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## Pressure Dependent Electrical Conductivity of Polypyrrole

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## PRESSURE DEPENDENT ELECTRICAL CONDUCTIVITY OF POLYPYRROLE

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abstract The results of pressure dependent electrical conductivity measurements in polypyrrole are consistent with a simple extension of the variable-range-hopping model of electronic transport in disordered media.

### INTRODUCTION

The pressure dependence of the optical absorption<sup>1</sup> and the electrical conductivity<sup>2</sup> in polyacetylene, (CH)<sub>x</sub>, have been reported previously. We have begun a study of the pressure-dependence of the electrical conductivity in boron-fluorid doped polypyrrole (PPy).

The issues addressed are: is there any pressure dependence?; if so, how large is it?; what functional form does it take?; and can any data be rationalized within the Mott-Davis variable range hopping (VRH) model<sup>3</sup>, which has been used previously to fit the  $\sigma(T)$  data for polypyrrole<sup>4,5</sup>.

### EXPERIMENTAL

Boron-fluoride doped polypyrrole (PPy) samples were prepared in Linköping according to standard procedures<sup>4</sup>, sent under inert atmosphere to Umeå, and studied using the 4-point contact method in a hydrostatic pressure apparatus described previously<sup>6</sup>.

At room temperature and atmospheric pressure, the polypyrrole samples had a dc conductivity in the range  $35 \leq \sigma \leq 55$  (ohm-cm)<sup>-1</sup>. A typical normalized curve is shown in Fig. 1, where one Giga Pascal = 10<sup>4</sup> bar. Upon cycling, the resistance returns to its initial value at  $p \approx 0$  GPa to within 10% lower resistance).

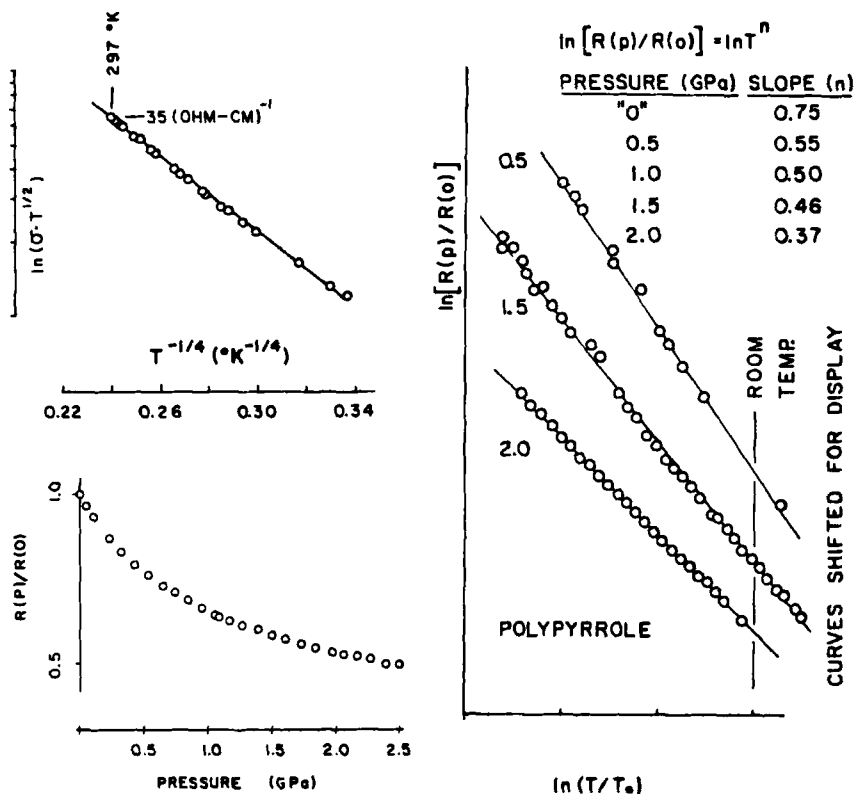


Fig.1: LEFT ABOVE: VRH plot; LEFT BELOW: Typical pressure curve; RIGHT: "Metals" conductivity plots,  $R \sim T^n$ .

## ANALYSIS

At  $p = 1$  bar (i.e.  $p \approx 0$  GPa), the  $T$ -dependence of  $\sigma$  does not fit to a straight line on a standard thermal activation model,  $\ln \sigma$  vs.  $T^{-1}$ , but do fit well to the VRH model<sup>3</sup>, a straight line on a  $\ln(\sigma \cdot T^{1/2})$  vs.  $T^{-1/4}$ , as shown in Fig. 1. Surprisingly, however, the  $\sigma(T)$  data also fit to  $R/R_0 = C \cdot T^n$ . For metals at  $T > \theta_{\text{DEBYE}}$ ,  $n = +1$ . We find that  $n$  is negative at  $P \approx 0$  GPa, but decreases with increasing pressure, Fig. 2. This behavior led us to consider the  $p$ -dependence in a VRH model.

