Pressure-Induced Phase Transition in the 1,2,4,5-Tetrabromobenzene Crystal

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The effects of pressure on the frequencies and band structures of the Raman active inter- and intramolecular vibrations of the 1,2,4,5-tetrabromobenzene crystal were studied under hydrostatic pressures upto 5 GPa at 300 K in a gasketed diamond anvil cell. Changes of the Raman frequencies and band structures of the inter- and intramolecular vibrations induced by pressure suggest that the phase transition takes place under about 0.7 GPa. Comparison of the pressure-induced frequency shifts of the inter- and intramolecular vibrations of the 1,2,4,5-tetrabromobenzene crystal with the frequency shifts observed in the 1,2,4,5-tetrachlorobenzene crystal indicates that the repulsive force between bromine atoms belonging to the adjacent molecules is fairly stronger than the force between chlorine atoms.

Schaum et al.[1] showed first that the phase transition of the 1,2,4,5-tetrabromobenzene crystal takes place above room temperature by microscopic methods. Johnson[2] measured the nuclear quardrupole resonance absorption of the crystal and indicated that the phase transition occurs at 46.5±0.22 °C. Gafner and Herbstein[3,4] studied the crystal structure of the γ and β phases and showed that the γ phase is stable above 46 °C and the β phase below 46 °C. Burgos and Bonadeo[5] and White and Eckhardt[6] studied the Raman active intermolecular vibrations of the 1,2,4,5-tetrabromobenzene crystal and made the assignment of the Raman bands observed for the γ and β phases. Very recently Shimada et al.[7] gave the assignment of the normal vibrations of 1,2,4,5-tetrabromobenzene through the analyses of the Raman and infrared spectra and through the normal coordinate calculation. Shimada et al.[8,9] also studied the pressure and temperature effects on the Raman active intermolecular vibrations of the 1,2,4,5-tetrachlorobenzene crystal and found the phase transitions from the γ to β phases and from the β to α phases.

In this work, the Raman active inter- and intramolecular vibrations of the 1,2,4,5-tetrabromobenzene crystal are studied under high pressure and the pressure-induced phase transition and frequency shifts of the inter- and intramolecular vibrations are discussed.

Experimental

Materials. 1,2,4,5-Tetrabromobenzene obtained from Wako Chemical Company was purified by zone-refining of about 100 passages.

Optical Measurement. The Raman spectra of the inter- and intramolecular vibrations were measured with a JEOL 400T laser Raman spectrophotometer under various pressures from 1 atm (1×10^{-4} GPa) to 5 GPa at 300 K by the backscattering observation method. The 514.5, 488.0, and 476.5 nm beams from an Ar^+ ion laser were used for the excitation. A diamond anvil cell obtained from Toshiba Tungaloy Co. was used for the measurement of the Raman spectrum under high pressure. The experimental methods are exactly the same as those described previously.[7] The pressure inside the gasket hole was determined by measuring the wavelength shift of the R_1 fluorescence line at 694.2 nm emitted from the ruby chips using the equation proposed by Mao et al.[10] The pressure inside the hole was confirmed to be hydrostatic by observing the shapes of the R_1 and R_2 (692.7 nm) fluorescence lines emitted from ruby.

Results and Discussion

Pressure Effect on Intermolecular Vibrations. It was shown that the 1,2,4,5-tetrabromobenzene crystal undergoes the phase transition from the β to γ phases at 46.5 °C and the crystal structures in the β and γ phases belong to the monoclinic space group $P2_1/a$ with two molecules in the unit cell.[3,4] According to the group theory the six rotational intermolecular vibrations are Raman active in both the β and γ phases and these six vibrations are classified into symmetry species A_g and B_g, three vibrations belonging to each species. The four and five Raman bands due to the rotational intermolecular vibrations were observed in the β and γ phase crystals, respectively, and their analyses were made by

the earlier workers.[5,6]

