Reversible phase transition between the metastable phases of tetracyanoethylene under high pressure

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Powder x-ray-diffraction patterns of the cubic and monoclinic phases of tetracyanoethylene have been measured up to 7 GPa at room temperature. The stable cubic phase showed no phase transition and polymerization occurred above 6 GPa. The monoclinic phase, which is a high-temperature phase metastably existing at room temperature, showed a structural transformation to a phase near 3.5 GPa. The high-pressure phase reversibly transformed to the metastable monoclinic phase on unloading. The reversible transition suggested that there were some similarities in molecular arrangement between the high-pressure and the monoclinic phases, and the transition into the stable cubic structure from them were possibly suppressed by large potential barriers. The structure of the high-pressure phase remained unsolved.

INTRODUCTION

Molecular solids often undergo phase transitions with re-arrangement of constituent molecules under pressure. Rotational or displacive molecular motions partly release the lattice energy of crystal lifted up by compression, realizing another molecular arrangement with a lower energy. Besides the magnitude of lattice energy, potential barriers lying along transition paths also play important roles in actual phase transitions. Large potential barriers would suppress spontaneous transitions into thermodynamically stable structures and sometimes allow existence of metastable structures over a wide pressure and temperature range. Such a kinetically controlled transition is expected to take place for large molecules rather than for small molecules. However very few works have been reported on kinetically controlled phase transition in molecular solids, and hence the transition behavior has not been well investigated.

Tetracyanoethylene (TCNE) is a planar model with a backbone of C=C double bond attached by four cyano groups and known to have two crystalline phases: a cubic ($Im3$, $z=6$) and monoclinic ($P2_1/n$, $z=2$) phase.[1,2] In the cubic phase, TCNE molecules stand perpendicularly to each other; C=C double bonds point to the center of the cubic lattice.[1] In the monoclinic phase molecules are aligned one by one in the same plane to form molecular chains, which are stacked zigzag.[2] The cubic phase transforms to the monoclinic phase at 318 K on heating at ambient pressure.[3] This transition is irreversible on cooling; the high-temperature monoclinic phase exists as a metastable phase at room temperature and even at a temperature of 5 K.[4] The reverse transition to the cubic structure is thus suppressed by a large potential barrier for the molecular motions associated with the transition.

Pressure-induced phase transitions in the monoclinic TCNE have been observed by x-ray-diffraction and infrared-absorption measurements at room temperature. The observed transition behavior, however, was very confusing and the high-pressure structure is still controversial. Powder x-ray diffraction[5,6] showed that the monoclinic phase transformed to the cubic phase via an amorphous state at 2–2.5 GPa. The cubic phase, which has once appeared at high pressure, maintained its structure after releasing pressure. On the other hand, infrared-absorption measurements revealed a transition from the monoclinic phase to a new high-pressure phase near 3 GPa,[7] which transformed to the monoclinic phase reversibly on unloading. The cubic phase did not appear in the monoclinic or the high-pressure phase under high pressure. By contrast to the exclusive transition behavior in the monoclinic phase, no phase transition was observed in the cubic phase. The presence of the cubic structure was confirmed to 7 GPa, at which polymerization took place.

In the present study we have performed high-pressure powder x-ray measurements for the cubic and monoclinic TCNE with a diamond-anvil cell. The purpose was to clarify the structural aspect of the pressure-induced phase transition. Careful attention was paid to the generation of hydrostaticity. Nonhydrostaticity often induces phase transitions different from those under hydrostatic condition. We obtained the compression data of the cubic and monoclinic TCNE and observed a reversible phase transition between the monoclinic and high-pressure phases in agreement with the previous infrared experiment.[7]

EXPERIMENT

Cubic and monoclinic crystals used in the present study were prepared from commercially available grade (98%) of TCNE (Tokyo Kasei Kogyo Co., Ltd.). Cubic crystals were grown from ethyl acetate solution at a temperature of 278 K,[1] and monoclinic crystals were prepared by sublimation at 373 K.[5]

High pressure was generated with a diamond-anvil cell.[8] Cubic crystals of TCNE were ground in a mortar together with liquid pentane. The ground powder was compacted into a small block and was put together with ruby chips in a

gasket hole 0.3 mm in diameter. The hole, which was drilled in a metal gasket of Inconel X-750 approximately 0.25 mm thick, was subsequently charged with a pressure-transmitting medium of n-pentane:isopentane (1:1) mixture. This pressure medium is capable of generating hydrostatic environment up to 7 GPa.[9] The same loading procedure was employed for the monoclinic crystals. The pressures were determined by the ruby fluorescence method.[10]

