THE UNIT CELL AND SPACE GROUP OF REALGAR

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Abstract

Realgar from Allchar, Macedonia, has been studied by the Weissenberg method. A new orientation is chosen by taking the a-axis in Goldschmidt's [101] direction; this gives the simplest cell. The cell characteristics are:

	absolute	ratio
$a=$	9.27Å	.6878
$b=$	13.50	1.
$c=$	6.56	.4858
$\beta=$	73°227′	
$Z=$	16 formula weights per cell	

Space group: C_{2h}^5, $P2_1/n$.
The monoclinic holohedral nature of realgar has been confirmed by purely x-ray methods.

The extremely unfavorable geometry of the space group prevents an immediate, complete determination of the structure.

Introduction

So far as the writer is aware, no study of the crystal structure of realgar has been published. The writer's investigation has proceeded to a unique determination of the general geometry of the cell of this mineral. It has been thought desirable to record the results to this point, inasmuch as they form a firm groundwork for further structural study, the pursuit of which must rest on somewhat less secure reasoning because of the extremely unfavorable geometry of the space-group.

Material and Method

The investigation was carried out on realgar from Allchar, Macedonia. The morphology of this particular material has received a thorough study by Goldschmidt,[1] who also furnished the following chemical analysis:

	found	calculated
S	30.55	29.91
As	69.57	70.09
	100.12	100.00

[1] Goldschmidt, V., Realgar von Allchar in Macedonien: *Zeit. Krist.*, vol. **39**, pp. 113–121, 1904.

The material is evidently nearly ideal AsS, but with a slightly low As:S ratio, corresponding to an empirical formula $As_{1.000}S_{1.028}$.

Small, well developed crystals of this material were studied by the Weissenberg method. Nearly equi-dimensional crystals of something less than ½ millimeter diameter were completely bathed in an unfiltered beam of CuK radiation of about one millimeter cross sectional diameter.

Unit Cell

The Weissenberg photographs have been studied, in the main, by the simple method of reciprocal lattice line curve-sketching directly on the original film,[2] but the actual reciprocal lattice has been reconstructed for the *b*-axis photographs. A study of these, together with Z measurements on pinacoid reflections, indicates that the simplest cell results by the choice of a new *a* axis in Goldschmidt's [101] direction. The geometry of the unit chosen by this Weissenberg study, and checked by rotation photographs, is given in comparison with Goldschmidt's elements in table I.

Table I

X-ray Data			Goldschmidt's Data	
Designation, Simplest Cell Axes	Dimension	Axial Ratio	Axial Ratio	Designation, Goldschmidt's Axes
a	9.27Å	.6875	.6878	[101]
b	13.50	1.	1.	*b*
c	6.56	.486	.4858	*c*
[101]			.7203	*a*
β			73°27′	$c\wedge[101]$
$c\wedge[101]$			66°15.6′	$\mu(=\beta$, Dana)
(Cell volume) V	788 $Å^3$			

The ideal formula weight of AsS is 106.9. The analysis given by Goldschmidt of the Allchar material indicates an empirical formula $AsS_{1.028}$. If the additional sulfur proxies for an arsenic deficiency, this is equivalent to $\left|\begin{matrix} As_{.986} \\ S_{\ .014} \end{matrix}\right| S$. which has a formula weight of 106.3. This differs from the ideal value by the order of half a

[2] Buerger, M. J., The Weissenberg reciprocal lattice projection and the technique of interpretating Weissenberg photographs: *Zeit. Krist.*, vol. **88**, pp. 356–380, 1934.

per cent. The number of formula weights per unit cell, Z, is given by the relation:

$$\text{measured density} = \frac{\text{cell mass}}{\text{cell volume}} = \frac{Z \times \text{formula wt}}{\text{cell volume}}.$$

With Dana's density value for realgar, this becomes:

$$3.56 = \frac{Z \times (\text{formula wt.}) \times 1.64 \times 10^{-24}}{788 \times 1.64 \times 10^{-24}}.$$

Use of the ideal formula weight leads to Z = 16.00, while assuming the excess sulfur, indicated by the analysis, proxies for arsenic, leads to Z = 16.09 formula weights per unit cell. Lack of coordination and precision in the measurements renders the difference between these two values non-diagnostic.

