High-pressure phases of SF₆ up to 32 GPa from X-ray diffraction and Raman spectroscopy

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Abstract

X-ray diffraction and Raman spectroscopy were employed to study the phase diagram of SF₆ at pressures up to 32 GPa. The known phase transformation of SF₆ phase I to phase II at around 2 GPa was confirmed. Discontinuities in the pressure dependence of the Raman frequencies and positions of X-ray reflections indicate further phase transitions at 10(1) and 19(1) GPa. The crystal structures of phases I and II were determined using single crystal X-ray diffraction. The structure of phase I corresponds to the “plastic” body-centred cubic low-temperature structure and the structure of phase II to the ordered monoclinic low-temperature structure. The bulk moduli of phase I and II were determined to be $B_{0,I} = 6.3(2)$ GPa with $B'_I = 4$ (fixed) and $B_{0,II} = 8.5(8)$ GPa with $B'_{II} = 7.4(9)$, respectively. The linear compressibilities of phase II showed a slight anisotropy, which can be rationalised by consideration of the packing of the SF₆ molecules.

Keywords: C. high pressure; C. X-ray diffraction; C. Raman spectroscopy;

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1. Introduction

Sulfur hexafluoride, SF_6 , is a very stable and chemically inert compound and hence widely used, for example as insulator material in electric equipment [1]. There are two different crystalline phases of SF_6 at ambient pressure and low temperatures [2]. Between 90 K and 230 K SF_6 crystallises in a so-called “plastic” phase in a body-centred cubic (bcc) structure with space group $Im\bar{3}m$ and $Z = 2$ (one molecule per lattice point) [3]. In the “plastic” phase the molecules are orientationally disordered. This disorder has been studied extensively, e.g. by molecular dynamics simulations [4, 5]. It has been found that the disorder is dynamic and that the origin of the disorder are short $\text{F}\cdots\text{F}$ distances which lead to repulsive forces between the molecules [4, 5]. Below 90 K SF_6 crystallises in an ordered monoclinic structure with space group $C2/m$ and $Z = 6$ [6]. The SF_6 octahedra are packed in a distorted hexagonal close packing arrangement. Each octahedron is surrounded by 12 octahedra, whereas in the cubic structure each octahedron has 8 neighbours. The unit cell of the monoclinic structure contains two SF_6 octahedra located on Wyckoff positions with site symmetry $2/m$ and four on a position with site symmetry m .

The phase diagram of SF_6 at high pressures has been explored by Stewart [7] up to 2 GPa using the direct piston displacement method and by Sasaki *et al.* [8] up to 10 GPa using Raman spectroscopy. At ambient temperature Sasaki *et al.* [8] found a liquid-solid transition to the so-called solid phase I at 0.25 GPa and a solid-solid phase transition from phase I to II at 1.8 GPa.

The solid-solid phase I to phase II transformation has also been observed by Stewart [7] at temperatures between 81 and 190 K and lower pressures. Sasaki *et al.* [8] proposed that the crystal structure of phase I corresponds to the known “plastic” bcc low-temperature structure and phase II to the ordered monoclinic low-temperature structure, but their suggestion, based on spectroscopic data, has not been confirmed by diffraction data so far.

This study presents the extension of the known phase diagram of SF₆ up to 32 GPa at ambient temperature by means of X-ray diffraction and Raman spectroscopy. We present the crystal structure determination of the phases I and II by single crystal X-ray diffraction and the bulk moduli of phases I and II, obtained by fitting Birch-Murnaghan equations of state to pressure-volume data.

2. Experimental details

Binary gas mixtures of SF₆ and He with 10.4(2) and 20.4(4) vol% SF₆ were obtained from Praxair and loaded without further purification with a gas loading system at 350 to 1800 bar into the pressure chamber of the diamond anvil cells (DAC). The He within the gas mixture served as pressure transmitting medium, as has been demonstrated in previous studies [9, 10]. Boehler-Almax [11] type DACs with opening angles of 48° to 85° and culet sizes of 350 μm were employed. Tungsten gaskets with an initial thickness of 200 μm were preindented to 45–53 μm and holes of 120–140 μm were drilled with a laser lathe. The pressure was determined using the ruby fluorescence method with the calibration after Mao *et al.* [12, 13]. For pressures up to around 20 GPa we used a B value of 7.665 for quasi-hydrostatic conditions

and above 20 GPa we used a B value of 5 for non-hydrostatic conditions.

Raman spectra of SF_6 between 0.5(1) and 32.4(6) GPa were measured with a Renishaw micro-Raman spectrometer (RM-1000) using a Nd:YAG laser ($\lambda = 532 \text{ nm}$, 200 mW). The positions and half widths (FWHM) of the Raman bands were determined by single-peak fits, which were performed with *KUPLOT* [14].

