

Compressibility of β -As₄S₄: an *in situ* high-pressure single-crystal X-ray study

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ABSTRACT

Ambient temperature X-ray diffraction data were collected at different pressures from two crystals of β -As₄S₄, which were made by heating realgar under vacuum at 295°C for 24 h. These data were used to calculate the unit-cell parameters at pressures up to 6.86 GPa. Above 2.86 GPa, it was only possible to make an approximate measurement of the unit-cell parameters. As expected for a crystal structure that contains molecular units held together by weak van der Waals interactions, β -As₄S₄ has an exceptionally high compressibility. The compressibility data were fitted to a third-order Birch–Murnaghan equation of state with a resulting volume $V_0 = 808.2(2) \text{ \AA}^3$, bulk modulus $K_0 = 10.9(2) \text{ GPa}$ and $K' = 8.9(3)$. These values are extremely close to those reported for the low-temperature polymorph of As₄S₄, realgar, which contains the same As₄S₄ cage-molecule. Structural analysis showed that the unit-cell contraction is due mainly to the reduction in intermolecular distances, which causes a substantial reduction in the unit-cell volume (~21% at 6.86 GPa). The cage-like As₄S₄ molecules are only slightly affected. No phase transitions occur in the pressure range investigated.

Micro-Raman spectra, collected across the entire pressure range, show that the peaks associated with As–As stretching have the greatest pressure dependence; the S–As–S bending frequency and the As–S stretching have a much weaker dependence or no variation at all as the pressure increases; this is in excellent agreement with the structural data.

KEYWORDS: β -As₄S₄, realgar, arsenic sulfides, high-pressure, crystal structure refinement, compressibility, thermodynamic properties.

Introduction

ARSENIC sulfides are widely studied because they have great technological potential; As₄S₄ compounds are of particular interest to material scientists due to their high infrared transparency, photo-structural sensitivity and doping ability (Kolobov, 2003). Most of them contain packed covalent cage-like As₄S_n ($n = 3, 4, \text{ and } 5$)

molecules held together by van der Waals forces (Bonazzi and Bindi, 2008, and references therein). Investigations of their thermodynamic properties, such as thermal expansion and compressibility, can make useful contributions toward understanding the interactions governing their structure and stability. The crystal structure of the α modification of As₄S₄ (i.e. the mineral realgar) has been investigated recently by energy-dispersive X-ray diffraction up to 8 GPa (Tuktaviet *et al.*, 2009) and *in situ* single-crystal X-ray diffraction and powder diffraction up to 45.5 GPa (Hejny *et al.*, 2012). However, no data on the compressibility and structural behaviour of

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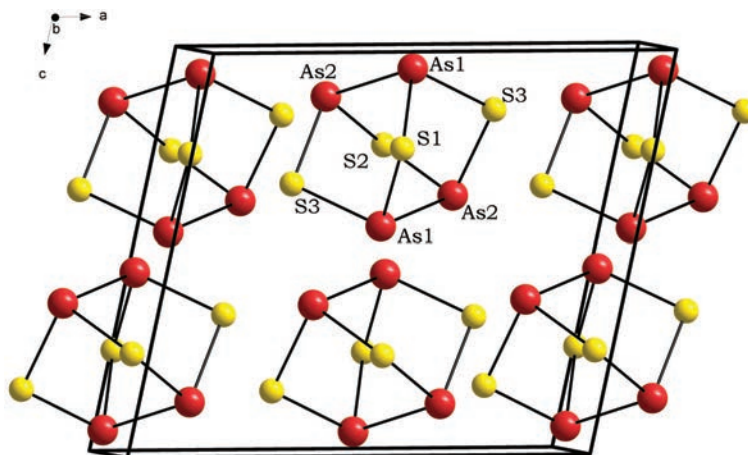


FIG. 1. The crystal structure of β -As₄S₄ projected approximately along [010].

β -As₄S₄ at high pressure have been reported. At ambient pressure, β -As₄S₄ crystallizes in the $C2/c$ space group with $a = 9.957(3)$, $b = 9.335(4)$, $c = 8.889(5)$ Å, $\beta = 102.48(4)^\circ$ (Porter and Sheldrick, 1972). The structure consists of packed cage-like As₄S₄ molecules (Fig. 1), which have $D2d$ molecular symmetry, with each As atom bonded to one As and two S atoms.

Experimental methods

Sample

To produce crystals of β -As₄S₄, a fragment of realgar from Shimen, Hunan Province, China, (from the mineralogical collection of the Museo di Storia Naturale, Università degli Studi di Firenze, catalogue no. 46768/G) was ground and heated in an evacuated silica tube in a horizontal furnace at 295°C for 24 h. The charge was then quenched to room temperature.

