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Pressure-induced transitions in tetracyanoethylene: a Raman scattering study

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Abstract

We report the results of high-pressure Raman scattering studies of the cubic and monoclinic polymorphs of tetracyanoethylene (TCNE). The evolution of the Raman spectrum at high pressures suggests that the cubic form is stable up to about 8 GPa. Subsequent pressurization leads to a gradual loss of transparency, and the sample becomes opaque to visible light above 14 GPa. In the monoclinic samples, qualitative changes are observed in the Raman spectrum above 3.6 GPa which indicate a subtle phase transition around this pressure. These changes are reversible when the pressure is reduced from peak values of about 4.5 GPa. At still higher pressures, the sample progressively becomes black, similar to what is observed in cubic TCNE. The Raman spectrum of the sample above 7 GPa is indicative of polymerization of TCNE. The spectrum of the pressure cycled opaque phase shows broad features characteristic of an amorphous phase, which is understood as being due to random cross-linking of TCNE in the pressure-reducing cycle.

1. Introduction

The molecular crystal tetracyanoethylene (TCNE) is widely studied in the interest of basic as well as applied research. Owing to its high electron affinity, this molecule forms many charge transfer complexes with a variety of electron donors. These charge transfer complexes are reported to exhibit exotic electrical, magnetic and other physico-chemical properties [1, 2]. Recently an interesting TCNE-based compound has been synthesized [3] wherein the magnetization states can be switched using visible light of different wavelengths. TCNE is also known to polymerize under different physical conditions and these polymeric films are expected to find applications in several electronic devices [4, 5].

Interest in basic research in TCNE stems from the rather unusual phase transition behaviour exhibited by this system. TCNE in solid form is known to exist in two crystalline phases, the cubic [6] and the monoclinic phase [7], of which the cubic form (space group: $Im3$; $Z = 3$) is supposed to be the stable form at ambient conditions. Experimental studies on the temperature-induced phase transition revealed that the cubic phase transforms into the monoclinic phase (space group: $P2_1/n$; $Z = 2$) above 318 K irreversibly [8]. The high-pressure behaviour of both polymorphs was also studied using Raman spectroscopic techniques [9]. These investigations, which were restricted to the external modes, revealed that the Raman intensities vanished completely above 3 GPa in the monoclinic samples and above 5 GPa in the cubic samples. High-pressure x-ray diffraction experiments in a piston-cylinder apparatus revealed that the monoclinic phase exhibits a unique pressure-induced transition to the cubic phase through an intermediate amorphous phase between 2 and 2.5 GPa [10]. As the cubic unit cell has volume lower than that of the monoclinic phase by about 5%, the application of pressure on the monoclinic phase was expected to induce a transition to the cubic phase [10]. Free energy minimization calculations by Chaplot [11] suggested that while the two phases have nearly the same static potential energy, the monoclinic phase is stable at high temperatures due to its higher vibrational entropy and the cubic phase is stable at high pressures due to its lower volume. However, high-pressure Raman spectroscopic measurements indicated that the monoclinic form did not exhibit a transition to the cubic form up to 3 GPa [9]. This behaviour was attributed to the effect of laser heating of the sample. High-pressure AC resistivity measurements [12] on monoclinic TCNE indicated a phase transition around 2.1 GPa. The kinetics of this transition was also investigated in detail from the time evolution of resistivity [12]. Subsequent infrared absorption [13] and powder x-ray diffraction measurements [14] on monoclinic TCNE indicated a reversible transition to a new high-pressure phase above 3.5 GPa, which was different from the cubic form. A recent neutron diffraction study on monoclinic TCNE suggested a transition to a disordered/nanostructured phase above 2.5 GPa [14]. Further, the sample recovered from pressures of about 5 GPa was found to have transformed into a graphite-like amorphous structure [15]. Raman scattering measurements by Chaplot *et al* [9] on the cubic polymorph indicated a subtle transition around 1.3 GPa, whereas their x-ray diffraction measurements suggested that the cubic phase was stable up to about 8 GPa. In addition to these structural changes, both these polymorphs have been claimed to polymerize [13, 14] beyond certain pressures.

