FLORE
Repository istituzionale dell'Università degli Studi di Firenze

How many alacranites do exist? A structural study of non-stoichiometric As8S9-x crystals.

How many alacranites do exist?
A structural study of non-stoichiometric As_8S_{9-x} crystals

Paola BONAZZI[1], Luca BINDI[1], Filippo OLMI[2] and Silvio MENCHETTI[1]

[1]Dipartimento di Scienze della Terra, Università degli Studi di Firenze, via La Pira 4, I-50121 Firenze, Italy
e-mail: pbcry@steno.geo.unifi.it
[2]CNR – Istituto di Geoscienze e Georisorse – sezione di Firenze, via La Pira 4, I-50121 Firenze, Italy

Abstract: Crystals of arsenic sulphide (reported as *alacranite*), coming from the burning dump of Kateřina Mine (Czech Republic), have been investigated by single crystal X-ray diffraction and chemical microanalysis.

Both analytical data and unit-cell parameters strongly suggest the existence of a continuous series between the high-temperature polymorph (β-As_4S_4) and the mineral alacranite (As_8S_9). As the S content increases in the series, the unit-cell volume increases accordingly. The structural model has been obtained for two crystals, exhibiting different unit-cell volumes (ALA15: a = 9.940(2), b = 9.398(2), c = 9.033(2), β =102.12(2), V = 825.0(3), R_{obs} = 6.12 %; ALA2: a = 9.936(2), b = 9.458(2), c = 9.106(2), β = 101.90(2), V = 837.3(3), R_{obs} = 6.41 %). We found that the non-stoichiometric compounds crystallize as a disordered mixture of two kinds of cage-like molecules, packed together as in the β-As_4S_4 phase. The first one is identical to the As_4S_4 molecule found in the structures of both realgar (α-As_4S_4) and β-As_4S_4. The second molecule is chemically and structurally identical to that found in the As_4S_5 compound. The simultaneous presence of As_4S_4 ($C2/c$) and As_8S_9 ($P2/c$) microdomains could be a reason for the observed gradual change of the translation symmetry from the β-phase to alacranite *s.s.*.

Key-words: alacranite, crystal structure, arsenic sulphides, chemical composition, Kateřina Mine.

Introduction

Three phases among the known crystalline modifications of tetra-arsenic tetrasulphide (*i.e.* realgar, pararealgar, and β-phase[1]) occur as minerals. Realgar is the low-temperature form, α-As_4S_4 (Hall, 1966; Clark, 1970; Roland, 1972; Blachnik *et al.*, 1980; Bryndzya & Kleppa, 1988), which commonly occurs as a sublimation product in active volcanic areas, in low-temperature hydrothermal deposits, and, to a lesser extent, as a minor constituent of lead, silver, and gold ore veins. Pararealgar occurs as a yellow film covering realgar crystals which have been exposed to light (Roberts *et al.*, 1980; Bonazzi *et al.*, 1995). The β-As_4S_4 phase is the high-temperature form, stable in the system As-S at temperatures higher than 256 ± 5 °C (Hall, 1966). The occurrence of a natural phase exhibiting a diffraction pattern quite similar to that of the synthetic β-As_4S_4 was first reported by Clark (1970), who found both low- and high-temperature forms in the Ag-As-Sb vein deposit at Alacràn (Chile). According to Clark (1970), the natural β-As_4S_4 phase forms irregular masses and exhibits optical properties similar to those of realgar, but the colour is slightly paler and more yel-

Table 1. Unit cell parameters for *alacranites* from Kateřina Mine together with data from literature.

	a (Å)	b (Å)	c (Å)	β(°)	*Vol.* (Å^3)
ALA11	9.968(4)	9.317(2)	8.906(4)	102.45(4)	807.7(5)
ALA12	9.963(9)	9.351(2)	8.984(5)	102.43(2)	817.4(9)
ALA15	9.940(2)	9.398(2)	9.033(2)	102.12(2)	825.0(3)
ALA1	9.95(1)	9.44(1)	9.07(1)	102.1(2)	833(2)
ALA2	9.936(2)	9.458(2)	9.106(2)	101.90(2)	837.3(3)
ALA7	9.941(6)	9.450(5)	9.110(2)	101.81(3)	837.7(7)
ALA6	9.918(5)	9.478(7)	9.145(6)	102.10(5)	840.6(9)
CL*	9.97(1)	9.29(1)	8.88(1)	102.6(1)	803(2)
PS	9.957(3)	9.335(4)	8.889(5)	102.48(4)	806.7(6)
PPV	9.89(2)	9.73(2)	9.13(1)	101.84(5)	860(3)
BP	9.943(1)	9.366(1)	8.908(1)	102.007(2)	811.4(1)
ZO	9.87(1)	9.73(3)	9.16(2)	101.52(4)	858(4)

