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**A refinement of the pseudo crystal structure of scleroclase  $\text{PbAs}_2\text{S}_4$ .**† By Y. IITAKA and W. NOWACKI, *Abteilung für Kristallographie und Strukturlehre, Mineralogisches Institut, Universität Bern, Schweiz*

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The crystal structure of scleroclase  $\text{PbAs}_2\text{S}_4$  (from the Lengenbach quarry, Binn Valley, Switzerland) was investigated by Nowacki, Iitaka *et al.* (1961), as a part of the study on sulfosalt minerals (Nowacki & Kunz, 1959, 1961). They noted the occurrence of superlattice reflections corresponding to the  $3 \times 1 \times 11$  times greater cell compared with the pseudo-cell. The cell dimensions and the space group of the pseudo-cell were

$$a' = 19.62 \pm 0.02, \quad b' = 7.89 \pm 0.01, \quad c' = 4.19 \pm 0.05 \text{ \AA};$$

$$\beta = 90^\circ, \quad C_{2h}^2 = P2_1/n.$$

They determined the pseudo-structure which is the average structure over the  $3 \times 1 \times 11$  such sub-cells, and found that the best agreement between the observed and calculated structure factors for the average structure is obtained when anisotropic temperature factors are introduced for individual atoms. The approximate values of the temperature factor coefficients were determined by difference Fourier syntheses, and the greatest values were observed on the  $B_{11}$  and  $B_{33}$  of certain atoms, which correspond to the r.m.s. displacement of about 0.3 Å from the mean position along the  $a$ - and  $c$ -axis.

It appeared likely that more precise determination of the temperature factor coefficients might indicate the orientation and the magnitude of the modulation which is responsible for the formation of the superstructure. The present communication describes the result of determining more accurate coordinates and temperature factor coefficients by the three-dimensional least-squares method (SFLS programme described by Mills & Rollett 1961, and Cruickshank *et al.*, 1961) which was carried out at the Oxford University Computing Laboratory.

The refinement was started with the atomic coordinates

† Structural investigations on sulfosalts from the Lengenbach, Binn Valley (Ct. Wallis). Part 4.—Contribution No. 122.

and anisotropic temperature factor coefficients which were listed in the previous paper (Nowacki, Iitaka *et al.*, 1961). The number of reflections which were used for the present calculation was 797. For the first three cycles the following weighting system was adopted:

$$\sqrt{W} = 1 \quad \text{if } |F_o| < F^*, \quad \sqrt{W} = F^*/|F_o| \quad \text{if } |F_o| \geq F^*$$

$F^*$  being taken as  $2.4 F_{o, \min.} = 12$ . For the 4th cycle this system was modified as

$$\sqrt{W} = |F_o|/F^* \quad \text{if } |F_o| < F^*,$$

$$\sqrt{W} = F^*/|F_o| \quad \text{if } |F_o| \geq F^* \quad \text{and}$$

$$\sqrt{W} = F^*/2|F_o| \quad \text{if } |F_o| \geq 200, \quad (F^* = 12)$$

so as to put smaller weight for the very large  $|F_o|$ .

Altogether four cycles of refinement were carried out; the process is outlined in Table 1.

Table 1. *The refinement process*

	R%	$\Sigma w( F_o  -  F_c )^2$
Start	18.7	18648
after 1st L.S. cycle	17.3	14038
after 2nd L.S. cycle	15.2	10892
after 3rd L.S. cycle	14.7	10085

The average parameter changes during the four cycles of refinement were about 0.03 Å and 0.02 Å in the  $a$ - and  $b$ -directions. However, the  $S_2$  atom moved as much as 0.1 Å and 0.04 Å along the  $a$ - and  $b$ -axis. At the same time, we noticed a significant increase in the temperature factors which had already been indicated as a residual anisotropy in the difference projections. The final atomic parameters and the standard deviations obtained from the 4th cycle are listed in Table 2.

The interatomic distances are summarized in Table 3.

Table 2. *Atomic coordinates and temperature factor coefficients with the standard deviations*

