ELECTRON SPIN ECHO INVESTIGATIONS ON TRAPPED EPR ACTIVE CENTERS IN OXYGEN CONTAMINATED POLYACETYLENE

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Abstract: In this work, investigations of the electron spin-lattice relaxation of he tr centers are presented. Electro- paramagnetic resonance (EPR) is a method fo sepa the spectrum of these centers to calculate the spin-lattice relaxation time T1. The e mental results suggest the conclusion that oxygen contaminated polyacetylen- und a structural phase transition of second order.

I. INTRODUCTION

Polyaxetylene is very active to react with oxygen with catalyses the cistrans is ization already at lower temperature close to room temperature [1]. The mobil the so formed neutral solitonlike paramagnetic conjugation defects in drastically re [2.3]. Time resolved EPR have been proved to be a powerful method for separatir spectrum of the trapped spin centers from that of the mobile centers [4.5].

The spin-lattice relaxation time T1 shows two peculiarities. It has an unusually temperature dependence below 200K which can be related with a strongly hamonic motion of the neighbored mobile centers contributing to the spin-lattice relaxation magnetic dipolar and hyperfine interaction. Furthermore, T1 showing at about 21 discussed to be attributed to a new second order phase transition in oxygen contami polyaxetylenes.

I. EXPERIMENTAL

Polyaxetylene was synthesized at 220 K following the procedure of Shrakav Immediately after the preparation the samples were 15 minutes exposed to ar an vacuum stored at room temperature. Sample A is the untreated cis-rich polyaxet whereas sample B was heat- treated at 150 C for 30 minutes and is trans-ric.

The T1 measurements were carried out with a electron spin echo heterodyne trometer working in X-band [7]. A three pulse sequence was used where the magneti recovery was monitored by the primary echo.

The sample temperature was varied using a nitrogen gas flow controlledto +(between 90 K and 300 K and a Oxford helium flow cryostat ESR 9 between4 K a K.

II. RESULTS

The electron spin-lattice relaxation rates $1/T_1$ of both samples A and B inthe lc high temperature range are nearly identical and in comparison with the mobile c in the pure polyacetylene [4,8]. by one order of magnitude lower. In the middle

20 K and 300 K the relaxation rate of sample A is some what higher. The ture dependence can be described by:

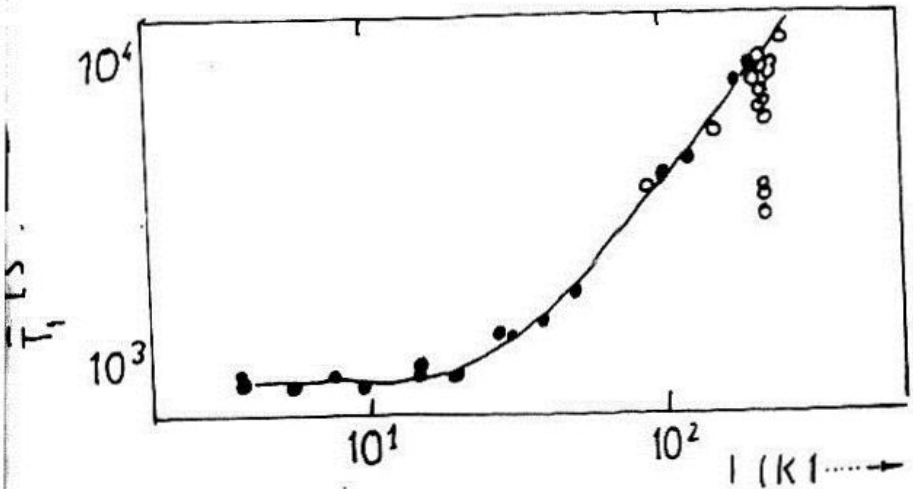
$$\frac{1}{T_1} = A_0 + A_1.M_1.\frac{\Theta ALM}{T} + A_2\frac{\exp(\Theta_0/T)}{[\exp(\Theta_0 T) - 1]^2} \quad (1)$$

he $A_i, i = 1, 2.$ are constants. The third term is a usual Raman process due to al lattice mode of energy $k\Theta_0$. The second term describes the contribution of anharmotic local motion (ALM) to the spin-lattice relaxation of the trapped as e. g. discussed in [9] for a phonon assisted relaxation process via vibrational f a particle within a square well potential.

$$M_1\frac{\Theta ALM}{T} = [\sum \exp(-m^2\Theta ALM/T)]^{-1}.\{\sum(2m+1)[1-(2m+1)^{-2}]^2 \times \frac{\exp(-m^2\Theta ALM/T)}{\exp[(2m+1)\Theta ALM/T] - 1}\} \quad (2)$$

in [9] where the characteristic temperature. $\Theta ALM = h/32kMa^2$ is related to states of a particle of mass M within an one-dimensional infinite well of the 2a. computer fit of the experimental data with equ. (1) gives $A_0 = 850s^{-1}$ and $A_1 = 1,6.10^3s^{-1}$ and $0,5.10^3s^{-1}$, $\Theta ALM = 25$ K and 19 K, $A_2 = 22.10^3s^{-1}$ and $^{-1}$, $\Theta_0 = 745$ K and 700 K for the samples A and B, respectively. Identifying the particle as a moving sliton in a neighbored chain the characteristic temperatures, corresponds to a range of the sliton motion of 44 and 50 c-c units sample A and

the temperature range between 200 K and 230 K a very striking anomaly of the tice relaxation is observed. Several sharp peaks in the T1 temperature dependence sured where t1 increase by more than 100 μs within a small interval of few Kelvin.



Temperature dependence of 1/T1 (sample A).
The drawn curve corresponds to equation (1)

e observed anomalies are far outside the limit of the experimental error. This type nomaly is similar to that observed by the authors on paramagnetic defect centers e crystals undergoing structural phase transitions of second order [10/. Therefore, erimental results suggest the conclusion that oxygen contaminated polyacetylene oes a structural phase transition of second order which take place at somewhat t temperatures due to the structural imperfections of the material.

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NGHIÊN CỨU ĐIỆN TỬ SPIN-MẠNG TRÊN CÁC TÂM HOẠT TÍNH EPR CỦA POLYAXÊTYLEN NHIỄM O

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Bài báo này trình bày việc nghiên cứu về thời gian hồi phục điện tử spin- m
với các tâm hoạt tính. Cộng hưởng từ điện tử (EPR) là một phương pháp hữu
xác lập phổ của các tâm này, từ đó tính được thời gian hồi phục spin-mạng T_1.
quả thực nghiệm thu được khẳng định rằng ô xy xâm nhập vào trong cácpolya
tạo nên một chuyển pha cấu trúc bậc 2.