

Thermal-history-dependent transition in pressed pellets of ClO_4^- -doped poly(3-methylthiophene)

E. C. Pereira and L. O. S. Bulhões

Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 679, CEP 13560, São Carlos, São Paulo, Brazil

A. Pawlicka, O. R. Nascimento, and R. M. Faria

Departamento de Física e Ciências dos Materiais, Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, CEP 13560, São Carlos, São Paulo, Brazil

L. Walmsley

Departamento de Física, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista, (UNESP) Caixa Postal 178, CEP 13500, Rio Claro, São Paulo, Brazil

(Received 22 February 1994)

Electron-spin-resonance and dc conductivity data show a thermal-history-dependent transition at 240 K in pressed pellets of ClO_4^- -doped poly(3-methylthiophene) (P3MT). We discuss the possibility of this transition to be a Peierls transition from a room-temperature-metallic to a charge-density-wave state driven by anions ordering at this temperature. Below 100 K, dc conductivity shows a change from linear to exponential decay. Nonlinear conductivity has also been observed in this system for very low electric fields.

INTRODUCTION

Polymers become conductors by *n* or *p* doping. The metallic state is characterized by room-temperature conductivity values as high as 10^3 S/cm, Pauli paramagnetism, linear dependence of thermopower with temperature and far-infrared absorption. The nature of this metallic state remains a controversial matter. Among many models that try to explain this finite density of states at Fermi level are bipolaron-polaron transition,¹ transition to a gapless Peierls insulator,² and bipolaron clusters.³ All those models stress the importance of disorder in the achievement of the metallic state.

In this work we show a thermal-history-dependent transition at 240 K observed from electron-spin-resonance (ESR) and dc conductivity data in pressed pellets of ClO_4^- -doped poly(3-methylthiophene) (P3MT). The possibility of this transition to be a Peierls transition of part of the system from a room-temperature-metallic to a charge-density-wave (CDW) state is discussed by comparison of the data with those of other low-dimensional systems, especially well-known CDW systems. The possibility of anions ordering to be the drive mechanism for this transition is discussed by comparison with cooling-rate-dependent transitions in other systems, especially in Bechgaard salts. The observed nonlinear dc conductivity at very low electric fields agrees with CDW depinning.

EXPERIMENT

The P3MT was deposited on Pt substrates at room temperature by a constant potential of 1.48 V from an acetonitrile solution with 0.1M methylthiophene and 0.1M LiClO_4 . The polymeric sample was scrapped and the resultant powder was pressed at a pressure of 6.2 kbar

to form pellets with thicknesses of a few hundred micrometers. The doping level was determined by using an energy-dispersive x-ray microanalysis system from Link Analytical (Model QX 2000) connected to a Zeiss 960 scanning microscope. The amount of anion in the sample showed to be dependent on the distance from electrode and current values, and the doping level in each pellet showed around 15% variation. We present data for four

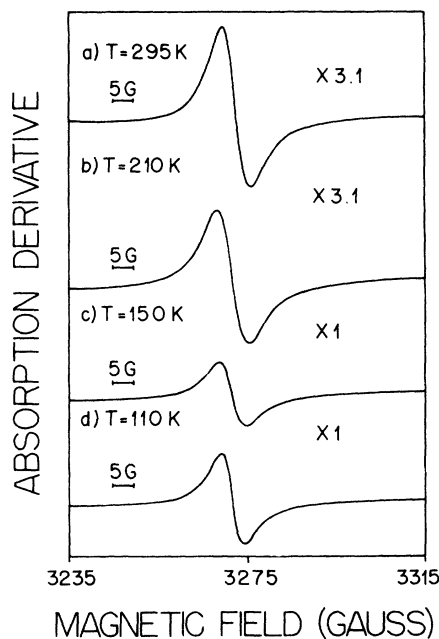


FIG. 1. ESR spectra of sample A. (a) $T=295$ K. After quenching to 110 K and raising fast the temperature at a rate of 10 K/min; (b) at 210 K; (c) at 150 K; (d) after quenching to 110 K.