In spite of considerable studies on the high-pressure behaviour of TCNE, there are still a few aspects that are not fully understood. In particular, there is no conclusive evidence for the existence of a structural transition around 2.5–3.5 GPa in monoclinic TCNE. Another aspect is the pressure-induced polymerization, which is one of the expected high-pressure phenomena in certain molecular crystals when the strength of the inter- and intra-molecular interactions becomes comparable. As this involves the formation of additional bonds, solid state polymerization is expected to be associated with a large activation barrier and is usually observed at high-pressure and high-temperature conditions, as also reported in C_{60} [16], CO_2 [17], etc. There are a few molecular solids such as acetylene [18] that are reported to polymerize solely under the application of pressure. Such systems are interesting from the point of view of theoretical investigation as well, to study the nucleation and growth of the polymerization process [19]. We have carried out Raman scattering studies at high pressures on both the cubic and monoclinic phases of TCNE to reexamine the stability range, the nature of the high-pressure phases and pressure-induced polymerization/amorphization properties.

2. Experimental details

Raman scattering measurements at high pressure were performed in a gasketed diamond anvil cell (DAC), Diacell Products, UK, Model B-05, with octagonal diamond flats of about 600 μm diameter culets. The cubic and the monoclinic crystals were grown by evaporation of TCNE solution in ethyl acetate, at temperatures of 270 and 320 K respectively. Transparent crystal bits of TCNE, typically of about 100 μm size, were loaded in the gasket hole along with ruby chips. TCNE dissolves in commonly used pressure-transmitting media such as methanol–ethanol mixture, and water. A large luminescence background was observed with silicone oil and hence no pressure-transmitting medium was used in the present set of experiments. The pressure inside the DAC was estimated using the standard ruby fluorescence technique. Pressure inhomogeneity across the laser spot size ($\sim$25 μm) was estimated from the width of the R_2 line [20], which was typically about ± 0.5 GPa at 5 GPa for the monoclinic samples and ± 1 GPa at around 12 GPa for the cubic samples. Raman spectra were excited using the 514.5 nm line of an Ar^+ laser. The power on the sample was kept at about 30 mW. Scattered radiation, collected in the back-scattering geometry, was analysed using a home-built 0.75 m double monochromator [21] with a 1800 lines/mm ruling holographic grating and detected by a cooled photomultiplier (GaAs photo cathode) operated in photon counting mode. Some of the high-pressure measurements were also carried out in a CCD-based (Andor Technology) multi-channel Raman spectrometer [22]. The instrument resolution for the scanning monochromator was $\approx$3 cm^{-1} with 250 μm slit width and the spectral reproducibility was within ± 0.5 cm^{-1} [21]. The instrument resolution in multichannel spectrometer is about 3 cm^{-1} for a 25 μm slit opening. The peak position and width (FWHM) of different modes were determined by fitting the profile using a Lorenzian line shape for individual modes.

3. Results

3.1. Vibrational characteristics of TCNE

As mentioned in the introduction, the cubic form of TCNE is stable at ambient conditions, and it transforms irreversibly into the monoclinic phase at 318 K. The molecular arrangement in the unit cell is considerably different in the two polymorphs. In the cubic phase, neighbouring molecules are perpendicular to each other [6] while in the monoclinic phase the arrangement of the molecules is planar [7]. The C$\equiv$N bond length is somewhat longer in the cubic phase. The molecular geometry is not altered much in the two forms; subtle differences are noted in some of the bond angles [1] in the two structures. An isolated molecule of TCNE has the symmetry D_{2h}, and hence the Raman and IR active modes are mutually exclusive. Out of the 12 distinct Raman active internal modes expected for the isolated molecule, 11 have been observed [23] and assigned. The centre of inversion is preserved in both the crystalline polymorphs at ambient conditions. Correlation splitting of the vibrational modes in the two polymorphs is given as $A_g \rightarrow (A_g + E_g)$, $B_g \rightarrow F_g$ for the cubic phase; each of the A_g and the B_g modes transform as $(A_g + B_g)$ in the monoclinic phase. Raman active vibrations in the crystalline phases transform as

$$\Gamma_{\mathrm{int}}(\mathrm{cubic}) = 5A_g + 5E_g + 8F_g; \qquad \Gamma_{\mathrm{ext}} = 3F_g$$

and

$$\Gamma_{\mathrm{int}}(\mathrm{monoclinic}) = 12A_g + 12B_g; \qquad \Gamma_{\mathrm{ext}} = 3A_g + 3B_g.$$

Table 1 gives the frequencies of the Raman active modes of the free molecule as well as in the crystalline phases. As the individual molecules are not influenced much by the crystal lattice, the prominent difference in the vibrational spectra of the two phases is reflected mainly in the external mode region. Figure 1 shows the Raman spectra of the cubic and monoclinic forms of TCNE at ambient conditions. In the cubic phase, the Raman modes observed at 67, 83 and 124 cm^{-1} are due to the librational lattice modes. It may be mentioned that the mode at 124 cm^{-1} has a predominant contribution from the (NC)–C–(CN) scissor mode [9] of E_g

