

## Phase transformation and electrical resistivity of tetracyanoethylene under pressure

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**Abstract.** This paper reports the phase transformation behaviour of tetracyanoethylene (TCNE) under pressure as revealed by AC electrical resistivity, its time evolution and X-ray diffraction studies. An irreversible transformation from monoclinic to cubic phase occurs at  $2.1 \pm 0.1$  GPa and is indicated by a sharp resistivity drop at this pressure. The time evolution of resistivity studies indicate that this transformation occurs via an intermediate phase having resistivity higher than either of the two crystalline phases. Finally, the kinetics of phase transformations obtained by time evolution of resistivity is compared with the X-ray studies on the pressure quenched TCNE.

**Keywords.** Tetracyanoethylene; high pressure; electrical resistivity; X-ray diffraction; phase transformation kinetics.

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### 1. Introduction

Tetracyanoethylene (TCNE) is an organic molecular solid with the chemical formula  $C_2(CN)_4$ . Recently, it has evoked much theoretical and experimental interest for a variety of reasons (Chaplot and Mukhopadhyay 1986; Mukhopadhyay *et al* 1986). TCNE is used as one of the most common acceptors in electron donor/acceptor complexes exhibiting one-dimensional semiconducting and metallic properties (Mukhopadhyay *et al* 1985). The most important feature of this material is its peculiar phase transformations seen under pressure and temperature. Depending on the preparation conditions, such as the solvent used, temperature and the rate of evaporation, TCNE can be obtained either in the cubic or in the monoclinic structure (Bekoe and Trueblood 1960; Little *et al* 1971). Both the phases have been studied extensively by X-ray diffraction, neutron diffraction, differential scanning calorimetry, dielectric susceptibility, nuclear quadrupole resonance and Raman scattering (Murgich and Pissanetzky 1975; Mukhopadhyay *et al* 1985; Chaplot *et al* 1985; Chaplot and Mukhopadhyay 1986). At 318 K, the cubic (c) phase transforms sluggishly to the monoclinic (m) phase, but the reverse transformation does not occur even after cooling the sample down to 5 K. This is striking especially in view of ~5% better molecular packing of the c phase. Pressure, naturally, can be expected to affect significantly the transformation behaviour. *In situ* high pressure X-ray diffraction studies (Chaplot and Mukhopadhyay 1986) indicate that the m TCNE transforms to the c phase via an intermediate amorphous (a) phase. In the following, we report high

pressure studies on the AC electrical resistivity and its time evolution. These measurements on TCNE are supplemented with the X-ray diffraction on pressure quenched samples.

## 2. Experimental

TCNE is first purified from the commercially available grade by sublimation and is then prepared into the *m* phase, following the procedure described by Mukhopadhyay *et al* (1985). The electrical resistivity of TCNE is very high,  $\sim 100 \text{ M}\Omega \text{ cm}$ , necessitating AC resistivity measurements. A lock-in amplifier with a resolution of 10 nV and having an internal oscillator for providing reference signal is used as the measuring instrument. Powdered sample of *m* TCNE is mounted in a metal anvil cell, and electrical contacts are obtained through the anvils. Mica serves as the gasket material since its resistivity is about 5 orders of magnitude higher than that of TCNE. Frequency dependence of the AC electrical resistivity is studied up to 40 kHz and the results are shown in figure 1 (inset). It is seen that the resistivity remains constant for frequencies up to 5 kHz. We have, therefore, chosen to carry out all subsequent measurements at 3.9 kHz. Pressure is applied to the sample in steps of  $\sim 0.3 \text{ GPa}$  and the measurements are carried up to 6.5 GPa. Time evolution of resistivity (TER) at each pressure step is monitored with a view to study the kinetics of the phase transformations. Finally, all the samples after the pressure treatment have been studied by X-ray diffraction. It may be pointed out that in contrast to the *in situ* high pressure X-ray diffraction measurement reported in the earlier work (Chaplot and Mukhopadhyay 1986), we have performed this study on pressure quenched samples to find out the resultant phase(s).

