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Structural changes in tetracyanoethylene at high pressures: neutron diffraction study

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Abstract

We report on structural changes in monoclinic tetracyanoethylene, $C_2(CN)_4$ as studied by *in situ* high-pressure (0–5 GPa) neutron powder diffraction experiments. Structural parameters were obtained by Rietveld profile refinement of the diffraction pattern up to $P = 2.5$ GPa. Above this pressure the width parameter is found to diverge, indicating pressure-induced disordering at 2.5 GPa. The recovered sample, on release of pressure from 5 GPa, is found to have transformed to a graphite-like amorphous structure. The transformation to a graphite-like material has been verified by an independent high-pressure x-ray diffraction experiment.

1. Introduction

Tetracyanoethylene (TCNE), C_2CN_4 , a member of the substituted ethylene group, shows a variety of interesting chemical and physical properties. The molecular conformation of TCNE is shown in figure 1. The interest here mainly stems from its peculiar phase transitional behaviour [1–7]. TCNE exists in a cubic phase [8] (space group = $Im\bar{3}$, $Z = 6$) at low temperature and in a monoclinic phase [9] (space group = $P2_1/n$, $Z = 2$) at high temperature. The cubic phase undergoes a sluggish phase transition to a monoclinic phase at 320 K [1] and it is irreversible on cooling down to 4 K [9]. It is a first-order transition and this is one of the few systems known so far showing a transition from a high-symmetry to a lower-symmetry phase on increase of temperature. The different phases of TCNE and its transition from one to the other were described in detail in [1]. Briefly, depending on the temperature of growth, different phases will result. Crystals grown by slow evaporation from the solution of TCNE in ethyl acetate kept at 270 K are in the cubic phase. Monoclinic TCNE was obtained from the solution kept at room temperature. Cubic-to-monoclinic transition could easily be initiated by heating the sample above 320 K, but the reverse transition was not observed even upon lowering the temperature to 4 K [1, 9]. This clearly indicates the existence of a large potential barrier along the transition path towards the monoclinic-to-cubic phase transition.

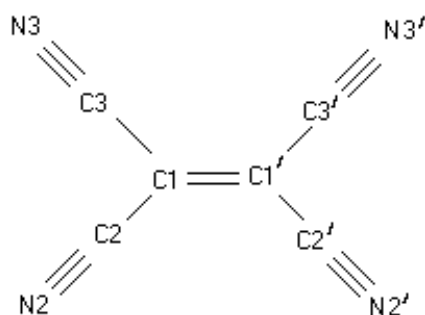


Figure 1. A schematic diagram of the molecular conformation of TCNE.

The molar volumes in the cubic and monoclinic phases are 154 and 162 Å³ respectively [1]. This means that the molecular packing in the cubic phase is denser by about 5% than in the monoclinic phase; therefore the reverse transition to the cubic phase was expected to initiate at high pressure [10]. *In situ* high-pressure x-ray diffraction experiments, at room temperature, showed that the reverse transition does indeed occur at about 2.1 GPa but via an intermediate phase [2]. The intermediate phase is found to be devoid of any sharp Bragg peak and only a few very broad peaks are seen. This phase had been identified as an amorphous phase, meta-stable in character, transforming slowly to the stable cubic phase. It may be noted that the high-pressure cubic phase was observed earlier in an independent experiment [3] and was confirmed later, when more details were revealed [2].

The kinetics of the phase transition was studied by monitoring the time evolution of the resistivity as a function of pressure [5]. At 2.1 GPa the resistivity was found to increase at first, reaching a maximum after 4 h, and then it started decreasing and settled down after 40 h. On decreasing the pressure from 2.1 GPa it was found that the resistivity was less than that of the monoclinic phase at any pressure. The increase of the resistivity as a function of time after pressurizing to 2.1 GPa was attributed to lattice disorder, and the phase with lower resistivity identified with the cubic phase. The topic of crystalline-to-amorphous transitions under pressure has recently received a lot of interest [11]. TCNE is a very simple molecular system showing crystal-to-amorphous transition at rather low pressure, and is probably the only system showing a phase transition sequence from a crystalline to an amorphous and again to another crystalline phase.