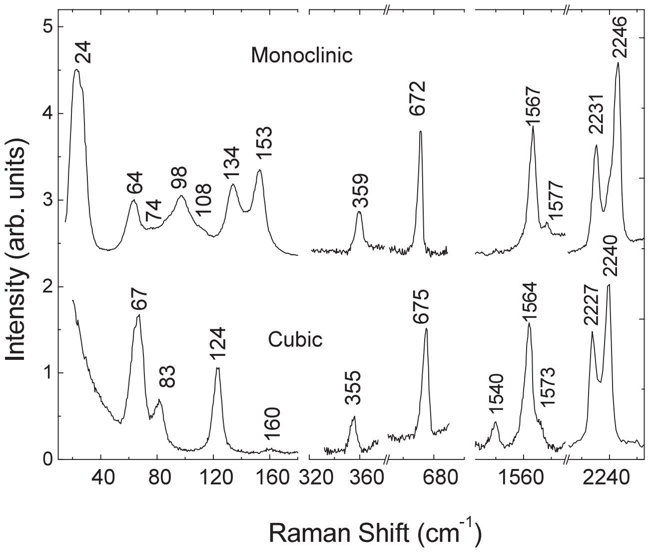

Figure 1. Raman spectra of the cubic and monoclinic phases of TCNE at ambient conditions.

Table 1. Raman active modes in the monoclinic and cubic forms of TCNE at ambient conditions.

Free molecule		Monoclinic	Cubic
ω (cm^{-1})	Symmetry	ω (cm^{-1})	ω (cm^{-1})
—	—	24	67
—	—	64	83
—	—	74	—
—	—	98	—
		108	—
130	A_g	134	124
		153	160
254	B_{3g}	—	—
251	B_{2g}	251	249
360	B_{1g}	359	355
490	A_g	505	499
535	A_g	527	529
674	B_{2g}	672	675
1282	B_{3g}	1278	1270
1569	A_g	1567	1564
—	—	1577	1573
2235	A_g	2231	2227
2247	B_{3g}	2246	2240

character. In the monoclinic phase, five out of the six expected librational modes [9] have been identified, which appear at frequencies below 120 cm^{-1}. In addition to the difference in the external mode region, the frequencies of some of the internal modes also show small but noticeable differences. Mode frequencies of the C–C≡N bending vibration in the two polymorphs may be expected to be different as the C–C≡N group has a more pronounced linear configuration in the monoclinic phase (179.1°) compared to the cubic phase (178.2°). The C–C≡N out of plane bending modes appear at 359 and 672 cm^{-1} in the monoclinic phase, and at 355 and 675 cm^{-1} respectively in the cubic phase. Similarly, the C–C–C angle is smaller

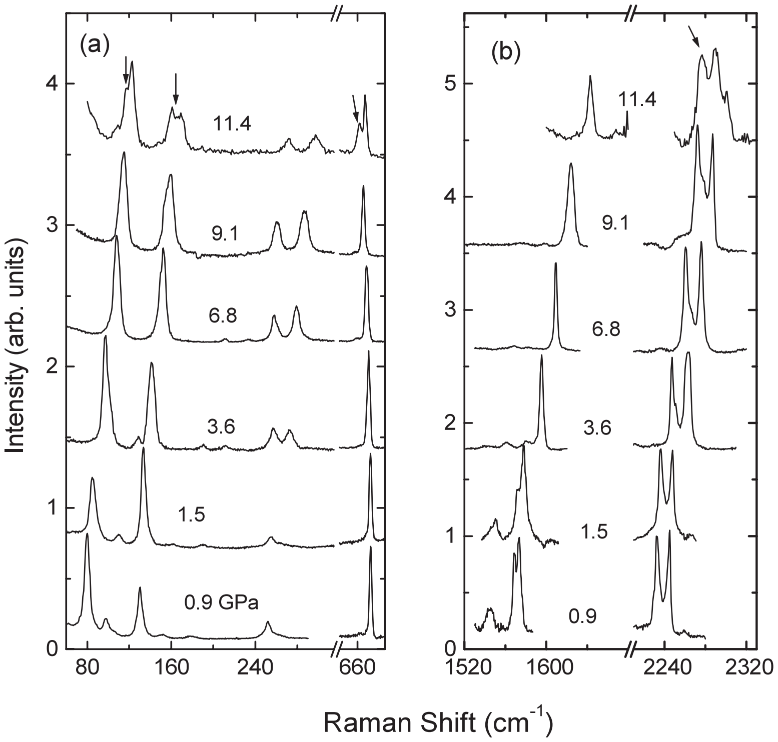

Figure 2. Raman spectra of cubic TCNE at various pressures. The intensity of the 1567 cm^{-1} mode in the C=C region decreases while that of the 1573 cm^{-1} mode increases continuously with increasing pressure, and beyond 2 GPa, only the latter could be observed. Arrows indicate the new peaks that appear above 9 GPa. In the C≡N stretching region, the mode indicated by an arrow increases in intensity above 8 GPa (see text).