Synchrotron X-ray diffraction experiments were performed at the Extreme Conditions Beamline [15] P02.2, PETRA III, DESY. We used radiation with energies of 42.4–42.8 keV (λ : 0.292–0.290 Å) and 59.8 keV ($\lambda = 0.207 \text{ Å}$). The beam was focused to about $2 \mu\text{m} \times 2 \mu\text{m}$ FWHM with Kirkpatrick-Baez mirrors, or $9 \mu\text{m} \times 3 \mu\text{m}$ to $16 \mu\text{m} \times 16 \mu\text{m}$ (for 59.8 keV) FWHM with a compound refractive lens system. A CeO_2 standard was used for calibration. Diffraction patterns were collected between 0.5(1) and 25.9(5) GPa with a PerkinElmer XRD 1621 (PE) detector and a MAR345 image plate. The sample-detector distances varied between 350 and 500 mm. The data collection times varied between 0.5 s and 60 s per frame. During the measurements of the “powder” diffraction patterns the DACs were rotated around ω up to $\pm 25^\circ$ in order to improve the counting statistics.

The X-ray “powder” diffraction data were processed with the *Fit2D* software [16]. Diamond reflections were masked and excluded from the integration. Le Bail [17] refinements were performed with the programs *GSAS* [18] and *EXPGUI* [19]. The background was interpolated with a shifted Chebyshev function between manually defined points. Profile parameters (GW and LX, profile function 2) and lattice parameters were refined. Pressure-volume data were fitted to a second-order Birch-Murnaghan equation of state (BM-

EOS) using the *Eosfit* software [20].

Single-crystal intensity data were collected at 0.8(1), 1.8(1) and 3.8(1) GPa in Frankfurt using the fixed-phi mode and a κ -diffractometer (XCalibur3, Agilent) equipped with a Sapphire3 CCD camera and a sealed tube with Mo-K $_{\alpha}$ radiation ($\lambda = 0.7107 \text{ \AA}$). Further experimental details are given in table 1. The single-crystal data were indexed and reduced with *CrysAlis* (Agilent). The absorption from the diamond anvils was corrected using the program *ABSORB* [21, 22]. The crystal structure refinements were carried out with the program *SHELXL-97* [23]. The known low-temperature structures of SF₆ served as starting models. The refinement of the bcc structure was performed with anisotropic displacement parameters. Due to the restricted opening angle of 48°, the number of observable unique reflections was limited to 51 at 3.8 GPa. Hence, the monoclinic structure was refined with isotropic displacement parameters which were constrained so that S and F atoms had the same displacement parameter, respectively. Moreover, octahedral S–F bond lengths and F···F edge lengths were restrained to the same length in each of the SF₆ octahedra using 99 restraints in order to obtain undistorted SF₆ octahedra. The volumes of the SF₆ octahedra were calculated using the program *IVTON* [24].

3. Computational details

The dynamically disordered phase I cannot be modelled by static total energy calculations. Phase II is ordered. As the molecules are only weakly bonded via van der Waals interactions, we employed the “on-the-fly” ultrasoft pseudopotentials from the *CASTEP* [25] database with a cut-off energy of 610 eV,

a $4 \times 4 \times 6$ Monkhorst-Pack [26] grid so that the distances between sampling points were $\leq 0.035 \text{ \AA}^{-1}$, and the PBE [27] exchange-correlation functional in conjunction with the dispersion correction suggested by Tkatchenko and Scheffler [28]. This leads to a systematic underbonding, and the lattice parameters are $\approx 2.5\%$ too large. However, as will be shown below, the computed compression behaviour is in excellent agreement with experimental data.

4. Results

4.1. Phase separation of the SF_6 -He mixture

The binary gas mixtures of SF_6 and He with 10.4(2) and 20.4(4) vol% SF_6 demixed at 0.5(1) GPa (figure 1). The difference in concentration did not have an influence on the phase separation pressure or on the following results. The SF_6 phase looked like a droplet after the phase separation (figure 1b). However, X-ray diffraction experiments confirmed that this phase was not liquid but crystalline. The SF_6 droplet seemed to grow during pressure increase from 0.5 to 0.8 GPa (figure 1c) and it was not possible to describe the composition of the He and SF_6 phases. It is possible that after the phase separation, there was still some SF_6 in the He-rich phase. At around 2 GPa the formation of crystal faces could be observed. Further pressure increase to around 4 GPa resulted in a breakage of the the crystal (figure 1d). It seemed, as if the amount of He was not enough to embed the SF_6 and thereby serve as pressure transmitting medium.

Figure 2 shows individual frames of a video which was recorded during the phase separation. During the demixing an initial dendritic crystal growth was

Figure 1: SF_6 -He mixture at high pressures in the DAC. The mixture was homogeneous below 0.5(1) GPa (a). At 0.5(1) GPa SF_6 and He separated (b). Solid SF_6 at 0.8(1) GPa (c) and 3.8(1) GPa (d).

observed. After several minutes the SF_6 dendrites formed spherical objects. The nucleation took place at the gasket wall and the growth velocity was $1.5(1) \cdot 10^{-3} \text{ m/s}$. Sasaki *et al.* [8] also described the shape of the SF_6 crystal of phase I as a “colorless sphere”.