X-ray diffraction

Two crystals of β -As₄S₄, labelled X1 (120 × 100 × 45 μm) and X2 (70 × 60 × 30 μm), were loaded into two different diamond-anvil cells (ETH-type and Bolher-Almax-type DACs) to measure the unit-cell parameters and X-ray intensity data, respectively. The DACs were loaded with a 4:1 methanol-ethanol mixture as an isotropic pressure medium (Angel *et al.*, 2007). The lattice parameters were measured using a STOE STADI IV four-circle diffractometer (MoK α radiation) equipped with a point detector and *SINGLE* software (Angel and Finger, 2011) at the University of Padova, Italy (Table 1). This allowed us to use eight-position centring, a procedure in which the effects of the crystal offset and diffractometer aberrations are eliminated from the refined peak positions (King and Finger, 1979). Full details of the peak-centring algorithms used are reported by Angel *et al.*

TABLE 1. Unit-cell parameters for β -As₄S₄ at different pressures.

P (GPa)*	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
0.0001 (air)	9.9670(5)	9.334(2)	8.8958(7)	102.426(5)	808.2(2)
0.290(8)	9.8858(6)	9.259(2)	8.8351(8)	102.548(6)	789.4(2)
0.695(7)	9.7920(6)	9.174(2)	8.7631(7)	102.659(5)	768.1(2)
1.002(9)	9.7329(7)	9.123(2)	8.7163(8)	102.743(6)	754.9(2)
2.001(8)	9.5850(6)	8.984(2)	8.5943(7)	102.954(5)	721.2(2)
2.86(1)	9.492(1)	8.903(3)	8.510(1)	103.152(9)	700.3(3)

* The pressure was calculated using the quartz EoS (Angel *et al.*, 1997).

(2000). The pressure was calibrated using a single crystal of quartz as an internal standard (Angel *et al.*, 1997). The measurement of the unit-cell parameters became impossible above 2.86 GPa because of a dramatic broadening of reflections. The intensity data collections were carried out at different pressures up to 6.86 GPa using an Oxford Diffraction Xcalibur2 diffractometer equipped with a CCD detector, using graphite-monochromated Mo-radiation ($K\alpha_1$, $\lambda = 0.71073 \text{ \AA}$) at the Bayerisches Geoinstitut, Germany. However, the quality of the data collected at 4.81 and 6.86 GPa did not allow the refinement of the structural parameters and only produced an approximate measurement of the unit-cell parameters. A crystal of ruby was enclosed in the DAC to calibrate the pressure using the laser-induced fluorescence technique (Mao *et al.*, 1986). Intensity integration and standard Lorentz-polarization corrections were done with the *CrysAlis RED* software package (Oxford Diffraction, 2006). The programs *X-Shape* and *X-Red* (Stoe and Cie, 2008) were used for the absorption correction. Reflections generated by diamond diffraction or attenuated by the gasket were removed from the datasets.

The crystal structure refinements were carried out in the space group *C2/c* starting with the atomic coordinates reported by Porter and Sheldrick (1972) and using *SHELXL-97* (Sheldrick, 2008). Full occupancy was assumed for all sites. Scattering curves for neutral atoms were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). Details of the data collections and structure refinements are reported in Table 2. Fractional atomic coordinates and anisotropic displacement parameters are listed in Tables 3 and 4, respectively. Structure factors and CIFs have been deposited with the Principal Editor of *Mineralogical Magazine* and are available at http://www.minersoc.org/pages/e_journals/dep_mat.html.

Raman spectroscopy

Changes in vibrational modes as function of pressure were monitored during the experiment on the X2 crystal. Micro-Raman spectra were collected using a LABRAM Raman spectrometer equipped with a helium-neon laser having a 632 nm red line excitation and a power of 20 mW. The sample was irradiated using a 20 × microscope objective. The beam power was

15 mW, with a laser spot size of $\sim 20 \mu\text{m}$ at the sample surface. The Raman spectra were collected by an air cooled 1024×256 pixel CCD detector. The acquisition time for each measurement was 10 s at low pressure but longer exposure times (up to 5 min) were necessary at higher pressure.

