



## Evidence of the existence of the $\text{As}_4\text{S}_6$ molecule produced by light exposure of alacranite, $\text{As}_8\text{S}_9$

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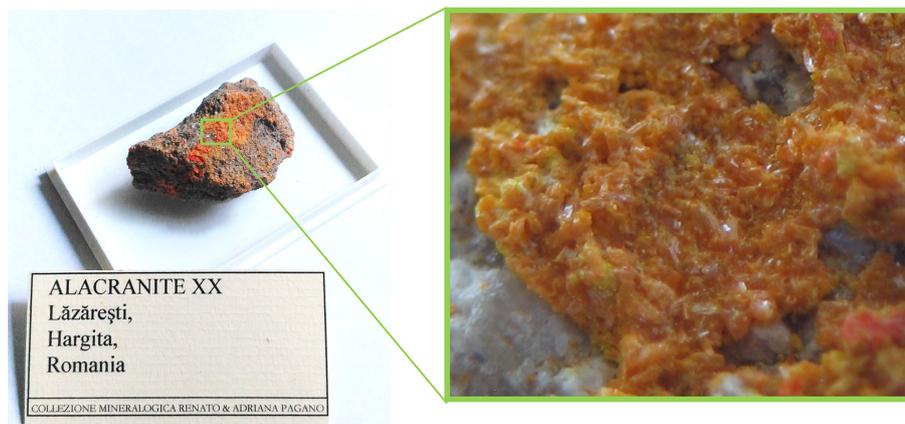
**Abstract.** The  $\text{As}_4\text{S}_6$  molecule, although theoretically predicted and supposed to occur in amorphous arsenic sulfides, was missing in the reported structures of crystalline As chalcogenides; the thermodynamic stable phase for this stoichiometry, in fact, is that of the mineral orpiment, which shows a layered structural arrangement based on trigonal  $\text{AsS}_3$  pyramids. Here we report the first possible occurrence of the  $\text{As}_4\text{S}_6$  molecule together with the other known  $\text{As}_4\text{S}_n$  ( $n = 3, 4, 5$ ) molecules randomly replacing each other in the crystalline structure of a new monoclinic product obtained by the light-induced alteration of the mineral alacranite,  $\text{As}_8\text{S}_9$ . Our findings are based on single-crystal X-ray diffraction experiments. The fact that  $\text{As}_4\text{S}_6$  formed in a crystalline light-induced alteration product could indicate a heretofore unknown role of this molecule in the photoinduced changes of the physico-chemical properties of both bulk glasses and thin films in the As–S system, widely studied in optics and optoelectronics.

### 1 Introduction

In the As–S system (Emelina et al., 2007), several compounds with different As : S ratios are known as minerals. They include duranusite,  $\text{As}_4\text{S}$ ;  $\alpha$ - and  $\beta$ -dimorphite,  $\text{As}_4\text{S}_3$ ; realgar and pararealgar,  $\text{As}_4\text{S}_4$ ; uzonite,  $\text{As}_4\text{S}_5$ ; alacranite,  $\text{As}_8\text{S}_9$ ; and orpiment,  $\text{As}_2\text{S}_3$  (Bonazzi and Bindi, 2008). The high-temperature polymorph  $\beta$ - $\text{As}_4\text{S}_4$ , i.e. bonazziite, was also found as a natural phase (Bindi et al., 2015). Non-stoichiometric sulfides with chemical composition ranging from  $\text{As}_4\text{S}_4$  to  $\text{As}_8\text{S}_9$  have also been reported (Bonazzi et al., 2003a). Most of the arsenic sulfides have a crystal structure consisting of a packing of cage-like, covalently bonded  $\text{As}_4\text{S}_n$  ( $n = 3, 4$  and  $5$ ) molecules held together by weak interactions of van der Waals characters (Bonazzi and Bindi,

2008). In contrast, duranusite (Bonazzi et al., 2016), with As : S = 4 : 1, and orpiment (Mullen and Nowacki, 1972), which fits the atomic ratio As : S = 4 : 6, exhibit a layered structural arrangement, despite the fact that ab initio quantum chemical calculations (Kyono, 2013) predicted the presence of molecular groups for both minerals.

All these As sulfides, as well as bulk glasses and thin films in the As–S system, are of interest for their potential or actual application in optics and optoelectronics, due to reversible and/or irreversible photoinduced changes of their physico-chemical properties (e.g. Holomb et al., 2005; Němec et al., 2005). Furthermore, as arsenic sulfide minerals were largely used as pigments, the study of their light-induced alteration finds application in the examination and conservation of



**Figure 1.** Alacranite sample from the As-sulfide-bearing sandstones of Lăzărești, in the northern part of the Ciomadu volcanic area, Romania (sample size  $6 \times 4 \times 4$  cm).

works of art (e.g. Trentelman et al., 1996; Vermeulen et al., 2015).