Note: CL = natural β-As_4S_4 from Alacràn Mine, Chile (Clark, 1970); PS = synthetic β-As_4S_4 (Porter & Sheldrick, 1972); PPV = alacranite from Kamchatka (Popova *et al.*, 1986); BP = natural β-As_4S_4 (Burns & Percival, 2001); ZO = *alacranite* from Kateřina Mine (Žáček & Ondruš, 1997).* indexed by the present authors.

lowish than realgar. At the Alacràn Mine the mineral occurs closely associated to smithite, orpiment and arsenolamprite. Although the main properties of the mineral (XRD data, chemical composition, optical properties and Vickers'

---

[1] Much confusion exists in literature for the use of α- and β-descriptors. Following Douglass *et al.* (1992) we will refer to the low-temperature form as α and to the high-temperature form as β.

hardness) were defined by Clark (1970), the proposal of a new mineral species corresponding to the natural β-As₄S₄ polymorph was not approved by the NMMN – IMA Commission (Popova *et al.*,1986). Later, a new arsenic sulphide was found at the Uzon caldera (Kamchatka, Russian Federation) by Popova *et al.* (1986).

These authors assumed this mineral to be identical to the species previously described by Clark (1970) due to the similarity of their XRD powder patterns. For this reason, the mineral was named alacranite (Popova *et al.*, 1986). As shown in Table 1, the lattice parameters of alacranite resemble fairly those of the synthetic β-As₄S₄ (Porter & Sheldrick, 1972) and those of the natural β-phase from Alacràn (Clark, 1970). In keeping with the greater unit-cell volume, alacranite exhibits a different chemical composition (As₈S₉). According to Popova *et al.* (1986), alacranite is monoclinic, *P*2/*c*, while the synthetic β-As₄S₄ crystallizes in the *C*2/*c* space group. During a recent sampling of the seafloor around Lihir Island (Papua New Guinea), a specimen mainly consisting of pyrite, sphalerite, and galena, together with red and orange arsenic sulphides, was recovered at the top of Conical Seamount (Percival *et al.*, 1999). According to these authors, the XRD analysis of both the deep-red and orange crystals revealed a mixture of realgar and alacranite. The subsequent detailed investigation (Burns & Percival, 2001) showed the mineral from Papua New Guinea to be structurally and chemically identical to the synthetic β-As₄S₄. However, one may wonder whether this mineral is actually the same mineral species defined as alacranite by Popova *et al.* (1986). Indeed, the *alacranite* described by Burns & Percival (2001) is quite similar to that from Alacràn (Clark, 1970), but, as also noted by Jambor & Roberts (2002), it appears to differ with respect to chemical formula, unit-cell volume and space group from the mineral approved with the name alacranite by the NMMN – IMA Commission (Hawthorne *et al.*, 1988).

The complexity of the problem is further increased due to the alteration induced by light on the tetra-arsenic tetrasulphides. It is long known that both polychromatic and monochromatic light alter realgar and the β-phase up to pararealgar through an intermediate product (χ-phase) (Douglass *et al.*, 1992; Bonazzi *et al.*, 1996; Muniz-Miranda *et al.*, 1996). The light-induced formation of the χ-phase obtained from the β-phase occurs with a strong anisotropic increase of the unit-cell volume. Therefore, crystals of β-phase partially altered by exposure to light exhibit unit-cell volumes greater than the unaltered crystals.

For these reasons, we were intrigued by a new recovery of *alacranite* coexisting with realgar, and other As-S phases (Žáček & Ondruš, 1997) from the burning dump of the Kateřina colliery, Radvanice (Czech Republic). On the basis of its lattice parameters (Table 1), this mineral appears to be very similar to the *true* alacranite described by Popova *et al.* (1986).

