PRESSURE EFFECTS ON ELECTRICAL CONDUCTIVITIES IN INTERCALATED GRAPHITE AND DOPED POLYPYRROLE

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Résumé - Nous avons mesuré la résistivité électrique, jusqu'à 2.5 GPa et à la température ambiante, des graphites intercalés $C_n FeCl_3$, $C_n SbF_5$ et $C_n HNO_3$. L'augmentation de la résistance jusqu'à 2.5 GPa est sensiblement la même dans les trois cas. On a constaté une transition de phase dans chacun des deux derniers matériaux, les caractéristiques de ces transitions étant différentes. Nos résultats sur la variation de la résistance du polypyrrole sont en accord avec la théorie de "sauts à pas variable". Il paraît que la densité d'états au niveau Fermi augmente avec la pression.

Abstract - We have measured the pressure dependence up to 2.5 GPa of the electrical resistance of the acceptor intercalated graphites $C_n FeCl_3$, $C_n SbF_5$, and $C_n HNO_3$. The slope of resistance versus pressure is approximately the same in all cases. Two different types of high pressure transitions are observed in $C_n SbF_5$ and $C_n HNO_3$. The results of electrical resistance measurements under pressure in polypyrrole are consistent with a simple extension of the variable-range-hopping model. We infer for this material that the density of states at the Fermi level increases with pressure.

INTRODUCTION

During the past year we have begun a study of the pressure dependence of resistance in graphite intercalated compounds (GIC's) and doped polypyrrole (PPy). A common behaviour of these organic materials is their large conductivity after doping with similar agents. Typical values are 10^5 S/cm for GIC's (in plane), and 10^2 S/cm for doped PPy, as compared to that of copper, $5.8 \cdot 10^5$ S/cm. Also, very few high pressure measurements have been performed on these materials and existing results are contradictory. As will be shown below our results on HNO_3-GIC are entirely incompatible with those of Iye et al /1/. Regarding polymers the pressure dependence of the optical absorption /2/ and the electrical conductivity /3/ in polyacetylene, $(CH)_x$, have been reported previously. In this first study of the pressure dependence of the electrical conductivity in boron-fluoride doped PPy we will examine the Mott-Davis /4/ variable range hopping (VRH) model, which has been used previously to fit the $\sigma(T)$ data for polypyrrole /5,6/.

EXPERIMENTAL

The high pressure experiments have been performed in a conventional piston-cylinder apparatus /7/. As pressure transmitting medium in a standard Teflon® cell we have used a 50/50 mixture of normal- and isopentane, providing hydrostatic conditions to about 7 GPa at room temperature. The temperature is limited to the range between 250 K to 300 K due to the massive nature of the apparatus.

Stage 2 $FeCl_3$ and stage 1 SbF_5 samples were obtained from Professor F. Lincoln Vogel, and stage 2 HNO_3 samples from Professor John E. Fischer, both of the Uni-

versity of Pennsylvania, Philadelphia, U.S.A. The conductivities of these samples, at room temperature and ambient pressure, were measured by a contactless open coil induction method /8/. Under pressure we used a contactless, closed toroidal core method /9/.

Boron-fluoride doped PPy samples were prepared in Linköping according to standard procedures /5/ and sent under inert atmosphere to Umeå for high pressure study using the 4-point contact method. Before pressurizing R(T) was measured between 77 K and 300 K.
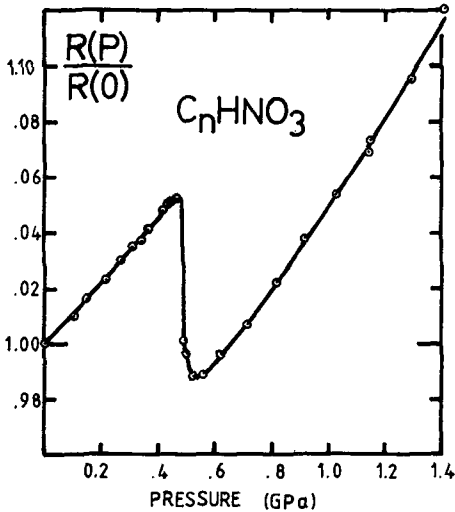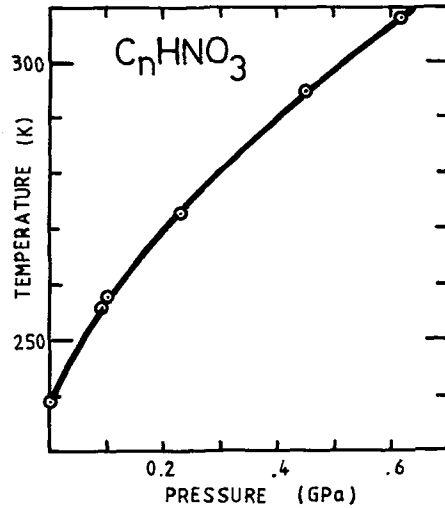

Fig. 1 - Relative resistance of C_nHNO_3 Fig. 2 - Phase diagram of C_nHNO_3.
          versus pressure.

RESULTS AND DISCUSSION

In all the acceptor intercalated samples, i.e. $FeCl_3$-, SbF_5-, and HNO_3-GIC's, examined here, the pressure coefficients of resistance, $(1/R(0))(dR(P)/dP)$, have about the same value, $+0.1$ GPa^{-1}, which contradicts that of Iye et al /1/, who report -1.0 GPa^{-1}. This discrepancy was noted in earlier measurements by the authors /10/ on the $FeCl_3$- and SbF_5-GIC's, and now on HNO_3-GIC for conclusive comparison.

