Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Synthesis, crystal structure, and phase transition of a Xe-N_2 compound at high pressure: Experimental indication of orbital interactions between xenon and nitrogen

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Experimental set-up

High-pressure experiments were carried out using a diamond anvil cell (DAC) with a culet size of 250 or 350 μm in diameter. A sample hole with 1/3 of the diamond culet size was prepared after the indentation of a stainless steel (SUS) or Re gasket. First, the gasket-equipped DAC was cooled to the temperature of liquid nitrogen. Then, gaseous xenon was slowly sprayed onto the sample hole. The sample chamber was closed after a large amount of solidified xenon had been deposited. The xenon-loaded DAC was then soaked completely with liquid nitrogen. Finally, the DAC was opened slightly to allow entry of liquid nitrogen into the sample chamber. The chamber was then closed. Some data collection runs used Au as a pressure maker loaded together with the xenon and nitrogen. The pressure of the sample chamber was reduced to less than 1 GPa to mix the liquid xenon and nitrogen homogeneously. The pressure was determined by the shift in the ruby fluorescence peak[1] or the diamond Raman scale.[2] The sample was examined by optical microscopy, high-pressure in-situ X-ray diffraction (Mo-K_α and synchrotron radiation), and Raman scattering experiments. The synchrotron X-ray diffraction experiments were carried out at NE1 (PF-AR) of the synchrotron facility of KEK, Japan and BL2S1 of the Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation, Aichi, Japan. For the experiments at NE1, the X-ray beam was shaped with a size of approximately 30 μm diameter, and the sample was irradiated parallel to the compression axis. The diffracted X-rays were recorded on an image plate with an exposure time of 15–30 min. In contrast, for the experiments at AichiSR, the incident X-rays were collimated to the size of a 100 μm square and the sample was irradiated parallel to the compression axis. The diffracted X-rays were recorded on a charge coupled device detector. The exposure time was 3 min. The sample-to-detector distance, wavelength, and degree-of-tilt of the detector were calibrated based on the diffraction pattern of a standard material (CeO_2) before the sample measurements. A two-dimensional diffraction image was integrated into the conventional one-dimensional diffraction pattern by using the IPanalyzer. An Ar^+-ion laser ($\lambda = 488$ nm) was used as an excitation source for the high-pressure, in-situ Raman scattering measurements. A finely focused Ar^+-ion laser irradiated the sample through the low-fluorescence diamond anvil, and Raman scattered light was collected with a spectrometer consisting of a diffraction grating with 1800 lines/mm and a liquid-nitrogen cooled charge-coupled device (CCD) detector. Data analyses, including the peak fitting, crystal symmetry determination, diffraction profile simulation, and depiction of the crystal structure, were carried out using dedicated software. More than 20 experiments were conducted to ensure the reproducibility of the results in this study.

