Acta Cryst. (1973). B**29**, 1986

The Crystal Structure of Caledonite, $Cu_2Pb_5(SO_4)_3CO_3(OH)_6$

By C. Giacovazzo, S. Menchetti* and F. Scordari
Istituto di Mineralogia dell'Università di Bari, Italy

(*Received* 13 *February* 1973; *accepted* 19 *April* 1973)

Caledonite, $Cu_2Pb_5(SO_4)_3CO_3(OH)_6$, is orthorhombic, space group $Pmn2_1$, with $Z=2$. Cell dimensions are: $a=20{\cdot}089\pm0{\cdot}007$, $b=7{\cdot}146\pm0{\cdot}003$, $c=6{\cdot}560\pm0{\cdot}005$ Å. The crystal structure was solved by the Patterson function and successive three-dimensional Fourier syntheses. The least-squares refinement led to a final R index of 0·052 for 858 measured reflexions. The edge sharing of the Cu–O 4+2 pseudo-octahedra builds, around the screw axis, a chain whose repeat unit is ${}_1^\infty[Cu(OH)_3O]^{3-}$. The three independent lead atoms are irregularly coordinated by oxygen atoms with a wide scattering of Pb–O distances. The CO_3 and SO_4 groups provide the connexions among the lead polyhedra, and between these and the copper oxygen chains. Some considerations about Pb–O distances are given.

Introduction

Caledonite is a basic carbonate–sulphate of lead and copper, first described by Brooke (1820). It occurs, as a secondary mineral, in the oxidized zone of copper–lead deposits, associated with other Cu–Pb compounds.

The carbonatic part was regarded for a long time as due to admixed cerussite, but since the analysis published by Berg (1901) the chemical formula $Cu_2Pb_5(SO_4)_3(CO_3)\,(OH)_6$ seems to be well defined. Many authors considered this mineral as belonging to the orthorhombic system; Schrauf and Jeremejev thought it monoclinic (Palache, Berman & Frondel, 1951), but this interpretation is not supported by any optical or X-ray evidence (Palache & Richmond, 1939). The first data on X-ray crystallography were determined by Richmond (1939) who assigned caledonite to the space group *Pnmm* with $a=7{\cdot}15$, $b=20{\cdot}10$, $c=6{\cdot}56$ Å and $Z=2$.

Experimental

Lattice parameters were refined by the application of the least-squares method using experimental data from a powder diagram and from Weissenberg photographs calibrated with a small quartz crystal. The results of both methods are in good agreement. The systematic absences on the Weissenberg photographs were the same as those observed by Richmond (1939); therefore the space group *Pnmm* seemed to be confirmed. Indeed this space group was initially assumed for the structural study. Later, because of difficulties found in the structure determination, a test for the piezoelectric effect was carried out with highly positive results; the correct space group is therefore $Pmn2_1$, as subsequently confirmed by the structure analysis.

Crystal data

$a=20{\cdot}089$ (7) Å
$b=\ 7{\cdot}14_6$ (3)
$c=\ 6{\cdot}560$ (5)
$\lambda(Cu\ K\alpha)=1{\cdot}5418$
$\mu(Cu\ K\alpha)=926{\cdot}8$ cm^{-1}
$\mu R(Cu\ K\alpha)=5{\cdot}79$

Space group $Pmn2_1$
F.W. 1613·4
$V=941{\cdot}7$ Å^3
$Z=2$
$D_m=5{\cdot}76$ g cm^{-3}
$D_x=5{\cdot}69$ g cm^{-3}

The above value for the measured density is that given by Palache & Richmond (1939).

A bluish green small crystal from Red-Gill, Cumberland, U. K., elongated along [001] was chosen for the structural study; because of the high absorption factor it was ground to a nearly perfect cylindrical shape (radius 0·0063 cm) in order to apply an easy and accurate correction. For intensity data collection the crystal was rotated about the c axis. Weissenberg equi-inclination photographs were recorded for the reciprocal levels with l from 0 to 6, using Ni-filtered Cu radiation and the multiple-film technique.

A total of 1102 reflexions were collected and measured by means of a microdensitometer; 244 were below the observational limit. The intensities were corrected for Lorentz–polarization, α_1–α_2 splitting and absorption.