Figure 2: Snapshots before and after the phase separation of a SF_6 -He mixture containing 20.4(4) vol% SF_6 at 0.5(1) GPa.

4.2. Single-crystal X-ray diffraction of SF_6 between 1 and 4 GPa

The crystal structures of the phases I and II were determined using single crystal X-ray diffraction (tables 1 and A.6). The starting models for the structure refinements consisted of the known low-temperature structures described above.

As proposed by Sasaki *et al.* [8], the crystal structure of phase I between 0.8(1) and 1.8(1) GPa corresponds to the low-temperature bcc phase and the crystal structure of phase II at 3.8(1) GPa to the monoclinic low-temperature phase. Figures 3 and 4 show the crystal structures at low temperature and ambient pressure as determined by Cockcroft and Fitch [6] and Dove *et al.* [29] and the high-pressure structures determined in this study. The corresponding SF_6 -He samples are shown in figure 1c and d. The packing, the site symmetries and the orientations of the octahedra of the low-temperature ambient-pressure structures are identical to those in high-pressure ambient-temperature structures. The atomic coordinates of the low-temperature and high-pressure structures are summarised in table A.6.

Figure 3: a) Crystal structure of SF_6 at 115 K and ambient pressure as determined by Cockcroft and Fitch [6] (S: yellow, F: green, atoms represented by displacement ellipsoids). b) Crystal structure of SF_6 at ambient temperature and 0.8(1) GPa (S: yellow, F: green, atoms represented by displacement ellipsoids).

Figure 4: Crystal structure of SF₆ at 85 K and ambient pressure as determined by Dove *et al.* [29] along *c* (a) and *b* (b) (S: yellow, F: green). Crystal structure of SF₆ at ambient temperature and 3.8(1) GPa along *c* (c) and *b* (d) (S: yellow, F: green, atoms represented by displacement ellipsoids).

In the “plastic” phase I, Cockcroft and Fitch [6] reported a S–F bond length of 1.556(3) Å at ambient pressure and 115 K. We found that the S–F bond lengths within the SF₆ octahedron was 1.53(1) Å at 0.8(1) and 1.8(1) GPa and ambient temperature (table A.7). The displacement parameters of the F atoms showed a significant anisotropy (table A.6) which is consistent with the orientational disorder of the SF₆ molecules mentioned above. The shortest intermolecular F···F distance decreased from 2.65(1) to 2.48(1) Å during pressure increase from 0.8(1) to 1.8(1) GPa.

In the ordered phase II, we found that the S–F bond lengths within the octahedra had an average value of 1.549(10) Å at 3.8(1) GPa and ambient temperature (table A.7). Bond lengths reported earlier at ambient pressure and 85 K are 1.562 Å and 1.563 Å and the bond angles deviate by a maxi-

Table 1: Crystal data and details of the data collection and refinement of phases I and II of SF₆.

	phase I			phase II			
p/GPa	0.0001	0.8(1)	1.8(1)	0.0001	0 [†]	3.8(1)	3.8 [†]
T/K	115 [6]	293(2)	293(2)	85 [29]	–	293(2)	–
space group	$Im\bar{3}m$	$Im\bar{3}m$	$Im\bar{3}m$	$C2/m$	$C2/m$	$C2/m$	$C2/m$
$a/\text{\AA}$	5.7951(3)	5.7127(9)	5.5448(15)	13.979(3)	14.2695	12.97(2)	13.2447
$b/\text{\AA}$	–	–	–	8.204(2)	8.4582	7.74(2)	7.88
$c/\text{\AA}$	–	–	–	4.8125(9)	4.9294	4.501(9)	4.5769
$\beta/^\circ$	–	–	–	94.997(6)	95.79	95.29(16)	95.78
$V/\text{\AA}^3$	194.62	186.43(5)	170.47(8)	549.8(1)	591.9	450.1(17)	475.25
Z	2	2	2	6	6	6	6
X-ray source	–	sealed tube	sealed tube	–	–	sealed tube	–
$\lambda/\text{\AA}$	–	0.7107	0.7107	–	–	0.7107	–
Detector	–	CCD	CCD	–	–	CCD	–
$\rho/\text{g cm}^{-3}$	2.492	2.602	2.845	2.647	2.458	3.233	3.062
$\sin \theta_{\text{max}} \lambda^{-1}/\text{\AA}^{-1}$	–	0.65	0.65	–	–	0.54	–
observed refl.	–	793	685	–	–	479	–
unique refl. ($I > 2\sigma$)	–	32	28	–	–	51	–
parameters	–	5	5	–	–	21	–
restraints	–	0	0	–	–	99	–
$R_{\text{int}}/\%$	–	5.6	4.1	–	–	7.0	–
$R1$ ($I > 2\sigma$)/%	–	9.4	7.8	–	–	4.4	–
$wR2/\%$	–	23.7	19.3	–	–	8.7	–
goodness of fit, S	–	1.24	1.34	–	–	1.18	–
$\Delta\rho_{\text{max}}/\text{e}\text{\AA}^{-3}$	–	0.39	0.48	–	–	0.21	–
$\Delta\rho_{\text{min}}/\text{e}\text{\AA}^{-3}$	–	–0.52	–0.44	–	–	–0.19	–