References

1. H. K. Mao, J. Xu and P. M. Bell, *J. Geophys. Res.*, 1986, **91**, 4673.

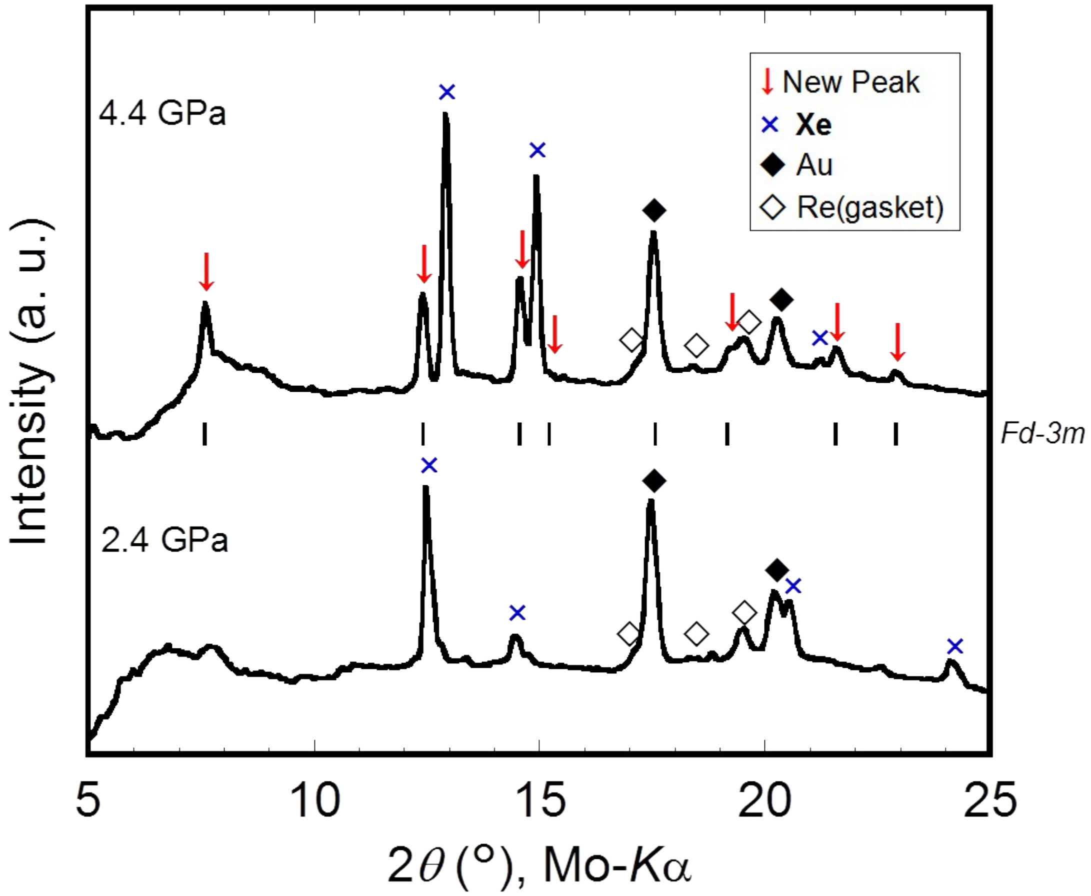
2. Y. Akahama, H. Kawamura, *J. Appl. Phys.*, 2004, **96**, 3748.

3. Y. Seto, D. Nishio-Humane, T. Nagai, N. Sata, *The Review of High-Pressure Science and Technology*, 2010, **20**, 269. (Japanese article with English abstract).

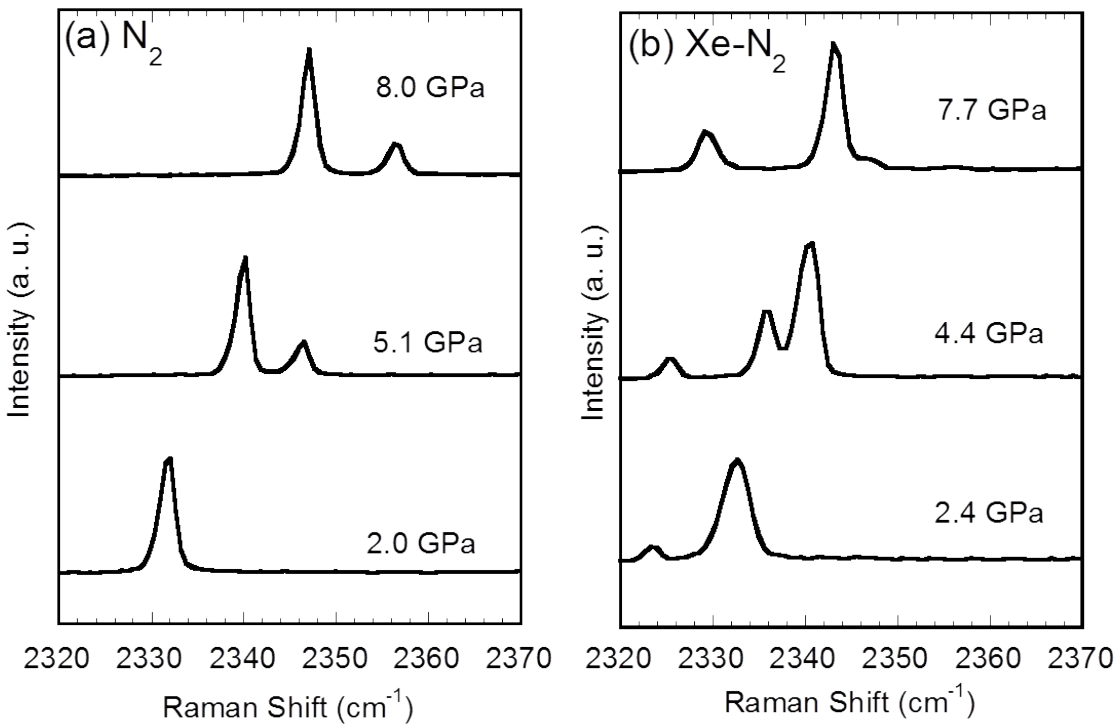
4. A. Boultif, D. Louer, *J. Appl. Crystallogr.*, 2004, **37**, 724.