Results

Compressibility

As the unit-cell parameters determined using the diffractometer equipped with a point-detector were more precise and accurate, we used the data reported in Table 1 to calculate the compressibility. The ‘normalized stress’ vs. the Eulerian finite strain (Jeanloz and Hazen, 1991; Angel, 2000) is shown in Fig. 2, indicating that the P – V data (Fig. 3) can be described adequately by a third-order Birch–Murnaghan (BM3) equation of state (Angel, 2000). The resulting bulk modulus and its first pressure derivative, calculated using *EoS-FIT5.2* (Angel, 2001) are $K_0 = 10.9(2) \text{ GPa}$ and $K' = 8.9(3)$. The refined V_0 parameter of $808.2(2) \text{ \AA}^3$ is identical to the measured value (Table 1), and the maximum ΔP is 0.001 GPa. The change in the unit-cell parameters with pressure (Fig. 4) is continuous, with no evidence of a phase transition up to the maximum experimental pressure.

A parameterized form of the BM3 was used to determine the moduli in the a , b , c and $a\sin\beta$ directions using *EoS-FIT5.2* (Angel, 2001). The BM3 coefficients are reported in Table 5. The linear axial compressibilities, β_a , β_b , β_c and $\beta_{a\sin\beta}$,

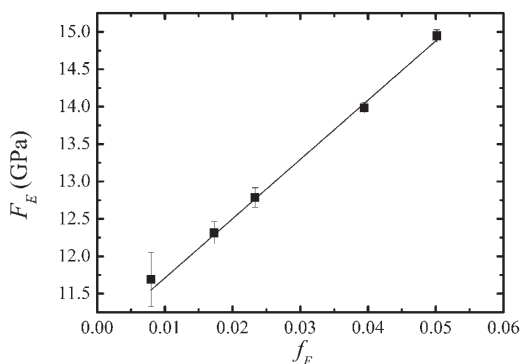


FIG. 2. A f_E – F_E plot for the P – V data, where the Eulerian strain $f_E = [(V_0/V)^{2/3} - 1]/2$ and the normalized stress $F_E = P/[3f_E(1 + 2f_E)^{5/2}]$. The regression fits the equation $y = 10.9(1) + 79(3)x$ ($R^2 = 0.996$).

TABLE 2. Crystal data and experimental details.

P_{meas} (GPa) [†]	0.0001 (air)	0.0001 (DAC)	0.82	1.43	2.04	2.70
a (Å)	9.9723(5)	9.969(2)	9.762(3)	9.660(3)	9.558(3)	9.500(3)
b (Å)	9.3213(4)	9.336(2)	9.142(5)	9.058(5)	8.969(5)	8.925(5)
c (Å)	8.8801(4)	8.879(1)	8.727(2)	8.647(1)	8.563(1)	8.512(1)
β (°)	102.514(5)	102.60(2)	102.76(2)	102.88(2)	103.06(1)	103.17(2)
V (Å ³)	805.84(6)	806.5(3)	759.6(5)	737.6(5)	715.1(5)	702.7(5)
P_{calc} (GPa)*	0.03	0.02	0.83	1.40	2.15	2.64
Theta range (°)	3.02–32.66	4.09–34.98	4.18–34.99	3.64–34.89	3.67–34.91	3.69–34.68
h range	-14 < h < 12	-14 < h < 14	-13 < h < 13	-13 < h < 13	-12 < h < 13	-13 < h < 12
k range	-12 < k < 14	-8 < k < 8	-9 < k < 9	-9 < k < 8	-8 < k < 8	-8 < k < 8
l range	-12 < l < 13	-14 < l < 14	-13 < l < 14	-12 < l < 13	-12 < l < 13	-13 < l < 12
Refined parameters	38	38	38	38	38	38
Collected reflections	4944	1806	1695	1993	1932	1912
Independent reflections	1445	688	656	538	526	507
Refl. with $F_o > 4\sigma(F_o)$	1189	497	513	454	450	454
R_{int} (%)	2.36	4.01	5.96	4.41	3.94	4.31
R_1 (%) [$F_o > 4\sigma(F_o)$]	2.53	5.96	5.80	4.94	4.56	6.42
R_1 (%)	3.41	8.19	7.53	6.20	5.76	7.40
$\Delta\rho_{\text{max}}$ (e ⁻ Å ⁻³)	0.81	0.86	1.53	0.93	1.06	1.20
$\Delta\rho_{\text{min}}$ (e ⁻ Å ⁻³)	-0.42	-0.91	-1.35	-1.02	-0.85	-1.14

These data were collected in air and in a DAC using sample X2 with a CCD-equipped diffractometer.

[†] P measured by ruby fluorescence shift (estimated standard deviations of 0.05 GPa).

* P interpolated on the basis of the EoS determined by the pressure-volume data of Table 1; the calculated values are in excellent accord with those measured by ruby fluorescence shift ($P_{\text{meas}} = 1.01(3)P_{\text{calc}} - 0.02(4)$; $R^2 = 0.997$).