In particular, realgar ( $\alpha\text{-As}_4\text{S}_4$ ) and bonazziite ( $\beta\text{-As}_4\text{S}_4$ ), the non-stoichiometric  $\beta\text{-As}_4\text{S}_{4+x}$  (Bonazzi et al., 2003a) and some adduct compounds ( $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ , Bonazzi et al., 2011;  $(\text{HgBr}_2)_3(\text{As}_4\text{S}_4)_2$ , Zoppi et al., 2013) containing the realgar-type (*r*-type) molecules, undergo structural modifications when exposed to filtered light. During this process, the *r*-type  $\text{As}_4\text{S}_4$  molecule irreversibly transforms into the pararealgar (*p*-type)  $\text{As}_4\text{S}_4$  molecule (e.g. Bonazzi et al., 2006). Surprisingly, stoichiometric alacranite, which also contains *r*-type  $\text{As}_4\text{S}_4$  molecules, does not experience any change when exposed to filtered visible light (Bonazzi et al., 2003b).

According to several authors (Bindi et al., 2003; Kyono et al., 2005; Naumov et al., 2007, 2010), such solid-state transformation occurs through a self-sustainable mechanism based on initial aerobic photo-oxidation (process 1:  $5\text{As}_4\text{S}_4$  (*r*-type) +  $3\text{O}_2 \rightarrow 4\text{As}_4\text{S}_5 + 2\text{As}_2\text{O}_3$ ) followed by release of an S atom by breaking an As–S–As linkage to form pararealgar:  $\text{As}_4\text{S}_5 \rightarrow \text{As}_4\text{S}_4$  (*p*-type) + S (process 2). Propagation of process 2 cyclically occurs by re-attachment of the free S to another *r*-type  $\text{As}_4\text{S}_4$  molecule to form  $\text{As}_4\text{S}_5$  and subsequent conversion to *p*-type  $\text{As}_4\text{S}_4$  + S. It is not clear what determines the number of  $\text{As}_4\text{S}_5$  molecules that can be stored within the structure and which are the main factors that may affect the kinetics of the autocatalytically induced conversion, which, as Naumov et al. (2007) pointed out, does not require further exposition to visible light. It is a fact, however, that different compounds containing *r*-type  $\text{As}_4\text{S}_4$  molecules show different routes of transformation. A common feature for all of them is an expansion of the unit cell, which was ascribed to the increment of  $\text{As}_4\text{S}_5$  molecules in light-exposed  $\beta\text{-As}_4\text{S}_{4+x}$  crystals (Bonazzi et al., 2006) and, to a much lesser extent, in realgar (Kyono et al., 2005; Naumov et al., 2010). On the other hand, the increase of the unit-cell volume was explained by a replacement of *r*-type with *p*-type

molecules in the case of the  $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$  adduct (Bonazzi et al., 2011). Similarly, it was demonstrated that, when the exposure to light takes place under anaerobic conditions,  $\beta\text{-As}_4\text{S}_4$  (Zoppi and Pratesi, 2012) and realgar (Pratesi and Zoppi, 2015) transform to pararealgar without evidence of storing  $\text{As}_4\text{S}_5$  molecules within the structure.

Conversely, the photoinduced alteration of the most S-rich among the studied non-stoichiometric  $\beta\text{-As}_4\text{S}_{4+x}$  crystal ( $x = 0.35$ ) resulted in a new phase with a *Pccn* crystal structure (Bindi and Bonazzi, 2007) consisting of discrete  $\text{As}_4\text{S}_5$  molecules, with a very minor number – if any – of coexisting *p*-type molecules. Since the  $\beta\text{-As}_4\text{S}_{4+x}$  crystals had been supposed to consist of different proportions of  $\beta\text{-As}_4\text{S}_4$  and  $\text{As}_8\text{S}_9$  (i.e. alacranite) coherent crystalline domains (Bonazzi et al., 2003a), it was inferred that light exposure causes conversion to pararealgar or to the *Pccn*  $\text{As}_4\text{S}_5$  structure starting from  $\beta\text{-As}_4\text{S}_4$  or  $\text{As}_8\text{S}_9$ , respectively. This conclusion, however, was not in agreement with the lightening experiments previously carried out on alacranite from the type locality (Bonazzi et al., 2003b).

