

APPENDIX

The summations involved in the evaluation of the structure amplitudes are of the type

$$\sum_i^N Z_i \frac{\cos 2\pi h x_i}{\sin 2\pi h x_i} \frac{\cos 2\pi k y_i}{\sin 2\pi k y_i} \frac{\cos 2\pi l z_i}{\sin 2\pi l z_i}$$

over the whole molecule (excepting the potassium ion and sulphur atom which are treated separately). The variation of scattering amplitude with θ was introduced after these preliminary summations.

For each atom the trigonometrical factors required are listed, and the sums

$$\sum_h^H \frac{\cos 2\pi h x_i}{\sin 2\pi h x_i}$$

etc. are derived. These sums provide the checks according to the formulae

$$T_1 \equiv \sum_h^H \cos 2\pi h x_i = \frac{1}{2} \cos 2\pi H x_i + \frac{1}{2} \cot \pi x_i \sin 2\pi H x_i + \frac{1}{2},$$

$$T_2 \equiv \sum_h^H \sin 2\pi h x_i = \frac{1}{2} \cot \pi x_i (1 - \cos 2\pi H x_i) + \frac{1}{2} \sin 2\pi H x_i.$$

If however $x_i \leq 0.1$ or $x_i \geq 0.9$ the magnitude of $\cot \pi x_i$ is large and the rounding-off errors disguise any real error in the tabulated values. In such cases the following formulae are to be preferred:

$$\sum_h^H (-1)^h \cos 2\pi h x_i = \frac{1}{2} + \frac{1}{2} (-1)^H \cos 2\pi H x_i - \frac{1}{2} (-1)^H \sin 2\pi H x_i \tan \pi x_i,$$

$$\sum_h^H (-1)^h \sin 2\pi h x_i = -\frac{1}{2} \tan \pi x_i + \frac{1}{2} (-1)^H \tan \pi x_i \cos 2\pi H x_i + \frac{1}{2} (-1)^H \sin 2\pi H x_i.$$

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The Crystal Structure of Realgar

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The crystal structure of realgar, AsS, has been worked out by the Fourier-synthesis method, using Weissenberg photographs (Cu $K\alpha$ $\lambda = 1.54 \text{ \AA}$). The signs for F^h 's were initially derived by the phase-inequality relations of Harker & Kasper. The unit cell has $a = 9.27$, $b = 13.50$, $c = 6.56 \text{ \AA}$, $\beta = 106^\circ 37'$. The space group is $P2_1/n$. The unit cell contains sixteen AsS. The structure is built up of separate As_4S_4 molecules of the cradle type held together by van der Waals forces. The cleavage and the relationships to orpiment, As_2S_3 , are explained in terms of the structure.

Introduction

The crystal structure of realgar, notwithstanding its simple chemical composition, defeated our repeated

The various factors having been checked in this way, the products

$$\frac{\cos 2\pi h x_i}{\sin 2\pi h x_i} \frac{\cos 2\pi k y_i}{\sin 2\pi k y_i}$$

are formed and checked in a similar way, e.g.

$$\begin{aligned} T_3 &\equiv \sum_h^H \frac{\cos 2\pi h x_i}{\sin 2\pi h x_i} \frac{\cos 2\pi k y_i}{\sin 2\pi k y_i} \\ &= \cos 2\pi k y_i \sum_h^H \frac{\cos 2\pi h x_i}{\sin 2\pi h x_i} = T_1 \cos 2\pi k y_i. \end{aligned}$$

The third stage, in which the triple products are formed, is checked in the same manner again, i.e.

$$T_4 \equiv \sum_h^H Z_i \frac{\cos 2\pi h x_i}{\sin 2\pi h x_i} \frac{\cos 2\pi k y_i}{\sin 2\pi k y_i} \frac{\cos 2\pi l z_i}{\sin 2\pi l z_i} = Z_i T_3 \frac{\cos 2\pi l z_i}{\sin 2\pi l z_i}.$$

For the final summation of these products, the check applied was of the form

$$T \equiv \sum_h^H \left(\sum_i^N Z_i \frac{\cos 2\pi h x_i}{\sin 2\pi h x_i} \frac{\cos 2\pi k y_i}{\sin 2\pi k y_i} \frac{\cos 2\pi l z_i}{\sin 2\pi l z_i} \right) = \sum_i^N T_4.$$

The nature of the expressions for the structure factors makes it convenient to separate odd and even values of the indices at various stages, but this has been omitted here in order to avoid confusion.