Occurrence and sample description

A sample from Kateřina Mine (Czech Republic) was submitted to our attention by Dr. Giovanni Pratesi (Museo di Storia Naturale – Università di Firenze, Italy).
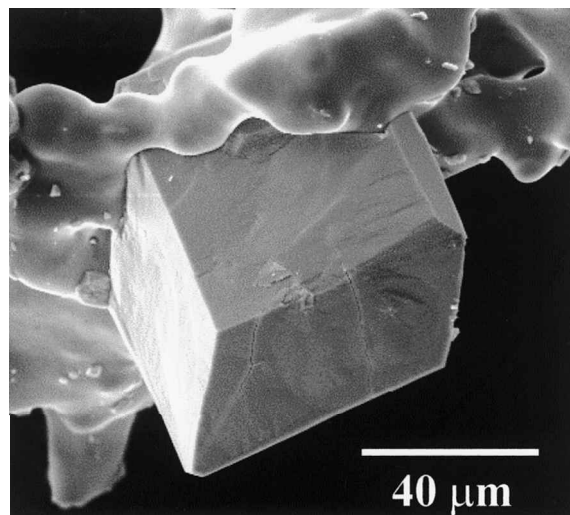

Fig. 1. SEM micrograph of a crystal of *alacranite* together with amorphous As-S alloy from Kateřina Mine, Czech Republic.

Kateřina Mine is located at Radvanice, near Trutnov and belongs to the Lower-Silesian coal basin in the north-eastern part of Bohemia (Czech Republic). Disseminated sulphide (pyrite, marcasite, pyrrothine, chalcopyrite, chalcocite, bornite, galena and sphalerite) and uranium (earthy uranium oxides and rare coffinite) mineralizations accompany the coal measures of the Radvanice Group of Coals (Žáček & Ondruš, 1997). A secondary mineralization originated as a consequence of more than a decade lasting subsurface fire of a large dump at the Kateřina colliery. According to Žáček & Ondruš (1997), several "minerals" were formed from escaping gasses and vapours, including native elements (sulphur, selenium, Bi-antimony, bismuth and lead), sulphides (galena, greenockite, antimonite, arsenic sulfides, and monoclinic GeSnS₃), oxides (molybdite, arsenolite, hexagonal GeO₂), halides (sal ammoniac, cryptohalite, bararite), sulphates (anglesite, mascagnite, letovicite), and organic compounds (kratochvilite, kladnoite). In addition, a variety of sulphates formed by alteration. Among the arsenic sulphides, As-S alloy, realgar, alacranite *s.s.*, orpiment and a "monoclinic As₄S₄" close to alacranite have been reported (Žáček & Ondruš, 1997).

The sample examined consists of a siltstone partially covered by acicular crystals of anhydrite. Scattered euhedral deep-red transparent crystals of realgar with a variable film of pararealgar are coexisting with orange-red to orange crystals, with pinacoidal prismatic habit (Fig. 1). Crystals are rarely transparent, with greasy luster. The orange mineral is extremely brittle, with orange-yellow streak; maximum size is approximately 100 μm. Associated minerals are mainly orpiment and native sulphur, together with botryoidal or dendritic aggregates of amorphous As-S alloy similar to those already described by Žáček & Ondruš (1997).

Experimental

Several well-formed crystals were selected for X-ray single-crystal investigations. On the whole, the diffraction quality

Table 2. Chemical compositions (wt. % el.) and atomic ratios for *alacranites* from Kateřina Mine.

	As$_4$S$_4$*	realgar	ALA 11	ALA 12	ALA 15#	ALA 7	ALA 2#	ALA 6
As	70.03	69.98	69.59	69.47	-	68.27	-	67.80
S	29.97	30.02	30.41	30.53	-	31.73	-	32.20
As	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
S	8.00	8.02	8.17	8.22	8.42	8.69	8.70	8.88

Note: values are averaged on three spots; * calculated values for stoichiometric As$_4$S$_4$; # atomic ratios obtained from structural data.

was found to be fairly good for the orange-red crystals, whereas reflections are weaker and broader for paler orange crystals. For some of these latter, no diffraction effects were detected, although long-time exposures were used. When possible, the unit-cell dimensions were determined by means of least-squares refinements using the same set of 25 reflections ($24 < 2\vartheta < 30°$) measured with a CAD4 single-crystal diffractometer. Surprisingly, a wide variety of parameters were obtained (Table 1). In particular, orange-red crystals (ALA11, ALA12) exhibit unit-cell parameters similar to those of a synthetic β-phase, whereas orange and pale-orange crystals show greater unit-cell volumes (up to 840.6 Å^3 for ALA 6).