[†]DFT, *CASTEP*

$$R_{\text{int}} = \frac{\sum |F_o^2 - \langle F_o^2 \rangle|}{\sum F_o^2}, R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$$

$$S = \sqrt{\frac{\sum w(F_o - F_c)^2}{m - n}}, m: \text{ number of reflections, } n: \text{ number of refined parameters}$$

mum of 0.05° from 90° and 180°, respectively. This is consistent with the results of the DFT calculations at 3.8 GPa, where the bond lengths varied between 1.579 and 1.582 Å and the bond angles deviated by a maximum of 0.1° from 90° and 180°. As stated above, the DFT calculations lead to a systematic underbonding, which results in larger S–F bond lengths. The shortest intermolecular F···F distances increased to 2.68(1) Å. As mentioned in the introduction, it has been found that the short F···F distances in the

bcc phase lead to repulsive forces between the molecules and therefore to the transition to the ordered monoclinic phase II. It is therefore expected, that the $F \cdots F$ distances increase compared to phase I.

The crystal chemical analysis of the known low-temperature structures and the high-pressure structures determined in this study showed, that the volumes of the octahedra vary by less than 6 %. The relative volume of the SF_6 octahedra compared to the unit cell volume increased with pressure, as the unit cell is compressed and the octahedral volume is nearly constant (figure 5).

Figure 5: Octahedra volumes relative to the unit cell volume. The data points at 85 K and 115 K were determined using structural models by Dove *et al.* [29] and Cockcroft and Fitch [6]. The crosses represent data of DFT-optimised models of phase II. The dashed line serves as guide to the eye.

The lattice parameters and space groups of the bcc and monoclinic structures were independently confirmed at several pressures by Le Bail refinements of “powder” diffraction data (see section 4.3).

4.3. X-ray diffraction of SF_6 between 2 and 26 GPa

Figure 6 shows 2D diffraction images of SF_6 between 2 and 26 GPa. The large and very intense reflections are caused by the diamond anvils, the smaller reflections are from SF_6 . At 2.3(1) GPa the sample was nearly single crystalline. The number of observed reflections increased when the sample was pressurised to 11.5(2) GPa, because the single crystal broke during pressure increase and several crystallites with different orientations were present. At 25.9(5) GPa the diffraction image shows reflection broadening and strong texture but no typical powder diffraction rings. As it was not possible to improve the quality of the crystals at higher pressures, we performed Le Bail refinements to determine the unit cell parameters.

Figure 6: 2D diffraction images of SF_6 at 2.3(1) GPa (left, ω rotation from 15° to -15°), at 11.5(2) GPa (middle, ω rotation from 25° to -25°) and at 25.9(5) GPa (right, ω rotation from 25° to -25°). Representative reflections from the diamond anvils are marked with white arrows.

Figure 7 depicts the Le Bail refinements of SF_6 at 1.6(1) and 7.4(1) GPa. The profiles of the reflections were not reproduced well at 1.6(1) GPa, because the sample was essentially a single crystal and not a powder. However, the positions of the reflections were reproduced very well with the metric and space group of the bcc phase I, which had been determined using single

crystal X-ray diffraction. The profile fit of the diffraction pattern measured at 7.4(1) GPa is excellent and unequivocally confirms the space group and lattice parameters of the monoclinic phase II. The refined lattice parameters of phase I and II up to 9 GPa are summarised in table 2.

Figure 8 shows the integrated diffraction data of a pressure series from 7 to 25 GPa. The diffractogram measured at 11.3(2) GPa shows new reflections and some reflections of phase II disappear. At 20.8(4) GPa the diffractogram changes significantly again and there are new reflections. With the diffraction data, it is not possible to unambiguously locate the phase transitions. However, the present observations indicate two additional phase transformations to phases III and IV at around 10(1) and 19(1) GPa, respectively.

The pressure dependence of two intense reflections from two different experiments (denoted as #4 and #13) is depicted in figure 9. The slopes of the linear fits differ significantly in the region of 2 to 10 GPa and 10 to 20 GPa. Moreover, the smaller value of the slope in the region of phase III indicates that this phase is less compressible than phase II. Due to a broadening of the reflections at high pressures it was not possible to determine the positions of the reflections accurately above 20 GPa. The positions of the reflections shown in figure 9 were slightly different. This is due to preferred orientation and large variations in the intensities of the reflections of the different DAC loadings which resulted in an inaccurate determination of reflection positions. However, the slopes were very similar for both experiments. Attempts to index the patterns of phase III and phase IV were also unsuccessful because of the very broad and overlapping reflections.

Figure 7: Le Bail fits of the SF_6 phases I and II at 1.6(1) GPa (a) and 7.4(1) GPa (b) (blue crosses: data, red line: simulated pattern, black line at the bottom: difference curve, tick marks: calculated reflection positions).