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$
Pb	0.19373 $\pm 0.00014$	0.08717 $\pm 0.00029$	0.25000	7.09 $\pm 0.13$	4.78 $\pm 0.07$	3.39 $\pm 0.07$	-0.40 $\pm 0.06$
As <sub>1</sub>	-0.12773 $\pm 0.00037$	-0.50402 $\pm 0.00079$	0.25000	5.12 $\pm 0.17$	4.25 $\pm 0.16$	7.76 $\pm 0.36$	-0.53 $\pm 0.14$
As <sub>2</sub>	0.00459 $\pm 0.00055$	0.80435 $\pm 0.00130$	0.25000	9.24 $\pm 0.35$	7.61 $\pm 0.30$	6.74 $\pm 0.31$	-4.73 $\pm 0.27$
S <sub>1</sub>	-0.22125 $\pm 0.00068$	-0.35874 $\pm 0.00131$	0.25000	4.74 $\pm 0.33$	2.82 $\pm 0.24$	2.92 $\pm 0.34$	-1.10 $\pm 0.25$
S <sub>2</sub>	0.15971 $\pm 0.00086$	0.67467 $\pm 0.00170$	0.25000	4.11 $\pm 0.45$	2.70 $\pm 0.31$	12.75 $\pm 1.22$	1.27 $\pm 0.30$
S <sub>3</sub>	-0.07790 $\pm 0.00064$	-0.97791 $\pm 0.00152$	0.25000	2.98 $\pm 0.30$	3.41 $\pm 0.30$	6.12 $\pm 0.54$	-0.75 $\pm 0.25$
S <sub>4</sub>	0.05195 $\pm 0.00083$	0.33385 $\pm 0.00139$	0.25000	3.89 $\pm 0.43$	2.07 $\pm 0.26$	19.02 $\pm 1.62$	-0.28 $\pm 0.26$

Temperature factors take the form,  $\exp - \frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^*)$  assuming the mirror planes exist at  $z = \frac{1}{4}$  and  $\frac{3}{4}$ .

Table 3. *Coordination of the Pb and As atoms*

Pb:	$2.95 \text{ \AA} (S_2) + 3.05(2S_1) + 3.22(2S_1) + 3.22(2S_3)$ $+ 3.33(S_2) + 3.42(S_4)$
As <sub>1</sub> :	$2.14(S_1) + 2.56(2S_2) + 2.92(2S_4)$
As <sub>2</sub> :	$2.36(S_3) + 2.59(2S_4) + 2.87(2S_3)$

It should be noticed that markedly large temperature factors are observed: the  $B_{11}$  of Pb, As<sub>2</sub> and the  $B_{33}$  of As<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub>, among them the value of the  $B_{33}$  for S<sub>2</sub> and S<sub>4</sub> are surprising. In view of the fact that this structure is the average structure over the  $3 \times 11$  sub-cells which are extended in the  $a$ - and  $c$ -axis direction, it may be considered that these values indicate the direction and a measure of the magnitude of the atomic displacements which would most likely occur within the superstructure.

Table 4. *R.m.s. displacement of the atoms along the three principal crystallographic axes*

	$\parallel a$	$\parallel b$	$\parallel c$
Pb	0.30 Å	0.25 Å	0.21 Å
As <sub>1</sub>	0.26	0.23	0.31
As <sub>2</sub>	0.34	0.31	0.29
S <sub>1</sub>	0.25	0.19	0.19
S <sub>2</sub>	0.23	0.19	0.40
S <sub>3</sub>	0.19	0.21	0.28
S <sub>4</sub>	0.22	0.16	0.49

In Table 4, the root-mean-square displacement of the atoms along the  $a$ - and  $c$ -axis are listed which are calculated by the formula  $B = 8\pi^2\mu^2$ .

It is interesting to note that as illustrated in Fig. 1, the sulfur atoms which have an extraordinary large  $B_{33}$  value are those which connect the pyramidal AsS<sub>3</sub>-groups to form a chain. If we assume that these sulfur atoms are displaced, say for example, 0.5 Å either upwards or downwards along the  $c$ -axis, some of the As-S distances would be about 2.17 Å (this is the normal As-S distance) while others would be about 2.98 Å which is too large to assume that a strong bonding exists between the As and S atoms. As discussed in the previous paper (Nowacki, Iitaka *et al.*, 1961), there is a morphological evidence to assume that the As-S-chains do not extend throughout the crystal.

However, as the environment of the Pb atoms is changed by the displacement of the S atoms forming a gap, it might happen that the Pb atoms are displaced (probably along the  $a$ -axis) so as to fill up the gap; the complete analysis of the super structure may be very complicated.

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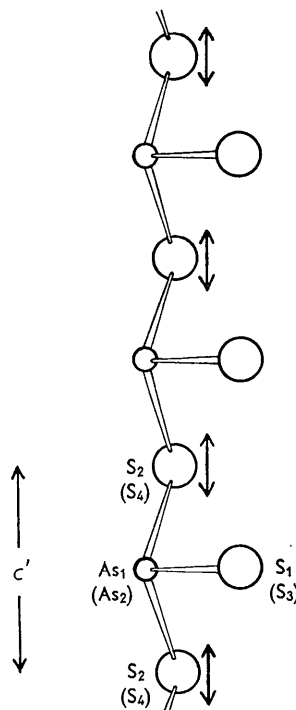


Fig. 1. The chain of the AsS<sub>3</sub>-group found in scleroclase (there are two kinds of chains each constituting As<sub>1</sub>S<sub>1</sub>S<sub>2</sub> and As<sub>2</sub>S<sub>3</sub>S<sub>4</sub>).

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