Supplementary info

Orthorhombic unit-cell values of a=7.4537(7), b=10.270(2), c=18.258(1) Å were found for the AsS phase. Other data collection and structure refinement details are presented in the Table 1. Starting atomic coordinates have been deduced from those of β-realgar, As_4S_4, which monoclinic unit-cell values are: a_m =9.909, b_m =9.655, c_m=8.502 Å, β =97.290°. For this purpose, atomic sites of β-realgar were expanded by the symmetry operators of the C12/c1 group, transformed to the basis c_m, a_m, $2b_m$ and then placed into the orthorhombic unit cell of AsS. The starting set was refined in the $P1$ group resulting in the displacement of about half of the atoms to new positions. Other part had to be removed from the set and new coordinates had to be taken from the difference Fourier synthesis of the electron density. As a consequence, by one means or another we could localize 64 atomic positions, hypothetically capable of containing eight molecules As_4S_4. The calculated density of 4.07 g/cm^3 agreed with the measured one, whence it could be concluded that the new phase does contain the As and S atoms in equal numbers, i.e., 32 atoms of each sort per the unit cell.

Some atomic sites were found to be split in stronger and weaker spots along the c-period on the Fourier maps. It was hard to understand what might create such a splitting effect: an atomic disordering, some kind of twinning or either. Because of that, it had taken some time before we managed to recognize the As- and S-sites with confidence and to determine any space symmetry group which would differ from $P1$. There was no way to do it except to examine the Fourier maps thoroughly. When the orthorhombic group $Pbc2_1$ had been taken, atomic positions separated into sorts and structure motif become clearly apparent. Diffraction pattern from very small and thin crystals of AsS contained only 3923 observed reflections with intensities more than $3\sigma(I)$ from the total number of 40652 reflections, i.e., less than 10%. High value of R_{int} = 20% for the total reflection number was referred to this fact, and R_{int} = 6.7% for the observed reflections was supposed to be acceptable also taking into account a complication of an accurate absorption correction for a needle-shaped crystal. However, the splitting effect did not disappear and additional proofs should be provided for the symmetry choice. Structure refinement was performed repeatedly in the $Pbc2_1$ symmetry group following various techniques: the splitting was either taken or not taken into account; the refinement was performed using either all or observed reflections; with or without any rejection of some "bad" reflections; with or without restrictions for various parameters. Original structure motif was confirmed repeatedly without any exception. Generally speaking, the splitting of the atomic sites could indicate a missing twin law. To verify this hypothesis, the structure was no once refined as monoclinic or even triclinic being twinned by one of the rejected symmetry elements. The twinning by the inversion center has also been testified (the Flack parameter is 0.27). Since no one transfer to lower symmetry did not give any new information and did not improve the results of the structure refinement, the choice of $Pbc2_1$ was found to be optimal. Atomic displacement parameters (ADP) were refined in an isotopic approximation owing to the above. Moreover, ADP of most the As- and all the S-atoms were assigned to be equal to prevent the splitting impact. Sole As8 position was kept split because of most remarkable splitting. The main results of the refinement are presented in the Table 2. All calculations were made using the JANA2006 software [Petricek, V., Dusek, M. & Palatinus L. (2006). Jana2006. Structure Determination Software Programs. Institute of Physics, Praha, Czech Republic].

Summarized Fourier map for $0.08 < y < 0.21$ (a thickness of the atomic xz-plane) is presented in Figure 2 for two adjacent unit cells. One can assume the As-chains provoke the formation of anti-phase domains shifted for $a/2$ one relative to other whereas the chains itself are invariant to the shift. Such a hypothesis could explain the observed splitting of the atomic sites.

Table 1. Data collection and structure refinement details

Chemical formula	AsS

M (g/mole)	107
Symmetry, sp. gr., Z	Orthorhombic $Pbc2_1$, 32
a, Å	7.4537(7)
b, Å	10.270(2)
c, Å	18.258(1)
V, Å^3	1397.6(3)
D_x, g/cm^3	4.066
Wave length, λ, Å	0.71069
μ, mm^{-1}	19.91
T, K	293
Crystal size (mm)	$0.028 \times 0.028 \times 0.24$
Diffractometer	XCalibur CCD Sapphire
Scan type	ω-scan
Absorption correction	Numerical (Gaussian)
T_{min}, T_{max}	0.099, 0.606
θ_{max}, deg.	37.81
Reflection limits	$-12 \le h \le 12$
	$-17 \le k \le 17$
	$-31 \le l \le 30$
Reflection numbers:	
Total / independent (all)	40652 / 7142
Total /independent (observed)	3923 / 927
R_{int} (all) / R_{int} (obs)	0.202 / 0.067
LS-refinement technique	Based on F
Weighting scheme $1/\sigma^2 + (kF)^2$, k	0.02
N refl(all) / N refl(obs) / parameters*	7041 / 829 / 57
R(all) / wR(all) / wR(obs)	0.347 / 0.116 / 0.078
GOF(all) / GOF (obs)	0.97 / 1.90

* "Bad" reflections with $|F_{obs} - F_{calc}| > 5\sigma(F_{obs})$ were omitted

Table 2. Atomic coordinates and equivalent atomic displacement parameters of U*eq* = Tr(||u_{ij}||)/3 in the AsS phase structure.