All calculations were carried out on a I.B.M. 360/65 computer.

Structure determination and refinement

A three-dimensional Patterson synthesis was computed from the complete set of measured reflexions. As mentioned above, the first space group assumed for structure solution was *Pnmm*. The most striking features of Patterson maps were represented by the highest peaks along the b axis with $w=0,\frac{1}{2}$. In *Pnmm* the general position is eightfold; therefore many atoms (heavy atoms included) should lie on special positions. The Patterson maxima seemed to confirm this requirement. In this

---

* Present address: Istituto di Mineralogia, Università di Firenze, Italy.

way, and by successive Fourier syntheses, the Pb, Cu and S atoms were located, but all attempts to determine the positions of the O and C atoms were unsuccessful. The mean *R* value was almost 0·20, this index showing a strong continuous increase from *hk*0 to *hk*6.

At this stage a test for a piezoelectric effect clearly showed the symmetry to be non-centrosymmetric: the correct space group is therefore $Pmn2_1$, provided that *a* and *b* are interchanged with respect to the original setting of Richmond (*Pnmm*). After this symmetry change all the atoms, except hydrogen, were easily determined; the Pb and Cu atoms, for instance, showed significant changes mainly on the z/c coordinates. Nevertheless these atoms are not far from the special positions in the former space group.

The parameters derived from Fourier maps were refined using a modified full-matrix least-squares *ORFLS* program (Busing, Martin & Levy, 1962) with equal weight for all observed reflexions.

Isotropic temperature factors were refined during the first cycles and seemed to behave normally except for a rather large variation in oxygen *B*'s. Anisotropic refinement was carried out only for lead and copper atoms. The final atomic parameters are given in Tables 1 and 2; the analysis of the anisotropic thermal parameters is in Table 3. An explanation of the magnitudes of individual *B*'s is difficult because of the dominance of lead. The average isotropic *B* values are all reasonable, except B_C which is larger than expected. The variations in individual B_O's are very large, but they are not significant because of the high σ values.

Table 1. *Atomic coordinates, equivalent isotropic temperature factors (lead and copper) and isotropic temperature factors (sulphur, oxygen and carbon)*

Standard deviations are in parentheses.

	x/a	y/b	z/c	B
Pb(1)	0·5000	0·0918	0·5000*	1·3
Pb(2)	0·3996 (1)	0·4146 (2)	0·0398 (5)	1·0
Pb(3)	0·3386 (1)	0·8870 (2)	0·0684 (5)	0·9
Cu	0·2511 (4)	0·4910 (14)	0·3121 (14)	0·9
S(1)	0·5000	0·5588 (15)	0·5552 (28)	0·9 (0·3)
S(2)	0·3367 (4)	0·1255 (11)	0·5566 (30)	0·9 (0·3)
OH(1)	0·164 (1)	0·372 (5)	0·352 (6)	0·2 (0·5)
OH(2)	0·340 (2)	0·608 (6)	0·274 (7)	1·2 (0·7)
OH(3)	0·275 (1)	0·356 (3)	0·060 (7)	0·5 (0·3)
O(1)	0·500	0·430 (10)	0·728 (11)	3·0 (1·5)
O(2)	0·500	0·435 (6)	0·358 (7)	0·3 (0·7)
O(3)	0·441 (1)	0·684 (3)	0·556 (7)	0·6 (0·4)
O(4)	0·284 (1)	0·274 (3)	0·566 (7)	1·2 (0·4)
O(5)	0·303 (1)	0·950 (4)	0·516 (5)	1·3 (0·5)
O(6)	0·375 (2)	0·109 (6)	0·763 (6)	2·3 (0·7)
O(7)	0·385 (2)	0·172 (5)	0·393 (6)	1·4 (0·5)
O(8)	0·446 (1)	0·753 (3)	0·051 (6)	1·0 (0·4)
O(9)	0·500	0·015 (6)	0·136 (8)	1·8 (0·8)
C	0·500	0·841 (7)	0·097 (12)	1·3 (0·9)

* The *z* parameter of Pb(1) was fixed at $\frac{1}{2}$ to establish a reference coordinate in the **c** direction.