High-pressure infrared studies [6] on TCNE reported that the monoclinic TCNE transformed reversibly to a high-pressure phase at about 3 GPa. The high-pressure phase was not identified as the cubic phase. Similar results were obtained in Raman experiments [4]. We believe that in both cases the laser heating prohibited the transition to the cubic phase, as the laser heating in Raman scattering or IR experiments may raise the sample temperature above $T_c = 320$ K when the monoclinic phase is the stable phase at ambient pressure. In another experiment [7], the monoclinic-to-cubic transition was observed and was believed to be caused by high-power x-rays. Reference [7] reports that a new crystalline phase is observed at 3.5 GPa, which is neither monoclinic nor cubic. This was not observed in our earlier x-ray diffraction studies [2]. Later in this paper we shall present a comparison of the data, which suggests that essentially similar structures were observed in the two previous x-ray experiments [3, 7] as well as in the present neutron work, although they were interpreted differently.

2. Experimental

Neutron diffraction experiments were carried using the POLARIS neutron diffractometer [12] at the ISIS facility and the Paris–Edinburgh high-pressure cell [13] in the pressure

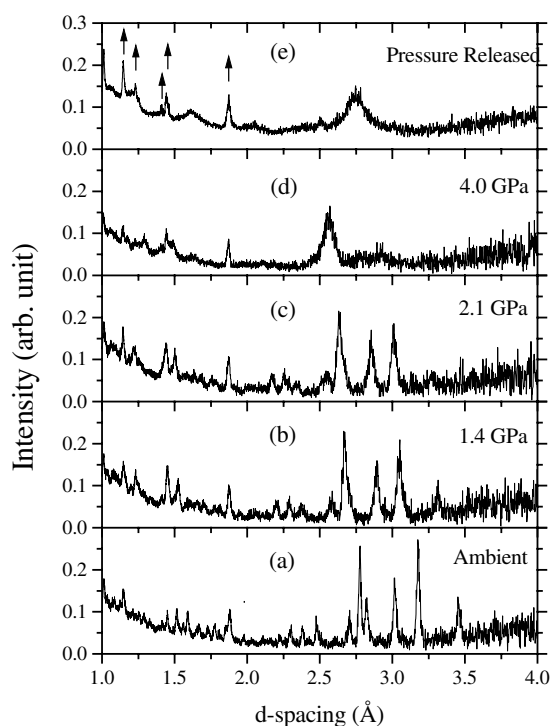


Figure 2. Evolution of the neutron powder diffraction pattern of TCNE with pressure: (a) at ambient pressure; (b) at 1.4 GPa; (c) at 2.1 GPa; (d) 4.0 GPa; and (e) after pressure was released (see the text). Arrows indicate diffraction peaks arising from the pressure-cell material.

range 0–5 GPa. The cell is an opposed-anvil device and the sample volume was about 90 mm^3 in spheroidal shape. Neutrons scattered at a fixed scattering angle of $2\theta = 90^\circ$ were analysed by the time-of-flight method.

Commercially available TCNE (Merck, Germany) was recrystallized into the monoclinic phase from a solution in ethyl acetate. Powder monoclinic TCNE samples were pre-compressed and then loaded in the pressure cell for diffraction experiments. No pressure calibrant was used, as mixing with the salt may have an effect on the phase transitional behaviour of TCNE; in particular when the system goes to the amorphous phase, the impurities (like salt) may change the path of transition. In our earlier x-ray studies also, no pressure calibrant was used. The pre-calibrated oil pressure is used as the measure of the pressure here.

3. Results and discussion

The diffraction data were analysed using the Rietveld profile refinement technique [14], assuming the monoclinic phase (space group $P2_1/n$, $Z = 2$). The refinements were carried out using the time-of-flight least-squares program TF14LS available at ISIS [15] in the time-of-flight range 6000–18 000 μs (corresponding d -spacings = 1.3–4 Å). Diffraction peaks due to the pressure cell were excluded from the refinement. To start with, the pattern obtained with the sample in a vanadium can was used for refinement. With the same set of parameters, the pattern for the sample in the high-pressure cell at ambient pressure was refined. Refinements obtained with the sample in the vanadium can and in the high-pressure cell were very similar.

