

Pressure Effect on the Raman Spectra of α - and γ -Glycine Crystals

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Pressure effects on the Raman active bands due to the inter- and intramolecular vibrations of α and γ -glycine crystals were studied at hydrostatic pressure up to about 4 GPa at room temperature in gasketed diamond anvil cell. The observed Raman spectra indicate the following facts. No change of orientation of molecules takes place in α -glycine crystal up to 4 GPa. In γ -glycine crystal, the Raman bands observed in orientation of molecules at ambient pressure decrease intensity with increasing pressure and are hardly observed above about 2.5 GPa. On the other hand, the new Raman bands observed above about 1.5 GPa increase intensity with increasing pressure and only the new bands are detected above about 2.5 GPa. These facts suggest that (1) molecular orientation in crystal becomes to change gradually at 1.5 GPa, (2) two different molecular orientations coexist at pressure region between about 1.5 and 2.5 GPa, and (3) a new molecular orientation is stable at pressure region between 2.5 and 4 GPa in γ -crystal.

Glycine has three polymorphs named α , β and γ . The mechanism of crystallization of glycine from its aqueous solution is complicated. α -Form crystallized from aqueous solution by evaporation of water and γ -form crystallized from basic aqueous solution are stable, but β -form crystallized by any method is quite unstable¹⁾⁻⁴⁾. The Raman spectra⁵⁾⁻⁹⁾, calculation of molecular vibrations¹⁰⁾, and crystal structures^{1),11)-13)} of α -, β - and γ -glycine crystals at ambient pressure were studied by many workers.

The phase transition induced by pressure was discussed for α -glycine crystal based on the pressure effect on the Raman spectra due to intermolecular vibrations¹⁴⁾. Study of pressure-induced lattice strains of α - and γ -glycine crystals was made through X-ray powder diffraction using a synchrotron radia-

tion source¹⁵⁾. No Raman study at high pressure for γ -glycine crystal was made and therefore, data for the pressure-induced phase transition of γ -glycine crystal are not available.

In this work, the Raman active inter- and intramolecular vibrations of α - and γ -glycine crystals are studied at high pressure, and the pressure-induced phase transitions are discussed.

Experimental

Materials.

Glycine was obtained from Wako Chemicals. α -Glycine crystal was crystallized by allowing to stand of neutral water solution of glycine for two months, and γ -glycine crystal was crystallized by leaving glycine in ammonium hydroxide water solution overnight.

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Optical Measurement.

The Raman spectra of α - and γ -glycine crystals due to the inter- and intramolecular vibrations were measured with a JOBIN YVON T64000-FU Laser Raman Spectrophotometer. The spectra were observed at various pressures from 1 atm (1×10^{-4} GPa) to about 4 GPa at 298 K by the backscattering observation method. A diamond anvil cell, obtained from Toshiba Tungaloy Co. , was used for measurements of the Raman spectra at high pressures. The 514.5 nm beam from an Ar⁺ ion laser of Spectra Physics was used for the excitation.

The method of observation of the Raman spectra is exactly the same as described previously^{16,17}. The pressure initially applied to sample being filled in the diamond anvil cell was almost 0.2 GPa for all cases. The pressure was applied gradually at the rate of about 0.1 GPa/day from 0.2 to 4 GPa. The sample was left overnight after pressure was applied. The pressure inside the gasket hole was measured by the wavelength shift of the R₁ fluorescence line at 694.2 nm emitted from ruby chips, using the equation proposed by Mao *et al*¹⁸. The pressure inside the hole was confirmed to be hydrostatic by observing the shapes of the R₁ and R₂ (692.7 nm) fluorescence lines emitted from the ruby.

Results and Discussion

A. Pressure Effects on Intermolecular Vibrations.

A-1. α -Glycine crystal

The melting point of glycine is 225°C at 1 atm. The crystal structure of α -glycine at ambient condition belongs to the monoclinic space group P2₁/n with four molecules in the unit cell¹³. In the α -glycine, zwitter-ions are linked by hydrogen bonds in double anti-parallel layers, the interactions between these double layers being purely van der Waals

force. Double layers of molecules is oriented perpendicularly to the crystallographic b-axis direction.