A small but significant improvement in *R* index was obtained using a correction for secondary extinction; the extinction coefficient is $4\,.\,10^{-7}$.

The atomic scattering factors used for Pb^{2+}, Cu^{2+}, S and C were derived from the values published by Cromer & Waber (1965) and for O^{-1} from those given in *International Tables for X-ray Crystallography*

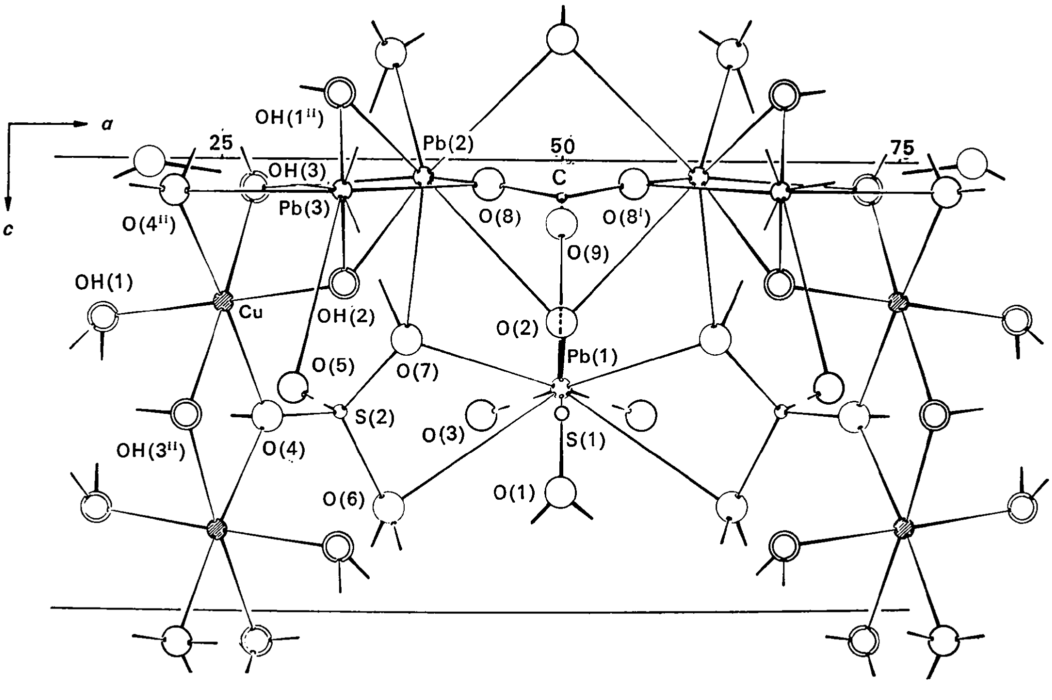

Fig. 1. The structure of caledonite projected along [010]. For clarity S(1)–O bonds are not drawn.

Table 2. *Final anisotropic temperature factors for lead and copper* (× 10⁴)

Standard deviations are in parentheses. The temperature factors refer to the expression

$$\exp\left[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)\right].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pb(1)	6 (0)	66 (4)	86 (10)	0	0	−9 (4)
Pb(2)	7 (0)	56 (2)	46 (4)	−6 (1)	−1 (1)	−3 (3)
Pb(3)	7 (0)	31 (2)	60 (5)	2 (1)	−1 (1)	−2 (3)
Cu	5 (1)	39 (9)	57 (14)	−2 (2)	2 (3)	14 (8)

Table 3. *Analysis of anisotropic thermal parameters*

α, β and γ are the angles of the principal axes of the thermal ellipsoids with respect to the crystallographic axes. Standard deviations are in parentheses.