Space Group

Equatorial Weissenberg photographs were taken for rotations about the *a*, *b*, *c*, and [101] axes, together with first and second layer photographs for the *b*-axis. All of these have been unequivocally indexed by the simple method of reciprocal lattice line curve sketching, directly on the film (plus reconstructing the *b*-axis, zero and first levels). A catalog of the resulting reflections is given in table II.

Table II

Catalog of Reflections

Indices are referred to new axes; to transform to Goldschmidt's axes, add *l00* to each index listed. Dashes indicate assured absences.

b-axis, 1st layer											
017	—										
016	116	—	316	416							
015	—	215	315	415	515						
014	114	214	314	—	514	614	714				
013	113	213	313	—	513	—	713	813			
012	112	212	312	412	512	612	712	812	912		
011	—	211	311	411	511	611	711	811	911	10.1.1	
	110	210	310	410	510	610	710	810	910	10.1.0	
	$\bar{1}11$	$\bar{2}11$	$\bar{3}11$	—	$\bar{5}11$	—	—	$\bar{8}11$	$\bar{9}11$	$\overline{10}.1.1$	—
	$\bar{1}12$	$\bar{2}12$	$\bar{3}12$	$\bar{4}12$	$\bar{5}12$	$\bar{6}12$	$\bar{7}12$	$\bar{8}12$	$\bar{9}12$	$\overline{10}.1.2$	$\overline{11}.1.2$
	$\bar{1}13$	$\bar{2}13$	$\bar{3}13$	$\bar{4}13$	$\bar{5}13$	$\bar{6}13$	—	$\bar{8}13$	$\bar{9}13$	—	
	$\bar{1}14$	$\bar{2}14$	$\bar{3}14$	$\bar{4}14$	$\bar{5}14$	$\bar{6}14$	$\bar{7}14$	$\bar{8}14$	$\bar{9}14$	$\overline{10}.1.4$	
	$\bar{1}15$	$\bar{2}15$	$\bar{3}15$	$\bar{4}15$	$\bar{5}15$	$\bar{6}15$	$\bar{7}15$	$\bar{8}15$	$\bar{9}15$		
	$\bar{1}16$	$\bar{2}16$	$\bar{3}16$	$\bar{4}16$	$\bar{5}16$	$\bar{6}16$	$\bar{7}16$	$\bar{8}16$			
	—	$\bar{2}17$	$\bar{3}17$	$\bar{4}17$	$\bar{5}17$	$\bar{6}17$	$\bar{7}17$				

TABLE II (*Continued*)

b-axis equator

—	107	—									
006	—	206	—	406	—						
—	—	—	305	—	505	—					
—	—	—	—	404	—	604	—				
—	103	—	303	—	503	—	703	—			
002	—	202	—	402	—	602	—	802	—		
—	101	—	301	—	501	—	701	—	901	—	
	—	200	—	400	—	600	—	800	—	10.0.0	—
	$\bar{1}01$	—	$\bar{3}01$	—	$\bar{5}01$	—	$\bar{7}01$	—	$\bar{9}01$	—	—
	—	$\bar{2}02$	—	$\bar{4}02$	—	$\bar{6}02$	—	$\bar{8}02$	—	$\overline{10}.0.2$	—
	$\bar{1}03$	—	$\bar{3}03$	—	$\bar{5}03$	—	$\bar{7}03$	—	$\bar{9}03$	—	$\overline{11}.0.3$
	—	$\bar{2}04$	—	$\bar{4}04$	—	—	—	$\bar{8}04$	—	$\overline{10}.0.4$	
	$\bar{1}05$	—	—	—	—	—	$\bar{7}05$	—	$\bar{9}05$	—	
	—	$\bar{2}06$	—	$\bar{4}06$	—	$\bar{6}06$	—	$\bar{8}06$	—		
	$\bar{1}07$	—	$\bar{3}07$	—	$\bar{5}07$	—					