References

- CROWFOOT, D., BUNN, C. W., ROGERS-LOW, B. W. & TURNER-JONES, A. (1949). *The Chemistry of Penicillin*. Princeton: University Press.
SHOEMAKER, D. P., DONOHUE, J., SCHOMAKER, V. & COREY, R. B. (1950). *J. Amer. Chem. Soc.* **72**, 2328.

attempts to work it out by the usual methods. The absence of any peculiar regularity in the X-ray reflexions, other than the space-group criteria, is partly responsible for this situation. However, the

very lack of characteristic spectra might indicate that atoms are arranged rather evenly in the structure. This, together with the fact that the structure is composed of no more than two sorts of atoms whose scattering factors differ only moderately (*c.* 2 to 1), suggested that the phase-inequality relations discovered by Harker & Kasper (1948) might possibly work here. Accordingly, following closely the procedure since developed (Gillis, 1948; Kasper, Lucht & Harker, 1950; Burbank, 1951), we tried to find if such relations existed in the experimental data at our disposal, and success was immediate. Without crystal-chemical or other assumptions, we have now arrived at the structure of realgar as described below.

Experimental

The specimens used came from Saimoku, Japan. They are fine red-coloured transparent crystals of prismatic habit with *e*(210), *m*(110) and *b*(010) well developed, and of up to 1 cm. in length (Ito, 1937, p. 6).

For Weissenberg and rotation photographs several cylindrical slips were made from these crystal with their axes parallel to a crystallographic axis and with a diameter less than 0.5 mm. Cu *K*α radiation was used throughout the experiments.

The unit cell has the dimensions

$$a=9.27 \pm 0.04, \quad b=13.50 \pm 0.02, \quad c=6.56 \pm 0.05 \text{ \AA} \\ (\lambda=1.54 \text{ \AA}), \quad \text{and } \beta=106^\circ 37' \pm 2' \text{ (goniometer measurement).}$$

There are 16 AsS per cell, the calculated density being 3.59 g.cm.⁻³ against 3.56 g.cm.⁻³ measured. The space group is *C*_{2h}⁵-*P*2₁/*n* with *h*0*l* and 0*k*0 reflexions absent respectively when *h*+*l* and *k* are odd. These results are in complete agreement with those of Buerger (1935).

Relative intensities of reflexions were measured on the Weissenberg-Buerger photographs, using the multiple photographic technique. They were corrected for the Lorentz and polarization factors but not for absorption or extinction.

Use of the Harker-Kasper relations

The relative *F*'_{*hkl*}'s were first converted into absolute *F*_{*hkl*}'s:

$$|F_{hkl}|^2 = |F'_{hkl}|^2 / K,$$

where

$$K = K_0 \exp - 2B \left[\left(\frac{\sin \theta}{\lambda} \right)^2 \right] = \frac{|F'_{hkl}|^2}{\sum_{j=1}^N f_j^2}$$

(Harker, 1948). We obtained for *hk*0 reflexions *B* = 1.33 Å² and *K*₀ = 1.45, and for 0*kl* reflexions *B* = 1.30 Å² and *K*₀ = 1.53.

We then derived the unitary structure factors, *U*_{*hkl*}, by dividing each *F*_{*hkl*} by the sum of the scattering factors of all the atoms in the cell. These *U*_{*hkl*}'s were further corrected by multiplying the term

exp [*M* (sin θ/λ)²], where we assumed *M* = 1.0 after several trials (see Burbank, 1951).

Of many inequalities applicable to the space group *P*2₁/*n*, the following two relations, in particular, have come into consideration for our purposes (Harker & Kasper, 1948):

$$2U_{hkl}^2 \leq \{1 + (-1)^{h+k+l} U_{0,2k,0}\}$$

and

$$(U_{hkl} \pm U_{h'k'l'}) \leq \{(1 \pm U_{h+h', k+k', l+l'}) (1 \pm U_{h-h', k-k', l-l'})\}.$$

By virtue of these relations we were able to determine the signs of seven *U*_{*hko*}'s unequivocally. We found, further, that the signs of 42 other *U*_{*hko*}'s are dependent on, and can be expressed as a product of, the signs, say *a*, *b*, *c*, of three definite *U*_{*hko*}'s which may be chosen arbitrarily. These results are listed in Table 1(a). Formally there are eight combinations of *a*, *b* and *c*, but we need consider only the following two, since the rest yield results identical with one or other of these two (see Harker & Kasper, 1948):

	<i>a</i>	<i>b</i>	<i>c</i>
(1)	+	+	-
(2)	-	+	-

As for the signs of *U*_{*okl*}'s, the results are as follows: Beside seven *U*_{*okl*}'s whose signs are fixed in consequence of the inequalities, there are 13 other *U*_{*okl*}'s with a sign, say *d*, *e* or *f*, which can be either positive or negative. These are given in Table 1(b). Here, again, we have to consider eight combinations of signs arising from the option, but, for the same reason as before, we need consider only the following two:

	<i>d</i>	<i>e</i>	<i>f</i>
(3)	+	+	-
(4)	-	+	-

Fourier synthesis

The first *xy* synthesis was carried out using the absolute *F*_{*hko*}'s with signs assigned, as obtained above, by means of the inequality relations. Of the two alternative combinations of the signs *a*, *b* and *c*, we have decided on (1); whereas the synthesis with (2) gave an utterly meaningless diagram, that with (1) resulted in a Fourier map with tolerably well-defined maxima of electron density which permitted an easy interpretation in terms of atomic positions. As this diagram was apparently capable of refinement we took further steps along this line. The second synthesis was made with 98, the third with 117, the fourth with 139, and the fifth and final with 147 terms (all including 30 zero terms), making successive adjustments of atomic sites by trial.

