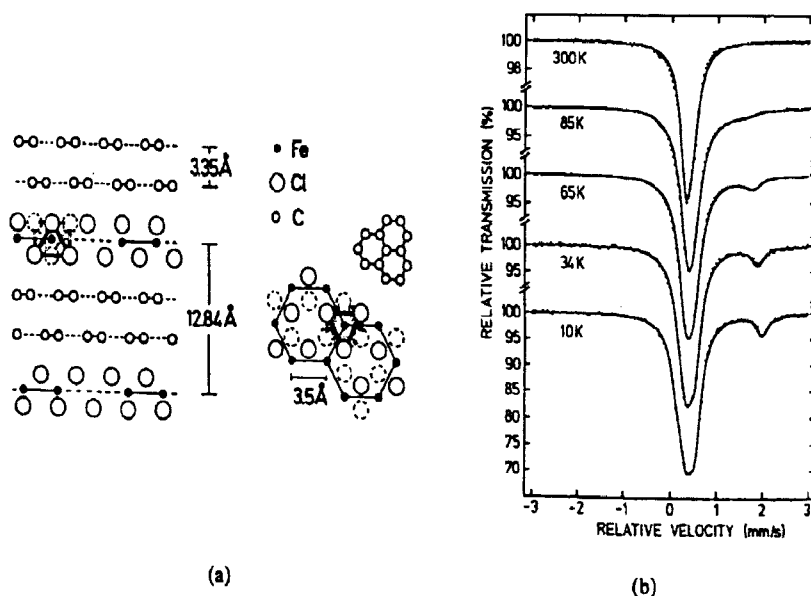


Fig. 3: (a) Structural model of stage-2 FeCl_3 -graphite viewed parallel and perpendicular to the graphite sheets. (b) Typical ^{57}Fe -Mössbauer spectra of an oriented FeCl_3 -GIC at various temperatures with the γ -rays parallel to the graphite c-axis /34/. The fit of the spectra with a relaxation model (see text) includes the transmission integral.

A large number of Mössbauer studies were performed on FeCl_3 -GICs and their derivatives, FeCl_2 -GICs (prepared from the former by reduction in hydrogen). They were concerned with the characterization and stability and the intercalant, the charge transfer and the magnetic properties /29-33/. Because of space limitations, we shall concentrate in the following on a recent study performed in our laboratories concerned mainly with the nature of the charge transfer /34/. As already demonstrated in the previous Mössbauer investigations, the charge transfer can be extracted from the Mössbauer spectra at low temperature, where a certain fraction of the Fe ions appear in the divalent state, easily distinguishable from the dominant Fe^{3+} component by the isomer shift and a large quadrupole splitting with the main axis of the EFG parallel to the graphite c-axis. Starting around 40 K, the Fe^{2+} subspectra show relaxation-like broadening effects and at temperatures above 100 K the Fe^{2+} spectral features have disappeared and only a single resonance line, typical for Fe^{3+} ions, is observable (see Fig.3b). In an earlier study /29/ this behaviour has been tentatively explained by a thermal activated electron-hopping of the transferred charge. A more recent study speculated about a temperature dependent charge transfer /33/. In order to clarify these points, we performed a detailed Mössbauer study of a stage-2 FeCl_3 -graphite sample, prepared from large natural graphite flake by a mild photochemical intercalation technique /31/. This resulted in a relatively homogeneous intercalant structure (large islands and small impurity/defect concentration). Typical resonance spectra taken between 10 and 300 K are shown in Fig.3b. The spectra were analyzed with a relaxation model assuming a temperature activated electron hopping between equivalent Fe-sites in octahedral chlorine surrounding. The relaxation processes are indicated in the top of Fig. 4, which shows resonance spectra at 10 and 300 K with different orientations of the textured absorber with respect to the y-rays. The assumptions of the relaxation models are strikingly confirmed by the spectra at 300 K (fast relaxation limit): the shape and position of resonance line change with the orientation of the sample! This proves that the isomer shift and quadrupole splitting experienced by the Fe^{2+} site, and clearly resolved at low temperatures (static limit), is still present at high temperatures, but now averaged in the common spectrum of the Fe^{2+} and Fe^{3+} sites (theoretical relaxation spectra for this special case are presented in Ref. 33). The charge transfer, corresponding to the relative fraction, r , of the Fe^{2+} ions, is found to be temperature independent ($r = 0.19(2)$)/34/. The fitted electron-hopping rates, when plotted in an Arrhenius presentation (Fig. 5), yielded an activation energy of the electron hopping process, $E_a = 45(20)$ meV. This value agrees nicely with the activation energy derived in a related intercalate system, FeOCl as host matrix with organic donors, studied by Herber and Eckert /35/. The f -factor data of this stage-2 FeCl_3 -GIC sample revealed a bonding strength, which is smaller than in anhydrous FeCl_3 and anisotropic /34,39/.