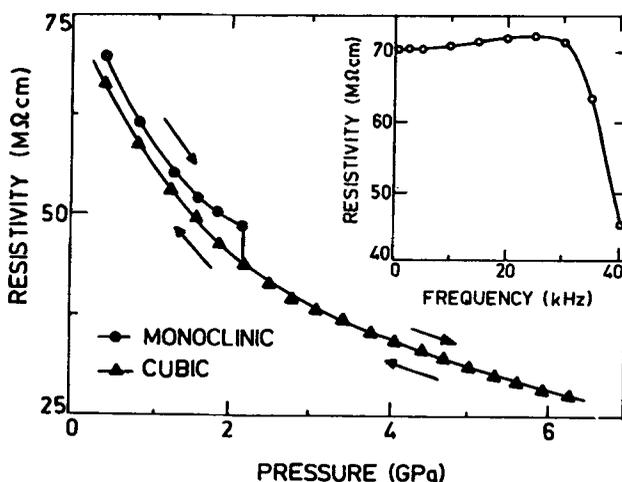


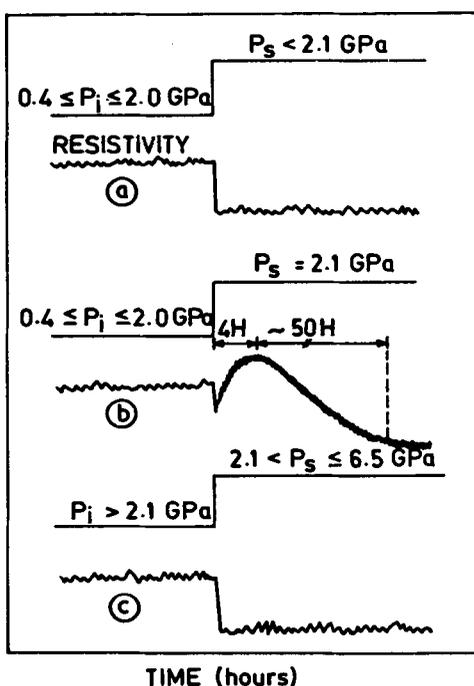
Figure 1. AC electrical resistivity behaviour of TCNE under pressure up to 6.5 GPa. Inset shows the frequency dependence of AC resistivity up to 40 kHz.

### 3. Results and discussion

Pressure variation of the AC electrical resistivity of TCNE is shown in figure 1. As reproducible electrical contacts are established only after 0.4 GPa, the data are presented above this pressure. It is seen that during the forward cycle, resistivity of the *m* TCNE decreases continuously with pressure. However, there is a sharp drop at 2.1 GPa, signalling a phase change. On further compression, resistivity again undergoes a normal decrease. This trend is noted up to 6.5 GPa.

On depressurising, in the range of 6.5 to 2.2 GPa, resistivity increases continuously along the path same as the forward one. Further, at 2.1 GPa, the resistivity does not exhibit any discontinuity in sharp contrast to the forward cycle. Finally, in the range of 2.1 to 0.4 GPa, there is a normal continuous increase. On recycling, from 0.4 GPa, the sample resistivity follows the lower path only.

In an effort to study the kinetics of phase transformation, TER has been investigated next. Defining the initial pressure, the soaking pressure and the soaking time as  $P_i$ ,  $P_s$  and  $t_s$  respectively, the treatment given to the sample is described by a set  $\{P_i, P_s, t_s\}$ . Here,  $P_s = P_i + \Delta P$ . As seen from figure 2a, for  $\{0.4 \lesssim P_i \lesssim 2.0 \text{ GPa}, P_s < 2.1 \text{ GPa}\}$ , TER shows normal feature and steady state is obtained within a very short  $t_s$ , typically, a few seconds. However, when  $\{0.4 \lesssim P_i \lesssim 2.0 \text{ GPa}, 2.1 \lesssim P_s \lesssim 6.5 \text{ GPa}\}$ , the TER indicates a strong time dependence. Specifically, the resistivity passes through a maximum and then decreases continuously with time attaining a steady state value which is smaller than its initial value. Figure 2b depicts a typical result which