5. K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2008, **41**, 653.

S1

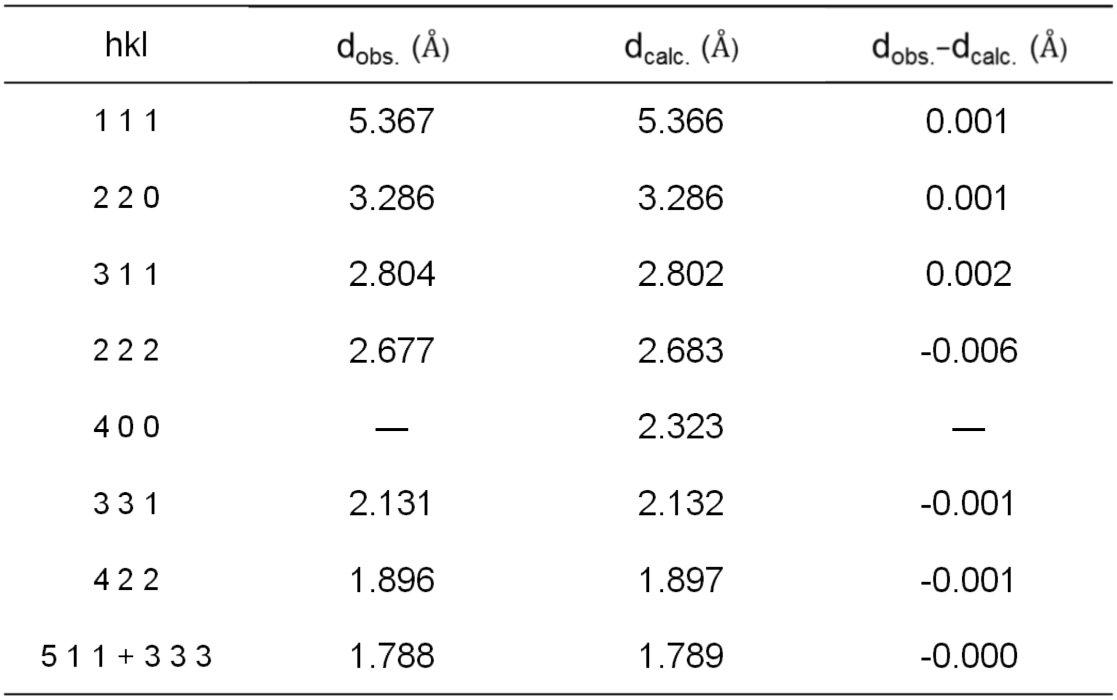


XRD profiles of the Xe-N_2 sample mixture measured at 2.4 and 4.4 GPa and room temperature.