The *yz* synthesis was made likewise, the first one with 32 terms obtained by the inequality relations (the combination (3)), the second with 53, the third with 85, the fourth with 90, and the fifth and the final with 92 terms (all counting 12 zero terms together).

Table 1(a). Phases of $hk0$ reflexions

hkl	U	Phase		hkl	U	Phase		hkl	U	Phase	
		initial	final			initial	final			initial	final
840	0·83	<i>a</i>	+	150	0·26	<i>ab</i>	+	810	0·11		+
080	0·64	+	+	370	0·25	<i>ab</i>	+	450	0·09		—
060	0·60	+	+	7,11,0	0·25		—	4,13,0	0·08		+
0,14,0	0·47	+	+	5,13,0	0·18		+	470	0·06		+
420	0·27	—	—	350	0·17	— <i>ab</i>	—	610	0·06		—
8,10,0	0·27	<i>a</i>	+	750	0·17	<i>ab</i> *	—	430	0·05		+
400	0·23	—	—	730	0·17		—	250	0·05	— <i>c</i>	+
240	0·23			190	0·16	— <i>ab</i>	—	210	0·05	<i>c</i>	—
2,10,0	0·23			770	0·15		+	650	0·03	— <i>ac</i>	+
2,12,0	0·21		+	3,15,0	0·14		+	1,12,0	0·67	<i>abc</i>	—
4,10,0	0·21		—	970	0·14		+	1,14,0	0·47	<i>abc</i>	—
480	0·20		—	530	0·12		—	780	0·46	— <i>bc</i>	+
260	0·18		+	930	0·12		+	720	0·43	— <i>bc</i>	+
620	0·18	+	+	950	0·12		+	5,14,0	0·42	— <i>abc</i>	+
280	0·18		—	170	0·11	— <i>ab</i>	—	580	0·33	— <i>abc</i>	+
0,12,0	0·17		—	510	0·08		—	760	0·31	<i>bc</i>	—
880	0·15		—	310	0·07		+	160	0·28	<i>abc</i>	—
800	0·13		—	3,13,0	0·05		+	180	0·26	<i>abc</i>	—
0,16,0	0·13		—	5,11,0	0·05		+	3,12,0	0·26	<i>abc</i>	—
460	0·12		—	570	0·05		+	320	0·25	— <i>abc</i>	+
820	0·12	<i>a</i>	+	550	0·04		—	140	0·24	<i>abc</i>	—
440	0·12		—	130	0·04	<i>ab</i>	+	520	0·24	— <i>bc</i>	+
4,12,0	0·12		+	710	0·04		+	340	0·21	<i>bc</i>	—
0,10,0	0·09		—	290	0·65	<i>c</i>	—	380	0·20		+
600	0·09		—	10,5,0	0·61	<i>ac</i>	—	360	0·19	<i>abc</i>	—
860	0·08		—	10,1,0	0·59	— <i>ac</i>	+	540	0·19		—
6,10,0	0·08		+	6,13,0	0·35	— <i>ac</i>	+	120	0·18	— <i>abc</i>	+
020	0·07	+	+	2,11,0	0·34	<i>c</i>	—	920	0·18		—
220	0·07		—	890	0·34		+	960	0·18		+
4,14,0	0·04		—	670	0·30	— <i>ac</i>	+	1,16,0	0·14		—
640	0·03		—	230	0·28	<i>c</i>	—	3,10,0	0·11		—
910	0·58	<i>b</i>	+	870	0·28		+	1,10,0	0·10		+
1,15,0	0·57	— <i>ab</i>	—	410	0·17		+	5,12,0	0·08		—
1,11,0	0·28	<i>ab</i>	+	850	0·16		—	560	0·07		+
330	0·27	— <i>ab</i>	—	6,11,0	0·16		—	940	0·05	<i>bc</i>	—
590	0·27	— <i>b</i>	—	830	0·15		+				

* Initial and final signs differ.