The Raman spectra of the 1,2,4,5-tetrabromobenzene crystal in the intermolecular vibrational region observed under various pressures upto 5 GPa at 300 K are shown in Fig. 1. The spectra due to the intermolecular vibrations observed at 100 °C and 77 K under 1 atm are shown in the top left-hand corner in Fig. 1. The spectrum at 100 °C was ascribed to the γ phase spectrum.[5,6] The spectrum observed under 0.2 GPa consists of three bands and shows the same spectral structure as that observed under 1 atm at 300 K, where the crystal exists in the β phase.[5,6] The spectral structure observed under 0.7 GPa is somewhat complex, while the structure observed under 0.8 GPa becomes simple again. Although the main structure of the 0.8 GPa spectrum consists of three strong bands, the spectral structure is different from that observed in the β phase. The three strong bands observed in the β phase will be referred to as bands β_1, β_2, β_3, the three strong bands observed in a new phase to as bands I, II, and III with increasing wavenumber, respectively, and the shoulder of the band II to as band II′. The spectral structures observed under 1, 2, and 5 GPa are essentially the same as that observed under 0.8 GPa except for the facts that the bands I and III were resolved into two bands, I and I′ and III and III′, and the separations between the bands I and I′ and between the bands III and III′ increase with increasing pressure.

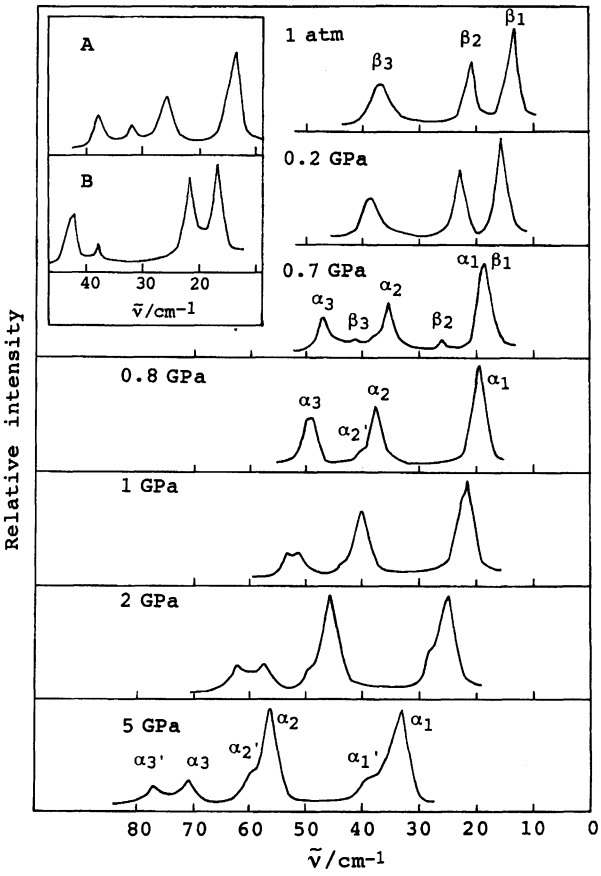

Fig. 1. The Raman spectra of the 1,2,4,5-tetrabromobenzene crystal in the intermolecular vibrational region observed under various pressures at 300 K. The figures given in the top left-hand corner are the spectra observed under 1 atm at 100 °C (A) and at 77 K (B).

The Raman frequency observed under various pressures at 300 K is given in Table 1 and the relationship between the observed frequency and pressure, which well be called as the pressure-frequency curve hereafter, is shown in Fig. 2. Figure 2 shows that (1) the frequency increases monotonically and continuously with increasing pressure from 1 atm (1×10^{-4} GPa) to about 0.7 GPa, (2) the discontinuity of the pressure-frequency curve is observed under about 0.7 GPa, and (3) the frequency increases monotonically again with increasing pressure from about 0.7 to 5 GPa. These observations indicate that (1) a phase transition of the 1,2,4,5-tetrabromobenzene crystal takes place under about 0.7 GPa, (2) comparing with the pressure-induced phase transition of the 1,2,4,5-tetrachlorobenzene crystal,[7] a new phase observed under pressures from 0.8 to 5 GPa are able to be ascribed to the α phase, and (3) the spectrum observed under 0.7 GPa can be explained by the overlap of the intermolecular vibrational bands in the β and α phases. The complex spectral structure may be given by the crystal in a transient state from the β to α phases under about 0.7 GPa. The band β_1 could not be resolved because of the overlapping of the strong band in the α phase under about 0.7 GPa. The bands