The Raman spectrum of α -glycine crystal in the intermolecular vibrational region observed at 298 K at 1 atm and the spectra observed at various pressures at 298 K are shown in Figs. 1 and 2, respectively. The spectral structures observed at various pressures up to 4 GPa are essentially the same as that observed at 1 atm. The pressure-frequency shift curves (the frequency plotted against pressure) are given in Fig. 2. The frequencies increase continuously with increasing pressure, and the slopes of the pressure-frequency shift curves show no clear discontinuity at pressure between 1 atm and 4 GPa. These behaviors support that no first-order phase transition takes place at pressure region between 1 atm and 4 GPa in α -glycine crystal. The vibrational frequencies observed at various pressures are given in Table 1.

A-2. γ -Glycine crystal

The crystal structure of γ -glycine at ambient condition belongs to the hexagonal space group P3₁ or P3₂ with three molecules in the unit cell¹¹. In the γ -glycine crystal, zwitter-ions form helix structure and lateral hydrogen bonds form a three dimensional network.

The Raman spectrum of γ -glycine crystal in the intermolecular vibrational region observed at 298 K at 1 atm and the spectra observed at various pressures at 298 K are shown in Figs. 1 and 3, respectively. The pressure-frequency shift curves are given in Fig. 3.

The spectrum consists of three bands at 1 atm. The spectral structure became much complex by successive application of pressure from about 1.5 GPa and seven bands (1, 1', 2, 3, 4, 5, 6) were observed at pressure region from 1.5 to 2.5 GPa. The spectra above 2.5

GPa consists of four bands and the spectral structure remained unchanged with increasing pressure from 2.5 to 4 GPa. The Raman frequencies of these bands are given in Table 1.

The observation of the change of the spectral structure and discontinuity in the pressure-frequency curves indicates that

some structural reorganization takes place gradually at pressure region between 1.5 and 2.5 GPa in γ -glycine crystal. The structural organizations existing below 1.5 and above 2.5 GPa are referred to as phases γ and γ' , respectively. The phases γ and γ' coexist at pressure region from 1.5 to 2.5 GPa.

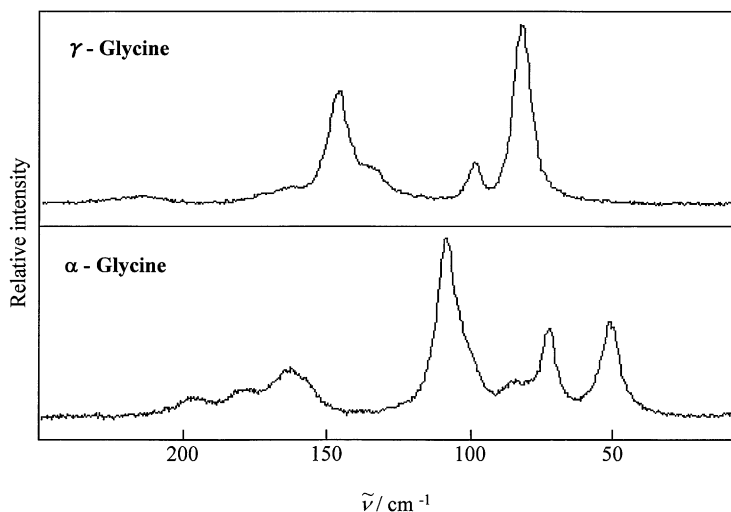


Fig. 1. The Raman spectra of α - and γ -glycine crystals in the intermolecular vibrational region observed at 1 atm. 1 atm corresponds to 10^{-4} GPa (≈ 0 GPa).