Atom	Occupation	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2
As1	1	0.8764(5)	0.3714(3)	0.25	0.0180(3)
As2	1	0.1288(5)	0.3807(3)	0.3327(3)	0.0180(3)
As3	1	0.3720(5)	0.3838(3)	0.2391(3)	0.0180(3)
As4	1	0.6231(5)	0.3738(3)	0.33394(17)	0.0180(3)
As5	1	0.1207(6)	0.1435(4)	0.1272(3)	0.0325(8)
As6	1	0.6136(6)	0.3555(4)	0.5780(3)	0.0357(11)
As7	1	0.3832(4)	0.1549(2)	0.4488(2)	0.0008(3)
As8	0.683(5)	0.8864(5)	0.1390(3)	0.5129(2)	0.0008(3)
As8a	0.317(5)	0.8756(11)	0.1415(7)	0.4618(4)	0.0008(3)
S1	1	0.1375(9)	0.1762(6)	0.3777(4)	0.0060(4)
S2	1	0.1378(8)	0.3528(8)	0.0968(4)	0.0060(4)
S3	1	0.8836(9)	0.1404(6)	0.2115(4)	0.0060(4)
S4	1	0.8600(8)	0.3571(6)	0.4991(3)	0.0060(4)
S5	1	0.3750(9)	0.1599(6)	0.2126(3)	0.0060(4)
S6	1	0.4016(8)	0.3651(7)	0.4846(4)	0.0060(4)
S7	1	0.6160(10)	0.1675(5)	0.3649(3)	0.0060(4)
S8	1	0.6348(9)	0.1382(7)	0.5997(3)	0.0060(4)

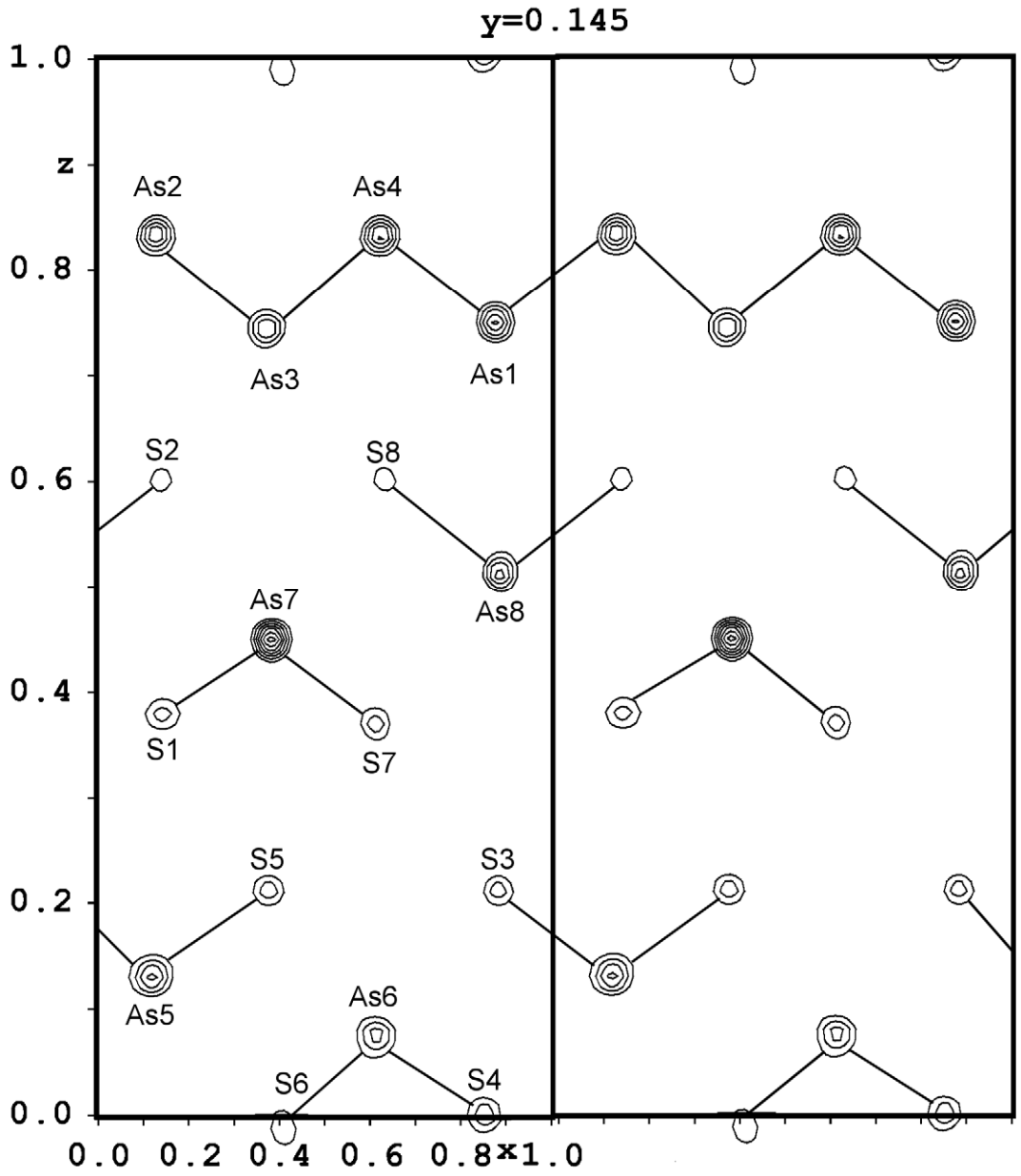

Fig. Fourier map of the electron density summarized through the cross-sections $0.08 < y < 0.21$ (mean y=0.145) of the AsS structure.