**Figure 2.** Time evolution of electrical resistivity (TER) of TCNE at 3 typical pressures. (a)  $\{0.4 \lesssim P_i \lesssim 2.0 \text{ GPa}, P_s < 2.1 \text{ GPa}\}$ , (b)  $\{0.4 \lesssim P_i \lesssim 2.0 \text{ GPa}, P_s = 2.1 \text{ GPa}\}$  and (c)  $\{2.1 \lesssim P_i \lesssim 6.5 \text{ GPa}, P_s \lesssim 6.5 \text{ GPa}\}$ .

**Table 1.** X-ray diffraction results obtained on pressure quenched TCNE indicating the kinetics of the phase transformations. Phases present in trace quantities are given within parantheses.

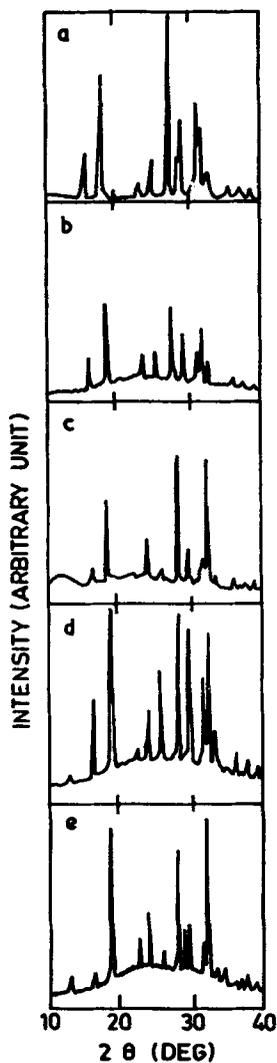
Initial pressure ( $P_i$ ) GPa	Soaking pressure ( $P_s$ ) GPa	Soaking time ( $t_s$ ) h	Remarks
As received sample		—	<b>m</b> (Figure 3a)
0.4–2.0	2.0	~ 50	<b>m</b> (Figure 3b)
0.4–2.0	2.1	4	<b>m*</b> (Figure 3c)
		~ 50	<b>m + (c)</b> (Figure 3d)
0.4–2.0	2.5	~ 50	<b>m + c</b> (Figure 3e)

\*A broad peak is seen at  $2\theta = 12.5^\circ$ .

corresponds to the condition  $\{0.4 \lesssim P_i \lesssim 2.0 \text{ GPa}, P_s = 2.1 \text{ GPa}\}$ . Further, when  $\{0.4 \lesssim P_i \lesssim 2.0 \text{ GPa}, P_s > 2.1 \text{ GPa}\}$ , a comparatively shorter  $t_s$  is required to complete the transformation. Finally when  $\{P_i \gtrsim 2.1 \text{ GPa}, P_s \lesssim 6.5 \text{ GPa}\}$ , as noted from figure 2c, features similar to that observed in the case of figure 2a are restored. On depressurising to 0.4 GPa and subsequent cycling, TER shows characteristics as depicted in figures 2a and 2c.

To learn more about the kinetics of the phase transformations, X-ray studies have been made on pressure quenched samples. Guided by the TER studies,  $t_s$  is varied appropriately for a given  $\{P_i, P_s\}$ , after which the pressure is released and X-ray diffraction pattern obtained.