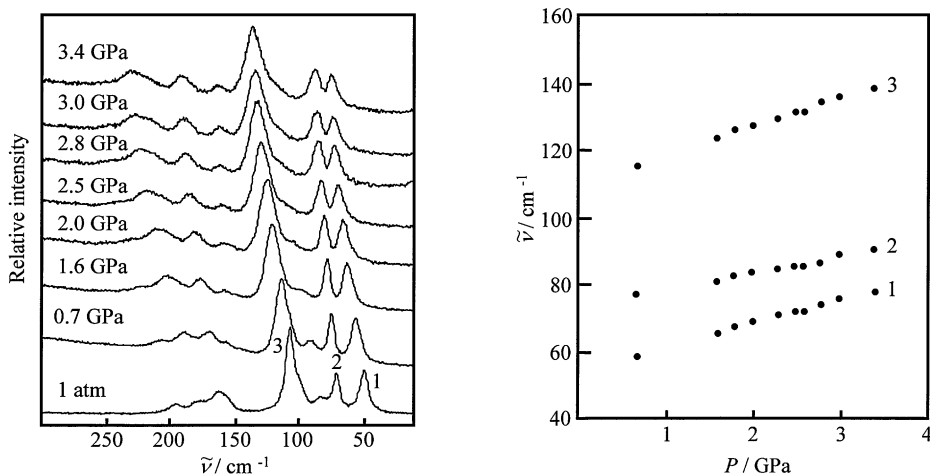


Fig. 2. The Raman spectra observed at various pressures and pressure-frequency curves of α -glycine crystal in the intermolecular vibrational region.

Table 1. Raman Frequencies of Intermolecular Vibrations of α - and γ -Glycine Crystals

α -glycine				γ -glycine				
	1 atm	2 GPa	4 GPa		1 atm	1.5 GPa	2 GPa	4 GPa
band	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	band	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$
1	51	72	82	1	89	96		
2	73	84	93	1'	29	32	98	106
3	109	129	142	2	105	110	112	
				3		122	125	127
				4			137	153
				5	139	149	155	167
				6	151	163	168	

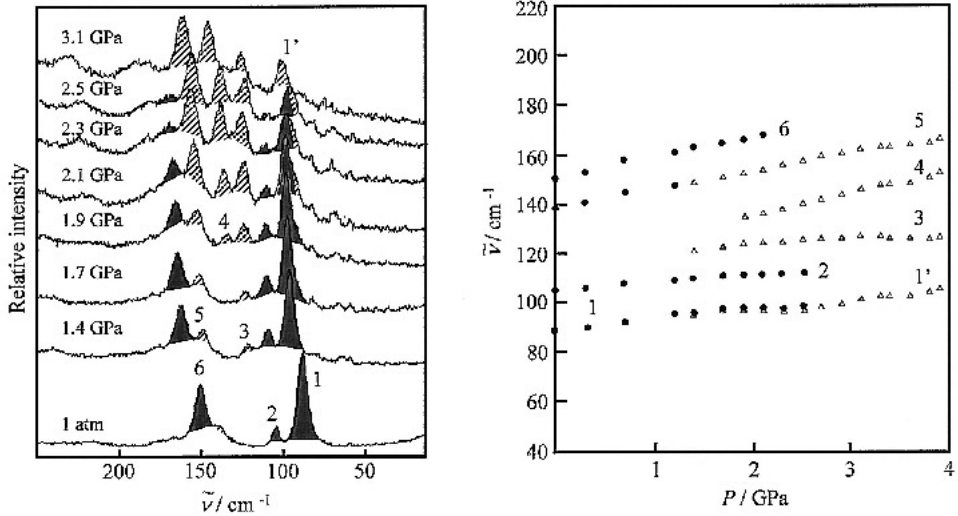


Fig. 3. The Raman spectra observed at various pressures and pressure-frequency curves of γ -glycine crystal in the intermolecular vibrational region.

B. Pressure Effects on Intramolecular Vibrations.

B-1. α -Glycine crystal

The Raman spectrum of α - and γ -glycine crystals in the intramolecular vibrational region observed at 1 atm at 298 K is shown in Fig.4, together with the assignments. The assignment was taken from those

given by Tsuboi et al. and Alper et al.^{9,10}, and that made in this work. The Raman spectra of α -glycine observed at various pressures are shown in Fig.5, together with the pressure-frequency curves. The Raman frequencies for the vibrational modes observed at various pressures are given in Table 2.