Table 1. Raman Frequencies of Intermolecular Vibrations of 1,2,4,5-Tetrabromobenzene Crystal

β Phase				α Phase			
	1 atm	0.2 GPa	0.7 GPa		0.7 GPa	2 GPa	5 GPa
	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}
β_1	14	16	19	α_1	19	25	32
β_2	21	23	26	$\alpha_{1'}$	19	28	39
β_3	37	39	42	α_2	36	45	56
				$\alpha_{2'}$	40	49	59
				α_3	47	57	71
				$\alpha_{3'}$	47	62	77

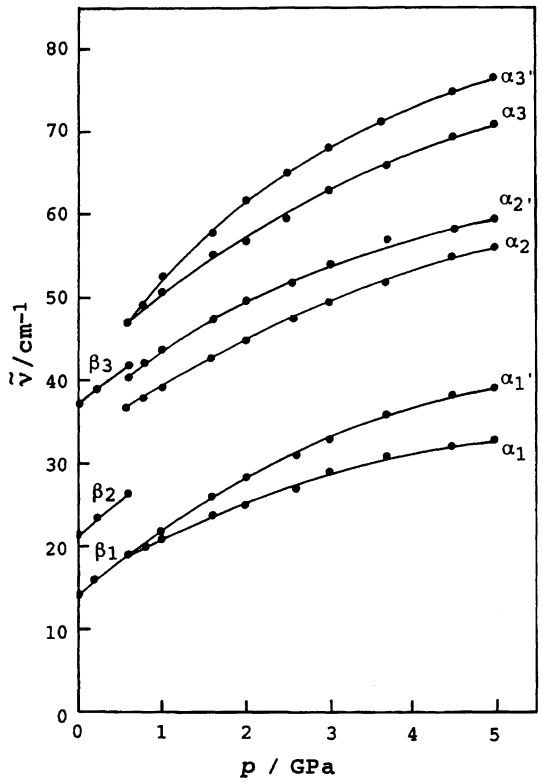

Fig. 2. Pressure effect on the intermolecular vibrational frequencies of the Raman bands of the 1,2,4,5-tetrabromobenzene crystal observed at 300 K. 1 atm corresponds to 1×10^{-4} GPa (Ca. 0 GPa).

I, II, and III are referred to as the bands α_1, α_2, and α_3, respectively.

Unfortunately the precise value of pressure inducing the transition from the β to α phases in the 1,2,4,5-tetrabromo- and tetrachlorobenzene crystals could not be determined and therefore, it could not be clear which of the 1,2,4,5-tetrabromo- and tetrachlorobenzene crystals undergoes the phase transition under lower pressure. The Raman spectrum due to the intermolecular vibrations of the 1,2,4,5-tetrabromobenzene crystal observed at 77 K under 1 atm can be ascribed to the β phase spectrum as can be seen in Fig. 1, while the Raman spectrum of the 1,2,4,5-tetrachlorobenzene crystal observed at 77 K under 1 atm was ascribed to the α phase spectrum.[7] This means that the phase transition from the β to α phases is already completed at 77 K in the 1,2,4,5-tetrachlorobenzene crystal, while the 1,2,4,5-tetrabromobenzene crystal still exists in the β phase at 77 K. These observed facts may suggest that the slope of the β phase–α phase equilibrium line in the pressure–temperatre phase diagram, dT/dp, for the 1,2,4,5-tetrabromobenzene crystal is greater than that for the 1,2,4,5-tetrachlorobenzene crystal.