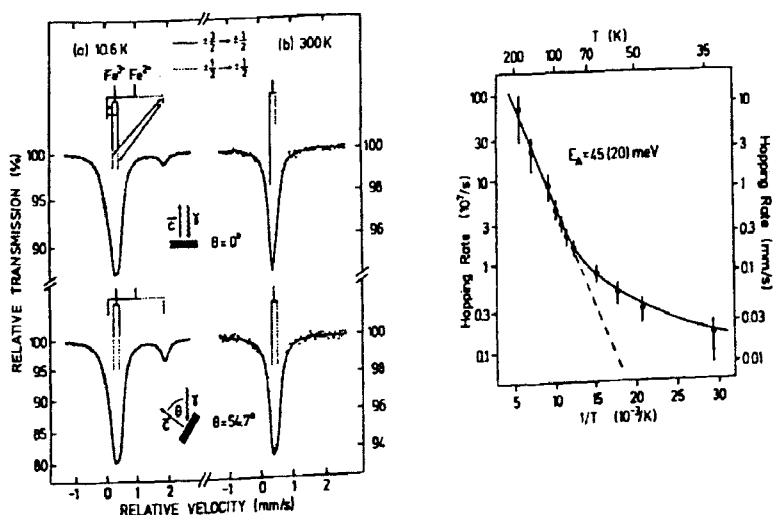


Fig. 4 (left hand side): ^{57}Fe -Mössbauer spectra of an oriented stage-2 FeCl_3 -GIC measured with different orientations in the slow (10.6 K) and fast (300 K) relaxation limit /34/.

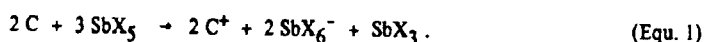
Fig. 5 (right hand side): Arrhenius plot of the electron hopping rate in stage-2 FeCl_3 -GIC /34/.

The specific 2D-magnetic properties of the various stages of FeCl₃-GICs are very interesting and are still the subject of actual debates /3,14,38,39/. Since Fe³⁺ has a S = 5/2 moment, one expects basically 2D magnetic interactions of the Heisenberg type. Anhydrous FeCl₃ ("stage-0") orders magnetically at 8.8 K /36/. The magnetic structure is rather complex, the Fe³⁺ moments are turned out of the Fe plane into a spiral structure. FeCl₃-GICs have been extensively investigated by Millman and coworkers /32,33,38/. Stage-1 FeCl₃-GICs orders at 4.2 K. The moments are now aligned in-plane. In stage-2 FeCl₃-GICs, magnetic ordering temperatures are difficult to derive from Mössbauer spectra because of magnetic relaxation effects starting around 4 K. Susceptibility measurements on stage-2 compounds exhibit field-dependent maxima, from which two ordering temperatures around 1.7 K were derived /37/. Stage-4 and stage-6 of FeCl₃-GICs were investigated by Mössbauer spectroscopy down to 65 mK. From the absence of magnetic polarization effects it was concluded that the fully-split magnetic hyperfine spectra were paramagnetic in origin /32a/.

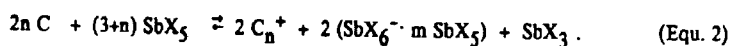
We investigated the magnetic properties of the stage-2 FeCl₃-GIC sample by taking Mössbauer spectra between 1.8 and 4.2 K in the presence of external magnetic fields. No dramatic changes in the spin alignment, expected for paramagnetic relaxations, were observed in fields up to 5.5 T. The Fe³⁺ spins are strongly coupled in a basal antiferromagnetic way within the Fe planes. An important aspect arises from the presence of 19% Fe²⁺ ions, which are distributed between the Fe³⁺ ions and do not have a magnetic moment. For that reason the magnetic interaction tracks in the Fe planes are cut in a rather random way. This has strong implications on the long-range magnetic order. We suggest therefore a magnetic order of spin-glass type /34/. This is in accordance with recent low-field susceptibility studies on stage-2 and stage-6 samples. The observed "cusp" in magnetic susceptibility increases strongly with Fe vacancies. These observations and current theoretical treatments may lead to new insights in the magnetic ordering mechanisms in FeCl₃-GICs /14/.

3.3. SbCl₅/SbF₅-Graphites

GICs prepared with Lewis-acid (oxidizing) molecules like AsF₅, SbF₅, and SbCl₅ belong to the most investigated acceptor systems. Following Bartlett and coworkers /40/, the intercalation (oxidation) reaction can be described for SbX₅-GICs (X = F, Cl) by



Since also neutral SbX₅ molecules were observed as intercalated species, the above equation was modified /41/ to



This equation (with n and m being stage dependent) already accounts for the tendency of SbX₅ to form macromolecules by halogen bridging.