Due to the brittleness of the mineral, it was not possible to obtain polished surfaces for crystals embedded in resin; therefore, semi-quantitative analyses were performed by means of an EDS-EDAX system. A crystal of realgar was used as standard. As shown in Table 2, the As/S ratio ranges from 8:8.0 to 8:8.9 for the crystalline material (ALA11, ALA12, ALA7, ALA6); amorphous material exhibits wider variation of the As/S ratio (ranging from 8:8.5 up to 8:14). Suspiciously high sulphur contents were locally found for single crystals having poor diffraction quality (*e.g.*, ALA1), probably due to intergrowth of *alacranite* and an amorphous S-rich phase.

Two crystals of relatively high diffraction quality (ALA15 and ALA2) were chosen for the structural study. Intensity data were collected up to $2\vartheta_{MoK\alpha} = 50°$ and subsequently corrected for Lorentz-polarization. Absorption correction was performed using the semi-empirical method of North *et al.* (1968). Experimental details are given in Table 3. (This table can be obtained from the authors or through the E.J.M. Editorial Office – Paris.)

Structure solution

For all the crystals tested (Table 1) the *h0l* reflections with $l = 2n+1$ were systematically absent. Moreover, most intensities were consistent with the *C*-centered lattice, although some *hkl* reflections with $h + k = 2n+1$ were observed. In particular, the most evident violations are the following: 5 0 0, $\overline{3}$ 2 1, $\overline{6}$ 1 1, 3 2 2, $\overline{1}$ 4 2, 3 0 4. It was also noted that the greater the unit-cell volume, the stronger and sharper the reflections violating the *C* lattice symmetry, thus suggesting a gradual change of the translation symmetry from the β-phase (*C*2/*c*; $V = 803(2)$ Å^3) to alacranite (*P*2/*c*; $V = 860(3)$
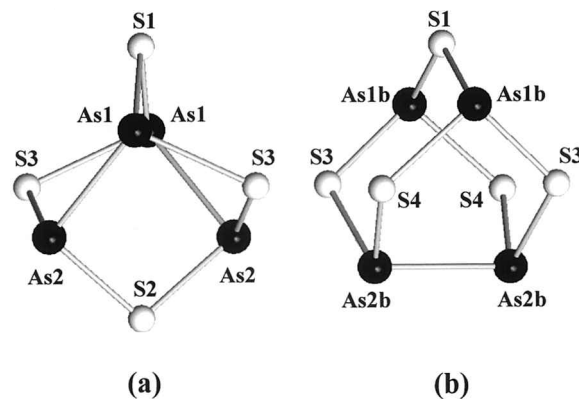

Fig. 2. As$_4$S$_4$ (a) and As$_4$S$_5$ (b) molecules in *alacranite* viewed along the **c** axis.

Å^3). Although these observations pointed towards a *P*2/*c* (or *Pc*) rather than *C*2/*c* (or *Cc*) symmetry, the number of the observed reflections with $h + k = 2n+1$ was too scarce to attempt a structure determination using a primitive unit-cell. Therefore, the *C*2/*c* structure of the synthetic β-phase (Porter & Sheldrick, 1972) was assumed as starting model. Structure refinements were performed on F$_o$^{2} using the SHELXL-97 program (Sheldrick, 1997). Isotropic full-matrix least-squares cycles were initially run assuming the atom sites as fully occupied, although the unusually high value of the isotropic displacement factor for the S2 atom strongly suggested partial occupancy at this site. An examination of the ΔF-Fourier map revealed the presence of residual peaks clearly indicating split positions for both As atoms (As1b and As2b) and an additional position for a sulphur atom (S4). The convergence was quickly achieved by adding these peaks to the atom array without constraint on their occupancy factors. For both ALA15 and ALA2 crystals the occupancy factors of As1, As2 and S2 resulted close to a common value (k), while the occupancy factor for As1b, As2b and S4 resulted approximately equal to 1-k. For both crystals, S1 and S3 appeared as fully occupied. An attempt to refine independently the split positions S1-S1b and S3-S3b did not lead any significant improvement due to the low number of observed reflections (Table 3). Furthermore, the coexistence of As1b + As2b with S2 and of As1 + As2 with S4 in the same molecule had to be excluded on the basis of the bond distances. Therefore, in order to reduce the number of free variables and to obtain a reliable model, only one parameter (k) was refined to constrain occ.(As1) = occ.(As2) = occ.(S2) = k, and occ.(As1b) = occ.(As2b) = occ.(S4) = 1-k. Successive cycles were run with an anisotropic model. Final R_{obs} were 6.12 % for ALA15 and 6.41% for ALA2, respectively. Fractional atomic coordinates and atomic displacement parameters are given in Table 4 and Table 5, respectively. (They can be obtained from the authors or through the E.J.M. Editorial Office – Paris.)

