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# Phase transitions of solid CF<sub>4</sub> at high pressures

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## Abstract

The pressure-induced phase transformation of solid CF<sub>4</sub> at room temperature was studied with x-ray and Raman scattering experiments. The space group of phase III was determined as  $P2_1/c$ . The pressure dependences of the intramolecular vibrational modes suggest phase transitions from phase III to IV at 8.9 GPa and from phase IV to V at 13.6 GPa.

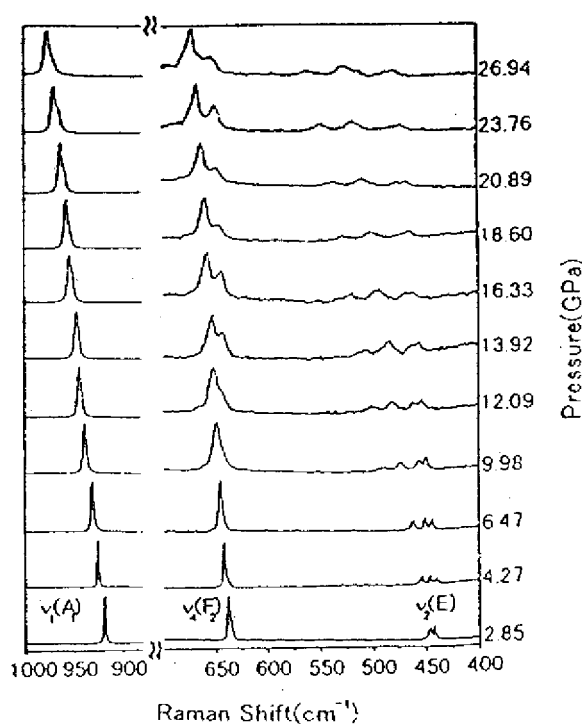
## 1. Introduction

Carbon tetrafluoride (CF<sub>4</sub>) has two crystalline phases at atmospheric pressure. It solidifies at 89.5 K to form a disordered plastic crystal (phase I) [1], the structure of which has been determined as rhombohedral, isostructural to phase Ib of CCl<sub>4</sub> [2]. Below 76.2 K, it transforms into a well-ordered monoclinic phase (phase II) with a space group of  $C2/c$  and four molecules per unit cell [2, 3]. Sasaki *et al* [4] have reported that under isothermal compression at 300 K, the liquid–phase I boundary is crossed at 1.86 GPa and the phase I–II transition is at 2.84 GPa. They have also found a transition at 3.5 GPa from phase II to III, due to the band splitting of an intramolecular vibrational mode ( $\nu_2$ ) into three peaks. In our previous work, we found phase III with a monoclinic lattice and another phase transition around 8.6 GPa [5].

In this paper, the crystal structure of phase III and phase transitions at higher pressures are investigated.

## 2. Experimental details

A diamond anvil cell (DAC) was used for generation of high pressure. Gaseous CF<sub>4</sub> was obtained from Nippon Sanso Co. Ltd. Its stated purity was of about 99.999%. It was sprayed on the metal gasket of the liquid-nitrogen-cooled DAC in a dry box and then liquefied CF<sub>4</sub> was loaded into the hole of the gasket with a tiny ruby chip. To prevent crystal growth, pressure was applied quickly up to about 3 GPa at a low temperature. An x-ray diffraction experiment at room temperature was carried out with a synchrotron radiation source on the beam line BL10XU at SPring-8. The wavelength was tuned with a Si(111) double-crystal



**Figure 1.** Raman spectra of intramolecular vibrational modes at pressures from 2.85 to 26.94 GPa. The  $\nu_1$  mode became asymmetric above 13.92 GPa.

monochromator to 0.4528 Å. Powder patterns were obtained by an angle-dispersive method with an image plate detector. The diffraction images obtained were analysed using integrated software, the 'Powder Pattern Analyzer for an Imaging Plate (PIP)' produced by Fujihisa *et al* [6].

High-pressure Raman spectroscopy at room temperature was carried out using a micro-optical system of a JASCO Model NR-1800 spectrometer equipped with a triple monochromator and a liquid-nitrogen-cooled CCD (Princeton Instruments Inc.) multichannel detector. The 514.5 nm line from an Ar-ion laser with a maximum power of 2 W was used for excitation. The pressure was determined by the ruby fluorescence method.

### 3. Results and discussion

Figure 1 shows the Raman spectra of solid  $\text{CF}_4$  under pressure from 2.85 to 26.94 GPa.

The spectra at pressures below 12.02 GPa are in good agreement with the previous results. At 13.92 GPa the  $\nu_1$  mode became asymmetric and with increase in pressure the shoulder appeared clearly on the low-frequency side. Figure 2 shows the frequency–pressure dependences of intramolecular vibrational modes of  $\nu_1$  and  $\nu_2$ . The band splitting of  $\nu_2$  into four peaks and also the band splitting of  $\nu_1$  above 13.6 GPa suggest phase transitions from phase III to IV and IV to V, respectively.