Figure 8: X-ray diffraction patterns of SF_6 between 7 and 25 GPa during pressure increase. The red and blue arrows mark new reflections, which indicate the occurrence of phase transformations. The right side is an enlargement of the Q region between around 1.5 and 4 $\text{\AA}^{-1}$.

Figure 9: Pressure dependence of the positions of two intense SF_6 reflections for two different experiments (denoted as #4 and #13).

Table 2: Lattice parameters of SF₆ phase I and phase II up to 9 GPa from Le Bail refinements and single-crystal data.

p/GPa	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$	$V/\text{\AA}^3$
phase I, $Im\bar{3}m$					
0.8(1) [†]	5.7127(9)	—	—	—	186.43(5)
1.6(1)	5.5640(4)	—	—	—	172.25(4)
1.6(1) [†]	5.5589(6)	—	—	—	171.78(3)
1.8(1) [†]	5.5448(15)	—	—	—	170.47(8)
2.0(1)	5.5455(6)	—	—	—	170.54(6)
phase II, $C2/m$					
1.7(2)	13.440(4)	7.920(4)	4.635(3)	94.61(3)	491.7(1)
1.8(1)	13.326(4)	7.895(2)	4.590(2)	94.97(3)	481.1(1)
2.3(1)	13.244(2)	7.869(2)	4.5750(8)	94.97(1)	475.0(1)
3.2(1)	13.012(2)	7.741(1)	4.499(2)	95.29(3)	451.2(2)
3.6(1)	12.959(3)	7.730(2)	4.451(2)	95.66(4)	443.7(2)
3.8(1) [†]	12.97(2)	7.74(2)	4.501(9)	95.29(16)	450.1(17)
4.4(2)	12.853(3)	7.663(1)	4.426(2)	95.58(2)	433.9(1)
4.7(1)	12.830(3)	7.642(1)	4.410(2)	95.53(3)	430.4(2)
5.1(1)	12.7894(7)	7.6200(5)	4.4166(3)	95.581(4)	428.38(3)
5.7(1)	12.713(3)	7.590(1)	4.389(2)	95.67(3)	421.4(2)
7.4(1)	12.5341(5)	7.4957(2)	4.3270(2)	95.763(4)	404.47(2)
8.1(9)	12.4803(5)	7.4735(2)	4.2978(2)	96.023(6)	398.65(3)
8.2(2)	12.4808(8)	7.4785(3)	4.3352(2)	95.756(3)	402.60(2)
9.1(2)	12.432(1)	7.4406(3)	4.3102(2)	95.810(4)	396.64(3)
9.3(2)	12.392(1)	7.4322(2)	4.2861(4)	95.773(8)	392.77(5)

[†]from single-crystal data

4.4. Equations of state

The pressure dependence of the volumes of the phases I and II and the corresponding fits of second and third order Birch-Murnaghan equations of state are presented in figure 10. The volume at ambient pressure, V_0 , was not refined and the volumes of the structures determined at low temperatures [30, 29] were used instead. The fits of the equations of state (figure 10) resulted in bulk moduli $B_{0,\text{I}} = 6.3(2)$ GPa with $B'_1 = 4$ (fixed) for phase I and $B_{0,\text{II}} = 8.5(8)$ GPa with $B'_{\text{II}} = 7.4(9)$ for phase II (table 3). The results from the DFT optimisation are also shown in figure 10. The absolute values of the DFT-optimised unit cell volumes are slightly larger than the experimental values from this study ($\approx 7\%$). However, the agreement between the bulk moduli determined from experimental data and DFT-optimised data is excellent (table 3).

The linear compressibilities of phase II show a slight anisotropy (figure 10). The b axis is less compressible than the a and c axes (table 4). This behaviour will be discussed in section 5.

Table 3: Isothermal bulk moduli of the phases I and II obtained by fitting second- and third-order Birch-Murnaghan equations of state.

	$V_0/\text{\AA}^3$	B_0/GPa	B'
phase I	$207^\dagger$ (fixed)	6.3(2)	4 (fixed)
phase II	$550^\ddagger$ (fixed)	8.5(8)	7.4(9)
phase II, DFT	592.2(9)	8.0(2)	7.3(1)

[†]Taylor and Waugh [30]; [‡]Dove *et al.* [29]

Table 4: Linear compressibilities of phase II obtained by fitting third-order Birch-Murnaghan equations of state.

	$B_{0,a}/\text{GPa}$	B'_a	$B_{0,b}/\text{GPa}$	B'_b	$B_{0,c}/\text{GPa}$	B'_c
phase II	7.7(4)	7.0(5)	9.9(6)	8.3(8)	7(1)	8(2)

Figure 10: Relative compressibilities of phase I and phase II fitted to second- and third-order Birch-Murnaghan equations of state.

4.5. Raman spectroscopy of SF_6 between 2 and 32 GPa

The Raman spectra of SF_6 between 2 and 32 GPa are presented in figure 11. The pressure dependences of the peak positions and FWHM are presented in figures 12 and 13. A group-theoretical analysis of phase I results in 3 Raman-active modes ($A_{1g}+E_g+T_{2g}$). All of these can be observed. Phase II has 30 Raman-active modes ($17A_g + 13B_g$). Of these 8–10 can be observed experimentally.