Results

The models obtained for both ALA15 and ALA2 are consistent with the coexistence in the structure of two kinds of

Table 6. Selected interatomic distances (Å) and angles (°) for the *alacranites* examined.

		ALA15				ALA2	
	As_4S_4	*mol.*			As_4S_4	*mol.*	
As1 -		S1	2.239(5)	As1 -		S1	2.252(6)
		S3	2.292(5)			S3	2.359(6)
		As2	2.593(7)			As2	2.58(1)
As2 -		S3	2.177(5)	As2 -		S3	2.124(7)
		S2	2.227(6)			S2	2.238(8)
		As1	2.593(7)			As1	2.58(1)
S1 –	As1 -	S3	94.6(2)	S1 –	As1 -	S3	93.2(2)
S1 –	As1 -	As2	99.8(2)	S1 –	As1 -	As2	100.1(2)
S3 –	As1 -	As2	97.8(2)	S3 –	As1 -	As2	97.5(3)
S3 -	As2 -	S2	95.4(2)	S3 -	As2 -	S2	96.6(3)
S3 -	As2 -	As1	99.4(2)	S3 -	As2 -	As1	100.1(3)
S2 -	As2 -	As1	99.1(1)	S2 -	As2 -	As1	99.5(2)
	As_4S_5	*mol.*			As_4S_5	*mol.*	
As1b -		S3	2.00(1)	As1b -		S3	2.046(8)
		S1	2.09(1)			S1	2.136(7)
		S4	2.17(4)			S4	2.19(2)
As2b -		S4	2.21(2)	As2b -		S4	2.19(2)
		S3	2.34(1)			S3	2.313(9)
		As2b	2.45(3)			As2b	2.48(2)
S3 -	As1b -	S1	109.0(6)	S3 -	As1b -	S1	106.5(3)
S3 -	As1b -	S4	96.4(6)	S3 -	As1b -	S4	96.1(4)
S1 -	As1b -	S4	107.8(8)	S1 -	As1b -	S4	105.4(5)
S4 -	As2b -	S3	100.6(6)	S4 -	As2b -	S3	101.2(5)
S4 -	As2b -	As2b	101.1(8)	S4 -	As2b -	As2b	101.7(5)
S3 -	As2b -	As2b	95.8(6)	S3 -	As2b -	As2b	95.6(3)

Fig. 3. The a, b, and c-$\sin\beta$ parameters plotted against unit-cell volumes. Filled circles refer to *alacranites* from Kateřina Mine (this study). Empty symbols refer to data from literature. Down triangle: synthetic β-As_4S_4 (Porter & Sheldrick, 1972); square: synthetic $As_2S_{2.15}$ (Kothiyal & Ghosh, 1976); circle: alacranite from Kamchatka (Popova *et al.*, 1986).

cage-like molecules. The first one (2As1 + 2As2 + S1 + S2 + 2S3) is identical to the As_4S_4 molecule found in the structures of both realgar and β-phase (Mullen & Nowacki, 1972; Porter & Sheldrick, 1972), in that each As atom links one As and two S atoms (Fig. 2a). The other molecule (2As1b + 2As2b + S1 + 2S3 + 2S4) is chemically and structurally identical to that found in the As_4S_5 compound (Whitfield, 1973). It can be derived from the As_4S_4 molecule by removing S2 (4*e* Wyckoff position) and adding two S4 atoms (8*f* Wyckoff position). In such a molecule, two As atoms link one As and two S atoms, whereas the other two As atoms link three S atoms (Fig. 2b). In both the molecules, the As atoms lie at the vertices of a disphenoid. In the As_4S_4 molecule, two edges of the disphenoid correspond to As-As bonds, while the other four edges are bridged by S atoms, which form a square parallel to (102). The As_4S_4 molecule possess a D_{2d} symmetry within the experimental errors. In the As_4S_5 molecule, five disphenoidic edges are bridged by S atoms, thus causing a lowering of the molecular symmetry to C_{2v} (approximately). Four S atoms lie at the vertices of a square parallel to (010).