The recent finding of a new sample of alacranite gave us the opportunity to repeat the lightening experiments by varying the exposure conditions. The results are reported in this study.

## 2 Results

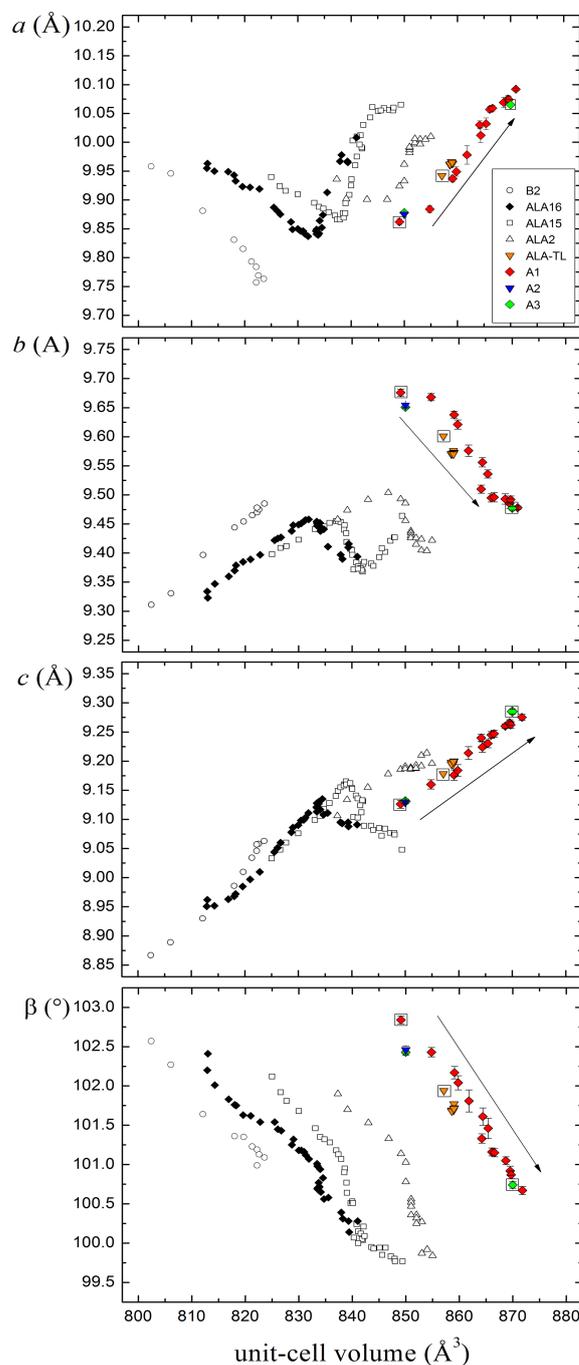
A new sample (Fig. 1), belonging to the private collection of Renato and Adriana Pagano, coming from the As-sulfide-bearing sandstones of Lăzărești, in the northern part of the Ciomadu volcanic area, Romania, was found to be rich in alacranite,  $\text{As}_8\text{S}_9$ , having a diffraction quality higher than that previously described for that locality (Kristály et al., 2006). Several single crystals were checked by means of X-ray single-crystal diffraction: the unit-cell parameters were found to match roughly those of alacranite from the type lo-

cality (Bonazzi et al., 2003b), with unit-cell volumes ranging from  $\sim 849$  to  $\sim 861 \text{ \AA}^3$ . Noteworthy, the smaller the unit-cell volumes, the higher the diffraction quality was.

