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NON–LINEAR CONDUCTION AND SWITCHING PHENOMENA IN QUASI–ONE DIMENSIONAL COMPOUNDS

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ABSTRACT

Quasi one dimensional compounds of Radical–Ion–Salts (RIS) type like Qn–$(TCNQ)_2$, Ad–$(TCNQ)_2$, K–TCNQ, and Cu_2O–TCNQ, were synthesized using different methods like electrochemical, diffusion and solution growth methods. The single crystals of Qn–$(TCNQ)_2$ and Ad–$(TCNQ)_2$ grown by electrochemical method were found to be largest in size (length) reported so far. The room temperature conductivity of these compounds was found to be in a wide range of 10^{-4} to 10^{2} ohm^{-1} cm^{-1}. For RIS with symmetric cations like K–TCNQ and Cu_2O–TCNQ, it was found that $\log \sigma \alpha T^{-\alpha}$ as is observed in conventional semiconductors. Besides these, semiconductor–metal phase transitions with temperature were observed. The investigation of the I–V characteristics of the four RIS synthesized were carried out in temperature range 10 to 300 K. All the four compounds show ohmic behaviour at low currents and transition to non–ohmic region at higher currents. In some cases (Qn–$TCNQ_2$ and K–TCNQ) a negative differential resistance region at higher currents was observed. In RIS with symmetric cations (K–TCNQ and Cu_2O–TCNQ), switching phenomena was observed at some particular temperatures.

Key words : Quasi one dimensional compounds, RIS, Non-linear conduction, Electrical switching, Negative differential resistance, Charge–density–wave, Solitons.

INTRODUCTION

Many quasi one–dimensional compounds exhibit interesting properties such as deviation from ohmic behaviour and switching from a low conducting state to a high conducting state[1]. Such behaviour has been reported previously in a wide variety of systems such as chalcogenides like $NbSe_3$ etc.[2], charge transfer complexes like TTF–TCNQ, $(TMTSF)_2PF_6$ etc[3]. Pronounced deviation from ohmicity under high pressure at high driving fields has also been observed in some organic charge transfer complexes like TMPD–TCNQ, TM bine–TCNQ, TEA–$(TCNQ)_2$ and o–tolidine–iodine[4] and Cu (TCNQ)[5,6].

To explain these observations, various theories have been reported. Prominent among them are the deepening of charge density waves (CDW) by Zenner type tunneling[7], space charge limited current[8], phonon assisted hopping through random barriers, impurity pinning[9] and sliding CDW[10].

In this paper, the investigations of I–V characteristics of quasi one–dimensional compounds of radical–ion–salts (RIS) type like Qn $(TCNQ)_2$, Ad $(TCNQ)_2$, K–TCNQ and Cu_2O–TCNQ in the temperature range from 10 to 300 K has been described. All the four compounds show ohmic behaviour at the low currents and transition to non–ohmic region at higher currents. In some cases, like Qn–$(TCNQ)_2$ and K–TCNQ, a negative differential resistance region was observed at higher currents. In RIS with symmetric cation like K–TCNQ and Cu_2O–TCNQ, switching phenomena at some particular temperature has been observed. An attempt would be made to discuss the above characteristics theoretically on the basis of space charge limited currents, tunneling models, decoupling of CDW, dynamics of charged solitons etc[11].

EXPERIMENTAL

Qn $(TCNQ)_2$ and Cu_2O–TCNQ have been prepared by the method given by Williams *et al.*[12] with acetonitrile as the solvent. The complexes are synthesized in powder form. Single crystals of Ad $(TCNQ)_2$ and K–TCNQ are synthesized by solution growth method[13] and electrochemical method[14]. It is found that the crystals grown by electrochemical method are largest in size reported so far[15,16]. The synthesized compounds have been characterized by the usual spectroscopic, NMR, X–ray diffraction and microanalysis techniques. Recently thin films of Cu–TCNQ have also been synthesized[17] which promise various kinds of applications in micro–electronics[18]. These complexes have unique properties that lead to application in optical recording disks, corrosion inhibition and molecular electronics devices[19].

All low temperature measurements were carried out using two probe and/ or four probe arrangements in a closed–cycle liquid He cryostat. Electrical connections are provided to the sample using silver paste and the Keithley current source is used as the driving source. The voltage across the two points on the samples is monitored as a function of current.