Table 6 reports selected intramolecular distances for both As_4S_4 and As_4S_5 molecules for ALA15 and ALA2, respectively. In the As_4S_4 molecule, the As-As distances (2.593(7), 2.5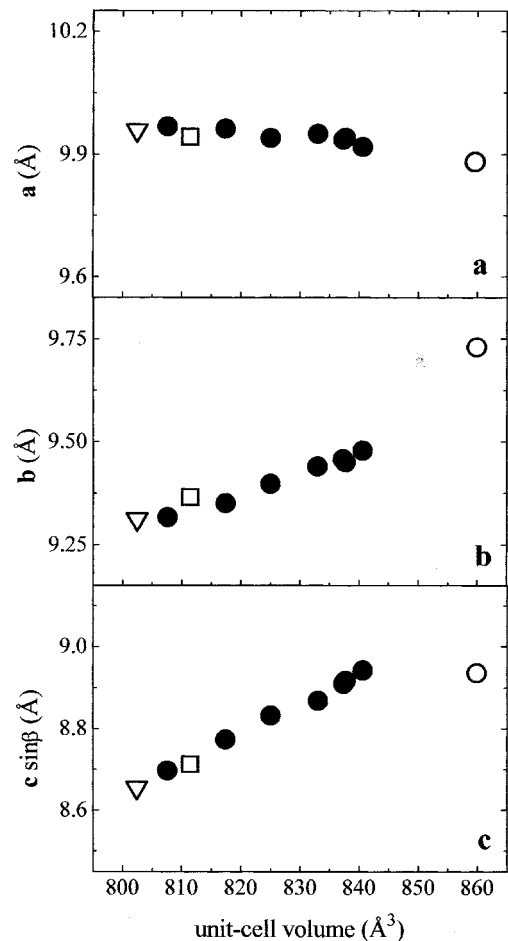8(1) Å) are very similar to those observed in the synthetic β-phase (2.593(6) Å; Porter & Sheldrick; 1972) and in the natural β-phase from Papua New Guinea (2.596(2) Å; Burns & Percival, 2001).

The As_4S_5 molecule closely resembles that observed in the structure of synthetic As_4S_5 (Whitfield, 1973). In both molecules, the As-S bond distances are in the range 2.00 to 2.36 Å, noticeably wider than that usually observed for intramolecular As-S distances. In particular, the As-S distances involving S2 and S4 are consistent with the sum of the covalent radii (1.21 + 1.02 Å, as reported in the Cambridge Structural Database), while those involving S1 and S3 deviate from the expected values. This is reasonably due to the fact that S1 and S3 are average positions for both As_4S_4 and As_4S_5 molecules; as pointed out above, in fact, an attempt to refine the split positions S1-S1b and S3-S3b was not successful.

The structural models obtained for ALA15 and ALA2 differ from each other mainly in the percentage of the As_4S_5 molecule (21 and 35 % for ALA15 and ALA2, respectively). Accordingly, the following chemical formulae can be

written: $As_8S_{8.42}$ (ALA15) and $As_8S_{8.70}$ (ALA2). The difference in the chemical composition estimated from the refinement is in accordance with the difference observed in the unit-cell volume for ALA15 ($V = 825.0(3)$ Å^3) and ALA2 ($V = 837.3(3)$ Å^3).

Discussion

Structural evidences (ALA15 and ALA2) together with chemical data and unit-cell parameters (ALA11, ALA12, ALA7, ALA6) indicate that *alacranites* from Kateřina Mine exhibit non-stoichiometric chemical composition ranging from As_8S_8 to As_8S_9. As the S content increases, the unit-cell volume increases accordingly. The expansion of the unit cell appears considerably anisotropic: in particular, a lengthening of c-sinβ and, to a lesser extent, of b is observed, whereas a remains almost unchanged (Fig. 3). In Figure 4 the unit-cell volume is plotted against the chemical composition for the crystals from Kateřina Mine together with data from literature. The data fit the regression line $V = 801(2) + 1.04(5)$ [% As_4S_5] (Å^3) (r = 0.989), thus confirming a continuous series between β-As_4S_4 (unnamed mineral) and alacranite (As_8S_9). The doubled unit-cell volume of synthetic As_4S_5 (2 x 453.0 Å^3 for 4 molecules; Whitfield, 1973), despite its different crystal structure (space group $P2_1/m$), is consistent with the model obtained (Fig. 4). *Alacranite* from Papua New Guinea should be close to a stoichiometric β-As_4S_4, as confirmed by the structural investigation (Burns & Percival, 2001). However, a content of $As_4S_5 = 10$ % ($V = 811.4$ Å^3) in this mineral can be predicted using the linear regression obtained in our study. Indeed, according to Burns & Percival (2001), the larger residual peaks in the final difference-Fourier map (3.21 e/ Å^3) were located within 1 Å of the As positions.