in the cubic phase (115.6°) compared to the monoclinic phase (118.1°) which is reflected in the internal modes involving C–C≡N scissoring vibrations. In the cubic phase, these appear at frequencies 124 and 160 cm^{-1}; the latter one is of very weak intensity as may be noted from figure 1. The corresponding modes in the monoclinic phase appear at 134 and 153 cm^{-1}. In the C=C stretching region, a strong band is observed at 1564 (1567) cm^{-1} and a weak band at 1573 (1577) cm^{-1} in the cubic (monoclinic) phase. In the case of cubic samples, in addition to these bands, one more is observed at 1540 cm^{-1}, which is not expected in the first-order Raman spectrum, and this could be a combination band. The C≡N stretch modes transform as $A_g + E_g + F_g$ in the cubic phase and as $2A_g + 2B_g$ modes in the monoclinic phase. Only two distinct bands are observed at ambient conditions in the cubic phase. In the monoclinic phase, two bands of strong intensities appear at 2231 and 2246 cm^{-1} and there is a weak shoulder at 2241 cm^{-1}. As mentioned earlier, the C≡N bond lengths are slightly longer in the cubic phase; the corresponding mode frequencies are found to be smaller and appear at 2227 and 2240 cm^{-1} (see figure 1).

3.2. High-pressure behaviour of the cubic phase

Figure 2 shows the Raman spectra of the cubic phase of TCNE at different pressures. The frequencies of all the Raman bands, except that of the C–C≡N mode at 675 cm^{-1}, increase

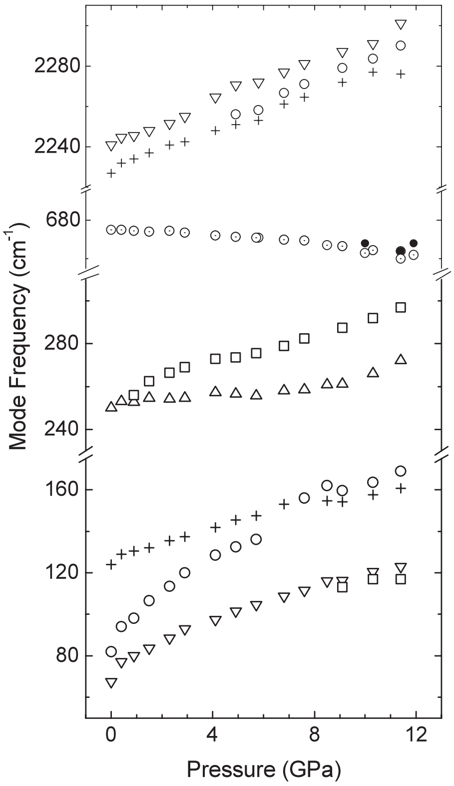

Figure 3. Pressure dependence of mode frequencies in the cubic phase of TCNE. The transition pressure evaluated from the pressure dependences of some of the mode frequencies is 8.0 ± 0.4 GPa.

monotonically with increasing pressure. The Raman bands ≈250 cm^{-1}, which arise due to the C–C≡N rock and wag, appear better resolved at high pressures. In the present studies, no additional splitting of any of the degenerate modes, lattice as well as the internal modes, was observed around 1.3 GPa or even at a somewhat higher pressure where the separation of the split components reportedly increase [9]. Analysis of the evolution of the full width at half maximum (FWHM) of the lowest frequency lattice mode also did not show any significant increase around this pressure. Pressure dependences of the Raman modes are shown in figure 3. It may be noted from the figure that the pressure dependences of many of the Raman modes, particularly the external and some of the low-frequency internal modes, show marked departure from a linear behaviour. The libration mode at 83 cm^{-1} shows larger pressure dependency compared to the one at 124 cm^{-1} and could not be observed as a distinct mode at pressures above 6 GPa. Evolution of the Raman spectrum is monotonic up to 9 GPa. At pressures above 9 GPa, the C≡N stretching mode at 2279 cm^{-1} starts gaining intensity. It may be mentioned that even around 3 GPa, a weak shoulder is noted in this region which is clearly visible only at higher pressures due to increased mode separation as well as intensity. In the external mode region, the bands at 116 and 154 cm^{-1} show splitting around 9 GPa; the two modes appear better resolved at higher pressures. It may be noted that the 154 cm^{-1} mode has contributions from two accidentally degenerate modes of E_g and F_g character even at ambient conditions. The F_g mode at 675 cm^{-1} also shows splitting at somewhat higher pressure, which clearly

