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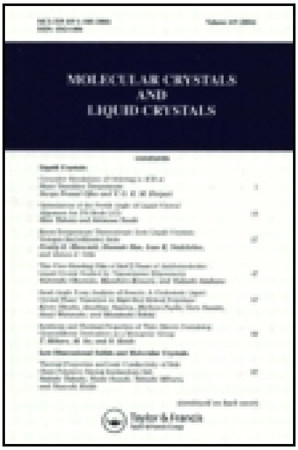

Molecular Crystals and Liquid Crystals

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

Mössbauer Spectroscopy Studies of Polyacetylene Doped With Selected Metal Halides

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Version of record first published: 17 Oct 2011.

To cite this article: Z. Kucharski , M. Józefowicz , J. Suwalski , A. Proń & S. Lefrant (1985): Mössbauer Spectroscopy Studies of Polyacetylene Doped With Selected Metal Halides, Molecular Crystals and Liquid Crystals, 117:1, 133-137

To link to this article: http://dx.doi.org/10.1080/00268948508074611

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Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 133-137
0026-8941/85/1174-0133/$10.00/0
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Printed in the United States of America

MÖSSBAUER SPECTROSCOPY STUDIES OF POLYACETYLENE DOPED WITH SELECTED METAL HALIDES

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Abstract Highly conducting derivatives of polyacetylene formed in the redox reactions with $FeCl_3$, $FeBr_3$ and $SnCl_4$ have been studied by Mössbauer spectroscopy. From the temperature dependence of the recoil-free fraction, the Mössbauer lattice temperatures θ_M, of the following binary compounds $\{CH(FeCl_4)_y\}_x$, $\{CH(FeBr_4)_y\}_x$ and $\{CH(SnCl_5)_y\}_x$, were calculated as 89K, 120K and 95K respectively. It has been also shown that it is possible to synthesize a ternary compound $\{CH(SnCl_5)_y(FeCl_4)_z\}_x$ through consecutive reactions of $(CH)_x$ with $SnCl_4$ and $FeCl_3$. ^{119}Sn and ^{57}Fe Mössbauer parameters of the ternary compound do not change significantly as compared to the ones of the corresponding binary compounds $\{CH(SnCl_5)_y\}_x$ and $\{CH(FeCl_4)_y\}_x$ indicating that the inserted species of different chemical nature do not influence mutually their coordination spheres.

INTRODUCTION

Mössbauer spectroscopy has proven to be an extremally useful technique in the studies of low dimensional system containing Mössbauer nuclei. In particular, from the examination of Mössbauer spectroscopic data extracted from the experiments covering an appropriate temperature range, significant information concerning charge transfer, oxidation state of the dopant and lattice dynamics can be gained.

To date the following conducting derivatives of polyacetylene have been studied by means of Mössbauer spectroscopy

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$\{CH(FeCl_4)_y\}_x$, (1),(2),(3) $\{CH(FeBr_4)_y\}_x$ (4), $\{CH(I_3)\}_x$ (5),(6), $\{CH(SbF_6)_y\}_x$ (7), $\{CH(SnCl_5)_y\}_x$ (8). In this communication we report Mössbauer lattice temperature, θ_M,measurements for $\{CH(FeCl_4)_y\}_x$, $\{CH(FeBr_4)_y\}_x$ and $\{CH(SnCl_5)_y\}_x$. In addition we have studied the possibility of a ternary compound formation through consecutive reactions of $(CH)_x$ with $SnCl_4$ and $FeCl_3$.

EXPERIMENTAL

All reactions and manipulations were performed using standard vacuum line technique or inert atmosphere. $(CH)_x$ film was prepared by a modification of the method of Ito et al. (9). The oxidations with $FeCl_3$ and $FeBr_3$ were carried out at RT in nitromethane solutions of 0.2 M and 0.3 M respectively whereas the oxidations with tin chloride were carried out in the solution consisting of 10 volume parts of $SnCl_4$ and 1 volume part of dry nitromethane. In all cases the samples were repeatedly washed with pure, dry nitromethane and then vacuum dried.

In the preparation of the ternary compound a strip of polyacetylene was first treated with $SnCl_4$ for 48 h., identically as described above, and then treated with 0.1 M solution of $FeCl_3$ for 5 min. The final product was washed with dry CH_3NO_2 and then pumped. The Mössbauer spectra were recorded in the temperature range 4.2 - 298K using standard transmission geometry. The spectra were fitted with Lorentz shape lines by the least square method.