The ratio of the pressure-induced frequency shift to the frequency observed under 1 atm or 0.7 GPa, $\Delta\tilde{\nu}/\tilde{\nu}$, for the intermolecular vibrations is discussed. The values of $\Delta\tilde{\nu}/\tilde{\nu}$ are defined as $(\tilde{\nu}_{p\ \mathrm{GPa}}-\tilde{\nu}_{1\ \mathrm{atm}})/\tilde{\nu}_{1\ \mathrm{atm}}$ and $(\tilde{\nu}_{p\ \mathrm{GPa}}-\tilde{\nu}_{0.7\ \mathrm{GPa}})/\tilde{\nu}_{0.7\ \mathrm{GPa}}$ for the β and α phases, respectively. The maximum and the minimum values among the values of $\Delta\tilde{\nu}/\tilde{\nu}$ for the six intermolecular vibrations of the 1,2,4,5-tetrachlorobenzene and 1,2,4,5-tetrabromobenzene crystals are plotted against pressure together with the maximum and the minimum values for the benzene crystal in Fig. 3. This figure shows that the values of $\Delta\tilde{\nu}/\tilde{\nu}$ for the 1,2,4,5-tetrabromobenzene crystal are smaller than the values for the 1,2,4,5-tetrachlorobenzene crystal in both the β and α phases.

The anharmonicity of the intermolecular potential plays an important role for the frequency shift of the intermolecular vibrations and the frequency shift is related to the anharmonic force constant and the change of the equilibrium intermolecular distance, which is related to the compressibility of the crystal. Vaidya and Kennedy[12] observed the compressibility of various molecular organic crystals under pressure from 1 atm to 4.5 GPa and found that the compressibility decreases with increasing molecular volume and the compressibility in the hexabromobenzene crystal is smaller than that in the hexachlorobenzene crystal. These facts might suggest that the rate of the decrement of the intermolecular distance between neighboring molecules with

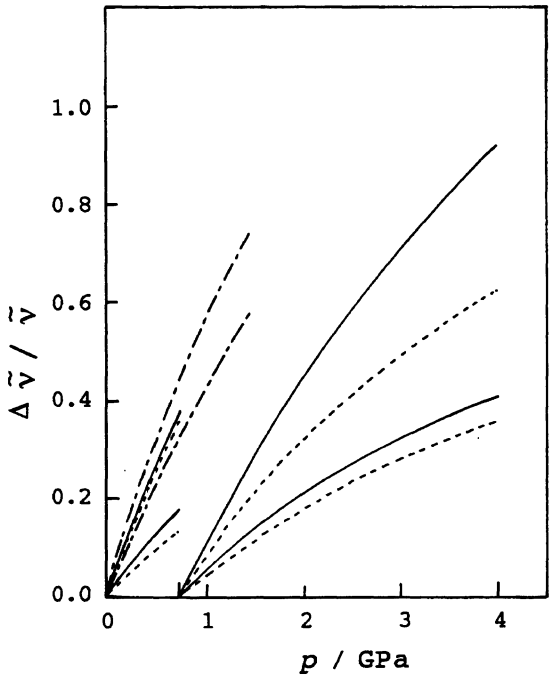

Fig. 3. Pressure effect on the maximum and minimum values among the six values of $\Delta\tilde{\nu}/\tilde{\nu}$ for the intermolecular vibrational Raman bands of the 1,2,4,5-tetrabromobenzene (---), 1,2,4,5-tetrachlorobenzene (—), and benzene (---) crystals. The values of $\Delta\tilde{\nu}/\tilde{\nu}$ are defined as $(\tilde{\nu}_{p\ \mathrm{GPa}}-\tilde{\nu}_{1\ \mathrm{atm}})/\tilde{\nu}_{1\ \mathrm{atm}}$ and $(\tilde{\nu}_{p\ \mathrm{GPa}}-\tilde{\nu}_{0.7\ \mathrm{GPa}})/\tilde{\nu}_{0.7\ \mathrm{GPa}}$ for the β and α phases of the 1,2,4,5-tetrabromo- and 1,2,4,5-tetrachlorobenzene crystals, respectively. For the benzene crystal the former definition is applied.

increasing pressure is smaller in the 1,2,4,5-tetrabromobenzene crystal than in the 1,2,4,5-tetrachlorobenzene crystal because of the larger van der Waals radius of the Br atom than the radius of the Cl atom. This circumstance may be ascertained by the observation that the values of $\Delta\tilde{\nu}/\tilde{\nu}$ (in particular the minimum values) for the 1,2,4,5-tetrachloro- and tetrabromobenzene crystals are fairly smaller than the minimum values for the benzene crystal as can be seen in Fig. 3.