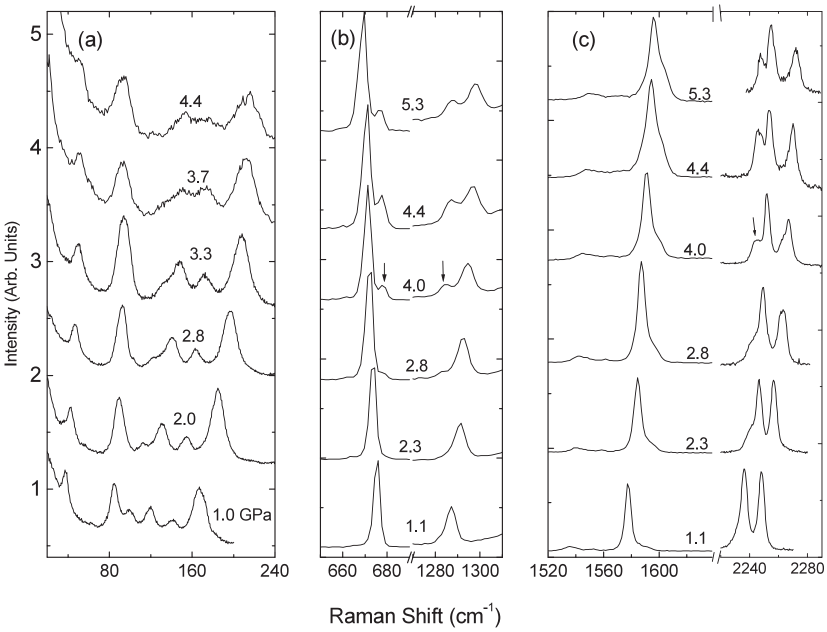

Figure 4. Raman spectra of monoclinic TCNE at various pressures. The arrows in (b) and (c) indicate Raman peaks which gain intensity above 3.6 GPa.

suggests that there is a phase transition to a new phase of lower symmetry, say P^cII. The superscript c indicates the ambient cubic structure. The transition pressure estimated from the pressure dependence of mode frequencies turns out to be 8.0 ± 0.4 GPa.

Above 7 GPa, the sample becomes highly sensitive to incident radiation, with the Raman intensities deteriorating rapidly with time when exposed to laser radiation. The sample became opaque gradually upon increasing the pressure, the dark regions being spatially inhomogeneous. Raman spectra could not be obtained from these regions; all the Raman spectra shown at pressures above 9 GPa in the figure are recorded from the transparent region of the sample. The opaque phase may be called P^cIII so as to distinguish it from the transparent phase P^cII. It may be mentioned that higher laser power was found to accelerate the process of darkening. However, the sample was found to become completely dark when the pressure was increased, even in the absence of any laser radiation, implying that this transformation is indeed pressure induced. The cubic–P^cII transition is observed to be reversible when pressure is released from values of about 12 GPa (when the sample has not fully turned black). Above 14 GPa, the sample turns completely black, irreversibly.

3.3. High-pressure behaviour of the monoclinic phase

Figure 4 shows the evolution of Raman spectra of the monoclinic phase of TCNE. Except for the mode at 672 cm^{-1}, the frequencies of all the modes increase with increasing pressure as in the cubic samples. Above 3.6 GPa, there is a considerable increase in line width and redistribution of intensities of the lattice modes in the region 130–180 cm^{-1}. In particular, the width of the lattice mode at 150 cm^{-1} increases from a value of 15 cm^{-1} at 2.7 GPa to ~30 cm^{-1} at 3.8 GPa. At this pressure, two new modes pick up intensity at 677 and 1283 cm^{-1}