Mössbauer spectroscopy using the 37.1 keV resonance of ¹²¹Sb has been applied quite often for an identification of the intercalated molecular species /42-47/. Sb³⁺ and Sb⁵⁺ valence states can be easily distinguished from their different isomer shifts (S(5⁺) - S(3⁺) = 8 ... 15 mm/s; all isomer shifts cited in this section are with reference to a Ca¹²¹SnO₃ source). It is, however, a more difficult task to distinguish more than one Sb³⁺ or Sb⁵⁺ species or to obtain additional informations from the most poorly resolved electric-quadrupole pattern. In an early work, Ballard & Birchall /42/ investigated SbCl₅- and SbF₅-GICs prepared from graphite powder. In both systems, Sb⁵⁺ and, to a smaller amount, Sb³⁺ species were found. They were attributed from their isomer shifts to SbX₃ and SbX₅ molecules. No information about the charge transfer or SbX₆⁻ acceptor molecules was derived. These questions were treated by Boolchand et al. /43/ in a study of stage-2 SbCl₅-GICs, prepared in part from HOPG slabs. Comparison with reference compounds led to a characterization of the Sb⁵⁺ species as SbCl₆⁻ acceptors. The Sb⁵⁺/Sb³⁺ ratio was found to be near 2, in agreement with Equ. 1, when the intercalation was performed in pure SbCl₅ atmosphere. Admixtures of SbCl₃ to the SbCl₅ vapour resulted in an increased intercalation of the (neutral) SbCl₃ molecules. This study found evidence for Sb³⁺ acceptor anion, namely SbCl₄⁻, being present at an amount of ~25% of the Sb³⁺ species. This observation, however, was questioned later in Mössbauer investigations cited below.

Friedt and coworkers presented detailed studies of stage-1 SbF₅-GICs /44/ and stage-2

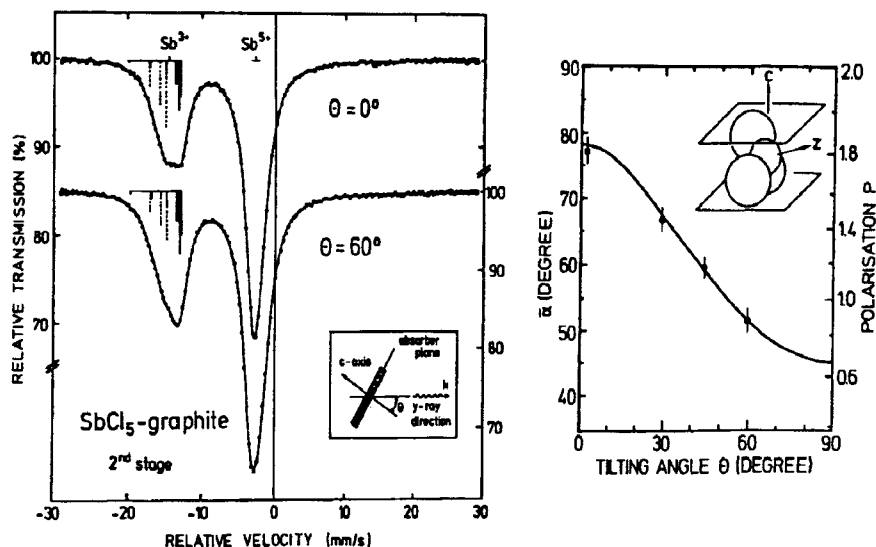


Fig. 6 ^{121}Sb -Mössbauer spectra of a textured SbCl_5 -GIC sample measured at different orientations with respect to the γ -rays /46/. The components of the quadrupole splittings are indicated by dashed ($\Delta m=0$ transitions) and solid ($\Delta m=\pm 1$ transitions) bars. The graph on the right shows the dependence of the averaged polarization angle $\bar{\alpha}$ on the tilting angle θ . The insert shows schematically the upright position of the SbCl_3 molecule. Measurements on a fully-aligned HOPG-sample reveal an angle of 90° between the molecular z-axis (main axis of the EFG) and the graphite c-axis /45/.

SbCl_5 -GICs /45/. Making use of the quasi single-crystalline properties of HOPG samples, the orientation and temperature dependence of the spectral components was determined. This procedure yields more detailed information about the specific properties of the species involved in the intercalation process. It was demonstrated that, in contrast to previous assumptions, the SbF_3 molecules are not intercalated into the SbF_5 -GICs, but presumably precipitates at the surface or in voids of the sample /44/. In SbCl_5 -GICs, on the other hand, the SbCl_3 molecules were found to be intercalated and oriented with their molecular axis (main axis of the EFG) parallel to the graphite planes. This structural information was derived from the polarization dependence of the quadrupole splitting of the Sb^{3+} site. This observation contradicts the interpretation of the Sb^{3+} site spectrum /43/ in terms of two molecular species. The existence of SbCl_4^- acceptor anions in a fractional amount of $\approx 25\%$ of the Sb^{3+} site is at variance with all reported Mössbauer spectra on SbCl_5 -GICs. The more convincing interpretation of a polarization-dependent structure of the Sb^{3+} -site has been given already in an earlier work of the Berlin group /46/ on a SbCl_5 -GIC prepared from large graphite flakes (see Fig. 6). The temperature dependence of the Sb^{3+} and Sb^{5+} sites in SbCl_5 -graphite was analyzed by Friedt et al. /45/ in terms of intermolecular and intramolecular vibrations and yielded rather low and anisotropic Debye temperatures ($\theta_{c,3} = 75$ K and 50 K, respectively).