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 TABLE 3. Refined atomic parameters for β -As₄S₄ at different pressures.

P (GPa) [‡]	0.0001 (air)	0.0001 (DAC)	0.82	1.43	2.04	2.70
As1						
x/a	-0.00182(3)	-0.0017(2)	-0.0022(1)	-0.0023(1)	-0.0028(1)	-0.0019(2)
y/b	-0.20545(3)	-0.2057(3)	-0.2045(2)	-0.2038(2)	-0.2038(2)	-0.2039(3)
z/c	0.05500(3)	0.0552(2)	0.0509(1)	0.0497(1)	0.0477(1)	0.0469(2)
U_{iso}	0.03441(9)	0.0377(7)	0.0310(7)	0.0282(5)	0.0285(4)	0.0240(6)
As2						
x/a	-0.16015(3)	-0.1601(2)	-0.1639(1)	-0.1655(1)	-0.1672(1)	-0.1685(2)
y/b	-0.40156(3)	-0.4013(3)	-0.4045(2)	-0.4052(2)	-0.4066(2)	-0.4065(3)
z/c	0.12616(3)	0.1263(2)	0.1224(1)	0.1211(1)	0.1194(1)	0.1178(2)
U_{iso}	0.03376(9)	0.0365(7)	0.0311(7)	0.0291(5)	0.0283(4)	0.0232(6)
S1						
x/a	0	0	0	0	0	0
y/b	-0.0537(1)	-0.055(1)	-0.0485(8)	-0.0477(6)	-0.0459(6)	-0.047(1)
z/c	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
U_{iso}	0.0395(2)	0.040(2)	0.033(2)	0.031(1)	0.031(1)	0.027(2)
S2						
x/a	0	0	0	0	0	0
y/b	-0.5535(1)	-0.553(1)	-0.5597(8)	-0.5619(6)	-0.5650(7)	-0.563(1)
z/c	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
U_{iso}	0.0415(2)	0.046(2)	0.037(2)	0.034(1)	0.037(1)	0.034(2)
S3						
x/a	-0.20154(7)	-0.2017(4)	-0.2058(4)	-0.2077(3)	-0.2096(3)	-0.2111(5)
y/b	-0.30378(9)	-0.3035(6)	-0.3044(5)	-0.3062(4)	-0.3058(4)	-0.3070(7)
z/c	0.34029(9)	0.3400(4)	0.3407(4)	0.3400(3)	0.3404(3)	0.3397(5)
U_{iso}	0.0400(2)	0.039(2)	0.036(1)	0.0323(9)	0.0321(9)	0.029(2)

[‡] The P value measured by ruby fluorescence shift (estimated standard deviations of 0.05 GPa).

calculated using $\beta = 1/3K_{\text{T0}}$, are 0.0327(6), 0.0320(12), 0.0256(4) and 0.0340(3) GPa⁻¹, respectively. The resulting compressibility ratios $\beta_a:\beta_b:\beta_c:\beta_{\text{asin}\beta}$ are 1.28:1.25:1:1.33 and indicate

an almost isotropic compressional behaviour with [001] being the least compressible direction.

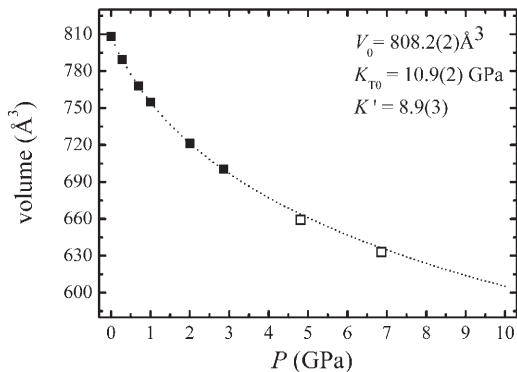


FIG. 3. Pressure dependence of unit-cell volume of β -As₄S₄. The dotted line represents the third-order Birch–Murnaghan EoS best fit. Full symbols refer to the lattice parameters reported in Table 1. Empty symbols refer to the lattice parameters measured at 4.81 and 6.86 GPa using a diffractometer equipped with CCD detector (these data were not used for the EoS fitting). The lattice parameters at the last two pressures are $a = 9.265(7)$, $b = 8.776(4)$, $c = 8.34(2)$ Å, $\beta = 103.5(1)^\circ$ at $P = 4.81$ GPa and $a = 9.14(1)$, $b = 8.694(6)$, $c = 8.20(2)$ Å, $\beta = 104.0(2)^\circ$ at $P = 6.86$ GPa. Errors are within the symbol size.