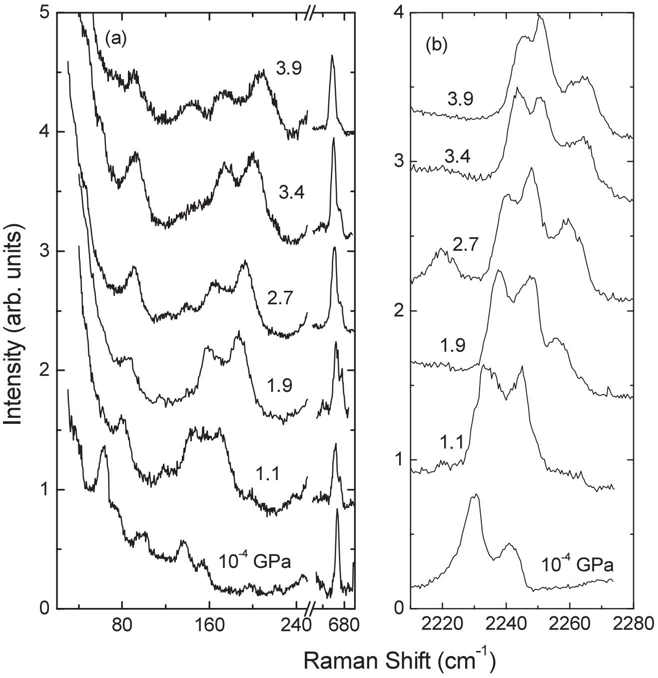

Figure 5. Raman spectra of monoclinic TCNE in the pressure-reducing cycle. Note that, even at 1.9 GPa, the spectrum resembles the high-pressure phase.

in the C–C≡N bending and C–C stretching region respectively, as shown in figure 4(b). In the C≡N stretching region, a continuous increase in intensity of the mode at 2246 cm^{-1} is observed above 3.6 GPa. Upon reducing the pressure from peak values of about 4.5 GPa, these changes observed in the spectra are found to be reversible with hysteresis, as shown in figure 5.

One might consider the qualitative changes around 3.6 GPa in the light of a possible phase transition. While the splitting observed in the degenerate modes in the cubic polymorph can be understood as being due to lowering of symmetry across the transition, the nature of changes expected across a transition starting from monoclinic phase is different. An increase in the number of modes, particularly in the lattice modes region, would arise only if the transition leads to an increase in the number of molecular units per primitive cell. It may be recalled that, in all the internal modes regions where new modes are observed above 3.6 GPa, the number of distinct Raman modes observed at ambient conditions is less than those expected for $Z = 2$. At the same time, evolution of Raman intensities is continuous within a phase, such as that observed for the 1563 cm^{-1} mode in the cubic samples (figure 2). Hence the appearance of new modes above 3.6 GPa is quite likely to be due to a phase transition. An increase in the intensity of the otherwise weak Raman bands may be interpreted as being due to changes in the relative molecular orientations in the new phase. In the earlier IR work [13], the strongest C≡N peak showed a decrease in mode frequency across the transition. In the present studies, however, no discernable discontinuities were noted in the Raman frequencies. Figure 6 shows the pressure dependence of the mode frequencies of monoclinic TCNE. The pressure dependences of two of the external modes are found to decrease considerably around 3.6 GPa while those of the internal modes do not show any significant change. Discontinuities in mode frequencies may be expected if the transition involves a considerable change in volume. The absence of a

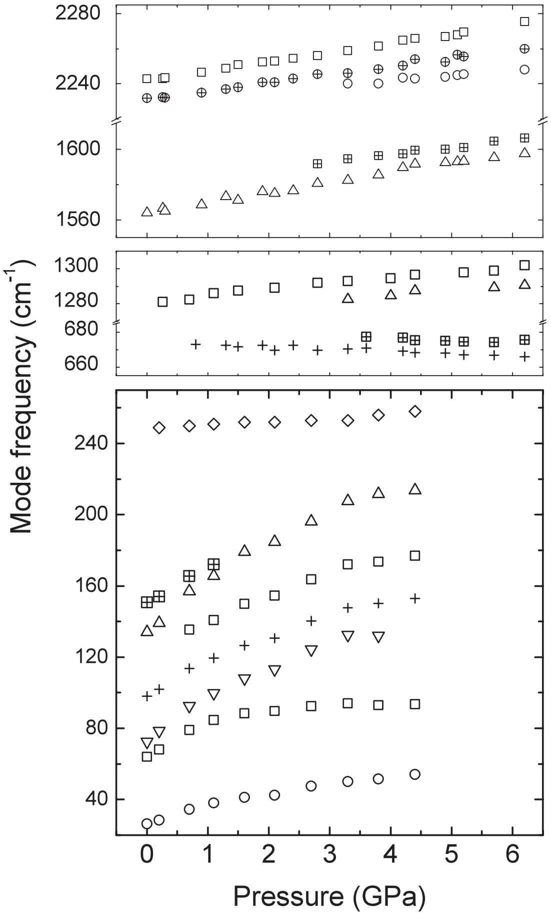

Figure 6. Pressure dependence of mode frequencies in monoclinic TCNE. Lattice modes could not be followed beyond 4.5 GPa.

discontinuity is in agreement with the neutron diffraction measurements [15], which indicated that all the lattice parameters, other than the monoclinic angle β, exhibit a smooth variation with increasing pressure.

