Pramāṇa – J. Phys., Vol. 26, No. 1, January 1986, pp. 61–66. © Printed in India.

Non-ohmic conduction and electrical switching under pressure of the charge transfer complex *o*-tolidine-iodine

HEMAMALINI NAIK and S V SUBRAMANYAM
Department of Physics, Indian Institute of Science, Bangalore 560012, India

MS received 15 April 1985; revised 9 October 1985

Abstract. The current voltage characteristics of *o*-tolidine-iodine, with stoichiometry 1:1 grown from benzene, have been studied under high pressures upto 6 GPa at $T = 300$ K and $T = 77$ K. The characteristics show a pronounced deviation from ohmicity beyond a certain current for all pressures studied. At room temperature, beyond a threshold field the system switches from a low conducting OFF state to a high conducting ON state with $\sigma_{ON}/\sigma_{OFF} \sim 10^3$. The OFF state can be restored by the application of an a.c. pulse of low frequency. The temperature dependence of the two states studied indicates that the OFF state is semiconducting while the ON state, beyond a certain applied pressure is metallic. The characteristics at $T = 77$ K do not show any switching.

Keywords. Non-ohmic conduction; electrical switching; high pressure; charge transfer complex.

PACS No. 72·15; 72·20; 72·80

1. Introduction

It has been found that charge transfer complexes grown with iodine as an acceptor have probably the least resistivity at room temperature. *o*-tolidine-iodine has a room temperature resistivity of about $10^3\,\Omega$ cm. The room temperature resistivity variation with pressure shows an initial increase in resistivity which reaches a maximum around 3 GPa and then decreases with further increasing pressure (Hemamalini and Subramanyam 1985). The current-voltage (I-V) characteristics of *o*-tolidine-iodine have been studied under pressures up to 6 GPa at $T = 300$ K and $T = 77$ K. At $T \sim 300$ K the I-V characteristics show a marked deviation from ohmicity. A switching from a low conducting OFF state to a high conducting ON state is observed when the applied bias exceeds a threshold field with $\sigma_{ON}/\sigma_{OFF} \sim 10^3$. The switching has been observed at 300 K for all pressures at suitable driving currents. The non-ohmic behaviour is explained based on the Zener tunnelling model. To understand the switching phenomena several mechanisms such as dielectric breakdown, thermal breakdown, Zener tunnelling, etc have been considered. The I-V characteristics at $T = 77$ K show only a slight deviation from ohmicity. No switching is observed at this temperature.

2. Experimental

o-tolidine-iodine has been prepared by the method due to Brass and Clar 1956, with benzene as the solvent medium. It has been characterized by using spectroscopic X-ray

diffraction and microanalysis techniques. All high pressure studies have been carried out in a clamp-type Bridgman anvil pressure cell (Bandyopadhyay *et al* 1980). Electrical connections are provided to the sample by pressure contacts. A four-probe arrangement is used for all conductivity measurements. Current is used as a driving force. The voltage across the sample is monitored as a function of the current. Low temperature measurements in the range $T = 300$ to 77 K are carried out in a bath-type cryostat. Temperature is monitored by a copper-constantan thermocouple.

3. Results

Figure 1 shows the I-V characteristics for various clamped pressures at $T = 300$ K. At very low currents the characteristics are linear. Pronounced nonlinearity is observed at higher currents for all clamped pressures. A switching from a low conducting OFF state to a high conducting ON state is observed when the current passing through the sample exceeds a threshold value. Before switching to the ON state a sudden rise in the voltage is observed, unlike in any other compound where switching has been observed. Once the system switches to the ON state it continues to remain in this state even after the driving current is reduced or removed. The observation of the memory of the switched state in this system is very similar to that observed earlier in TMBine-TCNQ. The system can be driven back to the low conducting OFF state by the application of an a.c. pulse of low frequency. The process of switching is fast and can be repeated for several cycles. After a large number of cycles, a degradation in this phenomena is observed. The temperature dependence of resistivity has been studied in the temperature range 300 to 77 K for the two states. Figure 2 shows the variation of resistivity (ρ) with temperature in the two states for clamped pressure of 0·98 GPa. The activation energy (E_a) is calculated by using the relation