Table 1(b). Phases of $0kl$ reflexions

hkl	U	Phase		hkl	U	Phase		hkl	U	Phase	
		initial	final			initial	final			initial	final
080	0·64	+	+	0,13,3	0·34	<i>d</i>	+	065	0·33		+
060	0·60	+	+	0,11,3	0·34	<i>d</i>	+	0,12,3	0·29		—
046	0·50		—	053	0·32	<i>d</i>	+	043	0·26	<i>e</i>	—
002	0·47	—	—	037	0·29		—	027	0·24		+
0,14,0	0·47	+	+	055	0·27		—	041	0·21	— <i>e</i>	+
062	0·37	—	—	095	0·21		+	083	0·19		—
0,12,4	0·31		+	011	0·18		+	0,16,1	0·17		+
082	0·29	—	—	017	0·18		+				
086	0·27		+	0,11,5	0·18		—	016	0·46	<i>f</i>	+
026	0·24		—	013	0·16		—	056	0·33	— <i>f</i>	—
044	0·23		+	0,11,1	0·16		—	096	0·33	<i>f</i>	+
024	0·19		+	0,15,1	0·16		+	094	0·27		—
022	0·18	—	—	0,10,3	0·60	<i>e</i>	—	036	0·26		+
064	0·18		+	0,12,1	0·56	— <i>e</i>	+	076	0·20		+
0,10,4	0·16		+	0,10,5	0·46	— <i>e</i>	+	034	0·19		—
				0,10,1	0·35	<i>e</i>	—	014	0·18		—
073	0·40	<i>d</i> *	—					054	0·17		+

* Marks that the initial and final signs differ.

The signs used in the final syntheses are given in Tables 1(a) and 1(b). Comparing these with those obtained by the inequality relations and used in the

initial syntheses we find that the latter are correct except for a few (marked * in the tables).

It should be noted that in these syntheses the effect

of cutting off the higher-order Fourier terms was minimized by the method of Cochran (1948), using 246 F_{hko} 's and 211 F_{okl} 's calculated.

Reading the Fourier maps of electron density

The final Fourier diagrams of electron density are given in Fig. 1, projected along the directions c and a , respectively, on to the planes normal to them.

The maxima of contours of nearly all the atoms in the cell are clearly resolved in these projections and we can easily locate the atomic positions (Booth, 1948, p. 62). Only the z parameter of one of the sulphur atoms does not lend itself to direct reading with the same precision as others since its maximum is overlapped in the [100] projection by that of an arsenic atom. This ambiguity was overcome by a graphical method by which the compound maximum was reduced to its component maxima of the same shape and height as those occurring in isolation elsewhere on the diagram.

The atomic coordinates finally determined are given

in Table 2. These are considered accurate probably to 0.02 Å in the a and c directions and to 0.03 Å in the

Table 2. *Coordinates of atoms*

Atom	No. of equivalent points in the cell	x/a	y/b	z/c
As(1)	4	0.118	0.024	-0.241
As(2)	4	0.425	-0.140	-0.142
As(3)	4	0.318	-0.127	0.181
As(4)	4	0.038	-0.161	-0.290
S(1)	4	0.346	0.008	-0.295
S(2)	4	0.213	0.024	0.120
S(3)	4	0.245	-0.225	-0.363
S(4)	4	0.115	-0.215	0.048

b direction. We give in Table 3 the structure factors calculated on the basis of these parameters contrasted with those observed. The reliability numbers, $R = (||F_o| - |F_c||) \div |F_o|$, are 0.26 for hkl and 0.18 for Ok reflexions with all observable (present and absent) reflexions counted.

Table 3. *Observed and calculated F values*

hkl	$\frac{1}{2}F_o$	$\frac{1}{2}F_c$	hkl	$\frac{1}{2}F_o$	$\frac{1}{2}F_c$	hkl	$\frac{1}{2}F_o$	$\frac{1}{2}F_c$
200	0	-1	2,12,0	17	20	540	17	-16
400	26	-18	2,13,0	0	5	550	3	-2
600	8	-9	2,14,0	0	0	560	6	3
800	11	-5	2,15,0	0	-4	570	4	6
10,0,0	0	-9	2,16,0	0	-13	580	27	28
020	13	10				590	21	-22
040	0	-7	310	10	11	5,10,0	0	4
060	70	63	320	32	27	5,11,0	4	7
080	61	49	330	35	-37	5,12,0	16	-10
0,10,0	9	-15	340	25	-27	5,13,0	13	15
0,12,0	13	-15	350	19	-17	5,14,0	29	29
0,14,0	34	27	360	20	-22			
0,16,0	9	-17	370	23	25	610	5	-6
			380	17	17	620	16	14
110	0	8	390	0	-5	630	0	0
120	32	45	3,10,0	9	-15	640	4	-5
130	6	11	3,11,0	0	0	650	3	1
140	35	-44	3,12,0	24	-19	660	0	3
150	33	38	3,13,0	4	10	670	24	27
160	33	-37	3,14,0	0	-1	680	0	3
170	11	-15	3,15,0	10	11	690	0	-1
180	24	-23	3,16,0	0	7	6,10,0	6	10
190	14	-16				6,11,0	12	-16
1,10,0	9	7	410	19	18	6,12,0	0	6
1,11,0	22	23	420	30	-28	6,13,0	25	34
1,12,0	52	-43	430	5	5			
1,13,0	0	2	440	12	-18	710	4	10
1,14,0	34	-26	450	8	-11	720	34	32
1,15,0	40	-37	460	11	-10	730	14	-25
1,16,0	9	-5	470	5	4	740	0	2
			480	16	-14	750	14	-12
210	8	-12	490	0	2	760	23	-21
220	10	-16	4,10,0	16	-14	770	11	9
230	40	-42	4,11,0	0	0	780	35	43
240	30	-30	4,12,0	8	12	790	0	3
250	7	8	4,13,0	6	7	7,10,0	0	5
260	20	22	4,14,0	4	-6	7,11,0	18	-25
270	0	1	4,15,0	0	-7	7,12,0	0	7
280	16	-17						
290	55	-45	510	7	-11	810	9	16
2,10,0	20	-21	520	23	29	820	10	10
2,11,0	26	-21	530	11	-8	830	11	11