As smaller unit-cell volumes seemed symptomatic of a higher diffraction quality, a crystal (A1) suitable for the whole intensity data collection and light exposure experiments was selected on this basis ( $a = 9.862(5)$ ,  $b = 9.676(6)$ ,  $c = 9.126(7) \text{ \AA}$ ,  $\beta = 102.84(5)^\circ$ ,  $V = 849(9) \text{ \AA}^3$ ). The X-ray studies were performed with an Oxford Diffraction Xcalibur 3 diffractometer equipped with a Sapphire 2 CCD detector, with graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), with working conditions  $50 \text{ kV} \times 50 \text{ mA}$  and with  $100 \text{ s}$  exposure time per frame; the detector-to-sample distance was  $6 \text{ cm}$ . The structure refinement of the A1 crystal ( $R1 = 8.25\%$ ) fully confirmed the  $P2/c$  model previously obtained for alacranite from the Uzon Caldera (Bonazzi et al., 2003b). Despite the smaller volume of the unit cell, all the sulfur positions were found to be fully occupied. It was then supposed that larger volumes could correspond to initial steps of light-induced alteration, which in molecular As sulfides usually produce an increase of the unit-cell volume due to the replacement of  $\text{As}_4\text{S}_4$  (*r*-type) molecules with  $\text{As}_4\text{S}_4$  (*p*-type) and  $\text{As}_4\text{S}_5$  molecules. The effect of the light exposure on the structure of alacranite was thus investigated employing either a  $550$  or a  $440 \text{ nm}$  long wavelength pass filter (LWPF). A Schott KL 1500 electronic apparatus equipped with optical fibres and a  $150 \text{ W}$  FFR Sylvania dichroic halogen lamp was used to irradiate the sample with polychromatic light at a distance of  $2.5 \text{ cm}$ . This apparatus, also equipped with a visible pass filter, prevented infrared radiation from reaching the sample (IR transmittance  $< 1/1000$ ). The LWPF  $550$  and  $440 \text{ nm}$  long-wavelength pass filters (Schott Germany) were used to cut the region of the visible spectrum. The emission spectrum of the filtered light ranged from  $\sim 500$  to  $\sim 800 \text{ nm}$ , with an emission maximum at about  $500/600 \text{ nm}$ . The power density on the sample, measured with a power-meter instrument (model 362; Scientech, Boulder, Colorado), was about  $70 \text{ mW cm}^{-2}$ .

The action of the light filtered using a  $550 \text{ nm}$  LWPF did not produce any significant effect on the unit cell, thus confirming what was previously observed for alacranite from the type locality (Bonazzi et al., 2003b, 2006). On the other hand, employing the  $440 \text{ nm}$  LWPF, remarkable variations of the unit-cell parameters were observed, producing an increase of the unit-cell volume of  $2.7\%$  after  $1520 \text{ min}$  of lightening (Table 1). In particular, the  $a$  and  $c$  parameters strongly increase, while the  $b$  parameter and the  $\beta$  angle decrease as a function of the light exposure time (Fig. 2). After  $1520 \text{ min}$ , a new diffraction experiment indicated that alacranite transformed into an orthorhombic phase (space group  $Pccn$ ) identical to that already obtained by the light-induced alteration of a non-stoichiometric  $\text{As}_4\text{S}_{4+x}$  crystal (Bindi and Bonazzi, 2007).

To follow the evolution of the transformation path, a second crystal (A2;  $a = 9.875(4)$ ,  $b = 9.654(3)$ ,  $c = 9.129(2) \text{ \AA}$ ,



**Figure 2.** Behaviour of alacranite crystals from Lăzărești (A1, A2, A3) compared with that of synthetic  $\beta\text{-As}_4\text{S}_4$  phase (B2) and non-stoichiometric  $\text{As}_8\text{S}_{9-x}$  crystals from Radvanice (ALA16, ALA15, ALA2; Bonazzi et al., 2003a); orange triangles represent alacranite from the type locality exposed to  $550 \text{ nm}$  LWPF light (Bonazzi et al., 2006). Symbols inscribed within empty squares indicate samples where a structural study was conducted. Arrows indicate increasing exposure times.

**Table 1.** Unit-cell values of alacranite (crystal A1) collected before and after exposure to filtered light.

Minute	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>V</i> (Å <sup>3</sup> )
0	9.862(5)	9.676(6)	9.126(7)	102.84(5)	849.1(1.0)
120	9.884(6)	9.668(6)	9.160(8)	102.43(6)	854.8(1.2)
240	9.937(6)	9.638(6)	9.176(9)	102.17(8)	859.1(1.5)
360	9.949(8)	9.621(8)	9.184(10)	102.04(9)	859.8(1.7)
480	9.978(16)	9.576(10)	9.214(11)	101.81(14)	861.8(2.6)
600	10.012(13)	9.556(8)	9.224(9)	101.61(11)	864.4(2.0)
720	10.032(10)	9.536(7)	9.230(7)	101.46(13)	865.4(2.3)
840	10.030(7)	9.510(7)	9.240(6)	101.33(6)	864.2(1.1)
920	10.057(5)	9.495(7)	9.245(6)	101.16(5)	866.1(9)
1040	10.059(5)	9.496(8)	9.247(6)	101.15(5)	866.6(9)
1160	10.069(8)	9.493(9)	9.260(4)	101.05(6)	868.7(1.0)
1280	10.075(6)	9.485(8)	9.266(5)	100.92(5)	869.5(1.0)
1400	10.074(5)	9.492(6)	9.262(6)	100.87(5)	869.7(7)
1520	10.092(2)	9.478(3)	9.275(5)	100.67(3)	871.8(6)