Figure 3 shows the diffraction profiles of solid  $\text{CF}_4$  at selected pressures. The diffraction patterns of the lowest two panels (figures 3(a), (b)) are from phase III. The patterns are assigned to a monoclinic lattice, except for two peaks marked by asterisks. In the monoclinic system

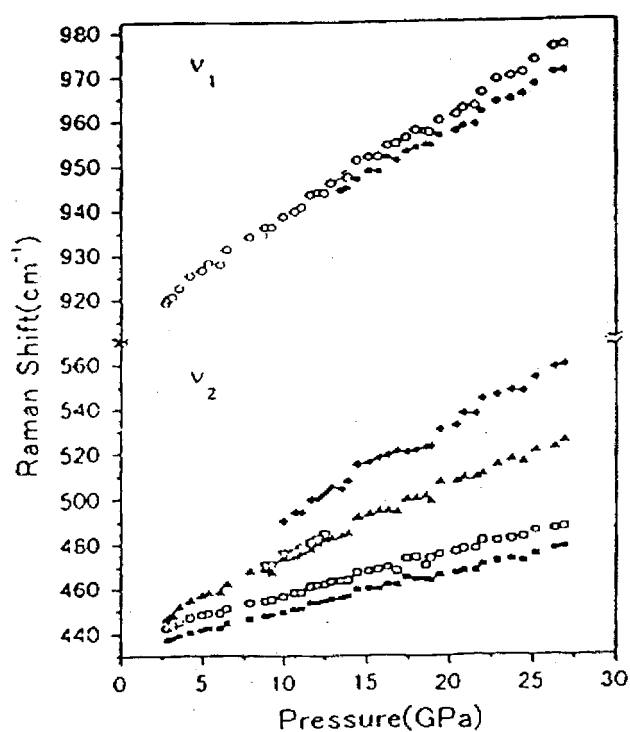


Figure 2. Pressure dependences of the  $\nu_1$ ,  $\nu_2$  Raman frequencies of CF<sub>4</sub> at room temperature.

Table 1. Observed and calculated  $d$ -values of CF<sub>4</sub> at 6.2 GPa. Lattice constants:  $a = 6.776 \text{ \AA}$ ,  $b = 4.423 \text{ \AA}$ ,  $c = 6.818 \text{ \AA}$  and  $\beta = 102.97^\circ$ .

$hkl$	$d_{obs}$	$d_{calc}$	$hkl$	$d_{obs}$	$d_{calc}$
*	5.510		$\bar{3}12$	1.867	1.8674
011	3.681	3.6818	022	1.841	1.8409
$\bar{1}11$	3.400	3.4006	221	1.831	1.8306
200	3.300	3.3016	113	1.799	1.8001
$\bar{1}02$	3.279	3.2776	311	1.794	1.7935
111	3.058	3.0580	$\bar{2}04$	1.639	1.6388
*	2.876		402	1.631	1.6314
102	2.731	2.7318	$\bar{1}14$	1.590	1.5899
012	2.657	2.6563	$\bar{3}21$	1.575	1.5755
$\bar{2}11$	2.626	2.6257	023	1.564	1.5649
211	2.319	2.3189	014	1.555	1.5550
$\bar{2}12$	2.279	2.2789	410	1.546	1.5466
020	2.212	2.2115	222	1.529	1.5290
021	2.098	2.0970	$\bar{3}22$	1.507	1.5074
$\bar{3}02$	2.059	2.0600	$\bar{3}04$	1.498	1.4972
$\bar{1}13$	2.011	2.0111	321	1.468	1.4677
$\bar{3}11$	2.002	2.0020	114	1.448	1.4473
013	1.980	1.9803	031	1.440	1.4409
121	1.960	1.9601			

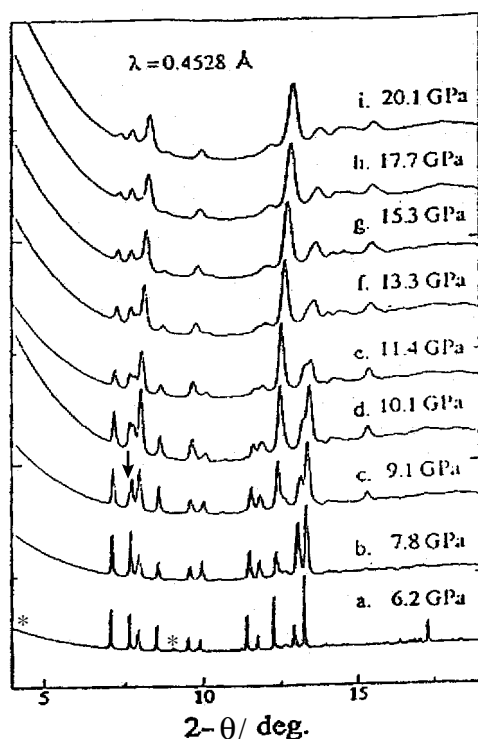


Figure 3. X-ray diffraction profiles of solid  $\text{CF}_4$  at selected pressures.

there are two space lattices, one with a primitive unit cell and the other with a base-centred one. A base-centred lattice ( $hkl$ ;  $h + k = 2n$ ) is ruled out because of the presence of 121 and 102 diffraction lines. The extinction rule permits three space groups,  $P2_1$ ,  $P2_1/m$  and  $P2_1/c$ , in view of the absence of the 010 reflection. Moreover, the absence of the 101 reflection rules out  $P2_1$  and  $P2_1/m$ . Thus the space group of phase III is determined as  $P2_1/c$ , which is isostructural to phase III of  $\text{CCl}_4$  [7]. The observed and calculated  $d$ -values are listed in table 1. The two peaks may be attributable to superlattice reflections.

With increasing pressure a new peak marked by an arrow appeared at 9.1 GPa and the strongest line was shifted to lower angle, which corresponds to the transition into phase IV.

The structure of phase IV, however, could not be clarified. At pressures above 13.6 GPa the diffraction patterns only became broader; they did not change appreciably. The application of pressure to molecular solids is apt to cause the deterioration of their crystallinity. Heat treatment may solve the problem.

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