The difference of the anharmonic force constant in the benzene, 1,2,4,5-tetrachlorobenzene, and 1,2,4,5-tetrabromobenzene crystals should also give a different contribution to the frequency shift. If overtone vibrations were observed, the contribution of the anharmonic force constant to the frequency shift could be estimated.

Pressure Effect on Intramolecular Vibrations. The Raman spectra observed under various pressures are essentially the same as that observed under 1 atm, which is shown in Fig. 4, except for the bands showing the blue shift with increasing pressure. The bands observed at 124, 219, 316, 667, 1124, 1526, 1542, and 3047 cm^{-1} under 1 atm are assigned to the ν_{9a} (Br bending), ν_{7a} (C–Br stretching), ν_{10a} (Br wagging), ν_{6a} (Ring), ν_1 (Ring), ν_{8a} (Ring), ν_{8b} (Ring), and ν_2 (C–H stretching) vibrations, respectively (Table 2).[9] These eight bands are clearly resolved under high pressures up to 5 GPa.

The observed pressure–frequency curves for these vibrations are shown in Fig. 5, where the differences of the pressure-induced frequency shifts, $\Delta\tilde{\nu}=\tilde{\nu}_{p\ \mathrm{GPa}}-\tilde{\nu}_{1\ \mathrm{atm}}$, are plotted in the ordinates. This figure shows that (1) the observed frequency shift in the β phase increases monotonically with increasing pressure at the rate of 7—25 $cm^{-1}\,GPa^{-1}$ depending on the vibrational modes up to about 0.5 GPa, while the rate of the observed frequency shift decreases abruptly from about 0.5 to 0.7 GPa for all vibrational modes, and (2) the observed frequency shift in the α phase increases monotonically again at the rate of 2—7 $cm^{-1}\,GPa^{-1}$ from about 0.7 to 5 GPa depending on the vibrational modes.

The ratio of the pressure-induced frequency shift to the frequency, $\Delta\tilde{\nu}/\tilde{\nu}$, under various pressures is given in Fig. 6 for the ν_{9a}, ν_{7a}, ν_{6a}, and ν_1 vibrations of the

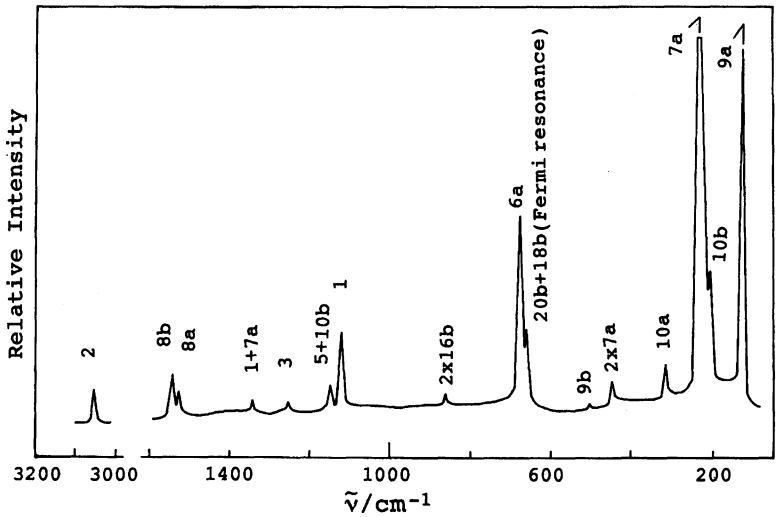

Fig. 4. The Raman spectrum of the 1,2,4,5-tetrabromobenzene crystal in the intramolecular vibrational region observed under 1 atm at 300 K.