Our Raman spectra of phase I show the characteristic ν_1 (A_{1g} , symmetric stretch), ν_2 (E_g , asymmetric stretch) and ν_5 (T_{2g} , bending) modes of SF_6 , which have been reported by Sasaki *et al.* [8]. The transformation from phase I to phase II took place at 1.9(2) GPa. This pressure is in excellent agreement with the phase transition pressure from Sasaki *et al.* [8] where $p_{\text{trans}} = 1.8$ GPa. The phase transformation can be detected by a splitting of the Raman modes. At around 10 GPa an additional splitting of the ν_5 mode was observed (figure 11, red arrows) and all ν_1 and ν_2 Raman frequencies discontinuously shift to smaller wavenumbers indicating the transformation to phase III. The magnitudes of the shifts are in the range of 1–8 cm^{-1} . At around 20 GPa the shape of the ν_5 mode changes again (figure 11, blue arrows) and there is a discontinuity in the pressure dependence of the Raman frequencies and of the FWHM (figures 12 and 13) indicating the transformation to phase IV. There is only a small ($\approx 1 \text{ cm}^{-1}$) discontinuous shift of the Raman frequencies during this phase transformation. The slopes, $\frac{d\nu}{dp}$, of the linear fits and the Grüneisen parameters, $\gamma = \frac{B_0}{\nu_0} \frac{d\nu}{dp}$, are summarised in table 5. The linear fits of the pressure dependence of the Raman mode positions of phases I and II were performed with data presented by Sasaki *et al.* [8]

and data measured in this study.

Figure 11: Raman spectra of SF_6 at 2 to 32 GPa. The red and blue arrows mark changes of the ν_5 mode. Left: Whole range of the ν_1 , ν_2 and ν_5 modes. Right: Enlarged range of the ν_5 mode.

In summary, the Raman spectra clearly showed the known phase transformation from phase I to phase II and indicate two additional phase transformations to phases III and IV at around 10(1) and 19(1) GPa, respectively. The pressures at which the discontinuities in the Raman spectra were observed coincide with pressures at which changes in the diffraction data were observed.

Figure 12: Pressure dependence of the positions of the ν_1 (a), ν_2 (b) and ν_5 (c) modes of SF_6 up to 32 GPa (closed symbols: this study, open symbols: data from Sasaki *et al.* [8]). The accuracy of the Raman shift is 1 cm^{-1} and the uncertainty of the pressure is 2 % or at least 0.1 GPa.

Figure 13: Pressure dependence of the half widths (FWHM) of the ν_1 mode of SF_6 up to 32 GPa (closed symbols: this study, open symbols: data from Sasaki *et al.* [8]). The largest numerical uncertainties of the FWHM from the fits were about 0.9 cm^{-1} and the uncertainty of the pressure is 2% or at least 0.1 GPa.

Table 5: Raman shifts of the ν_1 , ν_2 and ν_5 modes of the SF_6 phases I and II at ambient pressure and low temperatures, slopes of the pressure dependencies of the frequencies for phases I to IV and Grüneisen parameters for phases I and II. The low-temperature data have been determined by Gilbert and Drifford [31] and Shurvell and Bernstein [32].

	Raman shift ν_0/cm^{-1}	$\frac{d\nu}{dp}/(\text{cm}^{-1}\text{GPa}^{-1})$	$\gamma = \frac{B_0}{\nu_0} \frac{d\nu}{dp}$
phase I	223 K [31]		
ν_1	773	8.0(4)	0.0652
ν_2	645	7.8(5)	0.0762
ν_5	525	2.9(5)	0.0348
phase II	77 K [32]		
ν_1	777.4	4.4(1)	0.0481
	774.9	3.87(9)	0.0425
ν_2	653.2	4.1(1)	0.0534
	648.7	3.9(1)	0.0511
	646.7	3.5(1)	0.0460
ν_5	525.3	3.1(1)	0.0502
	524	2.9(1)	0.0470
	522.8	2.20(7)	0.0358
phase III			
ν_1	—	3.70(8)	—
	—	3.39(6)	—
ν_2	—	3.10(8)	—
	—	3.18(7)	—
	—	3.14(6)	—
ν_5	—	3.1(1)	—
	—	2.80(6)	—
	—	2.11(5)	—
	—	1.59(8)	—
phase IV			
ν_1	—	1.92(4)	—
	—	1.80(5)	—
ν_2	—	1.54(3)	—
	—	1.58(5)	—
	—	1.70(3)	—
ν_5	—	1.51(6)	—
	—	1.43(7)	—
	—	1.12(5)	—
	—	1.0(1)	—

5. Discussion

During the phase separation of SF₆-He mixtures dendritic crystal growth was observed. The growth velocity was calculated to be $1.5(1) \cdot 10^{-3}$ m/s. Dendritic crystal growth is usually observed in supercooled melts or supersaturated solutions. The crystal growth rate is strongly dependent on the supercooling or supersaturation. Camphene, for example, which is also a plastic crystal, forms dendrites during crystallisation [33]. Rubinstein and Glicksman [33] determined growth velocities of $0.031 \cdot 10^{-3}$ to $3.6 \cdot 10^{-3}$ m/s for undercooling of 0.3 to 2 K. Another well-known example for dendritic crystal growth is ice. Ohsaka and Trinh [34] determined growth rates of 1 to $11 \cdot 10^{-3}$ m/s for undercoolings of 1 to 10 K. These values are comparable to the growth velocity of the SF₆ dendrites in the present study. Thus, the moderate high pressure in the present study seems to have a comparable effect to undercooling of a few K and causes similar growth velocities.