X-ray-diffraction measurement was performed using a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.710\,69$ Å) from a rotating-anode x-ray generator and an image-plate detector 200 mm$\times$250 mm in dimension. The generator was operated at 10 kW (45 kV, 230 mA), and a typical exposure time was 7 h for the cubic phase. For the metastable monoclinic phase the power was reduced to 2.7 kW (45 kV, 60 mA) and instead exposure time was increased to 20 h. High-power x-ray irradiation transformed the monoclinic phase into the cubic phase. X-ray-diffraction patterns were recorded on an image-plate placed at a distance of 180 mm for the sample and converted into conventional 2θ-intensity data by integration of intensities along reflection rings. All measurements were made at room temperature.

RESULTS

The recrystallized and sublimated crystals were confirmed to contain single phases of the cubic and monoclinic structures, respectively, from x-ray-diffraction patterns measured at atmospheric pressure. Eleven diffraction peaks measured for the cubic structure at ambient pressure were completely indexed on the basis of the $Im3$ cubic structure, and 14 peaks of the monoclinic phase on the $P2_1/n$ structure in agreement with the literature.[1,2] The cell parameters are the following:

For the cubic structure,

a: 9.750(1) Å [9.736 Å],[1]

V_{mol}: 93.05(3) cm^3/mol,

and for the monoclinic structure,

a: 7.1495(6) Å [7.51 Å],[2]

b: 6.258(9) Å [6.21 Å],[2]

c: 6.990(7) Å [7.00 Å],[2]

β: 97.27(6) Å [97.10 Å],[2]

V_{mol}: 97.9(2) cm^3/mol,

where parenthesized figures represent estimated standard deviations. The values in square brackets are given in the literature. The molar volume of the cubic phase is 5% smaller than that of the monoclinic phase, showing a closer packing of TCNE molecules in the cubic cell.

Typical x-ray-diffraction patterns of the cubic and monoclinic structures taken at the same pressure of 3.2 GPa are shown in Fig. 1. Observed peaks were fitted with Gaussian functions and their positions were used for the calculation of the cell parameters. When the cubic phase was pressurized to about 6 GPa, a structural change associated with polymerization reaction was observed. The transparent crystals turned dark brown gradually. A phase transition accompanied with
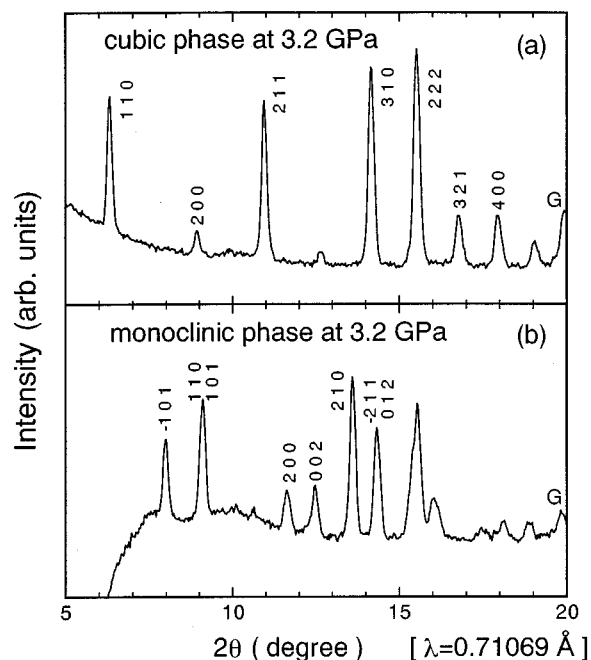

FIG. 1. The powder x-ray patterns of (a) the cubic and (b) monoclinic phases of tetracyanoethylene at 3.2 GPa. Indexed peaks were fitted by Gaussian functions and used for calculation of the cell parameters. Diffraction peaks from the metal gasket are marked by G.

molecular reorientation was found in the monoclinic phase near 3.5 GPa in agreement with the previous x-ray and infrared measurements.[5–7] Since the high-pressure phase has been shown to polymerize around 6 GPa as well as in the cubic phase,[7] we stopped x-ray-diffraction measurement at 5 GPa and released the pressure to examine reversibility of the transition.