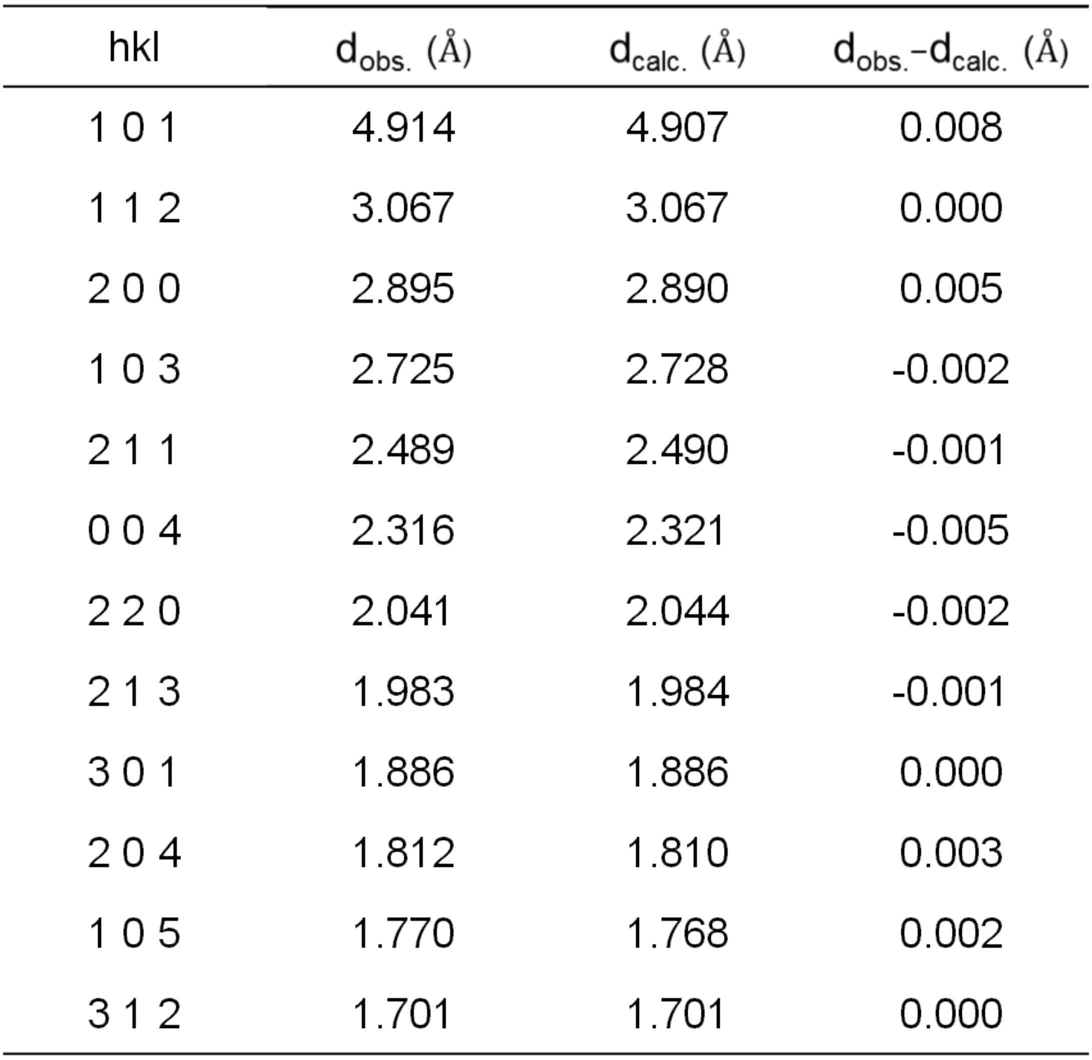
Raman spectra of (a) pure molecular nitrogen and (b) the Xe-N_2 sample up to approximately 8 GPa. The Raman peaks derive from the stretching vibrational modes of N_2.

S3



hkl	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	$d_{obs.}$–$d_{calc.}$ (Å)
1 1 1	5.367	5.366	0.001
2 2 0	3.286	3.286	0.001
3 1 1	2.804	2.802	0.002
2 2 2	2.677	2.683	-0.006
4 0 0	—	2.323	—
3 3 1	2.131	2.132	-0.001
4 2 2	1.896	1.897	-0.001
5 1 1 + 3 3 3	1.788	1.789	-0.000

