CRYSTALLOGRAPHY OF LANARKITE

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Lanarkite, Pb₂SO₅, has been found in measurable monoclinic crystals only from the Susanna Mine, Leadhills, Lanarkshire, Scotland (Heddle, 1901). The only complete description of these crystals was given by Schrauf (1877), who chose pseudorectangular axes ($\beta = 91^{\circ}49'$). Goldschmidt chose a setting with the axes considerably inclined ($\beta = 119^{\circ}23'$). Specimens in the Harvard collection from the type locality were examined by Richmond in connection with other work; these proved to be a rich source of new data. X-ray investigation revealed that neither the Schrauf nor the Goldschmidt settings were in agreement with that of the simplest structural cell.

X-Ray Determinations. A carefully selected crystal, approximately 0.5 millimeter long, was employed for rotation and Weissenberg photographs. The results of measurements and calculations of the photographs gave the following cell edge lengths for the base-centered lattice which was chosen: $a_0 = 13.73$ Å, $b_0 = 5.68$ Å, $c_0 = 7.07$ Å; $a_0: b_0: c_0 = 2.417: 1: 1.245$, $\beta = 116^{\circ}13'$.

The choice of the correct axial directions in this case, except for the b-axis, which is fixed by symmetry considerations, is not without ambiguity. If, in the reciprocal lattice, the three shortest translations, with c^* greater than a^* , are chosen, giving the cell with the least axial obliquity, the following reflections are observed on the Weissenberg pictures:

(hkl) —with h+k+l, even (h0l) —with h+k, even (0k0) —with k, even

The criterion, (hkl) with h+k+l, even, indicates a body-centered or "I" lattice. As there are, conventionally, only two types of monoclinic lattices, the primitive and the face-centered, it is advisable to choose a cell which may be referred to one of these lattice types.

A face-centered lattice may be obtained if the next shortest translation is taken for c^* , with a^* and b^* remaining identical with the a^* and b^* of the body-centered cell. The reflections appearing from this lattice are:

> (hkl) —with h+k, even (h0l) —with h, even (0k0) —with k, even

The criterion (hkl) with h+k, even, is that for the base-centered or "C" lattice, which is adopted for the mineral. The space group, fixed by the above criteria plus the fact that a morphological investigation showed

no hint of hemihedry, becomes $C_{2\hbar}^3-C$ 2/m. The transformations from the base-centered lattice to the body-centered lattice and vice versa are, respectively: 101/010/001 and 101/010/001.

The relation of the "C" lattice to the "I," Schrauf, and Goldschmidt cells is given in Fig. 1.



FIG. 1. Lanarkite. Structural lattice showing the chosen base-centered "C" cell with edges [100], [010], [001]; the body-centered "T" cell with edges [101], [010], [001]; Schrauf's cell with edges [$\overline{102}$], [$\overline{030}$], [$\overline{102}$]; and Goldschmidt's cell with edges [$\overline{104}$], [$\overline{030}$], [$\overline{102}$]. The volume of Schrauf's cell is 12 times, and that of Goldschmidt is 18 times that of the structural cell.

Morphology. As the structural study had disclosed that the old settings were incorrect, a further morphological study of the material in hand seemed advisable. Eleven well-developed crystals, varying in length from 1 mm. to 5 mm., were measured. On the basis of these measurements, new elements for the base-centered setting were calculated. A comparison between these elements and those of Schrauf, transformed to the base-centered setting, with those obtained by x-ray analysis is given below.

	a:b:c	β
Richmond and Wolfe	2.4137:1:1.2363	116°06′
Schrauf	2.4149:1:1.2424	115 48
X-ray	2.417 :1:1.245	116 13

There is essential agreement between the various elements, although Schrauf's value for β departs from the *x*-ray value by 0°25'. Because of this agreement, Schrauf's values are retained.

Schrauf's elements may be transformed to the base-centered setting by the method of Wolfe (1937), using the transformation formula, $\frac{1}{2}0\frac{1}{2}/0\frac{1}{3}0/\frac{1}{4}0\frac{1}{4}$. Similarly, Goldschmidt's elements, derived from Schrauf's work, may be transformed to the base-centered setting by the formula, $\frac{1}{3}0\frac{2}{3}/0\frac{1}{3}0/\frac{1}{6}0\frac{1}{6}$. The reverse transformations are, respectively: 102/030/102 and 104/030/102. The meaning of these transformations in the space-lattice is readily observed in Fig. 1.

Five new, well-authenticated forms were observed. In the discussion which follows, the indices refer to the "C" lattice. The new forms are: $c\{001\}$, $d\{103\}$, $E\{\overline{4}03\}$, $R\{\overline{8}01\}$, and $P\{\overline{1}11\}$. All were seen at least twice in good position and, except for $d\{103\}$, were sufficiently prominent to be figured (Fig. 2). In addition, the forms $m\{110\}$, $f\{201\}$ (with indistinct cleavage), $F\{\overline{2}01\}$ (with perfect cleavage), and $U\{\overline{4}01\}$ (with indistinct cleavage), first observed by Schrauf, were each observed several times in this study.

Five other forms—{100}, {101}, { $\overline{1}01$ }, {401}, and {601}—were each observed twice, but the reflections were of poor quality. These forms, therefore, require confirmation. σ {205} and s{9.10.3}, observed by Schrauf, were not seen by the authors.



FIG. 2. Lanarkite-Typical crystals from Leadhills, Scotland.