Variation of lattice plane spacings (d spacings) with pressure is shown in Fig. 2. The d spacings of the cubic phase decrease continuously up to 7 GPa [Fig. 2(a)], whereby polymerization occurred. Besides the diffraction peaks from
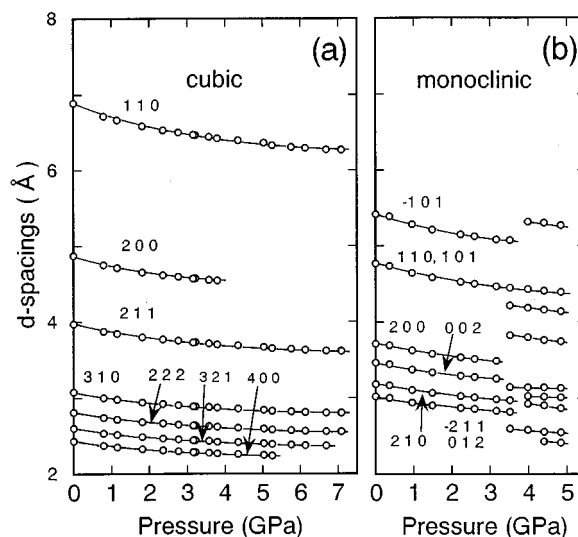

FIG. 2. Variation of the d spacings of (a) the cubic and (b) monoclinic phases with pressure. The monoclinic phase transforms to a new phase near 3.5 GPa.
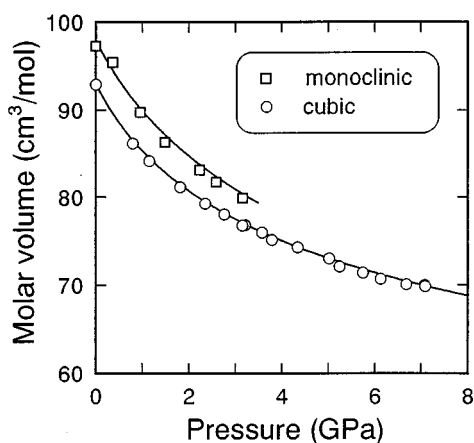
FIG. 3. Molar volumes of the cubic and monoclinic phases plotted against pressure.

nonreacted cubic phase, no additional peak appeared: the reaction products were noncrystalline polymers. The d spacings of the monoclinic phase and its high-pressure phase are plotted to 3.5 GPa [Fig. 2(b)]. The discontinuity at about 3.5 GPa is due to the phase transition. The cell parameters were calculated using the observed d spacings for the cubic and monoclinic phases. The fitting of the cubic cell parameter to a quadratic equation in terms of pressure gave

$$a = 9.6906 - 0.2165P + 0.0143P^2; \quad r = 0.9960,$$

where a is the magnitude of the cubic edge (Å), P is pressure (GPa), and r is correlation coefficient. For the monoclinic phase, the similar fitting gave the following results:

$$a = 7.511 - 0.225P + 0.0231P^2; \quad r = 0.9979,$$

$$b = 6.223 - 0.212P + 0.0252P^2; \quad r = 0.9979,$$

$$c = 7.003 - 0.224P + 0.0267P^2; \quad r = 0.9982,$$

where a, b, and c are the magnitudes of the monoclinic edges (Å). The angle between the a- and c-axes (β) is nearly constant: $\beta = 97.32 \pm 0.07°$. The three monoclinc edges have almost the same magnitudes of pressure coefficients, suggesting that the unit cell is isotropically compressed with keeping the molecular arrangement.