The spectral structure observed at vari-

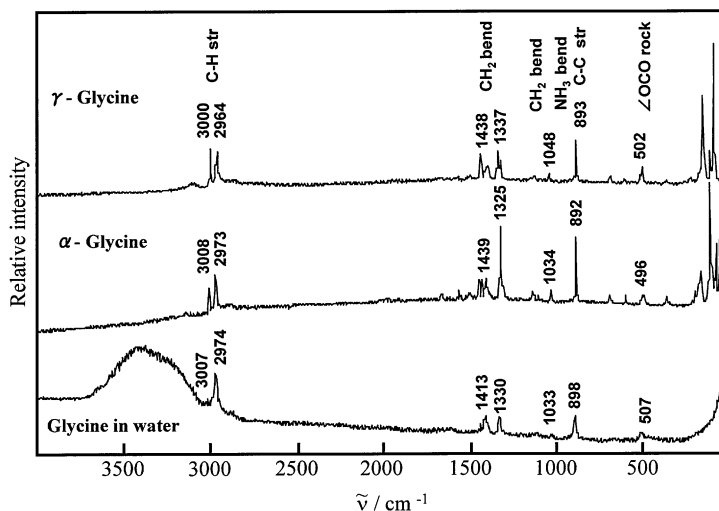


Fig. 4. The Raman spectra of α - and γ -glycine crystals in the intramolecular vibrational region observed at 1 atm.

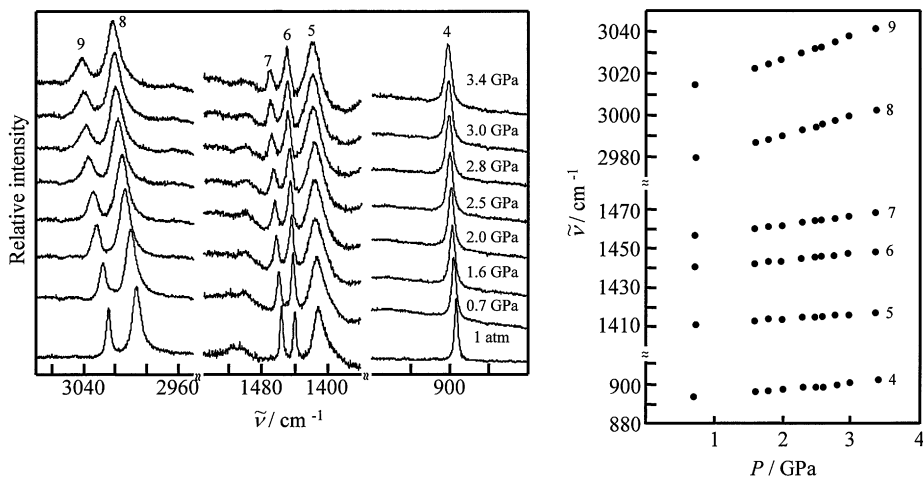


Fig. 5. The Raman spectra observed at various pressures and pressure-frequency curves of α -glycine crystal in the intramolecular vibrational region.

ous pressures is essentially the same as that observed at 1 atm. The pressure-frequency shift curves is given in Fig.5. The frequencies increase continuously with increasing pressure, and the slopes of the pressure-frequency shift curves show no clear discontinuity at pressure between 1 atm and 4 GPa as observed in the intermolecular vibrations. These behaviors support the fact that no first-order phase transition takes place at pressure

region between 1 atm and 4 GPa in α -glycine crystal as just suggested in the intermolecular vibrations.

B-2. γ -Glycine crystal

The Raman spectra of γ -glycine observed at various pressures are shown in Fig. 6, together with the pressure-frequency curves. The Raman frequencies for the vibrational modes observed at various pressures

Table 2. Raman Frequencies of Intramolecular Vibrations of α - and γ -Glycine Crystals

α -glycine				γ -glycine					
	1 atm	2 GPa	4 GPa	1 atm*		1 atm	2GPa	4 GPa	1 atm*
band	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	band	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$
9	3008	3031	3048		13	3000	3013		
8	2973	2993	3007		14		3033	3049	
7	1456	1465	1471	1450	11	2965	2972		
6	1439	1446	1451	1440	12		2999	3015	
5	1411	1415	1419	1395	9	1438			1435
4	892	900	905	895	10		1449	1457	
					7	893	902		893
					8		897	903	

* Taken from reference 9.