Table 2. Calculated and Observed Frequency Shifts of the Raman Active Intramolecular Vibrations of 1,2,4,5-Tetrabromobenzene

Mode	$\tilde{\nu}_{p\ \mathrm{GPa}}$ Obsd			$\tilde{\nu}_{0.7\ \mathrm{GPa}}-\tilde{\nu}_{1\ \mathrm{atm}}$ Obsd	Calcd
	1 atm	0.7 GPa	5 GPa		
	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$
9a	124	130	144	6	2.1
7a	219	225	234	6	8.7
10a	316	324	338	8	4.7
6a	667	669	676	2	1.2
1	1124	1130	1138	6	0.3
8a	1526	1534		8	0.3
8b	1542	1548	1562	6	0.3
2	3047	3049	3057	2	0.6

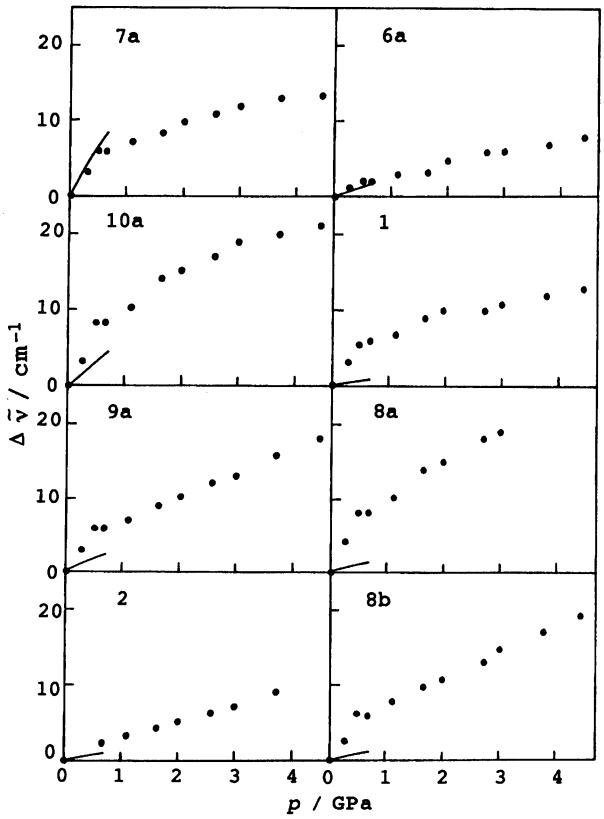

Fig. 5. Pressure effect on the intramolecular vibrational Raman bands of the 1,2,4,5-tetrabromobenzene crystal. The observed (····) and calculated (——) frequency shifts, $\Delta\tilde{\nu}=\Delta\tilde{\nu}_{p\ \mathrm{GPa}}-\Delta\tilde{\nu}_{1\ \mathrm{atm}}$, are plotted in the ordinate.

1,2,4,5-tetrabromobenzene crystal together with the ratio for the 1,2,4,5-tetrachlorobenzene crystal. The definition of the $\Delta\tilde{\nu}/\tilde{\nu}$ for the α and β phases are the same as those described in the frequency shift of the intermolecular vibrations. This figure shows that (1) the value of $\Delta\tilde{\nu}/\tilde{\nu}$ for the Br displacement vibrations is larger than the value for the Cl displacement vibrations, which in turn is much larger than the value for the ring vibrations and (2) the value of $\Delta\tilde{\nu}/\tilde{\nu}$ for the ring vibrations of 1,2,4,5-tetrabromobenzene is nearly equal to the values for tetrachlorobenzene.

The pressure-induced frequency shift of the intramolecular vibrations with neighboring six molecules was calculated for the ν_{9a}, ν_{10a}, ν_{7a}, ν_2, ν_{6a}, ν_1, ν_{8a}, and ν_{8b} vibrations under various pressures from 1 atm to 0.7 GPa in the β phase in the same way as described previously.[7] The parameters of the intermolecular potential were taken from the data given by Spackman.[11] The molecular geometry and the molecular orientation in crystal were assumed to keep unchanged under application of high pressure. The values of compressibility were not reported for the 1,2,4,5-tetrabromobenzene crystal and thus, the values were assumed to be the same as those given for the hexachlorobenzene