$\beta = 102.46(5)^\circ$ ,  $V = 850(8) \text{ \AA}^3$ ) was exposed to the 440 nm LWP light for 900 min. However, when the crystal was examined by single-crystal X-ray diffraction, it resulted to be completely transformed into the orthorhombic *Pccn* phase. The subsequent structure refinement of the *Pccn* phase ( $R1 = 12.05\%$ ) confirmed the model previously obtained (Bindi and Bonazzi, 2007) and led to the chemical formula As<sub>4</sub>S<sub>4.93</sub>.

Finally, a third crystal was selected (A3;  $a = 9.878(2)$ ,  $b = 9.651(2)$ ,  $c = 9.131(4) \text{ \AA}$ ,  $\beta = 102.43(4)^\circ$ ,  $V = 850(7) \text{ \AA}^3$ ) and exposed to the 440 nm LWP light for 600 min. At this step, the measured unit cell was  $a = 10.065(6)$ ,  $b = 9.477(3)$ ,  $c = 9.285(4) \text{ \AA}$ ,  $\beta = 100.74(4)^\circ$  and  $V = 870(8) \text{ \AA}^3$ . Single-crystal X-ray diffraction intensity data were collected and corrected for standard Lorentz and polarization factors with the *CrysAlis RED* package (Oxford Diffraction, 2006). The program ABSPACK in *CrysAlis RED* (Oxford Diffraction, 2006) was used for the absorption correction. A total of 888 unique reflections were collected. The analysis of the systematic absences together with the statistics tests on the distribution of  $|E|$  values led to the choice of the space group *C2/c*. The structure was solved by direct methods and refined using the Shelx software package (Sheldrick, 2008) and Fourier syntheses. All atoms were located on  $F_o$  Fourier maps. Isotropic full-matrix least-squares cycles were initially run with the atom sites fully occupied, although the unusually high value of the isotropic displacement factor for most of the As and S atoms suggested partial occupancy at these sites. Successive least-squares cycles were done by fixing, alternately, the site-occupancy factor and the isotropic displacement parameter for these atoms. In the last cycle, partial occupancy factors were fixed to the refined values, and an anisotropic model of the whole structure was refined. Convergence was achieved at  $R = 9.43\%$  for 468 observed reflections [ $F_o > 4\sigma(F_o)$ ] and 60 refined parameters. Scattering curves for neutral As and S atoms were

**Table 2.** Atomic coordinates and equivalent displacement parameters (Å<sup>2</sup>) of the new monoclinic phase.

Atom	<i>x/a</i>	<i>y/b</i>	<i>x/c</i>	<i>U</i> <sub>eq</sub>
As1a	0.0100(11)	0.2209(9)	0.9407(8)	0.121(3)
As1b	0.4385(10)	0.3308(10)	0.4317(8)	0.121(3)
As2a	0.191(3)	0.442(4)	0.855(4)	0.108(4)
As2b	0.3895(17)	0.044(2)	0.183(2)	0.108(4)
As2c	0.3436(17)	0.080(3)	0.152(2)	0.108(4)
S1	0	0.0605(10)	3/4	0.128(4)
S2	0	0.5679(18)	3/4	0.146(7)
S3a	0.2031(13)	0.3234(13)	0.6532(11)	0.112(3)
S3b	0.319(7)	0.212(7)	0.303(6)	0.112(3)
S4	0.3941(16)	0.1727(15)	-0.0066(14)	0.111(4)

taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). Inspection of the difference Fourier map revealed that maximum positive and negative peaks were 0.43 and 0.64 e<sup>-</sup>/Å<sup>3</sup>, respectively. Fractional atomic coordinates and equivalent displacement parameters are given in Table 2.

The resulting structural model is strongly disordered wherein different kinds of As<sub>4</sub>S<sub>*n*</sub> molecules replace each other.