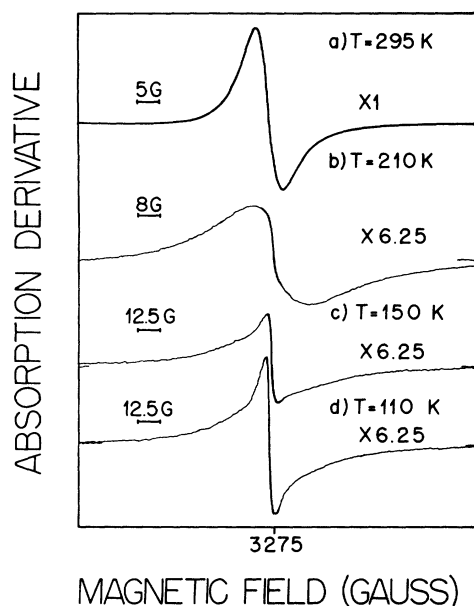


FIG. 2. ESR spectra of sample *A*. (a) $T=295$ K. After cooling slowly at a rate of 2 K/min: (b) at 210 K; (c) at 150 K; (d) at 110 K.

samples, with different thickness (d): *A* ($y=10\%$ and $d=140\ \mu\text{m}$), *B* ($y=15\%$ and $d=35\ \mu\text{m}$), *C* ($y=12\%$ and $d=540\ \mu\text{m}$), and *D* ($y=8\%$ and $d=300\ \mu\text{m}$).

The ESR measurements were performed in a conventional VARIAN E-109 reflection spectrometer using a TE_{102} rectangular cavity adapted to cold nitrogen gas flux system. Dc measurements were performed in silver painted pellets in a conventional capacitive setup, placed in a tubular cryostat system.

Figure 1 shows the ESR spectra after quenching sample *A* to 110 K and raising fast the temperature at a rate of 10 K/min. The dysonian room-temperature line is not saturable at klystron's ordinary powers although the line at 110 K saturates. Figure 2 shows the ESR spectra of the same sample when it is slowly cooled from room temperature at a rate of 2 K/min. For the composed spectra of Fig. 2(d) we were able to saturate the narrow line although the broad line did not saturate. Figure 3

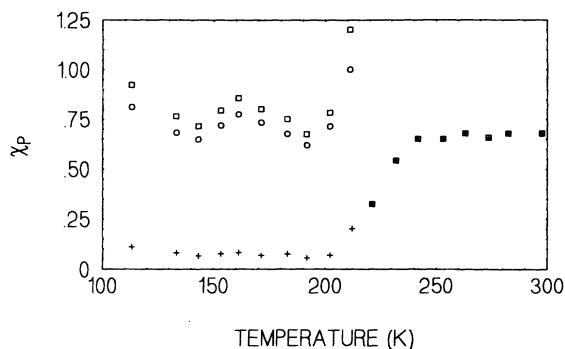


FIG. 3. Temperature dependence of paramagnetic susceptibility (in arbitrary units) for sample *B* which was slowly cooled from room temperature. (+), contribution from the narrow line; (O), contribution from the broad line; (□), total paramagnetic susceptibility.

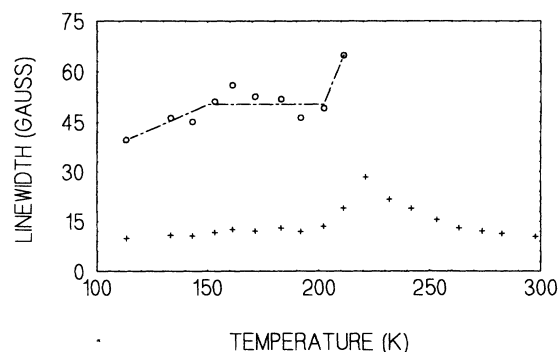


FIG. 4. (+), temperature dependence of linewidth for the narrow line; (O), the same for the broad line. Dashed line is a guide for the eyes.

shows the temperature dependence of paramagnetic susceptibility (in arbitrary units) for sample *B*, which was slowly cooled from room temperature at a rate of 1 K/min. Paramagnetic susceptibility was determined by double integration of the first derivative absorption line and the low-temperature data were fitted to a superposition of a narrow and a broad Lorentzian line. Crosses show the contribution of the narrow line, circles show the contribution of the broad line, and squares show the total paramagnetic susceptibility. In Fig. 4 we show $\Delta H \times T$ for the broad line (circles) and narrow line (crosses). In Fig. 5 we show the 9.4 GHz conductivity obtained from asymmetry ratio (A/B) of the ESR line and pellet's thickness (d):

$$\sigma = \frac{\lambda^2}{d^2 \pi \nu_0 \mu},$$

where we take $\mu = \mu_0 = 4\pi \times 10^{-7}\ \Omega\ \text{s}\ \text{m}^{-1}$, ν_0 is the microwave frequency, and $\lambda = d/\delta$ is taken from Dyson theory.⁴ The validity of this theory in the normal skin depth regime has already been established.⁵⁻⁷ Squares correspond to the experiment of Fig. 1 which was best fitted to a linear T dependence. Crosses correspond to the experiment of Fig. 2 and below 220 K the data were taken from the narrow line.