Table 1 contains a summary of the post pressurised resultant phase(s) of TCNE obtained for the set  $\{P_i, P_s, t_s\}$ . The corresponding X-ray patterns, as shown in figure 3, are depicted in the following sequence. The diffraction pattern of the starting material confirms it to be in **m** phase, figure 3a. For  $\{0.4 \lesssim P_i \lesssim 2.0 \text{ GPa}, P_s = 2.0 \text{ GPa}, t_s = 50 \text{ h}\}$ , it is seen from figure 3b that the **m** phase is still retained. A few interesting features such as sharpening of the peaks and change in the relative intensities as compared to those in figure 2a can be noted. This could possibly be related to annealing of defects under pressure and changes in molecular orientations (Yousuf *et al* 1986; Chaplot 1985). When  $\{0.4 \lesssim P_i \lesssim 2.0 \text{ GPa}, P_s = 2.1 \text{ GPa}\}$ , a broad peak starts appearing in the low angle region. Referring to figure 3c, obtained after a  $t_s$  of about 4 h, a broad peak is seen at  $2\theta = 12.5^\circ$ , the origin of which is not known. The other sharp peaks are completely indexable in terms of the **m** phase. When  $t_s \simeq 50 \text{ h}$ , complete transformation to the **c** phase occurs, as evidenced by the present resistivity and by earlier *in situ* X-ray diffraction studies (Chaplot and Mukhopadhyay 1986). However, X-ray diffraction of the pressure quenched samples revealed differences in that the pattern shown in figure 3d for  $\{0.4 \lesssim P_i \lesssim 2.0 \text{ GPa}, P_s = 2.1 \text{ GPa}, t_s \simeq 50 \text{ h}\}$  indicates the presence of mostly **m** phase with traces of **c** phase. Figure 3e depicts the X-ray diffraction result on the pressure quenched sample retrieved after the treatment  $\{0.4 \lesssim P_i \lesssim 2.0 \text{ GPa}, P_s = 2.5 \text{ GPa}, t_s \lesssim 50 \text{ h}\}$ . Here the gross features are similar to that of figure 3d, but an increased quantity of **c** phase is observed. It is worth noting at this juncture that we could not see any evidence for the **a** phase in our X-ray work on pressure quenched samples. We believe this to be due to the **a** phase being unstable and transforming either to the metastable **c** phase or to the stable **m** phase when pressure is released.



**Figure 3.** X-ray diffraction patterns of the pressure quenched TCNE samples. (a) initial **m** phase, (b) **m** phase for  $\{0.4 \leq P_i \leq 2.0 \text{ GPa}, P_s = 2.0 \text{ GPa}, t_s = 50 \text{ h}\}$ , (c) **m** phase for  $\{0.4 \leq P_i \leq 2.0 \text{ GPa}, P_s = 2.1 \text{ GPa}, t_s = 4 \text{ h}\}$  with an extra broad peak at  $2\theta = 12.5^\circ$ , (d) **m** + (c) phases for  $\{0.4 \leq P_i \leq 2.0 \text{ GPa}, P_s = 2.1 \text{ GPa}, t_s \approx 50 \text{ h}\}$ , and (e) **m** + (c) phases for  $\{0.4 \leq P_i \leq 2.0 \text{ GPa}, P_s = 2.5 \text{ GPa}, t_s \leq 50 \text{ h}\}$ . {In figures (b), (c), (d) and (e), the background is due to the glass sample holder.}

From the above TER studies, it is clear that at 2.1 GPa, the **m** TCNE transforms to **c** phase via an intermediate phase. It now remains to interpret figures 1 and 2 in the light of the present X-ray work on pressure quenched TCNE and the *in situ* high pressure X-ray work performed previously (Chaplot and Mukhopadhyay 1986). The sharp drop in resistivity at 2.1 GPa appearing in figure 1 can be due to the transformation **m**-**a**-**c**. Figure 2b now tells us that the appearance of the **a** phase is signalled by the increase in resistivity and that its conversion to the **c** phase starts when the resistivity reaches a maximum. Finally, it turns out that the resistivity of

the **a** phase is larger than either of the crystalline phases and that the resistivity of the **c** phase is smaller than the **m** phase.

#### 4. Summary

Under pressure, TCNE transforms from the monoclinic to the cubic via an amorphous phase at 2.1 GPa. The interesting observation is that the kinetics of the **m-a** transformation is an order of magnitude faster than that of **a-c**. Further, the transformation kinetics associated with the **m-a-c** becomes faster with increasing soaking pressure, and that the resistivities of **m** and **c** phases are smaller than that of the **a** phase. Also, the resistivity of the **c** phase is smaller than that of the **m** phase. Finally, absence of the **a** phase and retention of the **c** phase in pressure quenched samples are also noted.

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