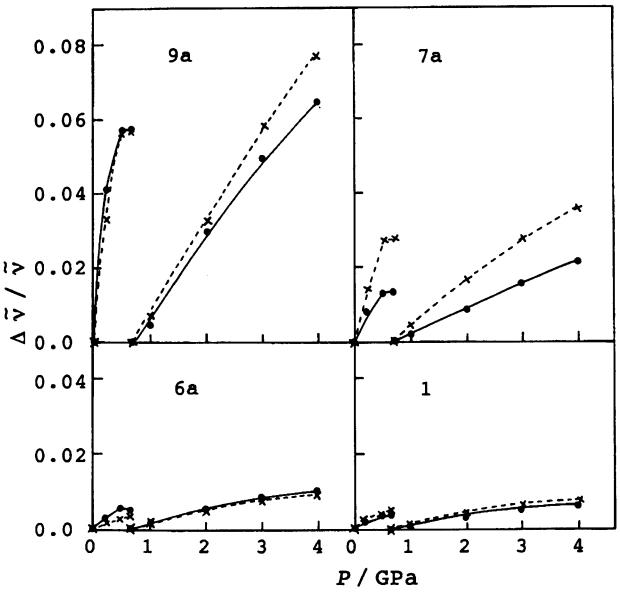

Fig. 6. Pressure effect on the values of $\Delta\tilde{\nu}/\tilde{\nu}$ for the intramolecular vibrational Raman bands of the 1,2,4,5-tetrabromo- (-× - -× -) and 1,2,4,5-tetrachlorobenzene (—•—) crystals. The values of $\Delta\tilde{\nu}/\tilde{\nu}$ are defined as $(\tilde{\nu}_{p\ \mathrm{GPa}}-\tilde{\nu}_{1\ \mathrm{atm}})/\tilde{\nu}_{1\ \mathrm{atm}}$ and $(\tilde{\nu}_{p\ \mathrm{GPa}}-\tilde{\nu}_{0.7\ \mathrm{GPa}})/\tilde{\nu}_{0.7\ \mathrm{GPa}}$ for the β and α phases, respectively.

crystal[12] just as the case for the calculation of the pressure-induced frequency shift of the 1,2,4,5-tetrachlorobenzene crystal.[7] The calculated frequency–pressure curves are shown in Fig. 5 together with the observed pressure–frequency curves. The calculated frequency–pressure curves show large discrepancy from the observed frequency shifts contrary to the results obtained for the 1,2,4,5-tetrachloro- and hexachlorobenzene crystals, where the agreement between the calculated and observed pressure-induced frequency shifts is fairly well.[7,13]

In order to improve the calculated frequency shift the parameters of the intermolecular potential for the Br atom, the changes of the molecular geometry and the molecular orientation in the crystal by pressure, and the anharmonicity of the vibration must be examined. The normal coordinate calculation was carried out by changing the C–Br distance from 0.1888 nm (under 1 atm)[3,4] to 0.17 nm (about 90 % of the C–Br distance under 1 atm). The decrease of the C–Br distance causes the considerably large increase of the vibrational frequency for the Br displacement modes (maximum increase is 16 cm^{-1} for the ν_{10a} mode) but hardly affects the change of frequency for the ring vibrational modes. Therefore, the change of the molecular geometry by pressure may not be a grave responsibility for the large discrepancy between the observed and calculated frequency shifts. The examination of the parameters of the potential is now carried out by studying the pressure effect on the inter- and intramolecular vibrations of hexabromo-

benzene crystal. The reexamination of the molecular orientation in the 1,2,4,5-tetrabromobenzene crystal is sincerely needed. We are now studying the pressure effect on the intramolecular vibrations for various organic molecular crystals, whose frequency shifts can not be explained only by examining the modification of the parameters of the potential and the molecular orientation in the crystal. The effect of the anharmonicity on the frequency shift will be discussed in further works. The calculation could not be made in the α phase because the crystal structure in the α phase was not available.

In conclusion the pressure effect on the Raman bands due to the inter- and intramolecular vibrations of the 1,2,4,5-tetrabromobenzene crystal indicates that (1) the crystal undergoes the phase transition from the β to α phases under the pressure of about 0.7 GPa (2) the intermolecular repulsive interaction in the 1,2,4,5-tetrabromobenzene crystal is fairly stronger than the interaction in the 1,2,4,5-tetrachlorobenzene crystal.

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