TABLE 4. Anisotropic displacement parameters, U_{ij} (\AA^2), at different pressures.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$P = 0.0001$ (air) GPa						
As1	0.0376(2)	0.0393(2)	0.0261(1)	0.0069(1)	0.0064(1)	0.0057(1)
As2	0.0265(2)	0.0373(2)	0.0333(2)	-0.0063(1)	-0.0028(1)	0.0005(1)
S1	0.0482(6)	0.0273(4)	0.0419(5)	0	0.0072(4)	0
S2	0.0401(5)	0.0265(4)	0.0515(6)	0	-0.0045(4)	0
S3	0.0284(3)	0.0544(5)	0.0396(4)	-0.0065(3)	0.0127(3)	-0.0046(3)
$P = 0.0001$ (DAC) GPa						
As1	0.040(1)	0.043(3)	0.0301(6)	0.0076(8)	0.0087(6)	0.0061(7)
As2	0.032(1)	0.038(2)	0.0367(7)	-0.0064(8)	-0.0001(5)	-0.0002(6)
S1	0.047(4)	0.027(9)	0.045(3)	0	0.006(2)	0
S2	0.040(4)	0.035(9)	0.055(3)	0	-0.003(2)	0
S3	0.034(2)	0.045(6)	0.040(2)	-0.003(2)	0.012(1)	-0.004(2)
$P = 0.82$ GPa						
As1	0.032(1)	0.036(2)	0.0253(6)	0.0037(5)	0.0056(6)	0.0041(5)
As2	0.024(1)	0.036(2)	0.0309(7)	-0.0034(5)	-0.0002(6)	0.0007(5)
S1	0.039(4)	0.022(7)	0.038(2)	0	0.005(2)	0
S2	0.039(4)	0.021(8)	0.047(2)	0	0.000(2)	0
S3	0.026(2)	0.051(6)	0.034(1)	-0.006(2)	0.010(1)	-0.006(1)
$P = 1.43$ GPa						
As1	0.026(1)	0.037(2)	0.0212(5)	0.0042(5)	0.0047(4)	0.0041(4)
As2	0.017(1)	0.040(2)	0.0271(6)	-0.0047(5)	-0.0017(4)	0.0002(4)
S1	0.031(3)	0.026(5)	0.033(2)	0	0.005(2)	0
S2	0.031(3)	0.022(5)	0.044(2)	0	-0.001(2)	0
S3	0.020(2)	0.047(4)	0.032(1)	-0.004(1)	0.010(1)	-0.005(1)
$P = 2.04$ GPa						
As1	0.0303(9)	0.033(2)	0.0223(5)	0.0040(5)	0.0055(4)	0.0038(4)
As2	0.0231(9)	0.031(2)	0.0277(5)	-0.0027(5)	-0.0004(4)	0.0018(4)
S1	0.034(3)	0.026(5)	0.031(2)	0	0.004(2)	0
S2	0.030(3)	0.034(6)	0.042(2)	0	-0.003(2)	0
S3	0.024(2)	0.044(4)	0.030(1)	-0.005(1)	0.009(1)	-0.007(1)
$P = 2.70$ GPa						
As1	0.024(1)	0.030(2)	0.0184(7)	0.0050(7)	0.0043(7)	0.0027(6)
As2	0.020(1)	0.023(2)	0.0240(7)	-0.0026(8)	-0.0003(6)	-0.0003(6)
S1	0.038(5)	0.011(8)	0.029(3)	0	0.002(3)	0
S2	0.029(5)	0.027(9)	0.040(3)	0	-0.006(3)	0
S3	0.020(3)	0.045(6)	0.024(2)	-0.005(2)	0.010(2)	-0.008(2)

The P value measured by ruby fluorescence shift (estimated standard deviations of 0.05 GPa)

Structural evolution under pressure

The intramolecular bond distances are relatively unaffected by increasing pressure (Table 6). The largest reduction is in the As1–As2 bond distance which changes from 2.5819(4) at ambient pressure to 2.564(3) Å at 2.70 GPa. The greatest reduction in the length of the molecule is almost parallel to (102); it results in a contraction of the

square formed by the four sulfur atoms (Fig. 5) and of the two As1–As2 bond distances (Table 6); the four As–As distances, corresponding to the long edges of the disphenoidic As_4 group, do not show any significant changes. The reduction in the molecular volume, compared with its standard deviation, cannot be considered to be significant (Table 6). Intramolecular length changes are negligible in comparison to reduction