### 3 Discussion

The atomic coordinates of the new monoclinic *C2/c* structure (Table 2) show similarities with those of bonazziite, natural  $\beta$ -As<sub>4</sub>S<sub>4</sub> (Bindi et al., 2015). The two As atoms of  $\beta$ -As<sub>4</sub>S<sub>4</sub> are here split into five partially occupied sites. In detail, As1 of bonazziite splits into two half-occupied sites (As1a and As1b), whereas As2 splits into three sites (As2a, As2b and As2c). More complex is the scenario for the S atoms. In  $\beta$ -As<sub>4</sub>S<sub>4</sub> there are three fully occupied S atoms. In

**Table 3.** Model of interacting molecules in the monoclinic phase.

	As1a	As1b	As2a	As2b	As2c	S1	S2	S3a	S3b	S4	%	V(As <sub>4</sub> )
	0.13 × 2			0.13 × 2		0.13		0.13 × 2			13 % As <sub>4</sub> S <sub>3</sub>	2.77
	0.37 × 2				0.37 × 2	0.37	0.37	0.37 × 2			37 % As <sub>4</sub> S <sub>4</sub>	3.33
		0.30 × 2		0.30 × 2		0.30		0.30 × 2		0.30 × 2	30 % As <sub>4</sub> S <sub>5</sub>	4.01
		0.20 × 2	0.20 × 2			0.20	0.20		0.20 × 2	0.20 × 2	20 % As <sub>4</sub> S <sub>6</sub>	6.47
(1)	1.00	1.00	0.40	0.86	0.74	1.00	0.57	1.60	0.40	1.00	As <sub>4</sub> S <sub>4.57</sub>	
(2)	1.00	1.00	0.40	0.86	0.74	1.00	0.60	1.60	0.40	1.00	As <sub>4</sub> S <sub>4.60</sub>	

(1) Atoms per formula unit (pfu) assigned on the basis of geometrical compatibility between split sites. (2) Atoms pfu obtained by the refinements of the occupancy factors.

the new monoclinic phase, only S1 remains fully occupied, S2 is partially vacant, S3 splits into two close partially occupied positions, and there is the appearance of a new, half-occupied sulfur atom (i.e. S4). All the atoms show very large atomic displacement parameters, indicating a strong disorder of the whole structure.

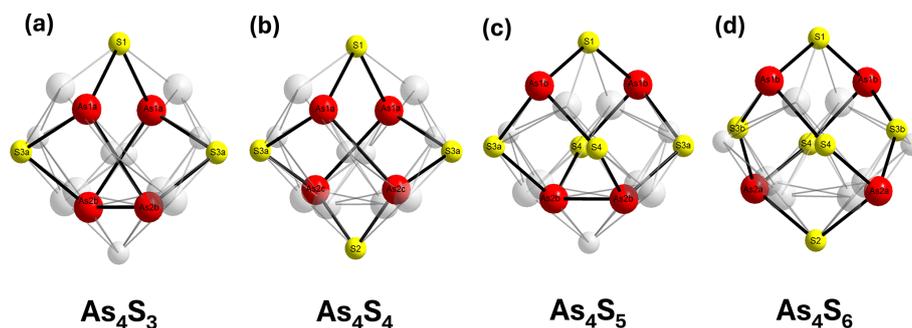
Taking into account the overall geometry and the partial occupancies of the structural sites, a complex model of interacting molecules was derived (Table 3). In detail, As1a links As2b, S1 and S3a, and As2b links As1a, As2b and S3a to form the As<sub>4</sub>S<sub>3</sub> molecules (Fig. 3a). The As–S bond distances (with errors between 0.01 and 0.03 Å) are in the range of 2.30–2.37 Å and the As–As distances in the range 2.34–2.78 Å. Then, As1a links As2c, S1 and S3a, and As2c links As1a, S2 and S3a to form realgar-type As<sub>4</sub>S<sub>4</sub> molecules (Fig. 3b). The As–S bond distances are in the range of 2.16–2.37 Å, and the As–As distance is 2.64 Å. As1b links S1, S3a and S4, and As2b links As2b, S3a and S4 to form uzonite-type As<sub>4</sub>S<sub>5</sub> molecules (Fig. 3c). The As–S bond distances are in the range of 2.09–2.30 Å, and the As–As distance is 2.34 Å. Finally, As1b links S1, S3b and S4, and As2a links S2, S3b and S4 to form the new As<sub>4</sub>S<sub>6</sub> molecule (Fig. 3d). The As–S bond distances are in the range of 2.00–2.32 Å.