RESULTS

In all cases studied, the resonant absorption strongly depended on the temperature. Since all $\ln\frac{A(T)}{A(4.2)} = f(T)$ plots were linear we were able to calculate the Mössbauer lattice temperatures, θ_M, for all three systems. In the calculations, we have followed

TABLE I Mössbauer parameters of ^{57}Fe and ^{119}Sn in $(CH)_x$ doped with iron chloride, iron bromide and tin chloride anion.

Sample	$e^2q\theta/2$ mm s^{-1} (4.2K)	I.S. mm s^{-1} (4.2K)	dlnA/dT	dIS/dT	θ_M	θ'_M
1. $\{CH(FeCl_4)_y\}_x$	0.33 ±0.01	0.30 ±0.03	-1.26×10^{-2}	-5.354×10^{-4}	104±5	89±8
2. $\{CH(FeBr_4)_y\}_x$	0.32 ±0.06	0.33 ±0.03	-	-	120	-
3. $(CH(SnCl_5\}_y)_x$	0.635±0.013	0.552±0.008	-1.98×10^{-2}	-	95±3	-

TABLE II ^{119}Sn and ^{57}Fe Mössbauer parameters of $\{CH(SnCl_5)_{0.035}(FeCl_4)_{0.011}\}_x$. Composition determined from mass uptake assuming $SnCl_5^-$ and $FeCl_4^-$ as the intercalated anions.

Type of Mössbauer nucleus	IS mm/s		QS mm/s		$\Gamma_{1/2}$ mm/s	
	4.2K	78K	4.2K	78K	4.2K	78K
^{119}Sn	0.524 ±.007	0.494 ±.011	0.612 ±.013	0.532 ±.021	0.927 ±.010	0.825 0.016
^{57}Fe	0.356 ±.012	0.341 ±.018	0.334 ±.026	0.381 ±.046	0.605 ±.019	0.588 ±.036

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a procedure recommended by Herber et al. (10). The θ_M was calculated according to the formula :

$$\theta_M = \frac{E_\gamma}{c}\left(\frac{-3}{M\ \mathrm{eff.}\ k d\ln A/dT}\right)^{1/2}$$

In the case of $\{CH(FeCl_4)_y\}_x$ we have estimated M eff. from the slope of the temperature dependence of the isomer shift. In the case of $\{CH(FeBr_4)_y\}_x$ and $\{CH(SnCl_5)_y\}_x$, similar corrections for M eff. were not possible due to low values of IS as compared to the half width of the peaks and their overlap. The reported values are therefore only rough estimates of θ_M. Mössbauer parameters of the ternary compounds are collected in Table 2. Similarly as in the case of the corresponding binary compounds, the resonant absorption is strongly temperature dependent increasing with the decrease of the temperature.

DISCUSSION AND CONCLUSIONS

Low Mössbauer lattice temperature, θ_M, is a general feature in intercalated low dimensional systems like lammellar compounds of graphite (11) or FeOCl (10). This low value indicates loose packing of the intercalated species and some degree of mobility at temperatures close to RT.

The Mössbauer lattice temperatures of all three polyacetylene - metal halide anions systems studied are similar and significantly lower than in the case of $FeCl_3$ intercalated graphite whose θ_M is 164K. It should be pointed out that only in the case of $\{CH(FeCl_4)_y\}_x$ the exact value of θ_M has been obtained since we were unable to calculate the corrections for M eff in the case of $\{CH(FeBr_4)_y\}_x$ and $\{CH(SnCl_5)_y\}_x$. In the presence of covalency, the correction for M eff. always lowers the θ_M by 10-20K so the true values of $\theta_M\ FeBr_4^-$ and $\theta_M\ SnCl_5^-$ are much closer to $\theta_M\ FeCl_4^-$. It can be therefore postulated that in doped polyacetylene θ_M does not depend on the inserted anion but is rather governed by the linearity of polycarbonium cation and

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its low value is determined by the two-fold coordination of carbon atoms in $(CH)_x$ chains.

The results of this research also prove that it is possible to from a ternary compound by consecutive reaction of $(CH)_x$ with $SnCl_4$ and $FeCl_3$.

Close similarity of the Mössbauer parameters of $\{CH(SnCl_5)_y(FeCl_4)_z\}_x$ with the ones of corresponding binary compounds $\{CH(SnCl_5)_y\}_x$ and $\{CH(FeCl_4)_y\}_x$ indicate that the inserted species of different chemical nature do not influence mutually their coordination spheres.

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