SF₆ is very compressible (table 3), which is typical for molecular solids or other van der Waals compounds such as noble gases, CO₂, etc. [35, 36, 37]. The pressure derivative of the bulk modulus of phase II, B'_{II} , has a comparatively large value of 7.4(9) which differs significantly from $B' = 4$ implied in a second-order Birch-Murnaghan equation of state and which is often observed for inorganic compounds such as silicates and oxides. However, earlier publications on the compressibilities of molecular solids indicate that these materials often have large B' values. Datchi *et al.* [37] determined the compressibility of CO₂-II and reported a bulk modulus of $B_0 = 8.5(3)$ GPa with $B'_0 = 6.29$. Likhacheva *et al.* [38] studied naphthalene (C₁₀H₈) at high pressures and found a bulk modulus of $B_0 = 7.9(3)$ GPa with $B'_0 = 7.5(3)$.

The noble gases follow a similar trend: Loubeyre *et al.* [39] studied helium at high pressures and temperatures and determined a bulk modulus $B_0 = 0.225$ GPa with $B'_0 = 7.35$. Dewaele *et al.* [36] determined the parameters for the equation of state of neon and found $B_0 = 1.070(16)$ GPa with $B'_0 = 8.40(28)$. Wittlinger *et al.* [40] studied argon at high pressures and found a bulk modulus $B_0 = 6.5(1.3)$ GPa with a fixed $B'_0 = 4$. These findings imply that the second-order Birch-Murnaghan equation of state is inapplicable for the molecular solids discussed here. The fit of Vinet equations of state to the pressure-volume data of phase II resulted in the same value for the bulk modulus and its pressure derivative. The slight anisotropy of the linear compressibilities of phase II can be explained by the packing of the SF₆ octahedra. The packing of the octahedra is more dense in the b direction compared to the a and c direction (figure 4). The sulfur atoms form a distorted hexagonal close packed arrangement with the hexagonal c_{hex} axis along the b axis. Therefore it is expected that the linear compressibilities of a and c are similar to each other and differ from b . A very similar behaviour has recently been found for the molecular compound W(CO)₆ [35].

The Grüneisen parameter γ is a quantity which describes the dependence of vibrational frequencies on the relative volume change. The Grüneisen parameters calculated for the SF₆ phases I and II vary between 0.04 and 0.08. These values are relatively small and typical for molecular crystals [41, 42]. Tolbert *et al.* [41] determined Grüneisen parameters for the molecular crystal C₆₀ and found very similar values around 0.06 for frequencies between 1400 and 1700 cm⁻¹. Zhao *et al.* [42] studied the molecular crystal anthracene at high pressure and determined Grüneisen parameters of 0.03 to 0.2 for

frequencies between 1600 and 400 cm^{-1} . The small value of the Grüneisen parameters of “molecular” vibrations can be rationalised by noting that the compression causes only small changes in the intramolecular bond lengths and large changes in the intermolecular spacings [41].

The phase diagram of SF_6 , which has been determined by Sasaki *et al.* [8] and Stewart [7] at high pressures and low temperatures, extended with the results of this study is depicted in figure 14. The liquid-solid phase transition of SF_6 at 0.25 GPa was not observed in this study, because the binary mixtures demixed at 0.5(1) GPa and SF_6 was solid after the phase separation. The solid-solid transition from phase I to phase II found by us is in excellent agreement with the data published by Sasaki *et al.* [8]. Here, the phase diagram was extended to 32.4(6) GPa. Both Raman spectroscopy and X-ray diffraction indicate further phase transitions at around 10(1) and 19(1) GPa, respectively.

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Figure 14: Phase diagram of SF_6 [7, 8] extended with the results of this study. The hatched areas denote the pressure range at which the corresponding SF_6 phases were observed in our experiments. The right side is an enlargement, showing the good agreement between values obtained earlier [7, 8] and data from the present study.