Although some drawbacks are present due to the low quality of the available data given the complex material (few very short bond distances and large atomic displacement parameters), the overall sum of the atoms per formula unit assigned on the basis of the geometrical compatibility between split sites produces the formula As<sub>4</sub>S<sub>4.57</sub>. This is in excellent agreement with that obtained by the refinements of the occupancy factors (i.e. As<sub>4</sub>S<sub>4.60</sub>). The assignment of the different molecules is also corroborated by the almost perfect match between the calculated polyhedral volumes of the As<sub>4</sub> disphenoidic group (2.77, 3.33 and 4.01 Å<sup>3</sup> for the As<sub>4</sub>S<sub>3</sub>, As<sub>4</sub>S<sub>4</sub> and As<sub>4</sub>S<sub>5</sub>, respectively) with those obtained for pure molecules (2.77, 3.23 and 4.38 Å<sup>3</sup> for the As<sub>4</sub>S<sub>3</sub>, As<sub>4</sub>S<sub>4</sub> and As<sub>4</sub>S<sub>5</sub>, respectively; Bonazzi and Bindi, 2008). The new As<sub>4</sub>S<sub>6</sub> molecule exhibits a volume of 6.47 Å<sup>3</sup>, well beyond the largest value observed for the As<sub>4</sub>S<sub>5</sub> molecule in the structure of wakabayashilite (4.89 Å<sup>3</sup>; Bonazzi et al., 2005).

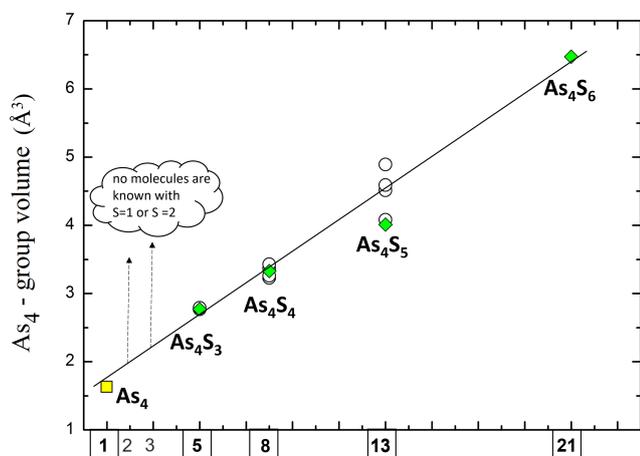
Interestingly, the Fibonacci sequence is related to an incredible variety of unrelated, natural phenomena. Docu-

mented phyllotaxic relationships follow the numbering, and many examples of spirals in natura – such as those of *Nautilus* seashells or the arrangement of seeds on flower heads (e.g. sunflower) and pinecones – can be built on Fibonacci sequences (Mitchison, 1977). It could be a simple coincidence, but it is intriguing to see as the volume of the As<sub>4</sub> group in the As<sub>4</sub>S<sub>n</sub> (0 ≤ n ≤ 6) molecules exhibits a linear trend (r<sup>2</sup> = 0.998) when plotted versus the range 1–21 with the known molecules falling exactly along the Fibonacci sequence (Fig. 4).

As shown in Fig. 2, the unit-cell volume increases as a function of the exposure time to light. The expansion is observed for all the crystals (B2 (β-As<sub>4</sub>S<sub>4</sub>; Bonazzi et al., 1996); non-stoichiometric As<sub>8</sub>S<sub>9–x</sub> crystals (ALA16, ALA15, ALA2; Bonazzi et al., 2003a)) but ALA-TL (Bonazzi et al., 2003b), where only a minor increment was observed. As documented by Bonazzi et al. (2006), the volume increase is not linear with time, being greater at the beginning of the lightening experiment. For non-stoichiometric crystals (i.e. ALA16, ALA15 and ALA2), the cell increase shows a decreased rate occurring at diverse volume values (~ 834, ~ 842 and ~ 851 Å<sup>3</sup> for ALA16, ALA15 and ALA2, respectively) persisting for various exposure times. To compare the unit-cell values in different arsenic sulfides, the lattice parameters were plotted against the unit-cell volume rather than the time of lightening. The expansion and/or contraction of the unit-cell parameters in the monoclinic phase here discovered has a roughly constant trend. This is in contrast with what observed for non-stoichiometric As<sub>8</sub>S<sub>9–x</sub> crystals (ALA16, ALA15, ALA2). Bonazzi et al. (2006) individuated two paths: path I (beginning of the process) with a decrease of the *a* parameter and an increase of *b* and *c* and path II with an increase of the *a* parameter and a decrease of *b* and *c*. The monoclinic phase shows instead a single path with increasing *a* and *c* and decreasing the *b* parameter (path II only). A possible explanation for the diverse observed behaviour can be found in the different way in which the various molecules are arranged. Unfortunately, owing to the inherent limit of X-ray diffraction together with the extremely low diffraction quality of the crystals, we can only detect disordered mixtures of the various molecules without a clear hint of the possible arrangement mechanisms. Several reactions were hypothesized (Bonazzi et al., 2006), but the