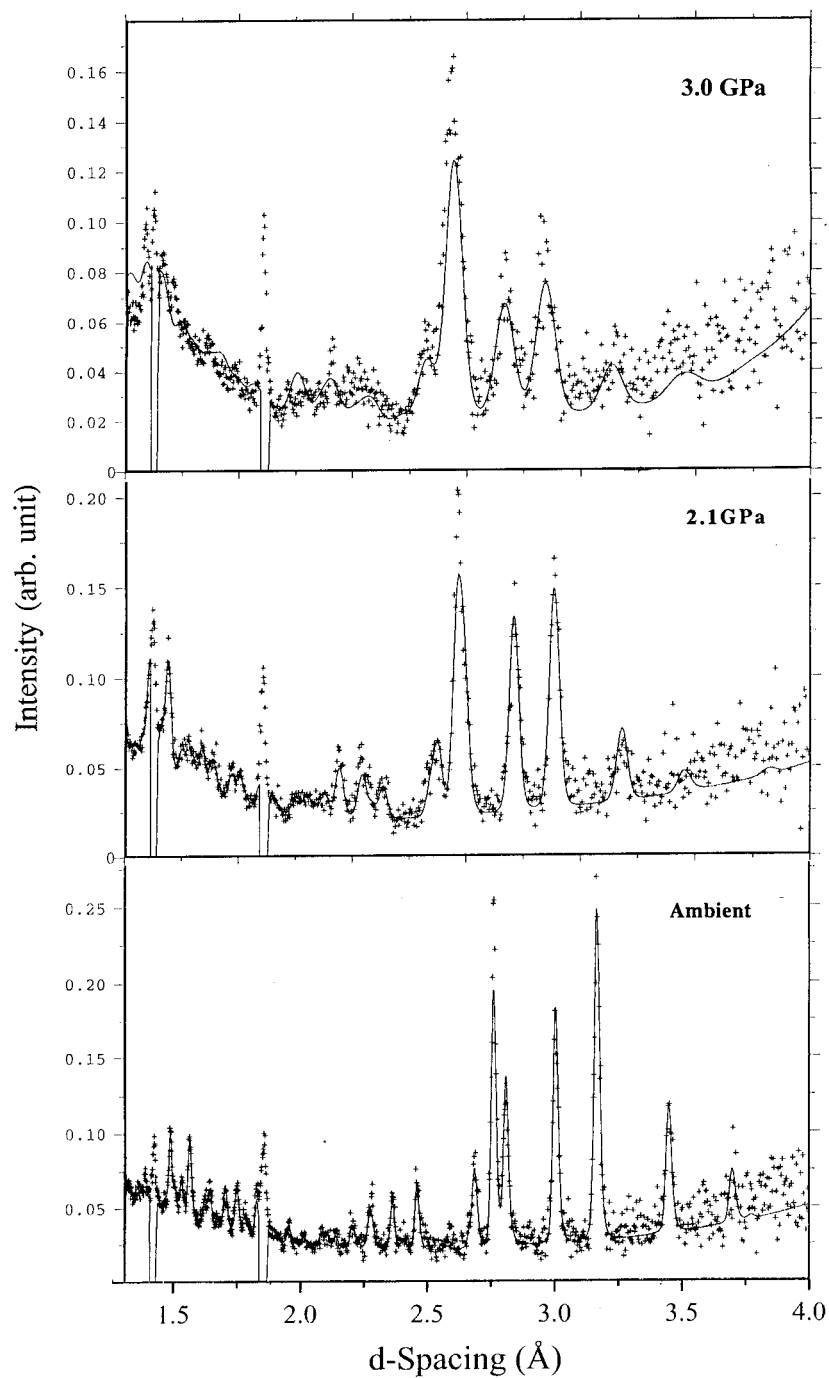


Figure 3. Typical Rietveld profile refinements of neutron powder diffraction patterns of TCNE at different pressures. Symbols show the experimental data and the solid curves represent the refined profile. The line broadening with pressure is clearly evident. Peaks contributed by the pressure cell (as shown by arrows) are excluded from the refinement.