In the SbF_5-GIC we have reported in Ref. /10/ a very slow (24 hours) phase (stage) transition at about 1.2 GPa, accompanied by a further increase in resistance. In the HNO_3-variety we observe an almost instantaneous order-disorder transition, accompanied by a sharp drop in resistance, as can be seen in Fig. 1. At room temperature the transition occurs at about 0.45 GPa. The hysteresis is about 0.05 GPa on decreasing the pressure. The corresponding hysteresis in C_nSbF_5 is about 0.5 GPa. At 1 bar the transition temperature is about 240 K, which is in agreement with reported data /11/, and also verified at our laboratory by differential scanning calorimetry. The phase diagram, showing the boundary between the low temperature ordered structure and the high temperature disordered one, is shown in

Fig. 2. The slope, dT/dP, of the phase boundary at room temperature and 0.45 GPa is 91 K/GPa, and at atmospheric pressure and 240 K, 132 K/GPa. According to the theory of DiVincenzo et al /12/, based on the Clausius-Clapeyron equation, the change in slope of the phase boundary indicates a ratio $\Delta\Omega(0.45)/\Delta\Omega(0) = 0.70$, where $\Delta\Omega$ equals the change in volume upon intercalation.
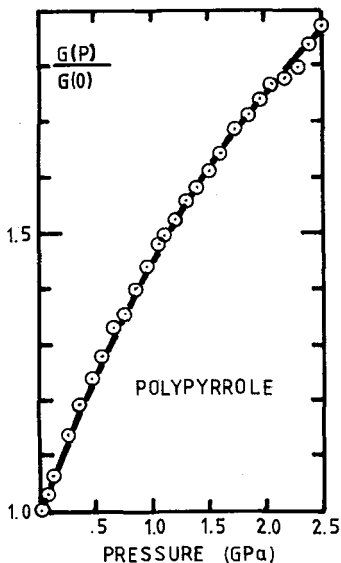

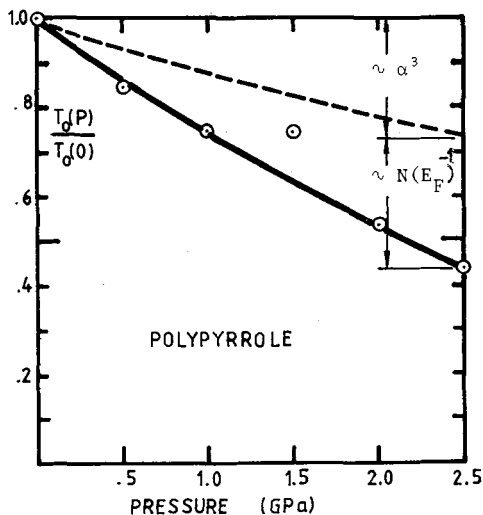Fig. 3 - Relative conductance of polypyrrole versus pressure.

Fig. 4 - The VRH parameter $T_0 \sim \dfrac{\alpha^3}{N(E_F)}$ versus pressure.

At room temperature and atmospheric pressure the polypyrrole samples had a dc conductivity in the range $35 \leq \sigma \leq 55$ S/cm. A typical normalised curve of conductance, $G = 1/R$, versus pressure is shown in Fig. 3 and indicates an increase in sample conductance by 85 % to 2.5 GPa.

In a previous paper /13/ we have shown that the T-dependence at P = 1 bar fits the VRH model /4/,

$$\sigma = A(T_0/T)^{\frac{1}{2}} \exp\{-(T_0/T)^{1/4}\}.$$

It was also shown that the data fit equally well a function of the type $\sigma(T) = \sigma_0 T^n$. However, instead of being a constant, as in polyacetylene ($n \approx 13$) /14/, n for PPy changes from 0.75 (at 1 bar) to 0.35 (at 2.0 GPa), and seems to be constant at P > 2.0 GPa. This behaviour led us to consider the P-dependence in the VRH model. As a first approximation we assumed that the characteristic decay length of the localized state $1/\alpha$ increases with pressure. Then, $\alpha = \alpha_0(1-h\cdot P)$, where h = 0.04 GPa^{-1} is the linear compressibility, here taken equal to that of (CH)$_x$ /3/, since the compressibility of PPy is unknown. $T_0(P)$ in the VRH equation now becomes $T_0(P) = T_0(0) (1-h\cdot P)^3$, where $T_0(0) = 24\alpha_0^3/\pi k_B N(E_F)$, and $N(E_F)$ is assumed constant. In our samples, $T_0(0) = 1.0 \cdot 10^5$ K, in agreement with previously published results /5/. At low pressure this model agrees roughly with experiment, but at higher pressures it deviates significantly. At each pressure, T_0 can be calculated from the slope of $\ln(\sigma T^{\frac{1}{2}})$ versus $T^{-1/4}$. Fig. 4 shows the variation of T_0 with pressure obtained in this way. Supposing the value of h used is reasonable, a best fit is

obtained for $T_0(P) \sim (1-h \cdot P)^8$. Since $\alpha^3 \sim (1-h \cdot P)^3$ it is reasonable to assume that the density of states, $N(E_F)$, increases considerably with increasing pressure.

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