Table 3 (cont.)

hkl	$\frac{1}{2}F_o$	$\frac{1}{2}F$	hkl	$\frac{1}{2}F_o$	$\frac{1}{2}F_c$	hkl	$\frac{1}{2}F_o$	$\frac{1}{2}F_c$
840	62	57	0,13,1	11	-12	034	17	-16
850	13	-12	0,14,1	11	-17	044	21	20
860	6	-8	0,15,1	12	17	054	14	20
870	20	20	0,16,1	12	10	064	15	15
880	11	-15				074	0	2
890	24	21	012	22	22	084	12	-12
8,10,0	18	25	022	30	-30	094	21	-18
			032	11	-15	0,10,4	12	10
910	42	31	042	5	6	0,11,4	0	2
920	14	-14	052	0	-2	0,12,4	21	15
930	9	13	062	39	-41			
940	14	-14	072	7	-11	015	4	-9
950	9	13	082	27	-30	025	5	14
960	15	21	092	9	-11	035	0	-1
970	9	16	0,10,2	6	14	045	0	1
980	0	-14	0,11,2	0	1	055	19	-17
10,1,0	42	30	0,12,2	10	-8	065	26	28
10,2,0	0	8	0,13,2	0	-6	075	9	-16
10,3,0	0	2	0,14,2	0	1	085	0	11
10,4,0	0	-4				095	16	18
10,5,0	41	-41	013	20	-20	0,10,5	33	30
			023	4	-8	0,11,5	13	-13
002	70	-73	033	9	7			
004	0	-1	043	29	-29	016	35	32
006	6	6	053	31	32	026	18	-18
011	29	26	063	7	-11	036	20	19
021	10	-14	073	35	-32	046	37	-32
031	11	-15	083	16	-19	056	26	-29
041	37	41	093	4	-6	066	10	-6
051	0	-5	0,10,3	49	-40	076	14	14
061	8	13	0,11,3	26	25	086	19	15
071	13	14	0,12,3	21	-18	096	24	26
081	7	-7	0,13,3	24	22			
091	7	8	0,14,3	6	-8	017	14	20
0,10,1	29	-29				027	17	13
0,11,1	13	-16	014	16	-16	037	20	-14
0,12,1	43	38	024	17	18			

Table 4. Intramolecular atomic distances and bond angles

(1) Covalent bond distances (Å)

As(1)-As(4)	2.59	As(1)-S(1)	2.25	As(3)-S(2)	2.25
As(2)-As(3)	2.59	As(1)-S(2)	2.27	As(3)-S(4)	2.19
		As(2)-S(1)	2.26	As(4)-S(3)	2.28
		As(2)-S(3)	2.20	As(4)-S(4)	2.25

(2) Bond angles* (°)

S(1)-As(1)-S(2)	89.0	As(4)-As(1)-S(1)	97.0	As(1)-S(1)-As(2)	103.4
S(1)-As(2)-S(3)	94.6	As(4)-As(1)-S(2)	98.8	As(1)-S(2)-As(3)	102.1
S(2)-As(3)-S(4)	95.9	As(3)-As(2)-S(1)	93.7	As(2)-S(3)-As(4)	100.9
S(3)-As(4)-S(4)	91.9	As(3)-As(2)-S(3)	99.0	As(3)-S(4)-As(4)	99.7
		As(2)-As(3)-S(2)	98.5		
		As(2)-As(3)-S(4)	96.7		
		As(1)-As(4)-S(3)	99.3		
		As(1)-As(4)-S(4)	99.8		

(3) Non-bonded distances (Å)

As(1)-As(2)	3.54	As(1)-S(3)	3.72	S(1)-S(2)	3.14	S(1)-S(4)	4.64
As(1)-As(3)	3.51	As(1)-S(4)	3.74	S(1)-S(3)	3.28	S(2)-S(3)	4.66
As(2)-As(4)	3.45	As(2)-S(2)	3.70	S(2)-S(4)	3.34		
As(3)-As(4)	3.40	As(2)-S(4)	3.59	S(3)-S(4)	3.26		
		As(3)-S(1)	3.52				
		As(3)-S(3)	3.68				
		As(4)-S(1)	3.65				
		As(4)-S(2)	3.68				