**Figure 3.** Different types of molecules present in the disordered monoclinic  $C2/c$  structure.



**Figure 4.** Volume of the  $\text{As}_4$  group in the  $\text{As}_4\text{S}_n$  ( $0 \leq n \leq 6$ ) molecules exhibits a linear trend ( $r^2 = 0.998$ ) when plotted versus the range 1–21 of the Fibonacci sequence. Green diamonds denote this study (A3 crystal); empty circles denote data from literature (Bonazzi and Bindi, 2008); yellow square denotes theoretical volume of a tetrahedral  $\text{As}_4$  group having an As–As edge (corresponding to As–As covalent bond) of 2.40 Å.

only clear evidence was the involvement of additional sulfur to the  $\text{As}_4\text{S}_4$  and  $\text{As}_4\text{S}_5$  molecules. In this study we have found the first direct evidence of the existence of the  $\text{As}_4\text{S}_6$  molecule, which can well take into account the increase of the unit-cell volume in alacranite as well as the inversion from path I to path II observed by Bonazzi et al. (2006) for non-stoichiometric  $\text{As}_8\text{S}_{9-x}$  crystals. However, the results obtained in this study suggest that the extent of sulfur incorporation is strictly controlled by the type of molecular packing and not only by the kind of molecule. Indeed, it should be taken into consideration that the packing of molecules (see Bonazzi and Bindi, 2008) in the structure of bonazziite,  $\beta\text{-As}_4\text{S}_4$  (Bindi et al., 2015), non-stoichiometric  $\text{As}_4\text{S}_{4+x}$  (Bonazzi et al., 2003a), alacranite (Bonazzi et al., 2003b), and the  $\text{As}_4\text{S}_{5-x}$  molecules in the orthorhombic  $Pccn$  phase (Bindi and Bonazzi, 2007) is substantially identical to the  $\text{As}_4\text{S}_4$  molecules in the new monoclinic phase and to that of the  $\text{As}_4\text{S}_4$  molecules in the structure of pararealgar (Bonazzi

et al., 1995). In these transformations ( $\beta\text{-As}_4\text{S}_4 \rightarrow$  pararealgar, and  $\text{As}_4\text{S}_5 \rightarrow$  monoclinic phase), the final phase is produced by a continuous, room-temperature, light-induced alteration process which does not require a complete rearrangement of the molecular packing and therefore does not imply the loss of coherency between crystalline domains.

#### 4 Conclusions

Over the past 40 years, many researchers have dealt with studies about structural modifications of arsenic sulfides belonging to the  $\text{As}_8\text{S}_8\text{--As}_8\text{S}_9$  series when exposed to light with appropriate wavelength radiation. In this work, the photoinduced structural modifications of alacranite have been investigated by exposing the mineral to a 440 nm wavelength radiation (at room temperature) and studied by means of single-crystal X-ray diffraction. The results of this study allowed confirmation of the increase of the unit-cell volume as a function of the light exposure. Besides, it was possible to observe that, by increasing the light exposure to at least 600 min, there is a structural transition from  $P2/c$  alacranite sensu stricto (Bonazzi et al., 2003b), through an orthorhombic  $Pccn$  phase (Bindi and Bonazzi, 2007) to a new, monoclinic  $C2/c$  phase where four discrete molecular clusters (i.e.  $\text{As}_4\text{S}_3$ ,  $\text{As}_4\text{S}_4$ ,  $\text{As}_4\text{S}_5$ ,  $\text{As}_4\text{S}_6$ ) coexist and constantly evolve. Noteworthy is the presence of the  $\text{As}_4\text{S}_6$  molecule, because it is the first time that such a molecule is reported in a crystalline compound of the As–S system.

This example conclusively corroborates the complexity of minerals in the natural kingdom, illustrating the intricate and multifaceted nature of their formation, composition and characteristics. This complexity underscores the rich diversity and sophistication inherent in Earth's geological processes (Bindi et al., 2020).

**Data availability.** Crystallographic data (CCDC 2366909) can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://doi.org/10.5517/ccdc.csd.cc2kfyxw> (Bindi, 2024).

**Author contributions.** The study was conceived by LB and PB. LB, PB, LC, MMNF, GOL, MM and AT carried out the diffraction experiments. LB, PB, GP, MZ and SM discussed the results. LB wrote the paper. All the authors commented on the final version of the paper.

**Competing interests.** At least one of the (co-)authors is a member of the editorial board of *European Journal of Mineralogy*. The peer-review process was guided by an independent editor, and the authors also have no other competing interests to declare.

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