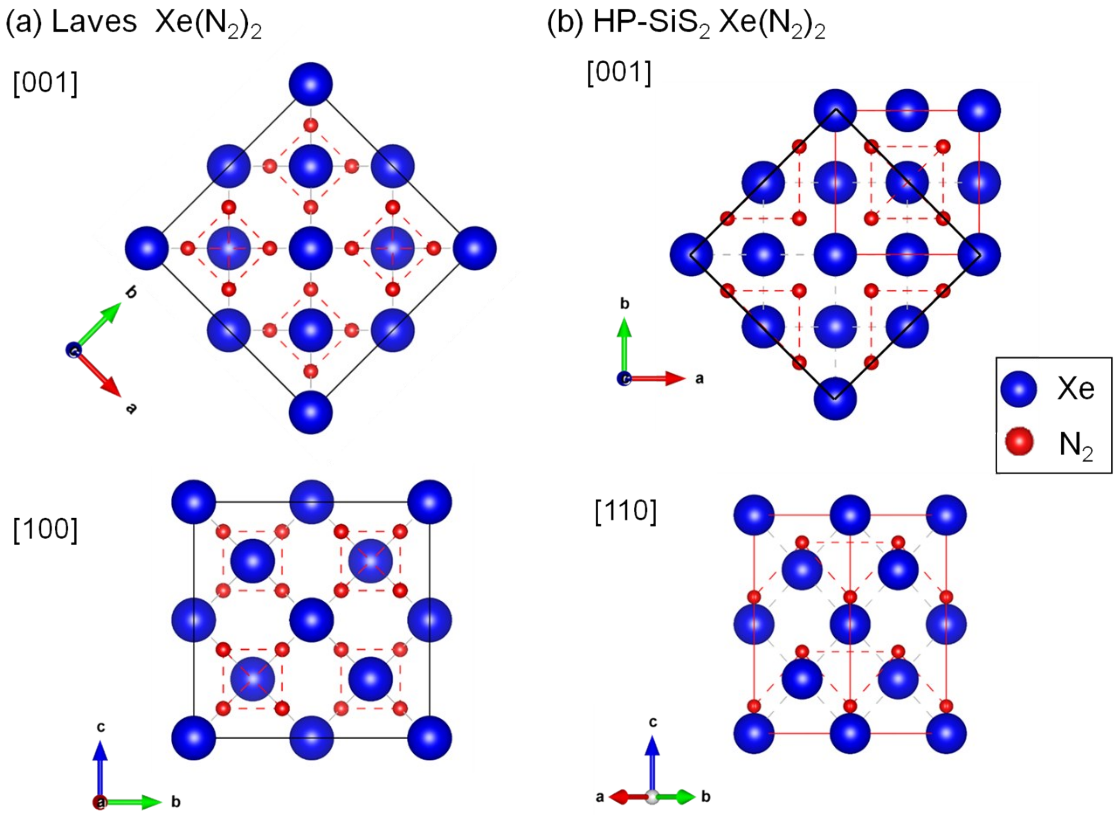
Results of peak indexing analysis and lattice parameters calculated using least-squares fitting.



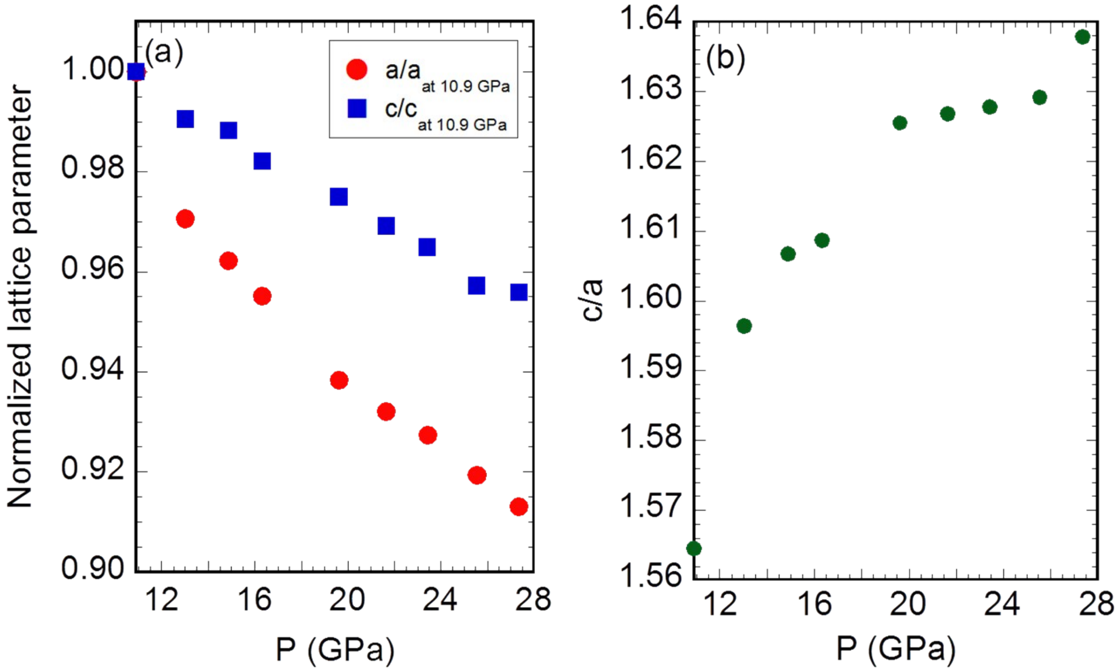
hkl	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	$d_{obs.}-d_{calc.}$ (Å)
1 0 1	4.914	4.907	0.008
1 1 2	3.067	3.067	0.000
2 0 0	2.895	2.890	0.005
1 0 3	2.725	2.728	-0.002
2 1 1	2.489	2.490	-0.001
0 0 4	2.316	2.321	-0.005
2 2 0	2.041	2.044	-0.002
2 1 3	1.983	1.984	-0.001
3 0 1	1.886	1.886	0.000
2 0 4	1.812	1.810	0.003
1 0 5	1.770	1.768	0.002
3 1 2	1.701	1.701	0.000

Results of peak indexing analysis and lattice parameters calculated using least-squares fitting.