* Bond angles obtained by construction

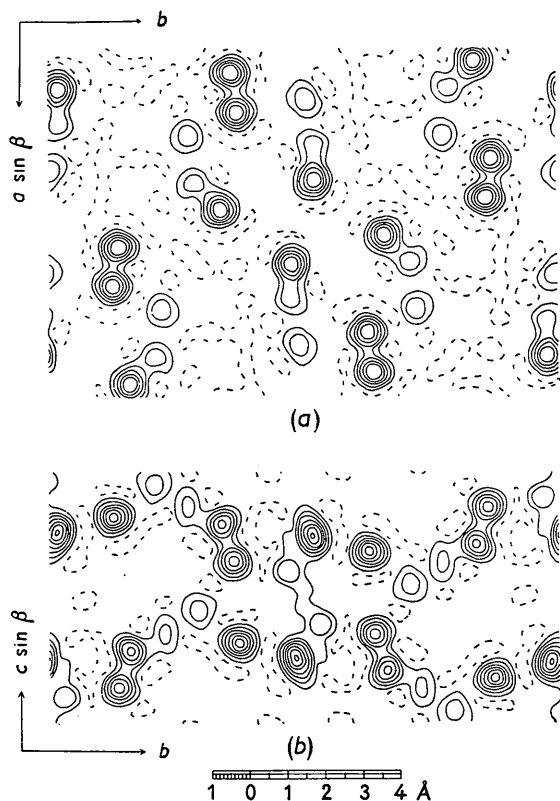


Fig. 1. Fourier projection of electron density of realgar. (a) [001] projection, (b) [100] projection. Contours at intervals of $10 \text{ e} \cdot \text{Å}^{-2}$, zero-electron lines being broken.

Description of structure

The structure of realgar is illustrated in Fig. 2, which, corresponding to Fig. 1, is projected on the planes perpendicular to the c and a axes. It is a molecular structure consisting of separate molecules As_4S_4 held together by van der Waals forces.

The molecule, clearly discernible especially in the [001] projection, is in shape and dimensions almost identical with one which was preferably ascribed to gaseous As_4S_4 (Lu & Donohue, 1944; see also Allen & Sutton, 1950) and is commonly called the cradle model. Four sulphur and four arsenic atoms in the molecule are bound one another by covalent bonds and form a square and a tetrahedron respectively. The sulphur square cuts through the arsenic tetrahedron in the middle.

The intra-molecular bond distances and angles are given in Table 4. The mean values of the covalent As-As and As-S distances are 2.59 Å and 2.24 Å respectively, against 2.49 Å and 2.23 Å as found in the gas. The bond angles, too, compare very favourably with those in the gaseous state, the mean values of the As-S-As, As-S-S and S-As-S angles being $101^\circ 5'$, $97^\circ 8'$ and $92^\circ 8'$ respectively, in contrast with 101° , 100° and 93° of the gaseous As_4S_4 molecule.

We give in Table 4 also the intermolecular atomic

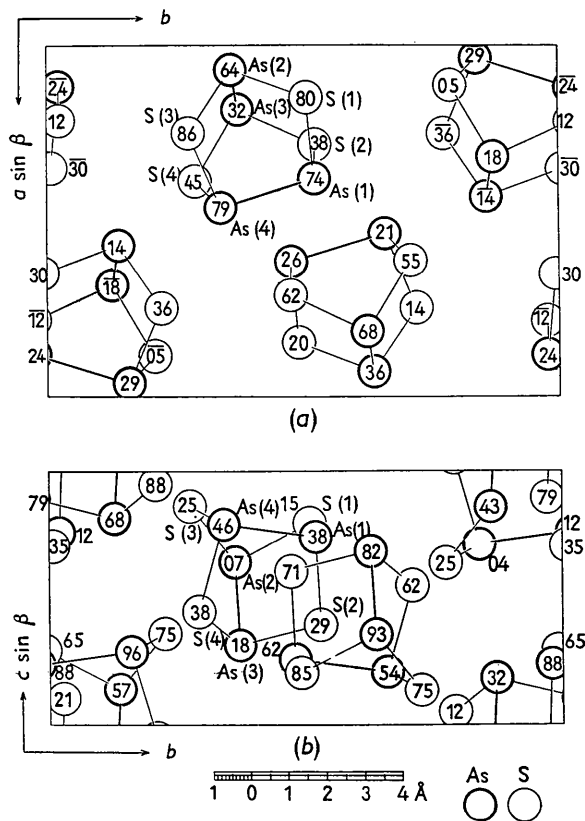


Fig. 2. The structure of realgar. The projections correspond to Fig. 1. (a) [001] projection, (b) [100] projection. Numbers give in a percentage of the c and a lengths, respectively, the heights of atoms from (001) and (100). As-As covalent bonds are traced by thick lines, As-S covalent bonds by thin lines.