Above 4 GPa, there is gradual reduction in the transparency of the sample, similar to that in the cubic phase, and the intensities of the lattice modes were too weak to be followed beyond this pressure. Other internal modes were observable up to pressures of about 7 GPa, beyond which only the C≡N and C=C modes could be detected with reduced intensities. A weak broad feature is noted at a frequency less than that of the strong C=C band. Figure 7 shows the Raman spectra of TCNE recorded in the pressure-reducing cycle from peak values of about 9 GPa. Note an increase in the intensity of a broad band around 1600 cm^{-1} as the pressure is reduced. The pressure-released sample showed only two broad bands centred around 1365 and 1563 cm^{-1} with very negligible intensities of C≡N and C=C modes. The overall spectrum of the recovered sample closely resembles that of the D and G bands in amorphous C:N [24], suggesting that the pressure-released phase is an amorphous phase wherein the identity of TCNE molecule is completely lost.

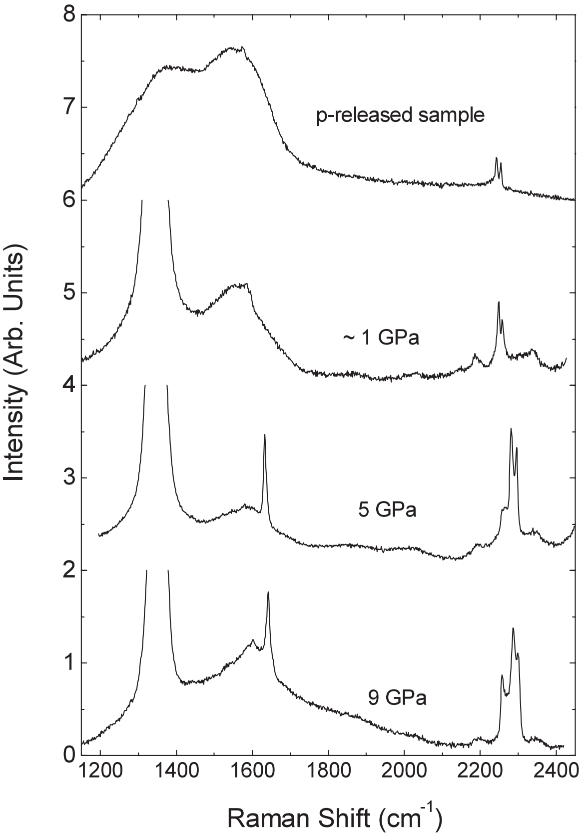

Figure 7. Raman spectrum of monoclinic TCNE in the pressure-reducing cycle from peak values of 9 GPa. Note the gradual weakening of the C≡N bands and an increase in intensity of the broad band at 1600 cm^{-1}.

4. Discussion

The present Raman scattering studies on the cubic form of TCNE reveal that the structure is stable up to 8.0 ± 0.4 GPa. In summary, the high-pressure behaviour of TCNE, from the present investigations, can be written as

$$\text{Cubic} \xrightarrow{8.0\pm0.4\ \text{GPa}} \mathrm{P^cII} \xrightarrow{>14\ \text{GPa}} \mathrm{P^cIII}$$
$$\text{Monoclinic} \xrightarrow{>3.6\ \text{GPa}} \mathrm{P^mII} \xrightarrow{>7\ \text{GPa}} \mathrm{P^mIII}$$

where the phase $\mathrm{P^cII}$ is the transparent phase which exhibits reversibility with hysteresis. The superscript m denotes the ambient monoclinic phase. While the overall behaviour of both the polymorphs agree with that reported by Chaplot *et al* [9], the transition pressures to the opaque phases, wherein no Raman spectra could be obtained, reported in [9] are much lower in both phases. It is further noted that the pressure dependences of the mode frequencies obtained in the present studies are lower compared to those reported from the earlier Raman work [9]. Table 2 gives the mode Grüneisen parameters calculated using the $(\partial\omega/\partial P)$ values for both cubic and monoclinic TCNE obtained from the present measurements and the bulk modulus values taken from the literature [15]. Further, the higher laser power (50 mW) used in the

Table 2. Mode Grüneisen parameters for both cubic and monoclinic TCNE derived from the present measurements using the bulk modulus values from the literature [15]. In the light of reported phase transitions, the values of $\partial\omega/\partial P$ given are obtained from the pressure dependence of the Raman modes up to 7 GPa for the cubic samples and up to 2.5 GPa for the monoclinic samples.