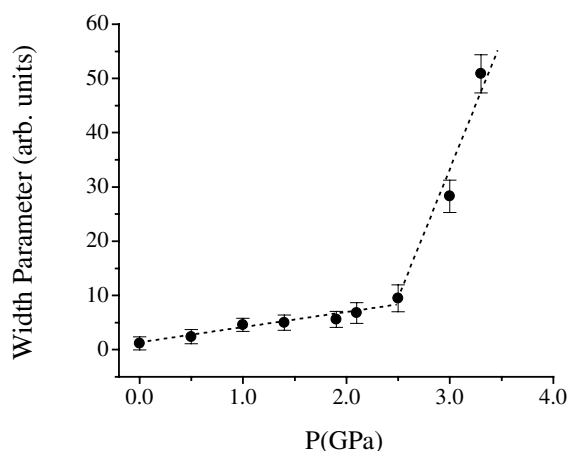


Figure 4. The variation of the width parameter with pressure. The dashed line is a guide to the eye. The width parameter increases abruptly above 2.5 GPa.

The data were not corrected for the attenuation by the pressure-cell materials. The refinement of the diffraction patterns at higher pressures needed larger and larger linewidth parameters. Up to 2.5 GPa the diffraction peaks broadened continuously and on further increase of the pressure the linewidths tended to diverge much faster. Profile refinement was carried out up to 3.3 GPa, although, with the diverging peak widths and noise in the data, the refined structural parameters—namely the bond lengths, thermal parameters etc—were not physically realistic above 2.5 GPa. Figure 3 shows the typical profile refinement of the patterns at different pressures. The variation of the width parameter with pressure is shown in figure 4. The diverging peak width above 2.5 GPa (figure 4) and dominance of only a couple of broad peaks in the diffraction patterns (figures 2 and 3) are indicative of a reduced particle size or amorphization. Above 3.3 GPa the peaks broadened considerably and the pattern (figure 2(d)) is dominated by one broad peak at about 2.6 Å (in d -spacing). The structure at 4 GPa may be described as a nanophase rather than a truly amorphous phase, since the peak widths are still smaller than typical widths for the amorphous structures. The average particle size estimated from the width of the peaks at 4 GPa is about 8 nm.

In figure 5, we show the diffraction patterns which indicated a structural change from the monoclinic phase at high pressure as obtained from the different experiments: (a) our earlier x-ray study (2.5 GPa) [2]; (b) present work (3.3 and 4 GPa); and (c) a recently reported x-ray study (4.8 GPa) [7]. The similarity of the patterns is obvious despite the differences in absolute value of the pressures indicated, which could be due to inappropriate pressure calibrations in (a) and (b). All the patterns are dominated by a broad peak at a Q -value of about 2.4 \AA^{-1} and also show a few weaker peaks, suggesting that the nature of the structures observed in the three experiments are essentially similar. We believe that the structure above 3 GPa should not be interpreted as a new crystalline high-pressure phase and is more likely to be an amorphous or a nanophase, modified from the low-pressure monoclinic phase.

From the refined structural parameters, we find that the smallest interatomic distance between neighbouring molecules occurs between a C1 of one molecule and an N3 atom of another molecule (figure 1). This smallest non-bonded separation reduces from 3.05 Å at $P = 0$ to 2.81 Å at 2.5 GPa. As the smallest non-bonded interatomic separation reduces significantly below the sum of the van der Waals radii of the corresponding atoms ($\sim 3.2 \text{ \AA}$), there is a possibility of a phase transition, amorphization or chemical changes such as polymerization etc.