A reliable information about the relative amount of SbCl_6^- anions would be most useful in order to elucidate the charge transfer in the SbCl_5 -GICs. The isomer shift of the Sb^{5+} species ($S = -3.1$ mm/s) in the study of Friedt et al. is roughly midway between those of the reference compounds, solid SbCl_5 and SbCl_6^- anions with $S = -3.4$ mm/s and -2.74 mm/s, respectively. In other SbCl_5 -GICs, the isomer shift of the Sb^{5+} site was reported as -2.9 mm/s /43/ and -2.8 mm/s /46/. This points to various $\text{SbCl}_5/\text{SbCl}_6^-$ compositions, depending on the preparation conditions. An extreme case, supporting this view, was observed recently in stage-1 SbCl_5 -GICs, where the isomer shift of the Sb^{5+} site, $S = -3.25(5)$ mm/s, was very near to that of pure SbCl_5 /46/. In addition, only small amounts of intercalated SbCl_3 molecules were detected ($\approx 6\%$ of the Sb^{5+} entities). There is experimental evidence that the $\text{SbCl}_5/\text{SbCl}_6^-$ ratio depends also on the stage and packing density of

the intercalant. The above mentioned stage-1 compounds were saturated with a composition near to $C_{14}SbCl_5$, which corresponds to a close packing of the intercalant /1,13,14/. In undersaturated $SbCl_5$ -GICs of higher stages, the isomer shifts were nearest to that of the $SbCl_6^-$ reference. It should be mentioned that a stage dependent charge transfer was also suggested for acceptor compounds /41/.

The analogous question about the SbF_5/SbF_6^- composition in SbF_5 -GICs was also investigated by the Cincinnati group on stage-2 SbF_5 -GICs /47/. From the observed isomer shifts as well as from chemical arguments the formation of macromolecules, $SbF_6^- \cdot nSbF_5$ with $n=1$, was proposed. Similar studies were performed on electrochemically-doped $NO_2SbF_6^-$ -GICs /48/. In this case the HOPG samples were loaded in a $NO_2SbF_6^-$ /nitromethane solution. This procedure avoids the intercalation of SbF_5 , but leads to a co-intercalation of solvent molecules, resulting in a composition $C_{23n}SbF_6(CH_3NO)_{1.7}$ for both stage-1 and stage-2. The isomer shift of the narrow Sb^{5+} resonance line is near to that of that of solid SbF_5 , which was explained by a complex formation of the SbF_6^- anion with the solvent molecules /48/.

Recently, a ^{19}F -NMR study on stage-1 SbF_5 -GICs was reported /50/. When oriented under the magic angle with respect to the external field, the resonance signal exhibit resolved splittings in the temperature interval 200 - 260 K, revealing the existence of three different F sites. They could be attributed by their shifts and intensities to the ligands of $(Sb_nF_{5n+1})^-$ polyanions (oligomers with $n = 3$ and 4) in bridging and terminal positions /50/. These results agree with a previous ^{19}F -NMR investigation of such polyanions in various solvents and of solid SbF_5 , in which the molecules form tetramers /51/. The assignment of $(Sb_nF_{5n+1})^-$ polyanions to the intercalant structure of SbF_5 -GICs has direct impact on the amount of charge transfer and, in our particular case, on the interpretation of the Mössbauer data, since one does not deal now with SbF_5 and SbF_6^- entities, but with rather similar sixfold-coordinated Sb^{3+} sites /51/. One of the above SbF_5 -GICs samples with $n = 3$ /50/ was studied also by the ^{121}Sb -Mössbauer resonance. The observed isomer shift, $S = -2.41(5)$ mm/s, agrees well with those of previous investigations /44, 46, 47/. Using the intercalate composition (corresponding to $SbF_6^- \cdot 2 SbF_5$ in the notation of Equ. 2), one finds fair agreement in composing the observed shifts from that of SbF_5 ($S = 2.1(1)$ mm/s) and SbF_6^- reference systems ($S = 2.7(2)$ mm/s) /44/. This calibration scheme, used up to now /44,47/ for an estimate of the SbF_5/SbF_6^- ratio, and thus for the charge transfer, is not very appropriate for the actually intercalated $Sb_nF_{5n+1}^-$ polyanions. Comparative studies on SbF_5 -GICs samples of different stages and composition would be most useful. The small scatter of the observed isomer shifts for the Sb^{3+} sites can be tentatively explained as sample dependent variations of the average size of the intercalated polyanions, for instance between $n = 3$ and 4, as demonstrated in stage-1 SbF_5 -GICs by ^{19}F -NMR /50/.

Finally we want to discuss in this section a point of actual debate concerning the intercalated structure in $SbCl_5$ -GICs. Electron diffraction studies reveal the presence of two superlattices assigned with $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ and $(\sqrt{39} \times \sqrt{39})R16.1^\circ$, which were attributed to Sb^{5+} and Sb^{3+} species, respectively. Their temperature- and pressure-dependent structural transitions are widely discussed /2,3,16,19,52,53,56/. The unusual commensurate-glass transition of the $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ phase observed around 200 K in TEM studies is now considered as being induced by the electron bombardment /54/. Two recent papers report on a spatial separation of the two phases, extending also in direction of the graphite c-axis /19/. It should be emphasized again that two assumptions /2,19, 53/ about the Sb^{3+} intercalant are in conflict with the present state of Mössbauer spectroscopy on these systems /45,46,49/: (i) there is only one intercalated Sb^{3+} species, namely (neutral) $SbCl_3$ molecules, with no evidence for $SbCl_4^-$ anions and (ii) these $SbCl_3$ molecules are arranged, at low temperatures ($T < 100$ K) and ambient pressure, with their molecular axes parallel to the graphite planes. This arrangement is similar to that at room temperature derived from an X-ray diffraction study /55/.