$$\rho = \rho_0 \exp(E_a/kT)$$

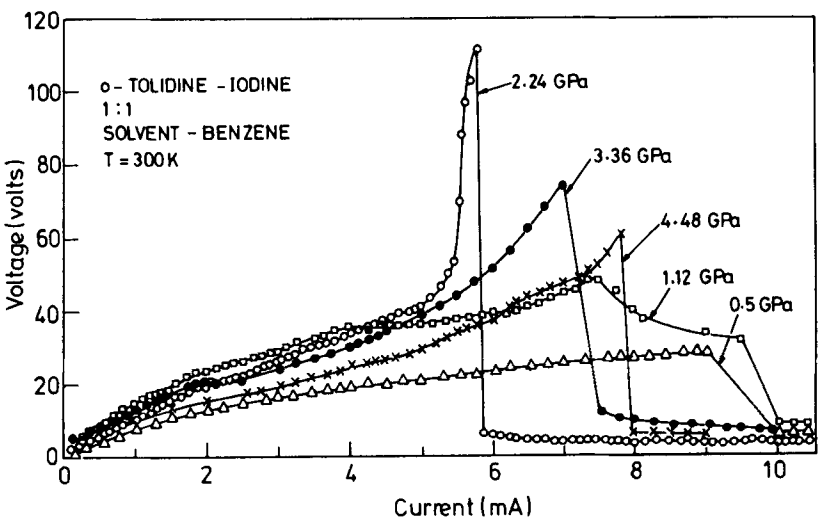

Figure 1. Current-voltage characteristics of *o*-tolidine-iodine at different pressures.

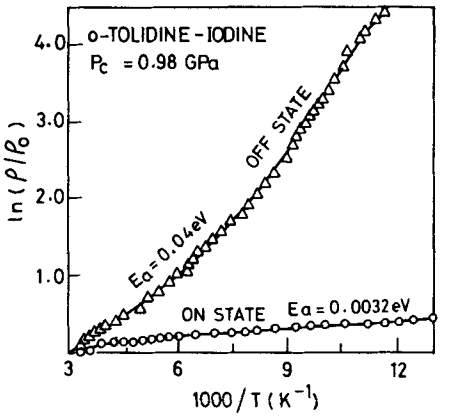

Figure 2. Variation of resistivity with temperature of *o*-tolidine-iodine in the two states at clamped pressure 0·98 GPa.

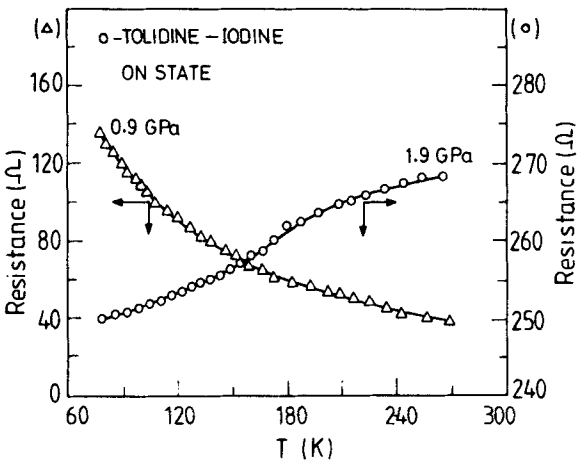

Figure 3. Variation of resistance with temperature of *o*-tolidine-iodine in the ON state.

where k is the Boltzman constant and ρ_0 the pre-exponential factor.

The conduction in the OFF state is found to be activated for all clamped pressures. In the ON state, in the low pressure region < 1 GPa the conduction is activated, while at high pressures the conduction is of metallic nature as seen in figure 3.