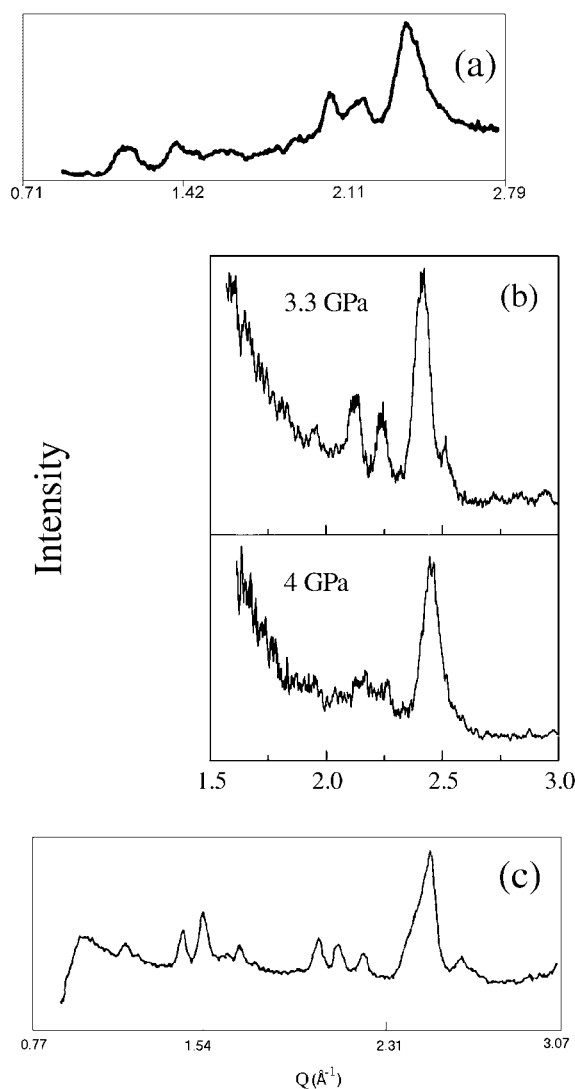


Figure 5. Comparison of the diffraction patterns which indicated a structural change from the monoclinic phase at high pressure as obtained from: (a) our earlier x-ray study [2] at 2.5 GPa; (b) the present study at 3.3 and 4.0 GPa; and (c) an x-ray study [7] at 4.8 GPa.

Tables 1 and 2 give the refined lattice parameters and the coordinates of the atoms in the asymmetric unit respectively. The interatomic distances at different pressures are given in table 3. The variation of the lattice parameters with pressure is shown in figure 6. Except the monoclinic angle β , the parameters show smooth variation with pressure. β shows a discontinuous change above 2.5 GPa, similar to that observed in the width parameter (figure 4). The variation of the unit-cell volume (V) versus pressure is shown in figure 7. The data were fitted to the Birch–Murnaghan equation of state [16]:

$$P = \frac{3}{2}K_0(\eta^{7/3} - \eta^{5/3})\left[1 + \frac{3}{4}(K' - 4)(\eta^{2/3} - 1)\right]$$

where K_0 is the bulk modulus at zero pressure, $K' = (dK/dP)_{P=0}$ and $\eta = V_0/V$. The solid curve in figure 7 is the least-squares fitted curve. The fitted values are $K_0 = 6.9 \pm 0.5$ GPa

Table 1. Refined lattice parameters of monoclinic TCNE (space group $P2_1/n$, $Z = 2$) at different pressures.

Parameter	Ambient	At 2.5 GPa
a (Å)	7.4843(5)	7.061(6)
b (Å)	6.1997(4)	5.808(4)
c (Å)	6.9858(5)	6.556(5)
β (deg)	97.25(5)	97.00(6)
V (Å ³)	321.5	267.0
R_p (%)	8.1	13.9

Table 2. Fractional atomic coordinates of monoclinic TCNE at different pressures.

Atom	Coordinates					
	Ambient			At 2.5 GPa		
	x	y	z	x	y	z
C1	0.0016(8)	-0.0335(11)	-0.0927(8)	0.009(3)	-0.028(6)	-0.089(4)
C2	0.0880(8)	0.0792(11)	-0.2227(10)	0.076(4)	0.093(6)	-0.246(6)
C3	-0.0752(8)	-0.2438(13)	-0.1495(10)	-0.082(4)	-0.285(6)	-0.144(6)
N2	0.1467(6)	0.1738(8)	-0.3387(7)	0.150(4)	0.177(3)	-0.358(3)
N3	-0.1371(6)	-0.4070(9)	-0.1895(7)	-0.143(2)	-0.427(4)	-0.213(4)

Table 3. Interatomic distances in monoclinic TCNE at different pressures and that of the recovered sample (graphite-like amorphous carbon).

Pressure	Bond lengths (Å)		
	C1–C1	Average C1–C2	Average C–N
Ambient	1.36 ± 0.01	1.42 ± 0.01	1.13 ± 0.01
2.1 GPa	1.34 ± 0.05	1.51 ± 0.04	1.06 ± 0.04
2.5 GPa	1.24 ± 0.06	1.52 ± 0.05	1.04 ± 0.05
Recovered sample	1.42 (first peak in $g(r)$)	2.46 (second peak in $g(r)$)	

and $K' = 7 \pm 1$. Our value of K_0 is higher than that reported from the Brillouin scattering measurements (5.6 GPa) [17] and lower than that reported in the recent x-ray diffraction study ($K_0 = 9.5$ GPa and $K' = 4.9$) [7].