TABLE II (*Continued*)

a-axis equator

	—	002	—	—	—	006	—
—	011	012	013	014	015	016	017
020	021	022	023	024	025	026	027
—	031	032	033	034	—	036	037
040	041	042	043	044	—	046	047
—	051	—	053	054	055	056	057
060	061	062	063	064	065	066	067
—	071	072	073	—	075	076	077
080	081	082	083	084	085	086	
—	091	092	093	094	095	096	
0.10.0	0.10.1	0.10.2	0.10.3	0.10.4	0.10.5	0.10.6	
—	0.11.1	—	0.11.3	—	0.11.5		
0.12.0	0.12.1	0.12.2	0.12.3	0.12.4			
—	0.13.1	—	0.13.3	0.13.4			
0.14.0	0.14.1	—	0.14.3				
—	0.15.1	0.15.2	0.15.3				
0.16.0	0.16.1						

TABLE II (*Continued*)

c-axis equator																
	—	020	—	040	—	060	—	080	—	0.10.0	—	0.12.0	—	0.14.0	—	0.16.0
—	110	120	130	140	150	160	170	180	190	1.10.0	1.11.0	1.12.0	—	1.14.0	1.15.0	1.16.0
200	210	220	230	240	250	260	—	280	290	2.10.0	2.11.0	2.12.0	—	—	—	
—	310	320	330	340	350	360	370	380	—	3.10.0	—	3.12.0	3.13.0	3.14.0	3.15.0	
400	410	420	430	440	450	460	470	480	—	4.10.0	—	4.12.0	4.13.0	4.14.0	4.15.0	
—	510	520	530	540	550	560	570	580	590	—	—	5.12.0	5.13.0	5.14.0		
600	—	620	—	640	—	—	670	580	690	6.10.0	6.11.0	—	6.13.0			
—	710	720	730	—	750	760	770	780	—	—	7.11.0	7.12.0				
800	810	820	830	840	850	860	870	880	890	8.10.0						
—	910	920	930	940	950	960	970	980	990							
—	10.1.0	—	10.3.0	—	10.5.0	—										

The Weissenberg photographs indicate a centro-symmetrical point group C_2^h, which confirms the monoclinic nature of realgar as deduced from morphological studies.

There are no systematic absences in the list of general, *hkl*, reflections, thus eliminating the body-centered monoclinic lattice, Γ_m', by reflections actually appearing. The primitive nature of the cell is confirmed by the identity of patterns of the *b*-axis first and second layer photographs. This leaves for consideration only the simple monoclinic lattice, Γ_m, upon which are based the space groups, C_s^1, C_s^2; C_2^1, C_2^2; C_{2h}^1, C_{2h}^2, C_{2h}^4, C_{2h}^5. The catalog of reflections plainly indicates the systematic absences:

$h0l$ when $h+l$ is odd
$0k0$ when k is odd.

These characteristics pertain only to C_{2h}^5 of the uneliminated list. This incidentally establishes the holohedral character of realgar by *x*-ray means, by elimination of lower symmetry space groups and therefor the point-groups upon which they are based.

Space group C_{2h}^5 is shown in figure 1. It is composed entirely of screw axes and glide planes. With the choice of unit adopted here, the orientation is indicated by the symbol, $P2_1/n$. This is not the conventional orientation, and the coordinates of equivalent positions are therefor not the ones usually listed in reference books. Coordinates referred to the orientation adopted here are given in table III.

Table III
Coordinates of equivalent positions of space group C_{2h}^5 referred to new realgar axes, orientation $P2_1/n$.

Equipoint designation	Coordinates
4	$[[xyz]];[[\bar{x}\bar{y}\bar{z}]];[[\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z]];[[\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z]]$
2_a	$[[000]];[[\frac{1}{2}\frac{1}{2}\frac{1}{2}]]$
2_b	$[[\frac{1}{2}00]];[[0\frac{1}{2}\frac{1}{2}]]$
2_c	$[[00\frac{1}{2}]];[[\frac{1}{2}\frac{1}{2}0]]$
2_d	$[[\frac{1}{2}0\frac{1}{2}]];[[0\frac{1}{2}0]]$

Possible Arrangements

Because of the low internal symmetry of C_{2h}^5, the general position contains only four equipoints, and the only special positions