3.4. Other Acceptor Systems: IF_5 -Graphite, $EuCl_3$ -Graphite, Eu/NH_3 -Graphite.

IF_5 -GICs were studied with the 57.6 keV resonance of ^{127}I /57/. The observed hyperfine parameters reveal the intercalation of (neutral) IF_5 molecules, with the absence of other molecular species of acceptor type, as IF_6^- , within the experimental resolution (5 mol% of the intercalated Sb -species). From the absence of polarisation effects in the quadrupole spectra of a HOPG sample, the orientation of the IF_5 molecules was derived. The square-pyramidal molecule lies with one of its triangular bases parallel to the graphite plane, which implies that the fourfold molecular axis (= main axis of the EFG) form an angle near 54.7° (magic angle) with the graphite c-axis. The spectra of the

HOPG sample taken at different orientations with respect to the γ -rays were used for a determination of the anisotropic Debye temperatures /57/.

A ^{151}Eu -Mössbauer study of EuCl_3 -GICs prepared by various methods from HOPG and natural graphite flake was reported by Boolchand et al. /58/. The Mössbauer spectra reveal the presence of only $\text{Eu}(3+)\text{Cl}_3$ with an isomer shift identical with the reference system $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$. No evidence for Eu^{2+} species indicating a charge transfer to the intercalant, as found in FeCl_3 -GICs was observed. The measured stoichiometry, $\text{C}_n\text{EuCl}_{3.2}$, gives strong evidence that a considerable chlorination of the graphite has occurred. This proves that the intercalation of (rare-earth)-chlorides can take place by the van-der Waals interaction alone, provided the graphite planes are "opened" by a concomitant chlorination. The same argument can be applied in the above case of IF_3 -GICs, where also a fluorination of the graphite has occurred /57/.

The preparation of Eu-NH_3 -GICs was investigated by Schäfer-Stahl & von Eynatten /59/. The ^{151}Eu -Mössbauer spectra reveal the presence of three different sites typical for Eu^{2+} and Eu^{3+} . The two Eu^{2+} sites were attributed to metallic Eu and Eu amines. A recent study of the Berlin group /60/ on the same system found evidence for magnetic ordering of the Eu^{2+} species below 50 K. The temperature variation of the relative intensities of the different sites could be explained solely by their Debye temperatures. The Eu^{3+} site was attached to oxide contaminations /60/.

Other Mössbauer investigations of GICs can be referred only briefly. Using ^{119}Sn Mössbauer spectroscopy, GICs prepared from SnCl_4 and $\text{Me}_{4-x}\text{SnCl}_x$ in a photochemical procedure, were investigated /61/. The observed changes in isomer shift and quadrupole interaction were attributed mainly to interactions with co-intercalated solvent molecules. These systems exhibit extreme low f -factors with indications of a solid-liquid transition in the intercalant layers at rather low temperatures. Preliminary investigations of IrF_6 -GICs were performed with ^{193}Ir -Mössbauer spectroscopy. The quadrupole-split resonance spectra of nominal pentavalent Ir indicate a strong variation of the molecular structure on intercalation. No indications of magnetic ordering are found at 4.2 K /62/.

To end up with this chapter on GICs, we want to stress again one point: The use of oriented samples, prepared from HOPG or larger graphite flakes, as well as measurements at various temperatures allows in a straight-forward way the distinction between *intercalated* species and non-intercalated impurities or reaction products. Intercalants exhibit *rather low* and *anisotropic* Debye temperatures which distinguish them from the other products.

4. MÖSSBAUER STUDIES OF DOPED POLYMERS

4.1. FeCl_4^- -PA and Related Systems

The FeCl_4^- anion belongs to the acceptor molecules, which can be inserted into PA. The doping of PA is performed chemically or electrochemically in a FeCl_3 /nitromethane solution, as described by Pron and coworkers /63,64/. The preparation process is very sensitive to minute amounts of water and degradation products like $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$, precipitating in separate phases, are often observed /63-65/. The delicate preparation process of FeCl_4^- -PA seemingly caused the recent controversy between Sichel et al. /66a/ and Pron et al. /66b/ about the chemical nature of the *inserted* species. The maximum amount of doped FeCl_4^- anions is relatively low, only up to ≈ 7 mol% can be inserted. All regular dopants and degraded products can be identified by their Mössbauer parameters. The FeCl_4^- anions exhibit a quadrupole splitting, which points to a distortion of the chlorine ligands from the tetrahedral coordination and/or to an interaction with the $(\text{CH})_x$ -chains. The FeCl_4^- anions do not exhibit any magnetic ordering effects down to 4.2 K /63-66/. Important informations are contained in the recoil-free fraction, f , observed at the FeCl_4^- anions. They exhibit a rather low Debye temperature of $\Theta_m = 104$ K, which distinguishes the FeCl_4^- anions from degradation products /63,64/. A Mössbauer study of FeBr_4^- -PA yielded similar Mössbauer parameters for the anion and a Debye temperature $\Theta_m = 120$ K. The Θ values were derived from the temperature dependence of the f -factor considering only the mass m of the Fe atoms. A more detailed analysis, which takes into account the larger effective mass of the rigidly-bond FeX_4 molecules yielded even lower values of effective Debye temperatures Θ_m^* /64/. A ^{119}Sn -Mössbauer study of SnCl_4 -doped PA suggested the existence of the SnCl_5^- anions as the only inserted species /67/. The extremely low Debye temperature, $\Theta_m = 95$ K, is responsible for the loss of the resonance signal in Mössbauer spectra at 300 K. The Debye