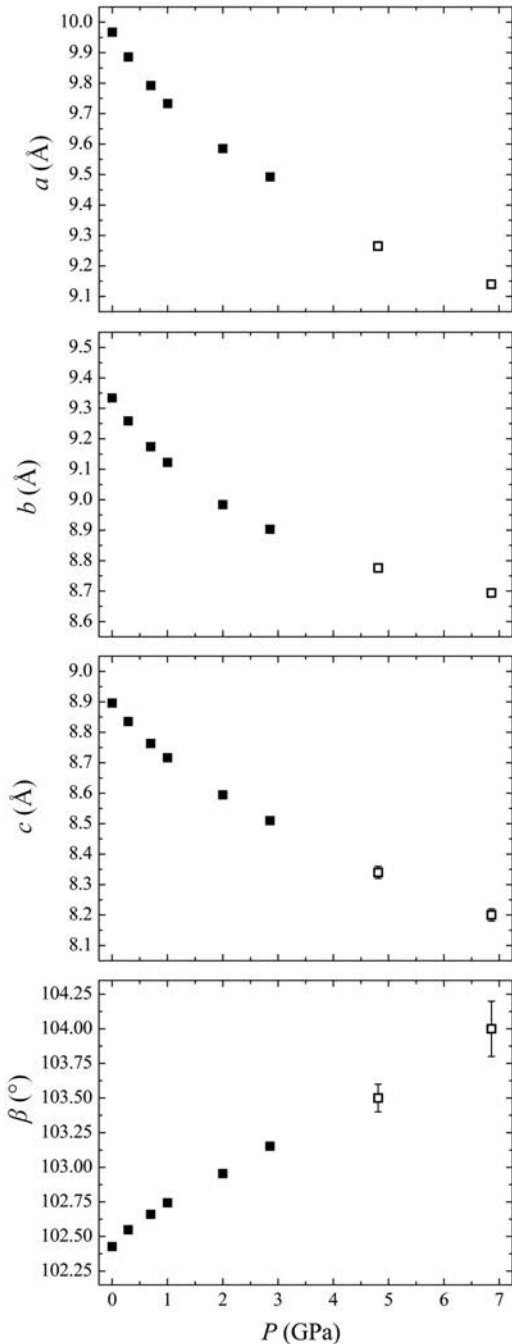
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FIG. 4. The variation in the unit-cell parameters of β -As₄S₄ as a function of pressure. Errors are within the symbol size if error bars are not present.

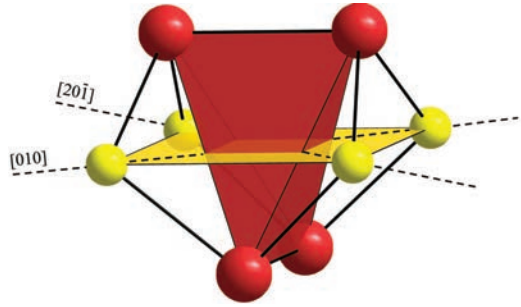


FIG. 5. Geometrical representation of the As₄S₄ molecule, the As₄ disphenoidic group (red) is interpenetrated by an S₄ square (yellow) laying on (102).

in the intermolecular distances, which are up to 8% (Table 6).

The frequencies of most of the vibrational modes in the Raman spectra at different pressures shift according to expectations (Fig. 6). Due to the strong photosensitivity of β -As₄S₄, which transforms into pararealgar when it is illuminated by visible light (Muniz-Miranda *et al.*, 1996; Bonazzi *et al.*, 1996; Bonazzi *et al.*, 2006), only the three main bands associated with intramolecular vibrations that do not overlap with those associated with pararealgar are considered (i.e.

TABLE 5. Coefficients obtained by fitting a third-order Birch–Murnaghan EoS to the data for β -As₄S₄.

Parameter	Fitted coefficient
a_0 (Å)	9.9671(6)
K_0 (GPa)	10.2(2)
K'	9.4(4)
b_0 (Å)	9.335(2)
K_0 (GPa)	10.4(4)
K'	7.7(7)
c_0 (Å)	8.8958(7)
K_0 (GPa)	13.0(2)
K'	7.9(3)
$a \sin \beta_0$ (Å)	9.7336(5)
K_0 (GPa)	9.8(1)
K'	8.5(3)
V_0 (Å ³)	808.2(2)
K_0 (GPa)	10.9(2)
K'	8.9(3)

TABLE 6. Molecular volume and selected interatomic distances and angles for β -As₄S₄ at different pressures.