The I-V characteristics at $T = 77$ K is shown in figure 4. For low pressures the characteristics are almost linear in the current range studied. For high pressures > 2 GPa, the characteristics are nonlinear. No switching has been observed at this temperature. The resistivity at $T = 77$ K is about $10^5\,\Omega$ cm, which is two orders of magnitude greater than that at room temperature. Probably the driving current necessary to cause switching is too high and the voltage across the sample before switching is more than 120 V at this temperature (OFF state resistivity may be very large).

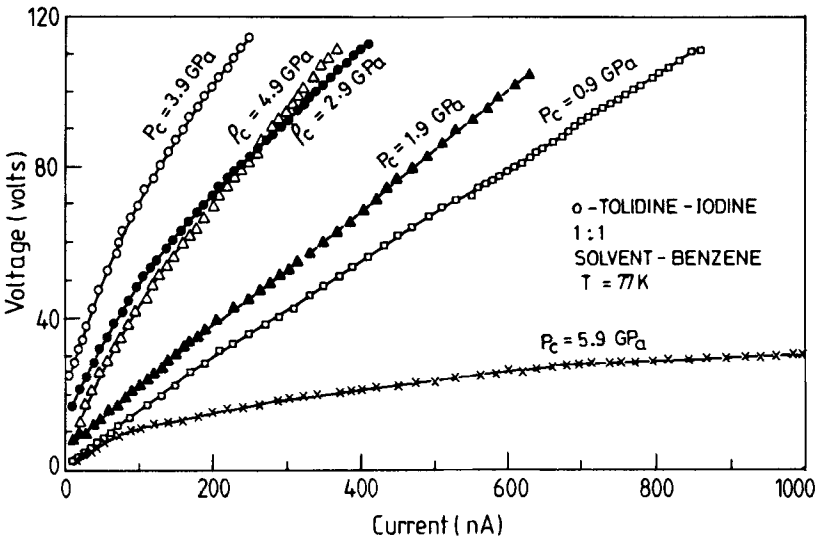

Figure 4. I-V characteristics of *o*-tolidine-iodine at $T = 77$ K for different clamped pressures.

4. Discussion

4.1 *Non-ohmic electrical conduction*

A deviation from ohmic behaviour has been reported before in a number of compounds such as TTF-TCNQ (Cohen and Heeger 1977), $Q_n(TCNQ)_2$ (Mihaly *et al* 1979) and $NbSe_3$ (Miller *et al* 1983). Non-ohmic electrical conduction has been attributed to tunnelling phenomena and the depinning of a charge density wave (CDW) (Bardeen 1980). A CDW may be pinned to impurity sites, lattice incommensurability, etc.

The nonlinear part of the I-V characteristics has been fitted to an equation of the following type for the field-dependent conductivity $\sigma(F)$

$$\sigma(F) = \sigma_a + \sigma_b \exp(-F_0/F),$$

where σ_a is the field independent conductivity and F_0 the characteristic Zener tunnelling field. Figure 5 gives the plot of $\ln(\sigma(F) - \sigma_a)$ as a function of $1/F$. Good linear fits have been observed for all clamped pressures. The non-ohmic conductivity has therefore been attributed to Zener tunnelling type of mechanism of CDW, as in $NbSe_3$. Though the formation of CDW at such high temperatures is doubtful, pressure plays an important role. It is possible that structural modulation is brought about by the application of high pressure resulting in nonlinear characteristics. Structural data after pressurization would yield a wealth of information. Unfortunately this has not been possible due to experimental limitations.

4.2 *Electrical switching*

There have been earlier reports on electrical switching in thin films of Cu-TCNQ (Potember *et al* 1979), anthracene (Elsharkawi and Kao 1977) and some charge transfer complexes, under pressure like TMPD-TCNQ and TMBine-TCNQ (TMPD = NNN'N' tetra-