temperatures observed on doped PA point to a loose bonding between the (isolated) anions and the $(\text{CH})_x$ chains. Measurements on oriented samples would be highly interesting, since anisotropic f -factors are expected from the PA structure.

4.2. Iodine-Doped PA: $(\text{CHI}_y)_x$

This system is one of the most stable and relatively easy to prepare. The transport and structural properties have been investigated by all applicable methods /4/. Mössbauer spectroscopy has contributed considerably to the understanding of these properties. Two Mössbauer resonances can be used: (i) the 57.6-keV resonance of ^{127}I , a 100% natural isotope, and (ii) the 27.7-keV resonance of ^{129}I , a long-living radioisotope ($T_{1/2} = 1.6 \cdot 10^7$ y). It is well known that the latter resonance is superior to the former because of its higher resolution power for hyperfine interactions and its lower γ -energy /70/. Its use, however, demands a laboratory with radioactive preparation facilities.

Two Mössbauer groups, one at the Kyoto university and one at the Free University Berlin, performed systematic studies of $(\text{CHI}_y)_x$ as function of the iodine content. Matsuyama and coworkers (including H. Shirakawa, who initiated the study of doped PA /20,21/) investigated samples doped with ^{129}I from CCl_4 -iodine solutions /71,73,74/. The Berlin group studied PA samples doped from the I_2 gas phase /72,75/. The results of both groups are in excellent agreement and can be summarized as follows: Three acceptor anions were found to contribute to the complex Mössbauer spectra, namely I^- , I_3^- , and I_5^- , the latter two as linear molecules (see Fig. 3). Their relative abundance depends strongly on the iodine content y . The I^- ions are only observable in small amounts at the lowest doping level ($y \leq 0.02$), the I_3^- anions are dominant up to $y = 0.1$, whereas mainly I_5^- anions are observed at high doping levels. According to this, the doping process can be described in the initial stage as $1/2 \text{I}_2 + e^- \rightarrow \text{I}^-$, followed by $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$. The I_3^- anions can be converted by additional I_2 to the larger I_5^- entities: $\text{I}_3^- + \text{I}_2 \rightarrow \text{I}_5^-$. This process dominates at higher doping levels and is reversible, as demonstrated by Mössbauer spectra of dynamically pumped samples /73,75/.

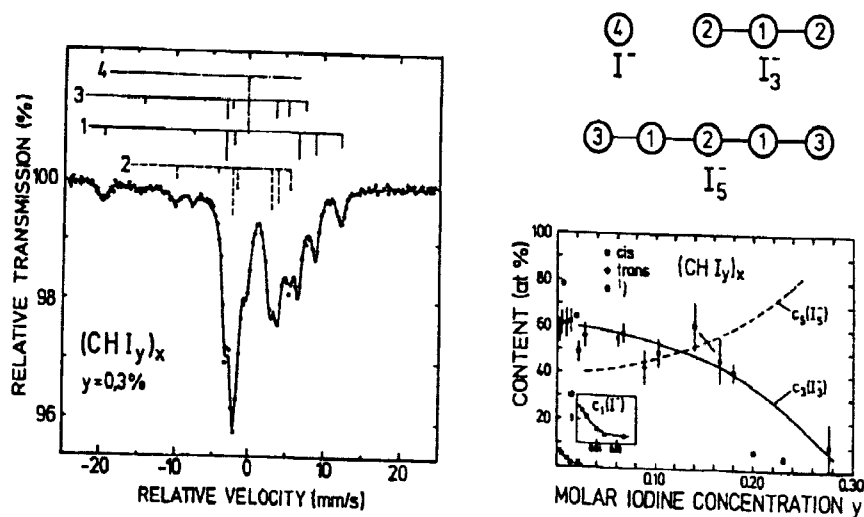


Fig. 7 ^{129}I -Mössbauer spectrum of iodine-doped PA at low doping level. Three acceptor anions contribute to the various subspectra 1-4, as indicated on the right hand side, where also the relative amount of the three anions is shown as function of iodine concentration y /75/.