S5

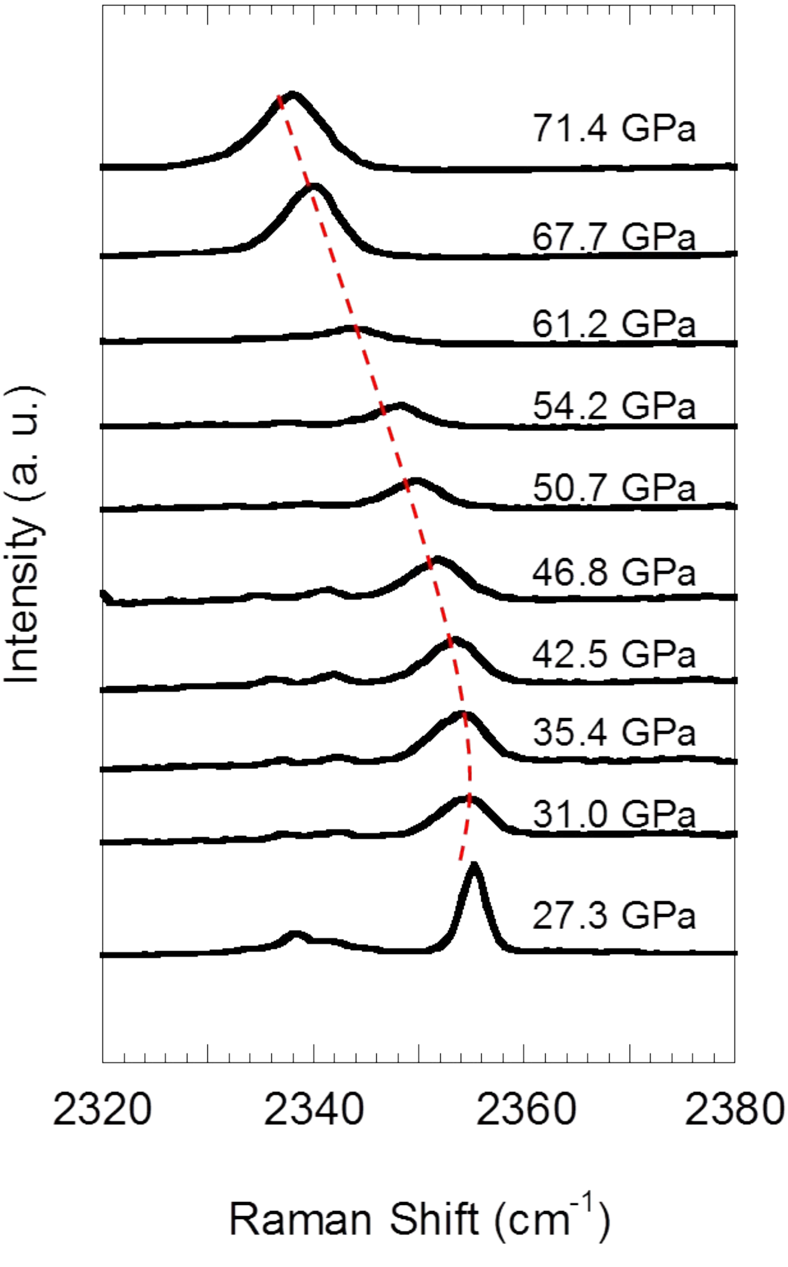


Schematic illustration of the crystal structures of (a) Laves and (b) HP-SiS$_2$-type Xe(N$_2$)$_2$ viewed from the [001] (or [100]) direction for Laves and the [001] and [110] directions for the HP-SiS$_2$ phases.



Pressure dependence of (a) the normalised lattice parameters and (b) tetragonal crystal for HP-SiS$_2$ Xe(N$_2$)$_2$ up to approximately 28 GPa.

S7



Pressure evolution of the Raman spectra for the Xe-N_2 system from 27.3 to 71.4 GPa. The pressure variation of the Raman peaks is indicated by a dashed line, which acts as a visual guide.