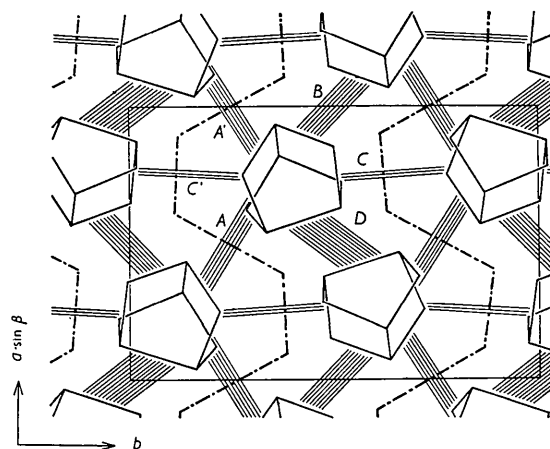


Fig. 3. Intermolecular (van der Waals) bonds and cleavage of realgar ([001] projection). As_4S_4 molecules are represented by the cradle models. The system of parallel thin lines indicate the number of bonds (each of a distance less than 4.0 Å) prevailing in the regions named A , B , C and D (cf. Table 5). Broken thick lines indicate the traces of planes on which the structure presumably gives way.

Table 5. *Intermolecular atomic distances* (cf. Fig. 3)

Primes denote equivalent atoms and asterisks those in the neighbouring unit cells. All distances are in Ångström units.

Region A			Region B			Region C			Region D		
S(4)	-As(3''')	3.76	S(1)	-As(3)*	3.39	S(1)	-S(3'')	3.90	As(4)*	-As(1')	3.50
As(4)	-As(3''')	3.49	S(1)	-As(2)*	3.51	As(1)	-S(3'')	3.61	As(1)*	-As(1')	3.52
As(4)	-As(2''')	3.50	S(1)	-S(2)*	3.95	S(2)	-S(3'')	3.85	As(1)*	-As(4')	3.50
S(3)	-As(2''')	3.50							S(2)	-As(4')	3.40
S(4)*	-As(2''')	3.61							S(2)	-As(1')	3.45
S(4)*	-S(3''')	3.72							S(2)	-S(4')	3.90
									S(2)	-S(2')	3.85
									S(4)	-S(2')	3.90
									S(4)	-As(1')	3.80
									As(4)	-S(2')	3.40
									As(1)	-S(2')	3.45
									As(1)	-S(4')	3.80

distances. The van der Waals radii of sulphur and arsenic are 1.85 Å and 2.0 Å (Pauling, 1940, p. 189). The interaction between atoms of the neighbouring molecules more than 4.0 Å distant, therefore, may not be held responsible for the cohesion of crystal. If we accordingly set aside these non-bonded distances and direct our attention only to the bond distances less than 4.0 Å, the bonds are then more concentrated in certain regions of the unit cell than in others, as given in detail in Table 4 and illustrated in Fig. 3. The crystal may be liable to break down right through these weaker regions, giving rise to the perfect cleavage on (010).

Relations to other kindred structures

Realgar changes very easily to orpiment on exposure to light. It is of interest to seek the reason for the alteration in the structures of these minerals.

The structure of orpiment, as analysed recently by the present writers (Ito, 1950, p. 161) and later confirmed and refined by means of a two-dimensional Fourier synthesis (unpublished), is made up of superimposed As_2S_3 layers in which each arsenic atom is surrounded by three sulphur atoms and each sulphur

atom is shared by two arsenic atoms. The layers are linked to each other by weak van der Waals forces. This structure appears to possess little apparent similarity to that of realgar except that practically the same bond distances and angles prevail in both. On a closer examination, however, we have found between them a striking resemblance that warrants the statement that they are in fact built from the same structural units upon different principles.

The cradle-type molecule of realgar is a closed one and may be divided into two halves which, though not exactly identical, could be brought into approximate coincidence by a digonal rotation axis passing through the centre of the group and connecting the middles of its two opposing As-As edges (Fig. 4(a)). The atoms in this half-molecule are arranged in the order S-As-S-As and form a spiral. If we take the spiral for a unit and subject it to a translation parallel to the spiral-axis, we obtain a chain extended indefinitely. Actually we can see in the layer structure of orpiment such spiral chains running parallel to each other and to the *c* axis with more sulphur atoms added in between so as to make its composition As_2S_3 instead of As_2S_2 (Fig. 4(b)).