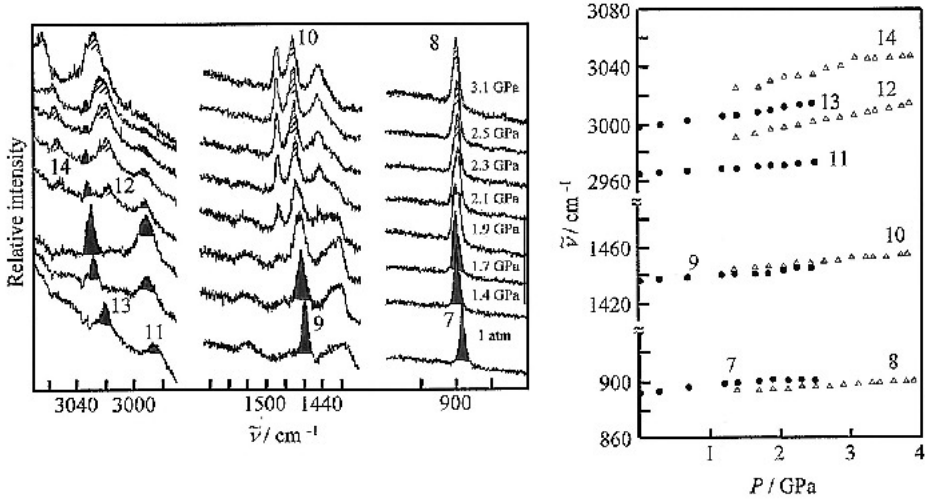


Fig. 6. The Raman spectra observed at various pressures and pressure-frequency curves of γ -glycine crystal in the intramolecular vibrational region.

are given in Table 2.

The four bands named as 7, 9, 11, and 13 (painted with black in Fig. 6) are observed strongly in the Raman spectrum at 1 atm. As increasing pressure from about 1.5 GPa, new band 8 is distinguished in lower fre-

quency side of band 7, band 10 in higher frequency side of band 9, and bands 12 and 14 are observed in lower and higher frequency sides of band 13, respectively. In these new bands, oblique lines are drawn in Fig. 6. The pressure-frequency curves of bands

shown with black paint and oblique lines are shown by closed circles and open triangles, respectively. The pressure-frequency curves indicate that closed circles and open triangles overlap in pressure region between about 1.5 and 2.5 GPa. This fact suggests that molecular orientation in γ crystal being stable at 1 atm becomes to change gradually to molecular orientation being stable in γ' crystal from about 1.5 GPa to above 2.5 GPa, and only γ' crystal is stable up to 4 GPa. The pressure-induced behaviors of the Raman bands are the same as those described for intermolecular vibrations.

The two factors are necessarily to be taken into account in the discussion of the pressure-induced frequency shift of the inter- and intramolecular vibrations. The first factor is the fact that in molecular crystals consisted of van der Waals force (composed of intermolecular repulsive and dispersive forces), repulsive and dispersive forces induce large blue and small red shifts, respectively, and, therefore, the frequency of the inter- and intramolecular vibrations in molecular crystals increases with increasing pressure for all vibrations. When phase transition takes place in molecular crystals, discontinuous frequency red-shift occurs since the large intermolecular repulsive forces are relaxed by phase transition^{16,17}. The second factor is the fact that the attractive force resulting from hydrogen bond gives various effects for the frequency shifts, that is, the red shift for the frequencies of the correlated stretching vibrations, and the blue shift for the correlated bending and wagging vibrations.

All vibrations observed in this work show relatively small blue frequency shifts compared with frequency blue shifts for vibrations of molecular crystals^{16,17}. This fact indicates that in α - and γ -glycine crystals, hydrogen bonds affect for pressure-induced frequency shift as well as the van der Waals

force.

Pressure-induced reorientation of molecules in γ -glycine crystal is detected, although the reorientation of molecules in α -glycine crystal is hardly detected in this work as described above. This fact may be due to the fact that the lateral hydrogen bond forming a three dimensional network in γ -glycine crystal would be stronger than the interlayer hydrogen bonds existing in the α -glycine crystal. Hence, strong intermolecular repulsive force induced by pressure may be absorbed by weak intermolecular hydrogen bonds in α -glycine crystal. On the other hand, the repulsive force may be relaxed by reorganization of molecular orientation.

In conclusion, the study of pressure effects on the Raman bands due to the inter- and intramolecular vibrations of α - and γ -glycine crystals gives the following results. (1) Hydrogen bonding force effects on the pressure-induced frequency shift for inter- and intramolecular vibrations as well as the intermolecular van der Waals force. (2) The pressure-induced frequency shift effected by hydrogen bonding forces is stronger in γ -glycine crystal than that in α -crystal.

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