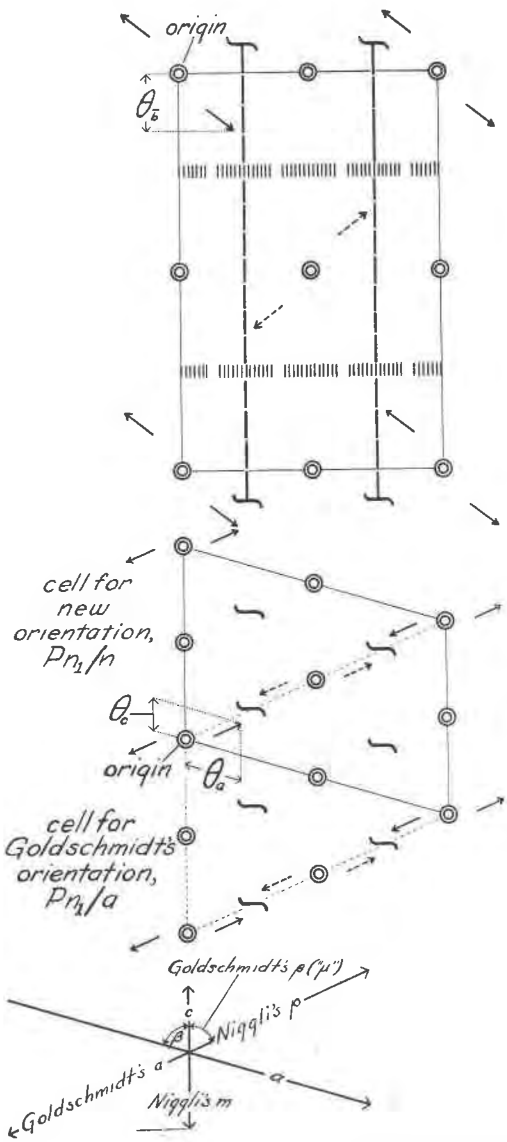

FIG. 1. The space group of realgar, showing the relations between the cell based on the new orientation, the cell based on Goldschmidt's orientation, and Niggli's space group coordinate directions. Double circles are symmetry centers; heavy dashed lines and "S's" are two-fold screw axes; broken ribbons are glide planes with components $a/2+c/2$ for the cell based on the new orientation, or $a/2$ for the cell based on Goldschmidt's orientation. The small full arrows represent molecules associated with symmetry centers on the zero levels, small dotted arrows molecules associated with symmetry centers on the halving levels.

are four 2-fold sets of symmetry centers. Sixteen formula weights of AsS, or 16 As and 16 S must be placed in this cell. Accordingly, there must be several kinds of each atomic species. The possible arrangements are given in table IV. The list is imposing. Of the twenty-one kinds of arrangements possible for realgar, the very simplest must be determined by fixing fifteen parameters, five at

TABLE IV

POSSIBLE ARRANGEMENTS FOR REALGAR

Combination designation	As		S		Parameters
1	2_a 2_b 2_c 2_d	4 4		4 4 4 4	18
2	2_a 2_b	4 4 4	2_c 2_d	4 4 4	15
3	2_a 2_c	4 4 4	2_b 2_d	4 4 4	15
4	2_a 2_d	4 4 4	2_b 2_c	4 4 4	15
5	2_b 2_c	4 4 4	2_a 2_d	4 4 4	15
6	2_b 2_d	4 4 4	2_a 2_c	4 4 4	15
7	2_c 2_d	4 4 4	2_a 2_b	4 4 4	15
8	2_a 2_b	4 4 4		4 4 4 4	18
9	2_a 2_c	4 4 4		4 4 4 4	18
10	2_a 2_d	4 4 4		4 4 4 4	18
11	2_b 2_c	4 4 4		4 4 4 4	18
12	2_b 2_d	4 4 4		4 4 4 4	18
13	2_c 2_d	4 4 4		4 4 4 4	18
14		4 4 4 4	2_a 2_b 2_c 2_d	4 4	18
15		4 4 4 4	2_a 2_b	4 4 4	21
16		4 4 4 4	2_a 2_c	4 4 4	21
17		4 4 4 4	2_a 2_d	4 4 4	21
18		4 4 4 4	2_b 2_c	4 4 4	21
19		4 4 4 4	2_b 2_d	4 4 4	21
20		4 4 4 4	2_c 2_d	4 4 4	21
21		4 4 4 4		4 4 4 4	24

a time. The least simple requires the fixing of twenty-four parameters, eight at a time. A unique determination of the structure by customary formal methods is, therefor, out of the question.

The study of the realgar structure is being continued, and it is hoped that a complete structure will be published shortly.