On increasing the pressure above 4.5 GPa, we made an unexpected observation: the load (oil pressure) was observed to reduce by 20% by itself; this was also reflected in the diffraction pattern. The broad peak observed at 2.55 Å at 4.5 GPa shifted to 2.75 Å on the reduction of the load, indicating a drop in sample pressure. The pattern did not show any further shift on release of pressure (figure 2(e)), suggesting that the sample pressure had already reduced to the ambient value. The recovered sample had turned black, whereas the starting sample was white. This probably corresponds to polymerization of TCNE molecules, as suggested earlier [3, 6]. It was a permanent change, which inhibited any possibility of the transition to the cubic TCNE phase.

Most surprisingly the diffraction pattern of the ex-pressure-cell sample taken after three days had elapsed showed several new broad peaks with no similarity to those of cubic or monoclinic TCNE. The structure factor, $S(Q)$, obtained from the neutron diffraction pattern of

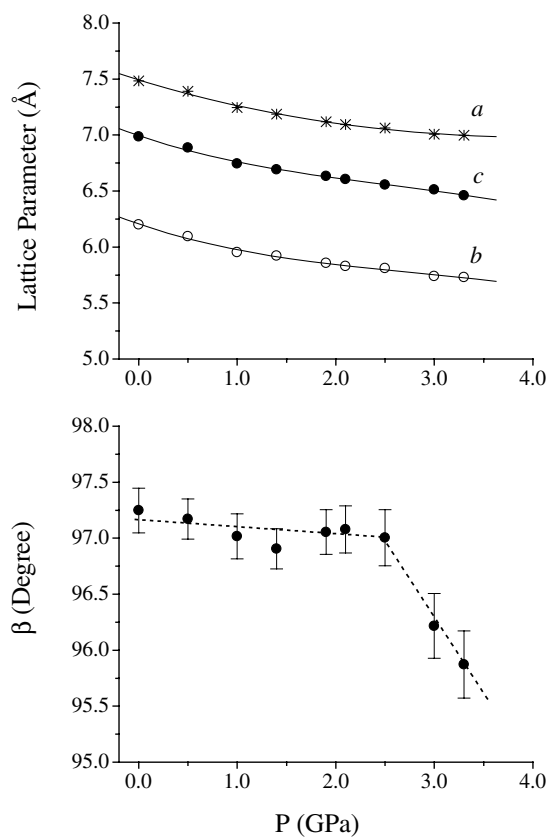


Figure 6. The variations of the lattice parameters of monoclinic TCNE with pressure as obtained from the refinements. Only the monoclinic angle shows a sharp variation at 2.5 GPa which is concurrent with the variation of the width parameter as shown in figure 4. Curves are guides to the eye.

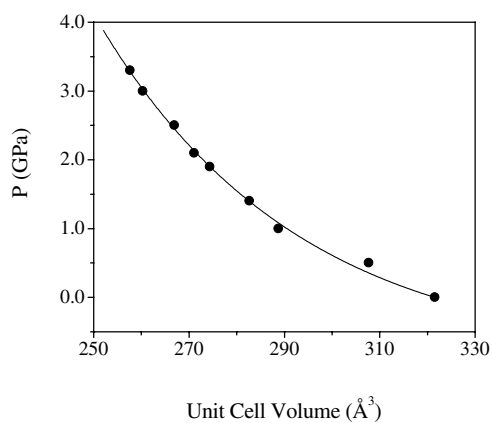


Figure 7. The pressure–volume relation of monoclinic TCNE. The experimental points are represented by solid circles and the curve is the fitted Birch–Murnaghan equation of state (see the text).