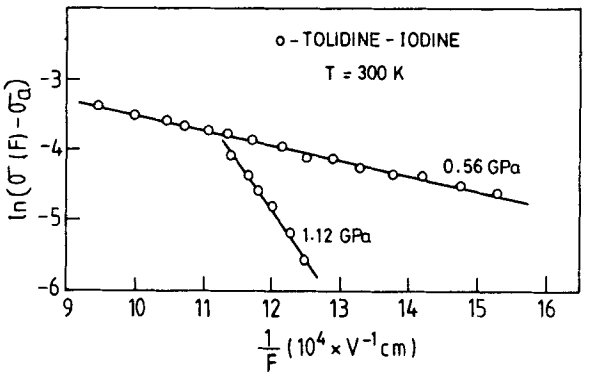

Figure 5. Variation of ln $(\sigma(F)-\sigma_a)$ of *o*-tolidine-iodine as a function of $1/F$.

methyl-*p*-phenylenediamine, TMBine = NNN'N' tetramethyl-benzidine) (Bandyopadhyay *et al* 1979). A very interesting aspect of the present results is the nature of conduction in the two states. The OFF state conduction is by an activated process. In the ON state, at low pressures, the conduction is activated with a very small activation energy. At pressures exceeding 1 GPa, the ON state conduction is metallic. This clearly demonstrates the difference in the manner of conduction in the two states. To explain the present data, various mechanisms of thermal and non-thermal origin have been considered.

A system switches to a high conducting state when the electron gains more energy from the electric field than what is dissipated to the lattice resulting in dielectric breakdown, elucidated by

$$p > \hbar\,\omega_D^2$$

where p is the power gained by each electron, $\hbar$ is the Planck's constant ($\hbar = h/2\pi$) and ω_D is the Debye frequency. p is expressed in terms of the switching power and the number of electrons/cc. Typical values at all pressures indicate that the breakdown condition is not satisfied.

The probability of Zener tunnelling from the valence band to the conduction band, as a result of switching has been considered as a possible mechanism where

$$P_{v-c} = \exp\left(-\frac{2}{3eF}(2m/\hbar^2)^{1/2}\,\Delta^{3/2}\right),$$

F being the switching field and Δ the activation energy after switching. For clamped pressure 1·12 GPa the Zener tunnelling probability is $\sim 10^{-3}$. It has therefore been ruled out as a mechanism responsible for switching.

When the joule heat generated by the current flow is greater than the heat lost by conduction an instability occurs resulting in thermal breakdown driving the system into a new state. This is not the case in the present case as the sample is firmly embedded in a steatite pressure transmitting medium between the tungsten carbide anvils. The total amount of heat supplied to the sample at the time of switching is less than 0·2 Watts. This heat is distributed over the entire sample and dissipated to its surroundings.

The mechanism has therefore been attributed to some form of electronic excitations in the system. Crystal structure data of the specimens in the ON state at high pressures and high driving fields should resolve this.

Acknowledgements

The authors wish to thank DST and ISRO for financial support, and the referee for his valuable comments.

References

Bandyopadhyay A K, Chatterjee S and Subramanyam S V 1979 *Nucl. Phys. Solid State Phys. India* **C22** 251
Bandyopadhyay A K, Nalini A V, Gopal E S R and Subramanyam S V 1980 *Rev. Sci. Instrum.* **51** 136
Bardeen J 1980 *Phys. Rev. Lett.* **45** 1978
Brass K and Clar E 1956 *Bull. Chem. Soc. Jpn* **29** 213
Cohen M J and Heeger A J 1977 *Phys. Rev.* **B16** 688
Elsharkawi A R and Kao K C 1977 *J. Phys. Chem. Solids* **38** 95
Hemamalini N and Subramanyam S V 1985 *Solid State Commun.* (communicated)
Mihaly G, Janossy A, Kurti J, Forro R and Gruner G 1979 *One-dimensional conductors-I* (eds) S Barisic, A Bjelis, J R Cooper and B Leontric (Berlin: Springer–Verlag) p. 297
Miller Jr J H, Richard J, Tucker J R and Bardeen J 1983 *Phys. Rev. Lett.* **51** 1592
Potember R S, Poehler T O and Cowan D O 1979 *Appl. Phys. Lett.* **34** 405