Cubic			Monoclinic		
Frequency (cm^{-1})	$(\partial\omega/\partial P)$ (cm^{-1} GPa^{-1})	Mode γ ($B_0 = 8.6$ GPa)	Frequency (cm^{-1})	$(\partial\omega/\partial P)$ (cm^{-1} GPa^{-1})	Mode γ ($B_0 = 9.5$ GPa)
—	—	—	24	7.5	2.97
67	5.25	0.67	64	11.8	1.75
83	8.97	0.93	98	14.8	1.43
124	3.92	0.27	117	13.9	1.13
			153	15.5	0.96
249	0.89	0.031	251	0.122	0.0046
256	2.98	0.10			
675	−0.77	−0.01	672	−1.5	−0.02
1564	3.67	0.02			
1573	5.93	0.032	1567	5.67	0.034
2227	4.53	0.02	2231	4.89	0.021
2237	5.89	0.02	2246	4.90	0.021
2240	5.40	0.02			

earlier work [9] might have accelerated the process of darkening, resulting in vanishing of the Raman signal.

The exact nature of the phase PIII is another interesting aspect to be discussed. Yamawaki *et al* [13, 14] have conjectured it to be a polymeric phase. The pressure-cycled opaque phase in the present studies is found to be insoluble in common solvents such as ethanol and acetone, in which the crystalline TCNE is soluble. There are similar reports on the solubility of pressure-polymerized benzene [25] suggesting that the opaque phase could be a polymeric phase. However, this cannot be taken as a conclusive evidence for identifying it as a polymeric phase. On the other hand, the increase in intensity of the broad band at ~1600 cm^{-1} together with a reduced intensity in the C≡N stretching mode in the Raman spectrum can be interpreted as being due to breaking of some of the C≡N bonds due to polymerization. In the light of this, the phase PIII at high pressures appears to be a pressure-induced polymeric phase. In the pressure-reducing cycle, it is noted that the intensities of the sharp C=C and C≡N modes decrease rapidly and the pressure-recovered sample has only very broad Raman bands. It may be mentioned that pressurization of crystalline polyacetylene resulted in the disappearance of sharp vibrational modes accompanied by discontinuous changes in the optical absorption spectrum [26]. Subsequent molecular dynamics simulations suggested that the polyacetylene gradually evolves into amorphous hydrogenated carbon as a result of chain interlinking [27]. Recent high-pressure Raman spectroscopic studies on the rhombohedral polymeric phase of C_{60} also reported an irreversible transformation to a new disordered state [28] resulting from random covalent bonding of the molecular cages in the adjacent layers. In view of these reports, the high-pressure phase of TCNE may be understood as a polymeric phase, which also explains the irreversibility of the starting monomeric phase. The amorphous nature of the pressure-cycled sample arises due to cross-linking of the TCNE molecules in the pressure-reducing cycle. This is in qualitative agreement with the neutron diffraction studies [15], where they reported that the pressure-cycled compound is more of a graphite-like *amorphous* structure. Neutron diffraction measurements reported the loss of nitrogen from the pressure-released samples, which however cannot be concluded from the Raman measurements as the small difference in the frequency of the bands due to C=C or C=N units is lost in the broad profile of the D and G bands in the amorphous structure.

5. Conclusion

High-pressure Raman scattering studies of the cubic and monoclinic forms of TCNE have shown that both the polymorphs eventually transform into a highly disordered phase irreversibly which is optically opaque. The evolution of the Raman spectra of the cubic phase suggests that, around 8 GPa, the compound transforms into a new phase which is reversible when the pressure is reduced from peak values of about 12 GPa (before the sample becomes completely black). The monoclinic TCNE exhibits a subtle transition around 3.6 GPa which is reversible when the pressure is reduced from peak values of about 4.5 GPa. At higher pressures, it transforms into an opaque polymeric phase irreversibly above 7 GPa. Comparison of the results of the present studies with those reported in other systems suggests that the polymer phase evolves into an amorphous phase in the pressure-reducing cycle due to cross-linking of the TCNE molecules.

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