RESULTS AND DISCUSSION

The room temperature conductivity (σ) of these compounds was found to be in a wide range of 10^{-4} to 10^{2} $ohm^{-1}\,cm^{-1}$. For RIS with symmetric cations like Qn$(TCNQ)_2$ and Ad $(TCNQ)_2$, it is found that $\log \sigma \;\alpha\; T^{-\alpha}$ where $\alpha = 1/4$ at low temperature and, $\alpha = 1/2$ at intermediate and higher temperatures. This indicates a crossover from 3d behaviour at low temperatures where $\log \sigma \,\alpha\, T^{-1/4}$ to 1d behaviour at intermediate and higher temperatures where $\log \sigma \,\alpha\, T^{-1/2}$ law is followed. The activation energy has different values in different temperature regions. On the other hand for RIS like K–TCNQ and Cu_2O–TCNQ, it was found that $\log \sigma \,\alpha\, T^{-1}$ as is observed in conventional semiconductors. The conductivity versus temperature studies have been carried out in temperature range from 10 K to 300 K.

The investigations of the I–V characteristics of the four RIS synthesized were carried out at some particular temperatures in the temperature range from 10 K to 300 K. These are shown in Figures 1–4. The experimental results obtained may be explained as follows :

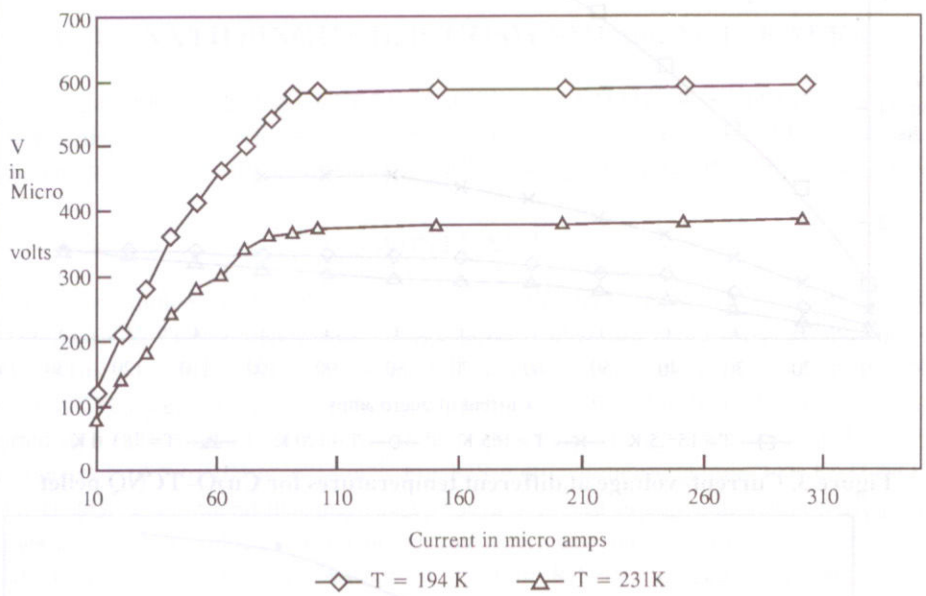

Figure 1. Current–voltage at different temperatures for Ad –$(TCNQ)_2$ crystal

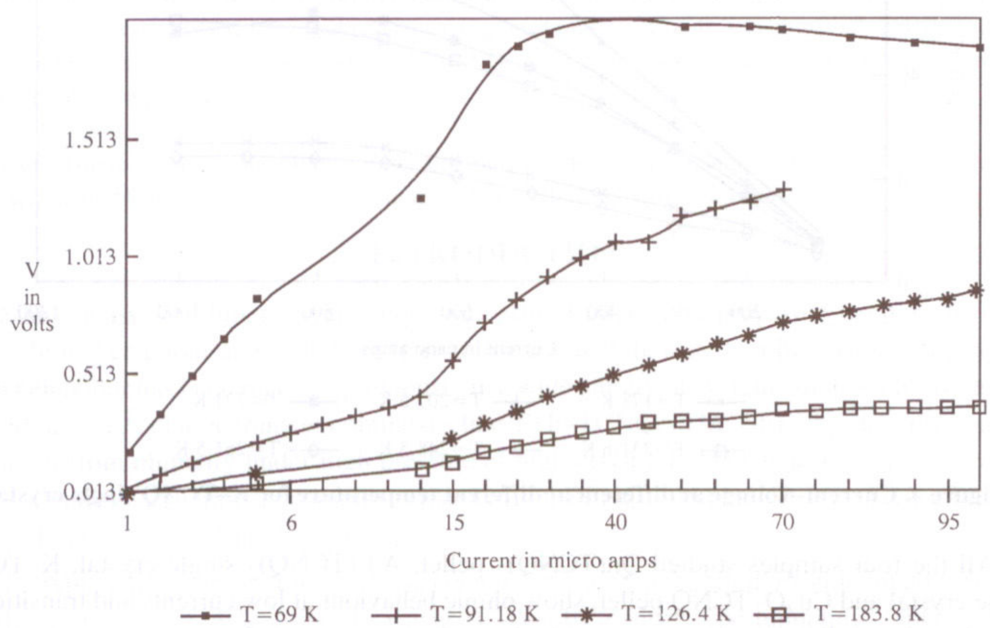

Figure 2. Current–voltage at different temperatures for Qn$(TCNQ)_2$ pellet

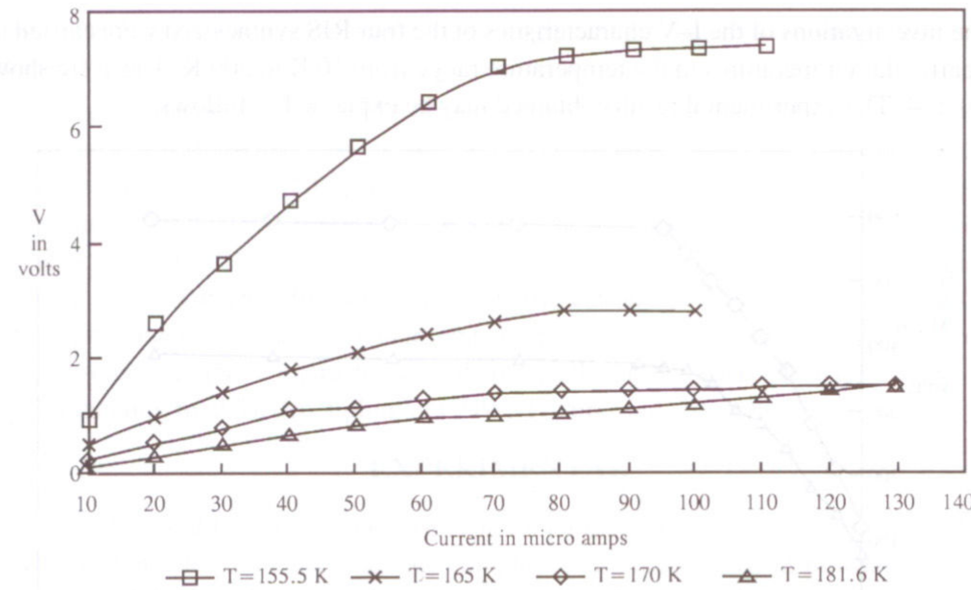

Figure 3. Current–voltage at different temperatures for Cu2O–TCNQ pellet

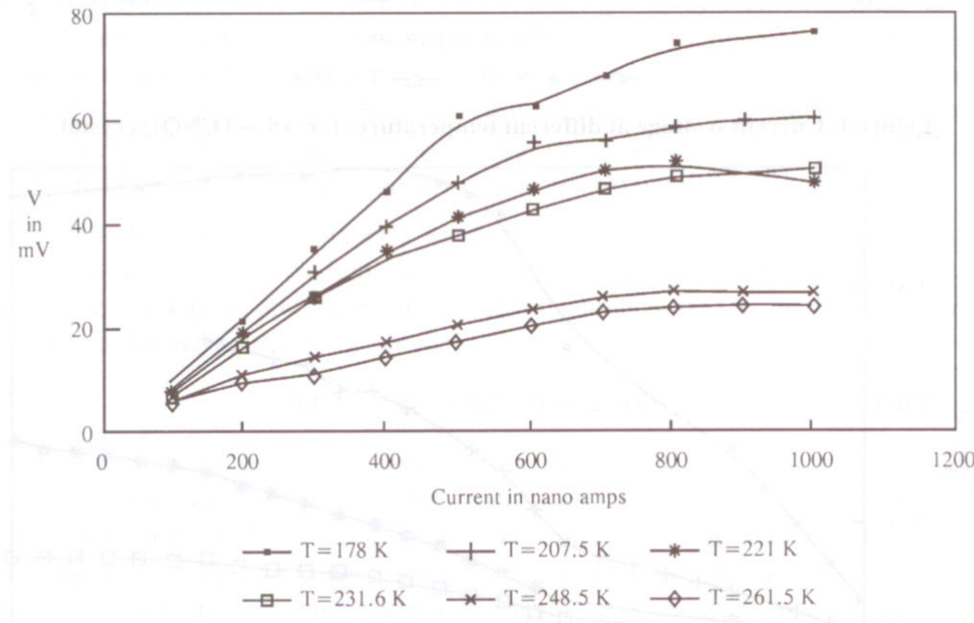

Figure 4. Current–voltage at different at different temperature for K–TCNQ single crystal