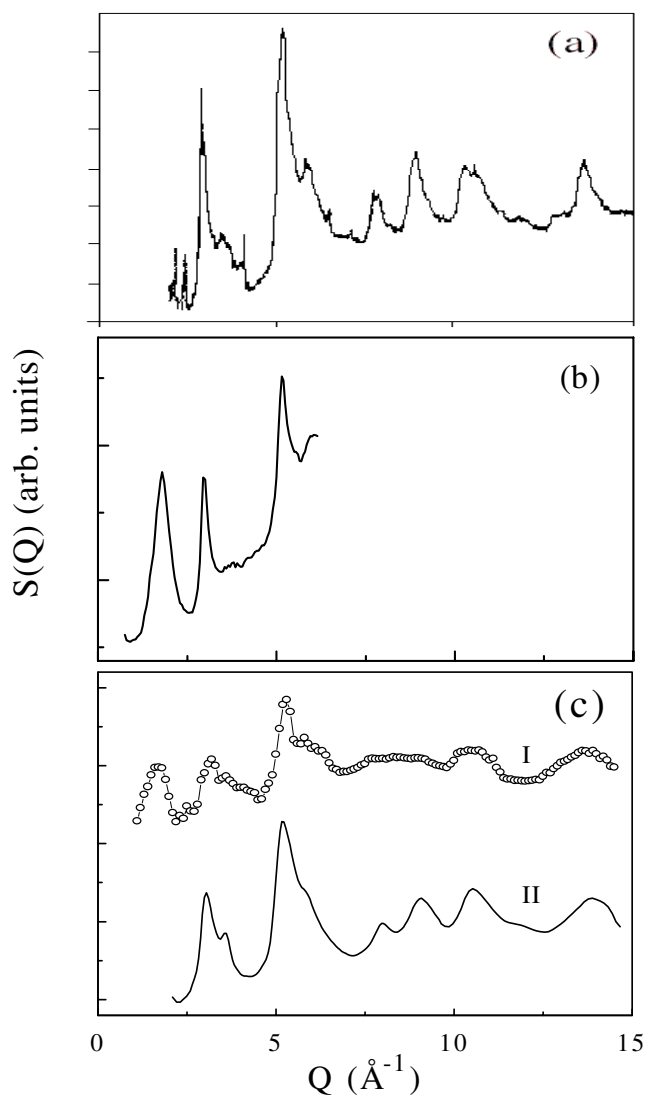


Figure 8. The structure factor, $S(Q)$, obtained: (a) from the neutron diffraction pattern of the ex-pressure-cell sample of TCNE taken after three days of pressure release; (b) from the x-ray diffraction pattern from a similar independent experiment; (c) (curve I) from neutron diffraction of amorphous carbon and (curve II) from the theoretical calculation by Guet and Tchoubar [19] for a graphite-like amorphous carbon phase containing very small polymeric domains.

the recovered sample at this stage is shown in figure 8(a). It compares well with that obtained from amorphous carbon (figure 8(c), curve I) prepared by a different method [18] and also with the $S(Q)$ calculated (figure 8(c), curve II) by Guet and Tchoubar [19] for a graphite-like amorphous carbon phase containing very small polymeric domains.

We carried out further experiments using the x-ray diffraction technique at Trombay, to investigate this unusual observation. The structure factor obtained from the x-ray diffraction pattern from a recovered sample after pressurizing TCNE to about 5 GPa is shown in figure 8(b). The clear correspondence of the recovered sample with amorphous

carbon (figure 8(c), curve I) is evident. A Fourier analysis of the recovered sample clearly demonstrates that the sample is graphite (table 3); no peak corresponds to the earlier C–N as in TCNE. It is clear that some chemical change has occurred in the sample; nitrogen somehow escapes from the sample. Chemical analysis of the recovered sample showed that the quantity of nitrogen remaining in the sample was much less (C:N=7:1) than that present in TCNE (C:N=3:2), which corroborated the observation of the diffraction techniques.

4. Conclusions

Structural changes in monoclinic TCNE at high pressures have been studied by *in situ* neutron powder diffraction in the pressure range 0–5 GPa. Data show that disordering in TCNE starts at ~2.5 GPa and completes at about 4 GPa. Rietveld profile refinement of the powder pattern carried out up to 3.3 GPa shows that the width parameter diverges above 2.5 GPa. The bulk modulus of 6.9 GPa obtained by fitting the pressure–volume result to the Birch–Murnaghan equation of state agrees fairly well with the earlier reported value. It is also found that TCNE probably polymerizes at about 4.5 GPa and it further transforms to a graphite-like amorphous carbon structure some time after the release of pressure.

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