TCNE crystals show large volume reduction with pressure, reflecting the weak bonds by the van der Waals forces (Fig. 3). The molar volume of the cubic phase decreases from 93.05 cm^3/mol at ambient pressure to 76.8 cm^3/mol at 3.2 GPa with a reduction of 17.5%, while that of the monoclinic phase decreases from 97.9 cm^3/mol to 79.9 cm^3/mol with 18.4% reduction for the corresponding pressure change. The rates of the volume reduction are almost the same between them and the molar volume of the cubic phase is held to be about 5% smaller than that of the monoclinic phase over the pressure range measured. The pressure-volume data were fitted with the Murnaghan equation of state, giving a bulk modulus B_0 of 8.6 GPa with pressure derivative $B_0' = 6.4$ for the cubic phase, and $B_0 = 9.5$ GPa, and $B_0' = 4.9$ for the monoclinic phase.
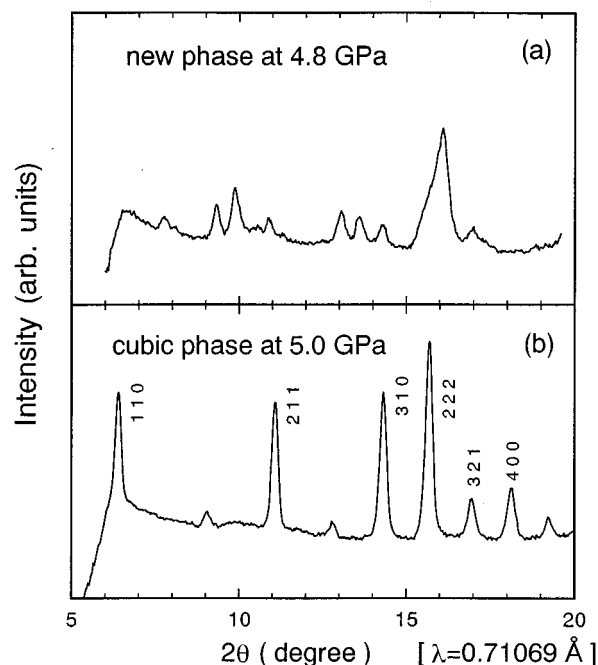

FIG. 4. The powder x-ray patterns of (a) the new high-pressure phase at 4.8 GPa and (b) the cubic phase at 5.0 GPa.

X-ray-diffraction patterns of the high-pressure phase and the cubic phase are shown in Fig. 4. They were measured at the corresponding pressures of about 5 GPa for comparison. A few remaining peaks from the monoclinic structure indicate that the transition into the high-pressure phase was not completed even at 4.8 GPa, about 1 GPa above the transition pressure. The newly appeared peaks, however, come apparently neither from the cubic structure nor from amorphous solids, showing appearance of a molecular phase of TCNE. These results are in contrast to the previous x-ray diffraction study, which reported the transition into the cubic phase via metastable amorphous states.[5,6] When the pressure was reduced stepwise from 4.8 GPa, the diffraction profile changed gradually. The change in the peak intensities was clearly recognized at 2.6 GPa, showing the start of the reverse conversion from the high-pressure phase to the monoclinic phase. The peaks of the high-pressure phase disappeared completely at 0.2 GPa and the monoclinic phase recovered.

DISCUSSION

X-ray-diffraction measurements of polymorphs of TCNE to 7 GPa revealed that no phase transition took place in the stable cubic phase, while the metastable monoclinic phase transformed into the high-pressure phase at about 3.5 GPa. The high-pressure phase did not show conversion from or into the cubic structure during pressure variation, but a reversible transition to the metastable monoclinic phase. Such a reversible transition between metastable states is very rare in molecular solids, and is considered to be a typical transition controlled kinetically.

We first consider the free-energy levels of the three polymorphs: the cubic, monoclinic, and high-pressure phases. It
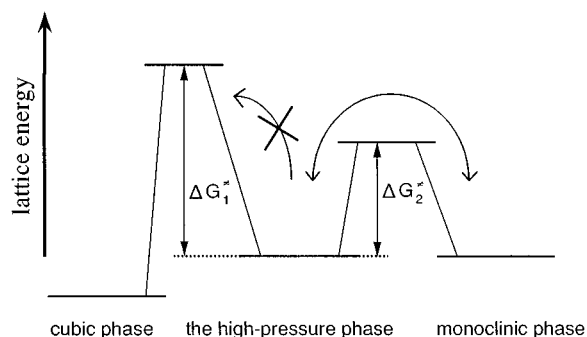
FIG. 5. A hypothetical energy diagram for the cubic, high-pressure, and monoclinic phases of tetracyanoethylene near 3 GPa. The transition to the cubic phase would be suppressed by a large potential barrier ($\Delta G_1^{\neq}$). Potential barrier ($\Delta G_2^{\neq}$) lying between the monoclinic and high-pressure phases should be sufficiently small to allow the mutual conversion.
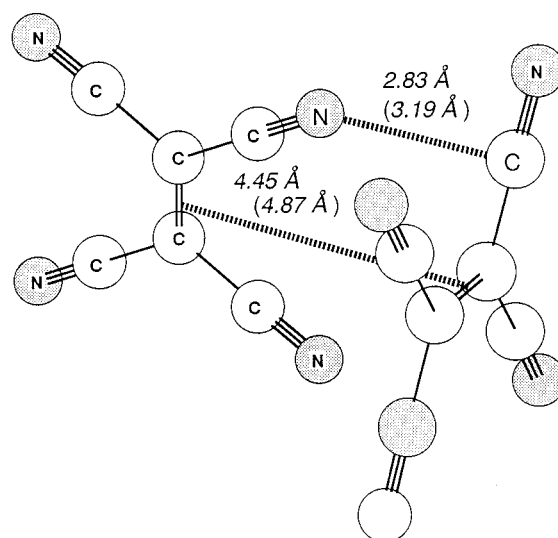