All the four samples studied Qn(TCNQ)$_2$ pellet, Ad (TCNQ)$_2$ single crystal, K–TCNQ single crystal and Cu_2O–TCNQ pellet, show ohmic behaviour at low currents and transition to non–ohmic (non–linear) region occurs at higher values of currents. In some cases at particular temperatures, a negative differential resistance region was observed e.g. for $Qn(TCNQ)_2$ at 69 K, and for K–TCNQ at 221 K. At very high values of currents either the voltage saturates or continues to increase, but not as in the non–ohmic region. In K–TCNQ and Cu_2O–TCNQ, we have observed switching at particular temperatures has been observed.

The non–linear behaviour of I–V characteristics in $Qn(TCNQ)_2$ and $Ad(TCNQ)_2$ has been explained on the basis of single carrier space charge limited current, where the current varies as some power of voltage. Mathematically, it can be expressed as

$$I = C V^K \quad ...(1)$$

where C and K are constants. Here, following three cases are there –

(i) $K \simeq 1$ (ohmic or linear region)

(ii) $K \simeq 2$ (square law region)

(iii) $K \simeq$ other than 1 and 2 (power law region)

The constants were calculated using least square fitting method. In $Qn(TCNQ)_2$ at 69 K, the values of C and K are found to be 7.95 and 0.412, respectively. For negative differential resistance region, the value of K in equation (1) is negative. In this region, C = 1.58 and K = – 0.068. This behaviour can be explained on the basis of Lampert and Rose model of double injection[20,21], whereas for higher values of currents, where voltage is continuously increasing with increase of current beyond non–linear power law region, it is clearly due to Schottkey emission.

The non–linear part of the I–V characteristics in two compounds K–TCNQ and Cu_2O – TCNQ has been fitted to equation

$$\sigma (E) = \sigma_a + \sigma_b \exp(-E_0 / E) \quad ...(2)$$

where σ_a is the ohmic conductivity and σ_b is the pre–exponential factor. E_0 being the characteristic electric field parameter; E is the applied electric field. The exponential dependence of σ on the applied electric field is suggestive of a tunneling mechanism. It has been proposed by Bardeen[22] that pinning of the charge density waves (CDW) can be represented by a small gap in the CDW excitation spectrum and Zenner type tunneling may occur across this gap.

It has been noted for both; K–TCNQ and Cu_2O–TCNQ that the saturation region comes at higher currents at all temperatures. This behaviour can be associated with a motion of CDW. Below the threshold field, the CDW is pinned to the lattice. A sufficient electric field is necessary to overcome this pinning energy, but the non–linear effects are strongly dependent on the crystal chemistry of the materials. It appears that pinning depends essentially on three factors, inter chain coupling, pinning by impurities and pinning caused by the gap to commensurability of the CDW with underlying lattice[23].

The negative differential resistance in K–TCNQ can be explained on the basis of dynamics of charged solitons and domain walls in the one dimensional molecular stacks of these types of crystals[24,25].

The switching has been observed in two samples, for K–TCNQ at T = 251.5 K and for Cu_2O–TCNQ at T = 183.6 K. There are different linear regions in which the system switches at particular values of currents. It is one conducting state (more resistive) to another conducting state (less resistive) through some intermediate highly conducting states. This can be seen more clearly in a plot of (dV/dI) versus I curves as shown in Figures 5 and 6.