Figure 6 shows dc conductivity versus temperature for samples *C* and *D* ($15 \leq T \leq 300$). For both samples the

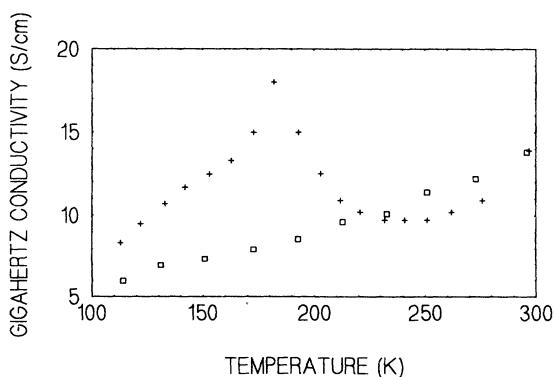


FIG. 5. Gigahertz conductivity vs temperature for sample *A*. (□), from the data of the experiment of Fig. 1; (+), from the narrow line of the experiment of Fig. 2.

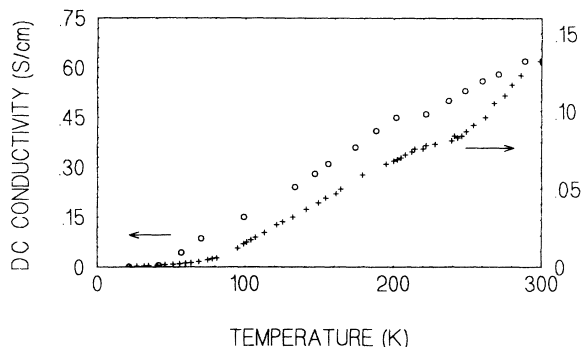


FIG. 6. Dc conductivity for samples C (circles) and D (crosses) slowly cooled from room temperature.

temperature was decreased very slowly and an anomaly was observed in the range 210–240 K. Below 100 K the conductivity data showed a change from a linear to an exponential decay. Although above 100 K we can already observe a nonlinear behavior in conductivity, below 100 K the nonlinearity is stronger and increases as the temperature is decreased. Figure 7 shows $I \times V$ curve for sample C at $T = 42$ K. We estimate the threshold dc electric field to be less than 20 mV/cm.

DISCUSSION

The transition from a single to a double line with a narrow and a broad component in Fig. 2 is the most striking feature of the ESR spectra. From Fig. 3 we observe that the broad line gives a Pauli contribution to the susceptibility meaning that part of the system remains in the metallic state. But the narrow line shows an $\exp(-E_g/k_B T)$ decay, best fitting yielding $E_g = 0.18$ eV. So there is a possibility of this behavior to be associated with a Peierls transition of this part of the system from a metallic to a CDW state. Concerning the total paramagnetic susceptibility, we observe that it closely resembles the paramagnetic susceptibility of the metal-insulator transition at 54 K in tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ).⁸ Similar features are also observed in the paramagnetic susceptibility of the metal-insulator transition at 60 K in NbSe_3 .⁹ In the latter, the temperature dependence of the ESR linewidth is similar to that of the narrow line in Fig. 4.

The dependence on cooling rate can be observed from comparison of Figs. 1 and 2. The effect of cooling rates in electric and magnetic properties has been observed in other low-dimensional systems, like graphite intercalation compounds,¹⁰ doped C_{60} compounds,¹¹ and Bechgaard salts.¹² In di(tetramethyltetraselenafulvalenium)perrhenate $[(\text{TMTSF})\text{RO}_4]$ this behavior is associated with ordering of the doping anions, with anion ordering occurring at the same temperature as the Peierls transition.¹³ The two curves in Fig. 5 can show the effect of disorder. When we quench the system we freeze the disordered state that exists at room temperature. No transition is observed and the linear T dependence is characteristic of ac thermally activated hopping.¹⁴ When we slowly cool the system the gigahertz conductivity ob-

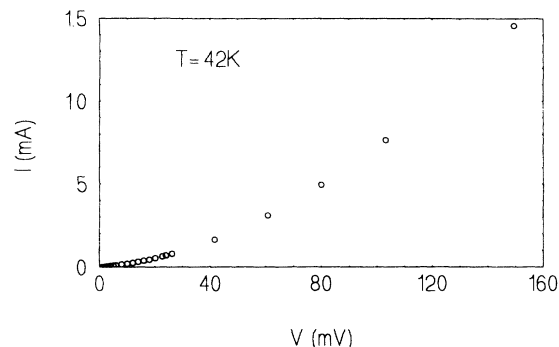


FIG. 7. I - V curve at $T = 42$ K for sample C.