Conclusions

Chemical and crystallographic data obtained for *alacranites* from Kateřina colliery strongly suggest the existence of a continuous series between natural β-As_4S_4 and alacranite *s.s.* As_8S_9. From the results of the structure refinements, it appears that non-stoichiometric compounds crystallize as disordered mixtures of As_4S_4 and As_4S_5 molecules packed in the same way as in the β-As_4S_4 phase. To establish whether this is a long- or a short-range disorder is an arduous task. However, a hypothesis can be made. Because the As_8S_9 stoichiometry (alacranite *s.s.*) seems to be the upper limit of the compositional range, one can speculate that alacranite (P lattice symmetry) consists of an ordered sequence of As_4S_4 and As_4S_5 molecules. The [½ ½ 0] translation vector can be eliminated by ordering As_4S_5 and As_4S_4 molecules along this direction. The simultaneous presence of As_4S_4 ($C2/c$) and As_8S_9 ($P2/c$) microdomains accounts for the observed gradual change of the translation lattice symmetry from the β-phase to alacranite *s.s.*.

Finally, an additional remark on nomenclature is due. Despite the first occurrence of natural β-As_4S_4 phase is that from Alacràn Mine (Clark, 1970), this mineral remained un-
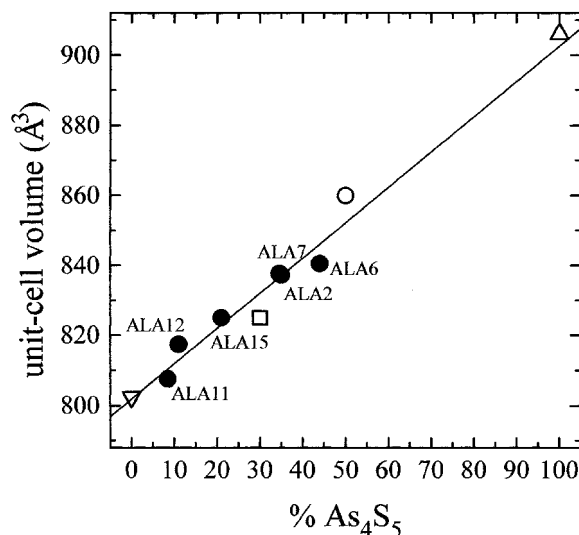

Fig. 4. Unit-cell volume plotted against the As_4S_5 percentage. Filled circles refer to *alacranites* from Kateřina Mine (this study). Empty symbols refer to data from literature. Down triangle: synthetic β-As_4S_4 (Porter & Sheldrick, 1972); square: synthetic $As_2S_{2.15}$ (Kothiyal & Ghosh, 1976); circle: alacranite from Kamchatka (Popova *et al.*, 1986); up triangle: synthetic As_4S_5 (Whitfield, 1973).

named. On the other hand, the name alacranite was approved for a mineral with the chemical formula As_8S_9 (Popova *et al.*, 1986). On the basis of their structural study, however, Burns & Percival (2001) stated that this formula had been incorrectly determined. It is now evident that minerals with chemical composition ranging continuously from As_8S_8 to As_8S_9 can crystallize.

Added in proofs: In the Strunz Mineralogical Tables recently published by Strunz & Nickel (2001), alacranite is reported with the chemical formula As_4S_4 and the space group $C2/c$, according to the results obtained by Percival *et al.* (1999). It appears evident that the name alacranite has to be referred to the mineral originally described by Popova *et al.* (1996).

References

Blachnik, R., Hoppe, A., Wickel, U. (1980): Die Systeme Arsen-Schwefel und Arsen-Selen und die thermodynamischen Daten ihrer Verbindungen. *Z. anorg. allg. Chem.*, **463**, 78–90.

Bonazzi, P., Menchetti, S., Pratesi, G. (1995): The crystal structure of pararealgar, As_4S_4. *Am. Mineral.*, **80**, 400–403.

Bonazzi, P., Menchetti, S., Pratesi, G., Muniz-Miranda, M., Sbrana, G. (1996): Light-induced variations in realgar and β-As_4S_4: X-ray diffraction and Raman studies. *Am. Mineral.*, **81**, 874–880.