Another interesting feature revealed by the present study is the intimate, though partial, analogy between the structures of arsenic sulphides and oxides. Arsenolite, As_2O_3 , has a molecular structure (Bozorth, 1923) and the groups, As_4O_6 , that constitute it are also of the cradle type, with two more (oxygen) atoms attached on top and at the bottom. On the other hand, claudetite, another form of dimorphous As_2O_3 , has turned out to have a layer structure (Frueh, 1951) like that of orpiment. The mode of linkage in these two minerals, if oxygen and sulphur atoms are looked upon as equivalent, is roughly the same. The only conspicuous difference is that the chains in claudetite are parallel but staggered, making the layer they form rather thick, while the chains in orpiment are arranged perfectly in a plane.

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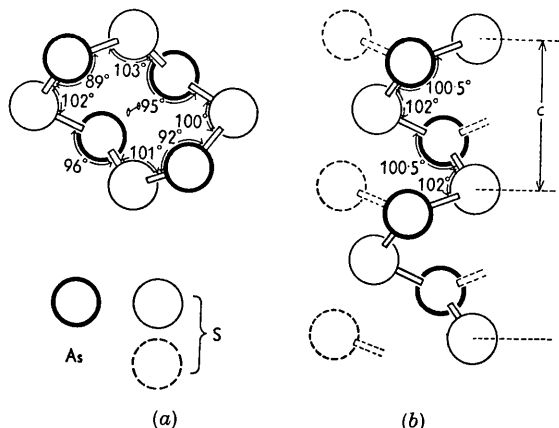


Fig. 4. The relation between the structures of realgar and orpiment. An As_4S_4 molecule of realgar (a) is seen from a direction that facilitates comparison with an As_2S_2 spiral chain (thick and thin full circles) and an As_2S_3 layer (thin broken circles in addition to thick and thin full circles) of orpiment (b).

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The Interpretation of Electron-Diffraction Patterns from One-Degree-Orientated Polycrystalline Deposits and Rotated Crystals

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Effective practical methods are developed for interpreting electron-diffraction patterns from one-degree-orientated polycrystalline deposits or rotating crystals, to determine their orientation, and their lattice form where this is not known previously. These methods apply to crystals of any symmetry; all apply to the case where the orientation axis is normal to the electron beam or nearly so, while some are of quite general application.

1. Introduction and general basis

Thin polycrystalline films of many materials are now much used in research and industry, and their properties depend much on structural characteristics such as crystal size, orientation, habit and purity. Many electron-diffraction investigations have shown that in such deposits formed under certain conditions on epitaxially inert substrates the crystals tend to grow in a 'one-degree' orientation, i.e. with a certain type of lattice row $[UVW]$ in common but otherwise with random disposition about this common axis. The deposit then yields an electron-diffraction pattern approximating to that which would be obtained by rotating a single crystal round the $[UVW]$ lattice row placed parallel to the orientation axis. The interpretation of such patterns obtained with fast electrons is now discussed, and an experimental study (Evans & Wilman, 1952) has also led to a clearer understanding of the causes and nature of preferred orientation in deposits condensed from the vapour.

The method of interpretation of such patterns first proposed by Kirchner (1932) (cf. also Thomson, Stuart & Murison, 1933; Nelson, 1937; and Thomson & Cochrane, 1939) is unduly laborious. A simpler Laue-zone method has been described (Finch & Wilman, 1937*a, b*) by which the theoretical pattern expected from the crystals in any suggested one-degree orientation can be constructed more easily for comparison with the recorded pattern. The present work describes a new generalized extension of this method which makes it easily applied to all types of lattice, and

further new methods which have proved useful in recent studies of orientation in deposits formed chemically (Goswami, 1950) or by condensation from the vapour (Evans, 1950; Evans & Wilman, 1952).

Single-crystal rotation patterns and also often one-degree-orientation patterns have, as in X-ray diffraction work, an important application for determining the lattice form and dimensions where these are not known initially, hence methods suitable for this purpose are also developed below for the case of patterns where the diffractions lie on elliptic or hyperbolic loci (see Finch & Wilman, 1936*b*, 1937*a, b*; Uyeda, 1938; Goche & Wilman, 1939). In the simpler case of patterns in which well-defined 'layer lines' (and often also 'row lines') occur, the methods described for analysis of the analogous X-ray patterns by Buerger (1942), Bunn (1945) and Henry, Lipson & Wooster (1951) are readily adapted and need not be discussed further here.

In polycrystalline deposits the criterion for one-degree orientation is (in reflexion patterns) that the diffraction pattern is unchanged as the azimuth of the electron beam round the orientation axis is varied, or (in transmission) that only a ring pattern is obtained when the beam is along the orientation axis, although the rings break up into arcs and arcs also appear on other ring positions on inclining the specimen (Thomson, 1930; Finch & Quarrell, 1933*a, b*). In certain cases the axis of one-degree orientation can be oblique to the substrate (Burgers & Dippel, 1934; Burgers & Ploos van Amstel, 1936; Beeching, 1936; Nelson, 1937; Schulz, 1949; Evans & Wilman, 1952).