tained from the line that undergoes the transition at 240 K is similar to the same frequency data of TaS_3 .¹⁵ In rubidium-doped C_{60} a cooling-rate-dependent transition was observed and ESR linewidth behavior also resembles that of the narrow line in Fig. 4.¹¹

Unfortunately, our ESR facilities do not allow to slowly drop the temperature below 110 K. In this sense, we cannot monitor, using ESR, the change from linear to exponential decay observed around 100 K from dc conductivity data. A rough estimation can be made from dc conductivity data for an additional gap $E_{g2} = 0.02$ eV, although the conductivity below 50 K, in the range of electric fields used, is increased by nonlinear effects. We believe that around 100 K, the part of the system that remained in the metallic state below 220 K, undergoes a transition and true semiconducting behavior is observed. The observation of nonlinear dc conductivity for very small electric field amplitudes (less than 20 mV/cm) as shown in Fig. 7 is suggestive of CDW depinning.

CONCLUSIONS

We have reported a cooling-rate-dependent transition at 240 K in pressed pellets of ClO_4^- -doped P3MT. We discussed the possibility of this transition to be a Peierls transition of part of the system to a CDW state, the true semiconductor behavior being attainable below 100 K. Nonlinear conductivity with threshold fields less than 20 mV/cm agree with CDW depinning. Thermal-history dependence shows evidence of anions ordering as the drive mechanism for the transition. We think the pressure of the pellets is a fundamental parameter since we did not observe a transition in P3MT-doped films. Influence of pressure on conductivity of conducting polymers has already been reported.¹⁶ We may stress that some questions remain unanswered needing further investigation by other techniques. The first one concerns the broad ESR line that can be only observed below the transition. Is it motional narrowed in the disordered room-temperature state or unobserved due to fast relaxation? The ESR line is also unobserved above the 145 K metal-insulator transition in NbSe_3 .⁹ The second problem concerns the part of the system that undergoes the 240 K transition. Since the degree of crystallinity of the samples is small to allow good x-ray experiments to be performed, this remains an open question.

ACKNOWLEDGMENTS

We are indebted to Marcelo A. P. da Silva for the doping levels determination. This work was partially sup-

ported by Fundação de Amparo à Pesquisa do Estado de São Paulo, Conselho de Desenvolvimento Científico e Tecnológico e Fundação para o Desenvolvimento da UNESP, Brazil.

-
- ¹S. Kivelson and A. J. Heeger, *Synth. Met.* **17**, 183 (1987).
²X. Q. Yang, D. B. Tanner, M. J. Rice, H. W. Gibson, A. Feldblum, and A. J. Epstein, *Solid State Commun.* **61**, 335 (1987).
³F. C. Lavarda, M. C. dos Santos, D. S. Galvão, and B. Laks, *Phys. Rev. B* **49**, 979 (1994).
⁴F. J. Dyson, *Phys. Rev.* **98**, 349 (1955).
⁵J. H. Pifer and R. Magno, *Phys. Rev. B* **3**, 663 (1971).
⁶L. Walmsley and C. Rettori, *Synth. Met.* **36**, 235 (1990).
⁷L. Walmsley, *Phys. Rev. B* **46**, 6256 (1992).
⁸Y. Tomkiewicz, A. R. Taranko, and J. B. Torrance, *Phys. Rev. Lett.* **36**, 751 (1975).
⁹M. C. Aronson and M. B. Salamon, *Phys. Rev. B* **38**, 10476 (1988).
¹⁰R. M. Stein, L. Walmsley, G. M. Gualberto, and C. Rettori, *Phys. Rev. B* **32**, 4774 (1985).
¹¹A. Jánossy, O. Chauvet, S. Pekker, J. R. Cooper, and L. Forró, *Phys. Rev. Lett.* **71**, 1091 (1993).
¹²T. Ishiguro and K. Yamaji, *Organic Superconductors*, edited by Peter Fulde, Springer Series in Solid State Physics Vol. 88 (Springer-Verlag, Berlin, 1990).
¹³R. Moret, J. P. Pouget, R. Comès, and K. Bechgaard, *Phys. Rev. Lett.* **49**, 1008 (1982).
¹⁴N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1971), p. 49.
¹⁵S. Sridhar, D. Reagor, and G. Grüner, *Phys. Rev. B* **34**, 2223 (1986).
¹⁶N. Basescu, Z.-Z. Liu, D. Moses, A. J. Heeger, H. Naarmann, and N. Theophilou, *Nature* **327**, 403 (1987).