To build in a  $p$ -dependence into a VRH model we make the following simplifying assumptions: the major effect of pressure is to reduce the distance between hopping sites; the underlying electronic structure is not changed; the density-of-states near  $E_F$  is a constant. The number of hopping sites per unit volume be-

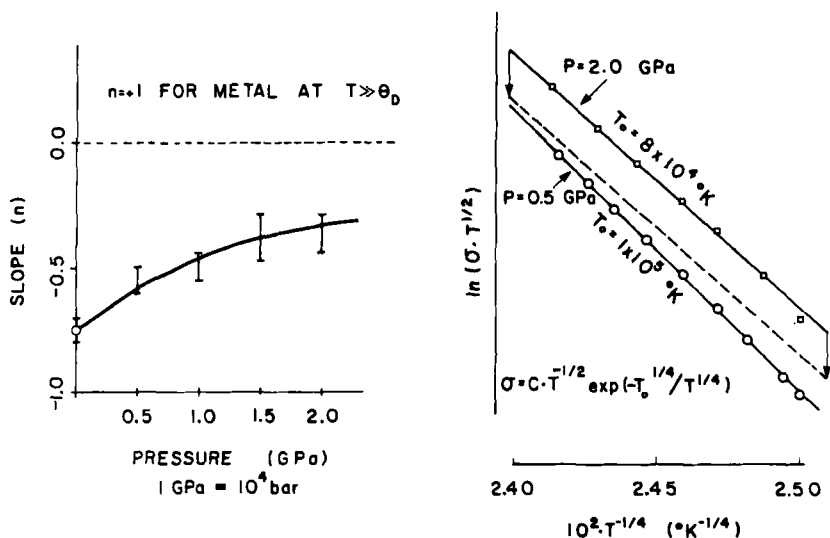


Fig.2: LEFT: Plot of exponent,  $n$ , from  $R \sim T^n$  versus pressure; RIGHT: Pressure-dependence of the VRH temperature parameter,  $T_0(p)$ .

comes  $n_F = N(E_F)/(4\pi a^3)$ , where "a" is the average distance between hopping sites. Then  $a = a_0(1-h \cdot p)$ , where  $p$  is the pressure in GPa, and  $h$  is the linear compressibility, taking  $h$  from the linear compressibility of (CH) in Ref. 2,  $h = 0.04 \text{ GPa}^{-1}$ . This value is constant up to about 3 GPa for (CH), and is equivalent to the value estimated using the bulk modulus of typical organic liquids. The resultant VRH equation becomes,

$$\sigma = A(1-h \cdot p)^{3/2} T^{-1/2} \exp(-T_0(p)^{1/4}/T^{1/4}),$$

where  $A = \text{constant}$ , and

$$T_0(p) = T_0(0) \cdot (1-h \cdot p)^3.$$

When  $h \cdot p \ll 1$ , the prefactor  $(1-h \cdot p)^{3/2}$  does not contribute significantly to the slope of a plot of  $\ln(\sigma \cdot T^{1/2})$  vs.  $T^{-1/4}$ . The term  $T_0(p)$ , however, is small but should be observable. In our samples,  $T_0(0) = 1.1 \times 10^3$  °K, in agreement with previously published results<sup>7</sup>. At  $p = 2.0$  GPa, our simple model predicts that  $T_0(2.0) = 0.78 T_0(0)$ , only a 22% change. The effect is small but in agreement with measurements, which could only be carried out over a limited  $T$ -range at  $p > 0$ , due to the massive nature of the pressure apparatus. The effect is seen in Fig. 2. At  $p \geq 2.5$  GPa, the  $\sigma(T)$  data are non-linear and our approximations break down.

## SUMMARY

Hydrostatic pressure-dependent electrical conductivity data on polypyrrole can be modelled by a simple extension to a pressure dependence of Mott's VRH model of electrical transport in disordered materials. The effect, a pressure dependence of the term  $T_0$  in the VRH model, is predicted to be small over the range of applicability of the approximations. Experimentally, a change in  $T_0$  is observed that is of the predicted sign and of approximately the predicted magnitude.

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7. In both Ref's 4 and 5, the conductivity was plotted as  $\ln(\sigma)$  vs.  $T^{-1/4}$ , where as in the VRH model one needs  $\ln(\sigma \cdot T^{1/2})$  vs.  $T^{-1/4}$ . The  $T^{1/2}$  term does not change the fit to straight line, but it does change the value of  $T_0$  deduced from the slope. When replotted including the  $T^{1/2}$ , the data of both Ref. 4 and 5 yield a  $T_0 \approx 1.1 \times 10^5$  °K.