<i>P</i> (GPa)	0.0001 (air)	0.0001(DAC)	0.82	1.43	2.04	2.70
Molecular volume (Å ³) [‡]	14.8(2)	14.7(2)	14.9(2)	14.8(2)	14.7(3)	14.5(2)
Intramolecular bond distances (Å)						
As1–S1	2.2329(7)	2.226(6)	2.244(5)	2.232(4)	2.233(4)	2.220(6)
As1–S3	2.2361(8)	2.234(4)	2.237(4)	2.241(3)	2.236(3)	2.232(5)
As1–As2	2.5819(4)	2.581(3)	2.581(3)	2.574(2)	2.568(2)	2.564(3)
As2–S3	2.2264(8)	2.224(4)	2.231(3)	2.214(3)	2.216(3)	2.207(5)
As2–S2	2.2372(7)	2.234(6)	2.242(5)	2.240(4)	2.239(4)	2.228(6)
Bond angles (°)						
S1–As1–S3	94.76(3)	94.7(2)	94.6(1)	94.6(1)	94.4(1)	94.4(2)
S1–As1–As2	99.28(2)	99.1(2)	99.5(1)	99.4(1)	99.5(1)	99.0(2)
S3–As1–As2	98.95(2)	99.1(2)	98.9(1)	98.6(1)	98.8(1)	98.9(2)
S3–As2–S2	94.82(3)	95.0(2)	94.7(1)	94.5(1)	94.6(1)	94.1(2)
S3–As2–As1	98.95(2)	99.0(2)	98.8(1)	99.1(1)	98.9(1)	99.3(2)
S2–As2–As1	99.16(2)	99.1(2)	99.3(1)	99.3(1)	99.4(1)	98.7(2)
As1–S1–As1	101.39(4)	101.7(4)	101.1(3)	101.4(2)	101.3(2)	102.0(4)
As2–S2–As2	101.44(4)	101.4(4)	101.5(3)	101.4(2)	101.3(3)	102.2(4)
As1–S3–As2	101.75(3)	101.7(2)	102.0(2)	102.1(1)	102.1(1)	102.2(2)
Intermolecular distances (Å)*						
S1 – S3	3.728(1)	3.736(7)	3.585(6)	3.519(5)	3.459(5)	3.429(8)
S2 – S3	3.730(1)	3.731(7)	3.588(6)	3.535(5)	3.464(5)	3.449(8)
As1–As2	3.5491(4)	3.548(2)	3.425(2)	3.368(2)	3.308(2)	3.277(3)
As1–S1	3.6322(7)	3.646(6)	3.503(5)	3.454(4)	3.398(4)	3.381(6)
As1–S2	3.5221(7)	3.528(6)	3.401(5)	3.354(4)	3.291(4)	3.275(6)
As2–S3	3.7020(9)	3.711(5)	3.585(5)	3.530(4)	3.476(4)	3.445(6)

[‡] Molecular volumes were calculated using *IVTON* (Balić-Zunić and Vicković, 1996).

* Only those contacts having distances shorter than the sum of the van der Waals radii [values from Bondi (1964)] of the connected atoms are reported.

bands at 184, 215 and 360 cm⁻¹). According to Muniz-Miranda *et al.* (1996), these are mainly due to the As–As stretching mode, S–As–S bending mode and As–S stretching mode, respectively. In agreement with the structural analysis, the peaks due to As–As stretching have the highest pressure dependence, whereas the S–As–S bending frequency and the As–S stretching mode show weaker or no variation with increasing pressure (Fig. 7).

Discussion

As expected for a crystal structure consisting of molecular units held together by weak van der Waals interactions, β -As₄S₄ has an exceptionally high compressibility. The unit cell contracts

without significant modifications to the cage-like As₄S₄ molecule; indeed, the dramatic reduction in unit-cell volume (~21% at 6.86 GPa) is caused by a reduction in the distances between the As₄S₄ molecules, which occurs without any phase transition in the pressure range reported in this study.

Making a comparison with other molecular arsenic sulfides, β -As₄S₃ is more rigid in compression [with $K_0 = 17$ GPa; Chattopadhyay *et al.* (1982)] whereas a very similar response to pressure is reported for realgar [with $K_0 = 8.1(5)$ GPa on the basis of energy-dispersive X-ray diffraction data up to 8 GPa (Tuktubiev *et al.*, 2009); $K_0 = 10.5(4)$ and 10.9(2) GPa on the basis of single crystal diffraction data up to 5.4 GPa and from density-functional theory