A tabulated comparison of the measured and calculated values for the new, certain forms is given in Table 1. As the crystals are always elongated parallel to the *b*-axis, measurement of the crystals was made with this axis vertical. The ϕ and ρ angles obtained in this orientation correspond to ϕ_2 and ρ_2 of the angle table, and direct comparison may thus be made.

12	No.	No.	Mea	asure	d Range	Weight	ed Mean	Calc	ulated
Form	xls.	times	ϕ_2		ρ_2	ϕ_2	$ ho_2$	ϕ_2	$ ho_2$
001	3	3	63°47′- 6	4°23′	90°00′-	64°07′	90°00′	64°12′	90°00′
103	2	2	55 50 5.	5 55	90 00	55 53	90 00	56 01 ¹ / ₂	90 00
403	2	2	105 13 10	5 20	90 00	105 18	90 00	105 34	90 00
801	7	11	164 38 16	5 05	90 00	165 15	90 00	166 15	90 00
Ī 11	5	9	94 03 9.	5 19	38 58 -39°07′	95 04	39 03	95 03	$38 56\frac{1}{2}$

TABLE 1. LANARKITE: MEASURED AND CALCULATED ANGLES

The indices for all of the forms noted in the literature in the basecentered, Schrauf, and Goldschmidt settings are given below. The new forms are marked with an asterisk.

Base-	centered	S	chrauf		Gol	dschmidt
с	001*		T01			201
m	110	z	131		z	131
d	103*		705			13.0.5
σ	205	σ	302		σ	$\overline{11.0.4}$
E	403*		105			405
f	201	a	100		a	100
F	201	С	001		С	102
U	401	u	103		U	001
R	801*		305			205
P	T11*		I 33			<u>T</u> 11
		Unc	onfirmed			
	100*		101			101
	101*		$\overline{3}01$			501
	<u>1</u> 01*		T 03			T 01
	401*		301			401
	601*		201			502
	9.10.3	S	1.10.5		S	T.10.5
		Di	scarded			
$\overline{2}$	34.4.57	V	10.1.29			1.2.58
1	75.4.18	w	13.4.37			1.4.37
	24.2.57	au	23.1.15			42.1.15

Vicinal forms similar to the last three listed above were observed on the larger crystals. In all cases they were too dull for accurate measurement, and are apparently solution forms. The faces on the smaller crystals, however, gave clear, bright reflections with rational indices. It seems advisable to discard the vicinal forms from the form list. An angle table, summarizing the crystallographic elements and angles, is given below.

	12:	a:b:c=2.4 $p_2:q_2=0.894$	Lanarkite—Pb ₂ SO ₅ Monoclinic; prismatic— $2/m$ 49:1:1.2424; β =115°48'; $p_0:q_0:r_0=0.5145:1.1186:1$ 0:0.4600:1; μ =64°12'; $p_0'=0.5714$, $q_0'=1.2424$, $x_0'=0.4834$					
	Forms	φ	ρ	ϕ_1	$\rho_1 = A$	ϕ_2	$\rho_2 = B$	Dana '92
с	001	90°00′	25°48′	64°12′	90°00′	0°00′	64°12′	
т	110	24 42	90 00	0 00	24 42	79 33	65 18	2
d	103	90 00	$33 58\frac{1}{2}$	56 $01\frac{1}{2}$	90 00	$8 \ 10\frac{1}{2}$	56 01 ¹ / ₂	
ø	205	90 00	35 27	54 33	90 00	9 39	54 33	σ
E	4 03	-90 00	15 34	105 34	90 00	41 22	105 34	
f	201	90 00	58 24 ¹ / ₂	$31 \ 35\frac{1}{2}$	90 00	$32 \ 36\frac{1}{2}$	$31 \ 35\frac{1}{2}$	a
F	201	-90 00	33 24	123 24	90 00	59 12	123 24	С
U	401	-9000	$60\ 58\frac{1}{2}$	150 581	90 00	86 461/2	$150\ 58\frac{1}{2}$	и
R	801	-90 00	76 15	166 15	90 00	102 03	166 15	
Р	<u>T</u> 11	- 4 03	51 14 $\frac{1}{2}$	95 03	$38 56\frac{1}{2}$	57 20	93 $09\frac{1}{2}$	

TABLE 2. LANARKITE: ANGLE TABLE

 $\label{eq:unconfirmed: 100} unconfirmed: -\{100\}, \{101\}, \{101\}, \{401\}, \{601\}, \{9, 10.3\} \\ Discarded: -\{6, 2, 57\}, \{234, 4, 57\}, \{75, 4, 18\} \\$

Optics

The refractive indices and optical orientation were determined by the immersion method, giving the following results:

	n(Na)	
X	1.928	negative
Y = b	2.007 ± 0.003	$2V = 60^\circ \pm 2^\circ$
$Z \wedge c = 30^{\circ}$	2.036	

CHEMISTRY

Using an existing analysis by E. Pisani (1873) and a density 6.92, determined here by the float method, together with the cell volume, $V_0 = 494.4$, the contents of the unit cell were determined and are given in the following table:

	1		2	3	4
PbO	84.63	Pb	0.379	7.86	8
SO_3	15.37	S	.191	3.96	4
		.0	.952	19.74	20

TABLE 3. LANARKITE: ATOMIC CONTENT OF UNIT CELL

1. Lanarkite, Leadhills, Scotland. Analysis reduced to 100%. Analyst, E. Pisani (1873).

2. Atomic proportions.

3. Number of atoms in unit cell yielding the formula Pb₈S₄O₂₀.

4. Theoretical number of atoms in unit cell for $M_0 = 2073.8$.

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