Appendix A. Crystal structure details of SF₆

Table A.6: Fractional atomic coordinates and displacement parameters of phase I at 0.8(1), 1.8(1) GPa and phase II at 3.8(1) GPa and at ambient pressure and low-temperatures.

atom	x	y	z	$u_{\text{iso}}/\text{\AA}^2$	$u_{11}/\text{\AA}^2$	$u_{22}/\text{\AA}^2$	$u_{33}/\text{\AA}^2$
phase I							
0.0001 GPa, 115 K [6]							
S1	0	0	0	—	—	—	—
F1	0.2685(5)	0	0	—	—	—	—
0.8(1) GPa, 293(2) K, this study							
S1	0	0	0	0.062(3)	0.062(3)	0.062(3)	0.062(3)
F1	0.2679(18)	0	0	0.158(6)	0.083(5)	0.195(9)	0.195(9)
1.8(1) GPa, 293(2) K, this study							
S1	0	0	0	0.045(2)	0.045(3)	0.045(3)	0.045(3)
F1	0.2760(15)	0	0	0.132(5)	0.052(4)	0.173(8)	0.173(8)
phase II							
0.0001 GPa, 85 K [29]							
S1	0	0	0	—	—	—	—
F11	0.0682	0	0.275	—	—	—	—
F12	0.063	−0.1347	−0.1236	—	—	—	—
S2	0.6687	0	0.5936	—	—	—	—
F21	0.7477	0	0.3831	—	—	—	—
F22	0.5896	0	0.8041	—	—	—	—
F23	0.725	0.8653	0.7695	—	—	—	—
F24	0.6123	0.8653	0.4177	—	—	—	—
3.8(1) GPa, 293(2) K, this study							
S1	0	0	0	0.019(3)	—	—	—
F11	0.0711(9)	0	0.296(2)	0.025(2)	—	—	—
F12	0.0683(6)	−0.1414(9)	−0.1262(18)	0.025(2)	—	—	—
S2	0.6678(5)	0	0.5828(15)	0.019(3)	—	—	—
F21	0.7500(7)	0	0.354(2)	0.025(2)	—	—	—
F22	0.5856(8)	0	0.812(2)	0.025(2)	—	—	—
F23	0.7296(6)	0.1415(7)	0.7660(18)	0.025(2)	—	—	—
F24	0.6060(6)	0.1415(7)	0.400(2)	0.025(2)	—	—	—

Table A.7: Bond lengths and bond angles in the structure of phase I at 0.8(1), 1.8(1) and phase II at 3.8(1) GPa (bond angles within the octahedra of the cubic structure at 0.8(1) and 1.8(1) GPa are exactly 90° and 180°, respectively).

atoms	bond length/Å	atoms	bond length/Å
phase I			
0.8(1) GPa, 293(2) K			
S1–F1	1.530(10)		
1.8(1) GPa, 293(2) K			
S1–F1	1.530(8)		
phase II			
3.8(1) GPa, 293(2) K			
S1–F12 ⁱ	1.547(10)	S2–F23 ⁱ	1.548(9)
S1–F12 ⁱⁱ	1.547(10)	S2–F24	1.548(9)
S1–F11 ⁱⁱⁱ	1.549(10)	S2–F21	1.549(8)
S1–F11	1.549(10)	S2–F22	1.549(8)
S1–F12 ⁱⁱⁱ	1.550(10)	S2–F23	1.551(9)
S1–F12	1.550(10)	S2–F24 ⁱ	1.551(9)
atoms	bond angle/°	atoms	bond angle/°
phase II			
3.8(1) GPa, 293(2) K			
F12 ⁱ –S1–F12 ⁱⁱ	180.0(10)	F23 ⁱ –S2–F24	179.99(12)
F12 ⁱ –S1–F11 ⁱⁱⁱ	90.1(2)	F23 ⁱ –S2–F21	89.9(2)
F12 ⁱⁱ –S1–F11 ⁱⁱⁱ	89.9(2)	F24–S2–F21	90.1(2)
F12 ⁱ –S1–F11	89.9(2)	F23 ⁱ –S2–F22	90.1(2)
F12 ⁱⁱ –S1–F11	90.1(2)	F24–S2–F22	89.9(2)
F11 ⁱⁱⁱ –S1–F11	180.0(8)	F21–S2–F22	179.99(10)
F12 ⁱ –S1–F12 ⁱⁱⁱ	90.00(19)	F23 ⁱ –S2–F23	90.0(2)
F12 ⁱⁱ –S1–F12 ⁱⁱⁱ	90.00(19)	F24–S2–F23	90.00(19)
F11 ⁱⁱⁱ –S1–F12 ⁱⁱⁱ	90.1(2)	F21–S2–F23	90.1(2)
F11–S1–F12 ⁱⁱⁱ	89.9(2)	F22–S2–F23	89.9(2)
F12 ⁱ –S1–F12	90.00(19)	F23 ⁱ –S2–F24 ⁱ	90.00(19)
F12 ⁱⁱ –S1–F12	90.00(19)	F24–S2–F24 ⁱ	90.0(2)
F11 ⁱⁱⁱ –S1–F12	89.9(2)	F21–S2–F24 ⁱ	89.9(2)
F11–S1–F12	90.1(2)	F22–S2–F24 ⁱ	90.1(2)
F12 ⁱⁱⁱ –S1–F12	180.0(6)	F23–S2–F24 ⁱ	179.99(12)

i) $x, -y, z$; ii) $-x, y, -z$; iii) $-x, -y, -z$

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