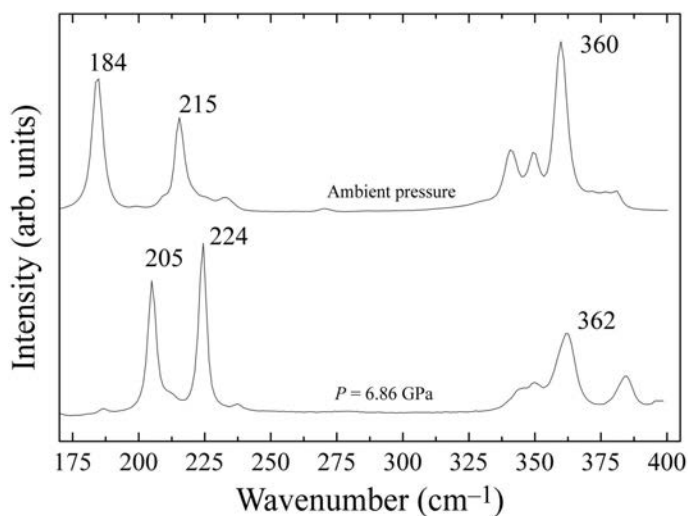


FIG. 6. Micro-Raman spectra collected at ambient pressure and 6.86 GPa.

calculations, respectively (Hejny *et al.*, 2012)]. There is disagreement in the literature about the presence of a pressure-induced phase transition in realgar. According to Tuktabiev *et al.* (2009), realgar undergoes a monoclinic–orthorhombic transition at $P \sim 7$ GPa. However, Töbrens *et al.* (2010) carried out single-crystal X-ray diffraction and powder diffraction experiments on realgar at pressures up to 5.4 GPa and 43 GPa, respectively, and did not observe any phase transition. As observed in β -As₄S₄, the intramolecular distances in realgar do not show any appreciable shortening, the compression is mainly intermolecular, and is greatest between the rods stacked along [010] (Hejny *et al.*, 2012). Indeed, as shown by Bonazzi

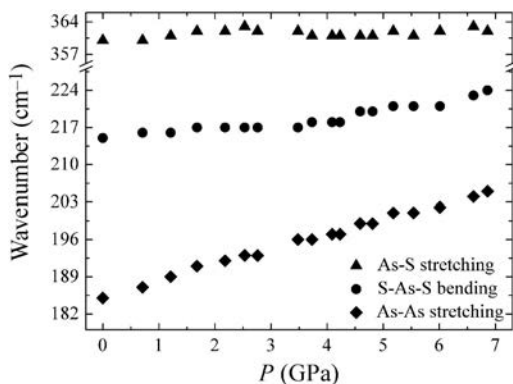


FIG. 7. Pressure dependence of selected Raman peaks.

and Bindi (2008), the structure of realgar can be described as a sequence of layers stacked along [010]. Each of these layers, in turn, can be described as a sequence of rods parallel to [100]. Within these rods, pairs of molecules show the shortest distances between molecular barycentres ($B-B = 5.62$ Å), whereas along the stacking axis the $B-B$ distances are significantly longer (7.03 Å). Therefore, the compressibility scheme

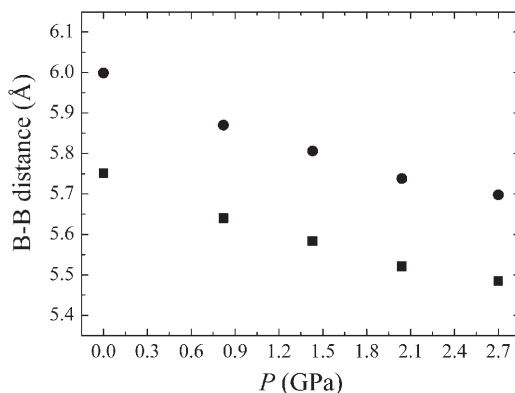


FIG. 8. Variation of the distances between the barycentres of the molecules ($B-B$) with pressure. The $B-B$ distances within rods are marked as circles and distances in the direction of layer stacking are indicated as squares. The barycentre of the molecules was calculated using *IVTON* (Balić-Žunić and Vicković, 1996). Errors are within the symbol size.

$\beta_b > \beta_c > \beta_a$, deducible from the lattice parameters published by Tuktatiev *et al.* (2009), is a consequence of the structural arrangement, with the smallest compressibility being along the direction where molecules are most closely packed. The structure of β -As₄S₄ can be described using the same kind of layers and rods found in realgar, in β -As₄S₄ they are parallel to $(\bar{1}11)$ and $[101]$, respectively. However, the distances between barycentres within the rods (B–B = 6.00 Å) are quite similar to those along the axis of layer stacking (B–B = 5.75 Å). Accordingly, as the pressure increases, the B–B distances within rods (circles in Fig. 8) decrease as much as those in the direction of the stacking axis (squares in Fig. 8), which accounts for the more isotropic response of the structure to increasing pressure.

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