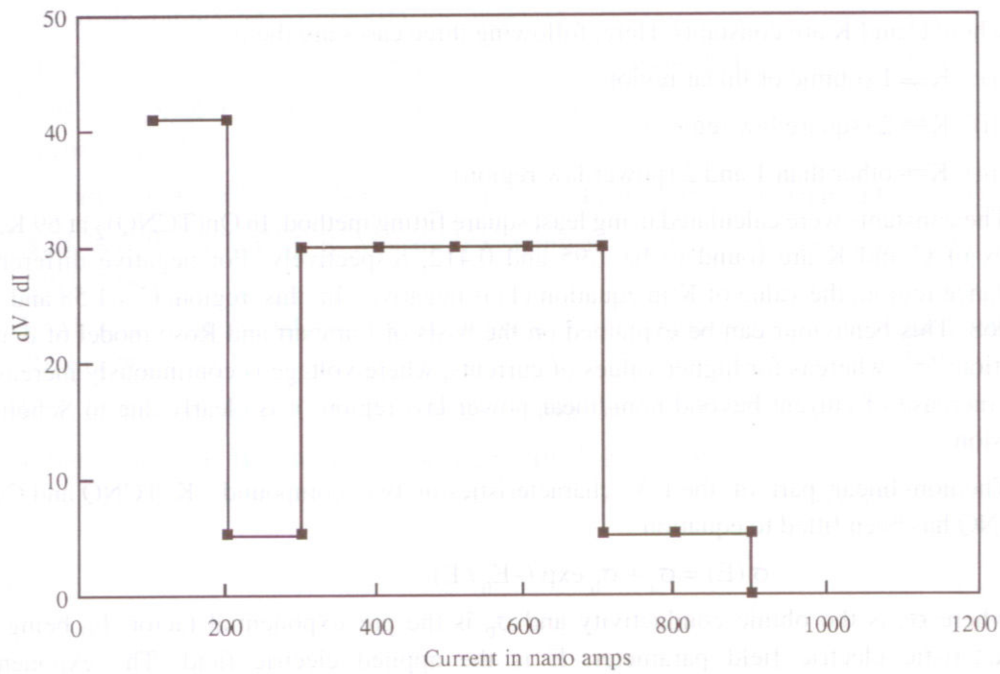

Figure 5. dV / dI Versus I of K–TCNQ Crystal at 251.5 K

To explain the above mentioned switching, it seems that the tunneling occurs between various macroscopically occupied states. A random distribution of CDW segments may be there due to inhomogenities, grain boundaries etc. The distribution of these CDW regions leads to a distribution of pinning energies. With the application of current, the various CDW regions are coupled together to develop a coherent current carrying state. Some of the regions, which remain uncoupled at lower values of currents may be coupled at higher values of currents to give another current carrying state. However, these explanations require further experimental investigations in presence of (DC + AC) electric field.

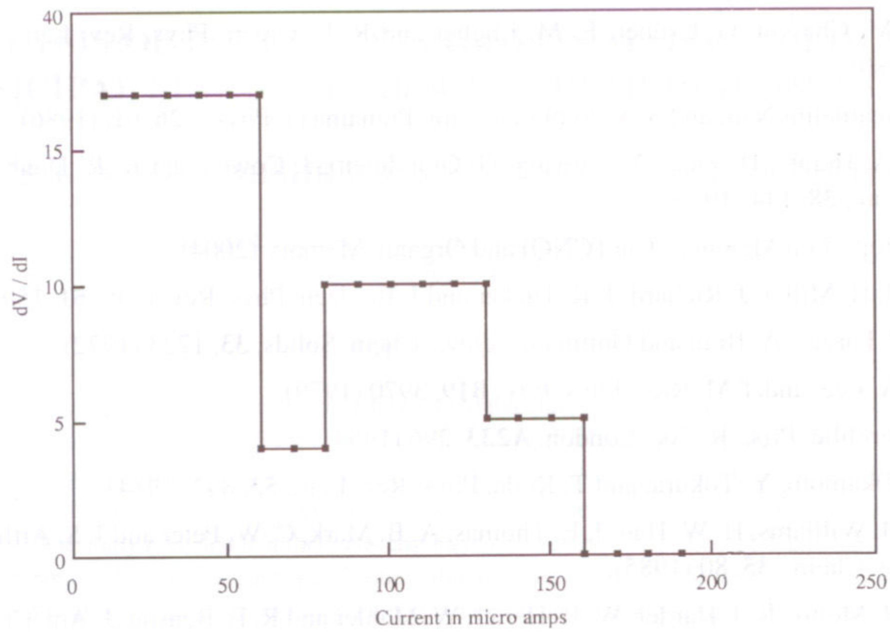

Figure 6. dV / dI versus I of Cu_2O – TCNQ

CONCLUSION

The basic feature of non–linear conduction observed in all the compounds $Qn(TCNQ)_2$, $Ad(TCNQ)_2$ K–TCNQ and Cu_2O–TCNQ are similar, however, their origins are different. The I–V characteristics are analyzed on the basis of space charge limited current and Schottkey emission for compounds having asymmetric donor molecules, which have disorder for example $Qn(TCNQ)_2$ and $Ad(TCNQ)_2$ and on the basis of tunneling model for compounds having symmetric donor molecules like K–TCNQ and Cu_2O–TCNQ. The negative differential resistance observed in $Qn(TCNQ)_2$ is explained on the basis of Lampert and Rose model of double injection, however, the negative resistance observed in K–TCNQ can be explained by dynamics of soliton type defects in bond ordered (dimerized) stacks of TCNQ molecules.

The switching observed in K–TCNQ and Cu_2O–TCNQ at particular temperatures is explained on the basis of different CDW current carrying states appearing at different values of applied currents due to coupling of various CDW regions.

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