FIG. 6. The arrangement of two adjacent TCNE molecules in the cubic phase at 6 GPa. Intermolecular distances between the molecular centers and that between the nearest-neighbor atoms at 6 GPa are represented. The distances at ambient pressure are given in parentheses.

is immediately derived from the experimental and theoretical results that the energy level of the cubic phase is located below that of the monoclinic phase over all the pressure region studied. At atmospheric pressure the relative stability of the cubic phase to the monoclinic has been confirmed from an exothermic transition at 318 K by a differential scanning calorimetry measurement.[3] In addition, the cubic lattice has been shown to become much more stable in a high-pressure region by comparison of the lattice energies calculated for the two polymorphs.[11] No experimental data are available for the energy level of the high-pressure phase. However, the reversible conversion to the monoclinic phase suggests that its lattice energy is located closely to that of the monoclinic phase and hence above that of the cubic phase. The relative locations of the lattice energies for the three phases are drawn in Fig. 5.

Conversion of the monoclinic phase into the cubic phase is suppressed probably by a large potential barrier separating the two phases. In spite of the general tendency that high-density structures are preferable at high pressure and the theoretical prediction that the cubic lattice becomes much more stable by compression, the monoclinic phase remains as a metastable phase in the pressure region of 0.1 MPa–3.5 GPa. This is because thermal energy is insufficient to pass through the potential barrier for the structural conversion. The similar situation can be seen in the temperature variation experiment at ambient pressure. The recovery of the high-temperature monoclinic phase at low temperatures suggests the presence of a large potential barrier that blocks the transition path.[4] The large potential barrier can be attributable to the significant difference in molecular packing, if we look into their crystal structure in detail. TCNE molecules are packed with their planes perpendicular and parallel to each other in the cubic and monoclinic phases, respectively.[1,2] Large energies should be required to make the planar molecules stand up perpendicularly.

In contrast, the potential barrier lying between the monoclinic and high-pressure phases should be sufficiently small to allow the mutual conversion between them. The transition from the monoclinic to the high-pressure phase proceeds sluggishly on loading, and the reverse transition does also

sluggishly on unloading. This reversibility is due to the small potential barrier, which the thermal energy can go over to initiate the transition. Furthermore, the small potential barrier to molecular reorientation suggests a planar packing of TCNE molecules for the high-pressure phase similar to that in the monoclinic phase. Hence, the transition to the cubic phase would be blocked by a large potential barrier as discussed for the monoclinic phase. This is consistent with the experimental results.

A comprehensive picture for the kinetically controlled phase transition in crystalline TCNE is drawn in Fig. 5. To discuss precisely the transition mechanism, we need experimentally measured thermodynamic data such as magnitudes of the lattice energies and the potential barriers. High-pressure measurements of reaction rate and thermal analysis will be required.

Molecular arrangement at the polymerization pressure will provide a valuable insight into the reaction process in the TCNE crystals. As observed by the high-pressure infrared measurement,[7] crosslinking reactions may occur between cyano groups in neighboring TCNE molecules. Intermolecular distances were estimated from the observed x-ray data. For simplicity, we assumed the rigid molecule and used the intramolecular bond lengths of TCNE determined at ambient pressure.[1] This assumption yields the intermolecular distances using the cubic cell parameter of 8.906 Å at 6 GPa. The distance between the C=C double bonds on the adjacent molecules perpendicularly standing is calculated to be 4.45 Å (Fig. 6). The reaction takes place between cyano groups. The distance between the reacting carbon and nitrogen atoms is 2.83 Å, which is shorter than the van der Waals distance by 13%, and about two times longer than the usual C—N bond length of 1.4 Å. The observed C$\cdots$N contact of 2.83 Å just before polymerization well agrees with a

C···N limiting value of 2.9 Å. Below this limiting distance for nonbonded carbon and nitrogen atoms in organic crystal, polymerizations or other phase transitions are expected to occur.[12] Such experimentally derived criterions explain also pressure-induced solid-state polymerizations of acetylene and benzene.[12]

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