Bryndzya, L.T. & Kleppa, O.J. (1988): Standard molar enthalpies of formation of realgar (α-AsS) and orpiment (As_2S_3) by high-temperature direct-synthesis calorimetry. *J. Chem. Thermodyn.*, **20**, 755–764.

Burns, P.C. & Percival, J.B. (2001): Alacranite, As_4S_4: a new occurrence, new formula, and determination of the crystal structure. *Can. Mineral.*, **39**, 809–818.

Clark, A.H. (1970): Alpha-arsenic sulfide, from Mina Alacràn, Pampa Larga, Chile. *Am. Mineral.*, **55**, 1338–1344.

Douglass, D.L., Shing, C., Wang, G. (1992): The light-induced alteration of realgar to pararealgar. *Am. Mineral.*, **77**, 1266–1274.

Hall, H.T. (1966): The system Ag-Sb-S, Ag-As-S, and Ag-Bi-S: Phase relations and mineralogical significance. Ph. D. Thesis, Brown University, Providence, Rhode Island.

Hawthorne, F.C., Burke, E.A.J., Ercit, T.S., Grew, E.S., Grice, J.D., Jambor, I.L., Puziewicz, J., Roberts, A.C., Vanko, D.A. (1988): New mineral names. *Am. Mineral.*, **73**, 189–199.

Jambor, I.L. & Roberts, A.C. (2002): New mineral names. *Am. Mineral.*, **87**, 355–367.

Kothiyal, G.P. & Ghosh, B. (1976): Preparation of non-stoichiometric arsenic sulphide crystals $As_2S_{2.15}$, and measurement of their electrical conductivity. *J. Cryst. Growth*, **32**, 29–32.

Mullen, D.J.E. & Nowacki, W. (1972): Refinement of the crystal structures of realgar, AsS and orpiment, As_2S_3. *Z. Kristallogr.*, **136**, 48–65.

Muniz-Miranda, M., Sbrana, G., Bonazzi, P., Menchetti, S., Pratesi, G. (1996): Spectroscopic investigation and normal mode analysis of As_4S_4 polymorphs. *Spectr. Acta*, **A52**, 1391–1401.

North, A.C.T., Phillips, D.C., Mathews, F.S. (1968): A semiempirical method of absorption correction. *Acta Cryst.*, **A24**, 351–359.

Percival, J.B., Hannington, M.D., Herzig, P.M., Jonasson, I.R. (1999): Clay mineral associations in sulphide-bearing volcanic rocks and sediments from the Lihir area, Papua New Guinea. *In* Clays for our future (H. Kodama, A.R. Mermur, J.K. Torrance, eds.). Proc. 11th Int. Clay Conf. (Ottawa, 1997). ICC97 Organizing Committee, Ottawa, Canada, 689–696.

Popova, V.I., Popov, V.A., Clark, A., Polyakov, V.O., Borisovski, S.E. (1986): Alacranite As_8S_9; a new mineral. *Zap. Vses. Mineral. Obshchest.*, **115**, 360–368 (in Russian).

Porter, E.J. & Sheldrick, G.M. (1972): Crystal structure of a new crystalline modification of tetra-arsenic tetrasulphide (2,4,6,8-tetrathia-1,3,5,7-tetra-arsatricyclo[3,3,0,0^{3,7}]-octane). *J. Chem. Soc.*, *Dalton Trans.*, **13**, 1347–1349.

Roberts, A.C., Ansell, H.G., Bonardi, M. (1980): Pararealgar, a new polymorph of AsS, from British Columbia. *Can. Mineral.*, **18**, 525–527.

Roland, G.W. (1972): Concerning the α-AsS realgar inversion. *Can. Mineral.*, **11**, 520–525.

Sheldrick, G.F. (1997): SHELXL-97. A program for crystal structure refinement. University of Göttingen, Germany.

Strunz, H. & Nickel, E.H. (2001): Strunz Mineralogical Tables. Chemical-Structural Mineral Classification System. 9th ed. Schweizerbart Publ., Stuttgart, Germany.

Whitfield, H.J. (1973): Crystal and molecular structure of tetra-arsenic pentasulphide. *J. Chem. Soc.*, *Dalton Trans.*, 1740–1742.

Žáček, V. & Ondruš, P. (1997): Mineralogy of recently formed sublimates from Kateřina colliery in Radvanice, Eastern Bohemia, Czech Republic. *Bull. Czech Geol. Survey*, **72**(3), 289–302.