These results provide detailed informations about the charge transfer in $(\text{CHI}_y)_x$ as function of the doping level /71-75/. The occurrence of large acceptor anions at high doping level is a direct consequence of a limited charge transfer from the $(\text{CH})_x$ chains to the acceptors; the charge transfer already starts to saturate around $y = 0.1$, though the transferred electron is shared by larger polyiodine anions. The maximum charge transfer is -0.04 electrons per (CH) unit. The occurrence of two

polyiodine species, namely I_3^- and I_5^- , is independent of the doping procedure, e.g. doping from gas-phase or solution, slow or fast doping; therefore the use of the formula $(CH(I_3)_y)_x$ is misleading with respect to the morphology and charge transfer in iodine-doped PA.

The question about the orientation of the linear I_3^- and I_5^- anions with respect to the $(CH)_x$ chains is of actual interest, since some of the proposed structural models demand a strictly parallel insertion /23,77/. Mössbauer studies on oriented $(CHI_y)_x$ samples could clarify this point by using the polarization dependence of the quadrupole splittings observed in Fig. 7. In contrast to the expectation, a study of stress-oriented $(CHI_y)_x$ samples by Matsuyama et al. /74/ yielded no polarization dependence of the quadrupole spectra, which was interpreted as evidence for a random insertion of the polyiodine molecules, eventually caused by a doping-induced loss of crystallinity in the samples. A similar study of the Berlin group, however, exhibited the expected polarization dependence of the quadrupole pattern, pointing to an - at least preferred - orientation of the I_3^- and I_5^- anions parallel to the $(CH)_x$ chains (see Fig. 4). The same group applied also another microscopic method, namely X-ray absorption spectroscopy (XAS) for studying the local structure and orientation of the iodine species /76/. For example, the iodine L_1 -edge absorption spectrum, taken from the Mössbauer absorber of Fig. 8a, is shown in Fig. 8b. The near-edge structure (NEXAFS) is dominated by an excitation of a 2s electron into an unoccupied $5p(\sigma^*)$ orbital of the I_3^-/I_5^- molecules. Since these σ^* -orbitals lie in the direction of the molecular axes, the use of linear-polarized synchrotron light allows an easy determination of the orientation of linear molecules in oriented (textured) samples. The analysis of both the Mössbauer and the L_1 -XA spectra yielded a mean angle of $45(3)^\circ$ between the I_3^-/I_5^- molecules and the texture axis of the PA film. The orientation of the molecules with respect to the $(CH)_x$ -chains is certainly at a smaller angle, since the alignment in this samples was rather incomplete. An XA study of better aligned $(CHI_y)_x$ samples yielded indeed larger polarization effects, especially on samples with low iodine content /76/. The analysis of the extended fine structure (EXAFS) of iodine L_3 -XA spectra reveal I-I distances typical for I_3^- and I_5^- molecules, however no defined I-C distances. This points to a random or incommensurate insertion of the iodine molecules with respect to the $(CH)_x$ chains. It should be mentioned that XA spectroscopy has been successfully applied to bromine-doped PA, $(CHBr_y)_x$, where one finds Br_3^- acceptor anions - aligned parallel to the $(CH)_x$ chains - and Br ions which had reacted with the $(CH)_x$ chains /78,79/.

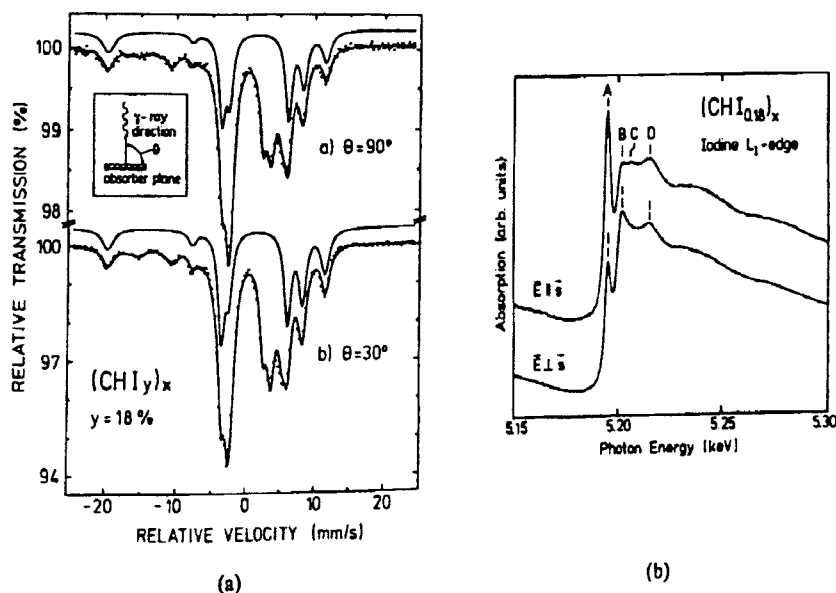


Fig. 8: (a) Polarization dependence of the quadrupole spectra of a textured $(CHI_{0.18})_x$ absorber /75/. For convenience, only the subspectra of site 1 (see Fig. 79) are shown. (b) Iodine L_1 -XA spectra of the same absorber with the texture axis parallel and perpendicular to the polarization vector E of the synchrotron radiations (for details, see Ref. 76).

4.3. SbF_5 -PA and SbCl_5 -PA

Similar to the case of SbF_5 -graphite, ^{121}Sb -Mössbauer spectroscopy can identify the molecular species inserted into the $(\text{CH})_x$ matrix by gas-phase doping with SbF_5 . The doping reaction is expected to be analogous to that for SbF_5 -GICs described above. One expects SbF_6^- acceptor anions and possibly SbF_3 and SbF_5 . These three species are indeed observed in the ^{121}Sb -Mössbauer spectra of a series of SbF_5 - $(\text{CH})_x$ samples with dopant concentration ranging from 0.1 to 8 mol% /80/. At the lowest doping level, a large fraction of SbF_6^- is observed, while at higher levels SbF_5 and SbF_3 molecules dominate. In contrast to the SbF_5 -GICs, the SbF_6^- and SbF_5 molecules are clearly distinguishable in the Mössbauer spectra by their partially resolved resonance lines. This points to separated Sb^{5+} species, as expected in the structural models for doped PA, and not to macromolecules, as suggested in SbF_5 -GICs. Recent experiments on SbF_5 -PA samples, performed at temperatures up to 150 K (f-factor measurements) indicate that in the gas-phase loaded SbF_5 -PA samples the SbF_5 and SbF_3 entities are actually not inserted in the $(\text{CH})_x$ matrix, but precipitate in clusters inside the PA foils. One should have in mind that PA prepared by the Shirakawa method consists to $\approx 2/3$ of cavities and only to $1/3$ of the PA fibrils. Recent structural investigations of electrochemically doped SbF_5 -PA, prepared from highly-oriented PA foils synthesized by the "Durham route" /24/ report a detailed crystal structure with incommensurate arrays of SbF_6^- anions /25/. A preliminary ^{121}Sb -Mössbauer study /82/ on a similar prepared sample confirms the assignment of the SbF_6^- sites in the previous Mössbauer studies /80,81/.

Friedt et al. reported on a study of SbCl_5 -PA by Mössbauer effect and other methods /83/. Up to a weight uptake of 5 mol%, only SbCl_3 species were observed in the Mössbauer spectra, while ^{13}C -NMR revealed a strong chlorination of the $(\text{CH})_x$ chains. This demonstrates that an increase in the electrical conductivity is not necessarily caused by acceptor molecules, but can also originate from the chlorination (oxidation) of the $(\text{CH})_x$ chains. The use of Lewis acid molecules like AsF_5 , SbF_5 , and SbCl_5 for gas-phase doping is always accompanied by such (unwanted) degradation reactions. For the preparation of undistorted counterion- $(\text{CH})_x$ structures, electrochemical doping is superior to gas-phase doping (the term "doping" should be read as oxidation" from a chemical point-of-view /4,23/).

4.4. Other Polymers: Polypyrole (PPy) and Polyparaphenylene (PPP)

Despite of the wide interest in PA as model substance for the understanding of conducting polymers, possible applications are limited because of its intrinsic instability, its extreme sensitivity to air and moisture and its poor crystallinity (as long Shirakawa PA is concerned). Other polymers are more stable also in doped forms, and/or can be prepared in more regular structures or larger quantities /5-7/. Mössbauer spectroscopy has been again successfully applied to the investigations of the inserted species. In many ways the dopants behave similar to the case of PA /68,69/. Pron and coworkers performed Mössbauer studies on PPy doped with FeCl_3 , SnCl_4 and SbCl_5 /69/. The inserted species were identified as FeCl_4^- , SnCl_5^- , and $\text{SbCl}_3/\text{SbCl}_6^-$, respectively (for details, see the contribution of Kucharski et al. in this volume). The Mössbauer spectra of FeCl_3 -doped PPP exhibit the presence of two different Fe^{3+} species, the dominant one again as the FeCl_4^- anion with Debye temperatures similar to FeCl_4^- -PA ($\Theta_m = 124$ K) /68/.

5. CONCLUSIONS

The presented and, of course, selected examples of Mössbauer studies on synthetic metals show that this spectroscopy provides a sensitive tool for the identification of the *chemical form (or forms)*, the *structural properties* and the *bonding strength* of the intercalated or inserted species. The *quality* of the samples can be easily checked by determining the *low* and *anisotropic* Debye temperatures characteristic for all dopants in GICs and conducting polymers.

The *charge transfer* can be elucidated in many systems; the studies on Cs-GICs, FeCl_3 -GICs, and $(\text{CH})_x$ may be cited as best examples. Mössbauer spectroscopy probes only the one side of these systems. The properties of the matrix have to be investigated by other methods, for instance by magnetic resonance (NMR and ESR) and optical spectroscopies, by electron energy-loss spectroscopy /84/ and XPS /85/. Most useful are comparative studies with different techniques on identical samples.

One of the intrinsic limitations of Mössbauer spectroscopy lies in the small number of applicable resonances and in the relatively low temperatures, at which the experiments have to be performed. X-ray absorption studies do not suffer from these limitations and can be also effectively applied to the study of the forms and local structure of the dopants /76,78,79,86/. The Mössbauer effect, however, is well suited for the study of the specific low-dimensional *magnetic properties* of the GICs.

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