	R.m.s.	α	β	γ
Pb(1)	0·108 (4)	180 (0)	90 (0)	90 (0)
	0·125 (5)	90 (0)	35 (15)	55 (15)
	0·142 (6)	90 (0)	54 (15)	144 (15)
Pb(2)	0·095 (5)	120 (12)	118 (11)	137 (18)
	0·105 (4)	58 (11)	60 (11)	133 (18)
	0·135 (2)	133 (3)	43 (3)	91 (5)
Pb(3)	0·088 (3)	80 (4)	169 (4)	94 (9)
	0·114 (6)	76 (15)	92 (9)	14 (14)
	0·124 (2)	162 (12)	100 (4)	76 (14)
Cu	0·09 (1)	91 (72)	145 (28)	125 (30)
	0·10 (1)	19 (19)	80 (67)	106 (45)
	0·12 (1)	109 (20)	57 (16)	141 (17)

(1962). A correction for anomalous dispersion was applied to the scattering factors for lead and copper (Cromer, 1965). Because of the dominant weight of Pb and Cu atoms, no attempt was made to locate H atoms on difference Fourier maps.

The final R value is 0·052 for 858 observed reflexions and 0·088 including the non-observed ones.†

Interatomic distances, angles and their standard deviations (Tables 4 and 5) were calculated by the program *ORFFE* (Busing, Martin & Levy, 1964) using the variance-covariance matrix for atom coordinates.

Description and discussion of the structure

The atomic arrangement in caledonite is shown in Fig. 1, where Pb–O bonds up to 3·17 Å are drawn; for clarity, S(1)–O bonds are omitted.

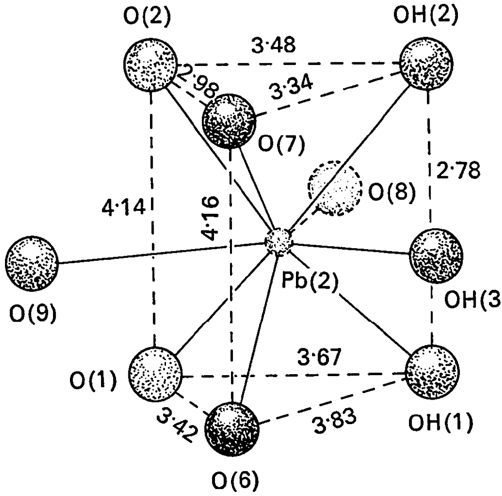

Fig. 2. Idealized Pb(2) polyhedron. OH(1), OH(2), OH(3) and O(8) form the basis of a distorted pyramid with the apex at Pb(2).

Table 4. *Interatomic distances in caledonite*

(±0·03 Å for Pb–O, Cu–O, S–O distances; ±0·05 Å for C–O and O–O distances).

Pb(1)–O(9)	2·45 Å	Pb(2)–OH(1^{ii})*	2·34 Å	Pb(3)–OH(1^{ii})*	2·33 Å
Pb(1)–O(7)	2·47 (2×)	Pb(2)–OH(2)	2·38	Pb(3)–O(8)	2·37
Pb(1)–O(2)	2·63	Pb(2)–OH(3)	2·54	Pb(3)–OH(2)	2·41
Pb(1)–O(1)	2·84	Pb(2)–O(8)	2·60	Pb(3)–O(6)*	2·66
Pb(1)–O(6)	3·05 (2×)	Pb(2)–O(1)*	2·88	Pb(3)–O(4^{ii})	2·73
Pb(1)–O(3)*	3·17 (2×)	Pb(2)–O(6)*	2·89	Pb(3)–O(5)	3·05
		Pb(2)–O(2)	2·91	Pb(3)–O(7)	3·09
Cu–OH(1)	1·97	Pb(2)–O(7)	2·91	Pb(3)–O(5^{ii})*	3·10
Cu–OH(2)	2·00	Pb(2)–O(9)	3·55	Pb(3)–O(9)*	3·40
Cu–OH(3)	1·97				
Cu–OH(3^{ii})	2·03	S(1)–O(1)	1·46	S(2)–O(4)	1·49
Cu–O(4)	2·37	S(1)–O(2)	1·56	S(2)–O(5)*	1·44
Cu–O(4^{ii})	2·44	S(1)–O(3)	1·48 (2×)	S(2)–O(6)	1·55
				S(2)–O(7)	1·49
C–O(8)	1·29 (2×)	Postulated H bonds:			
C–O(9)*	1·27	OH(1)···O(3^{ii})	2·90		
		OH(2)···O(3)	2·80		
		OH(3)···O(5^{ii})	2·72		

Labelling scheme for symmetry related atoms

None	x	y	z
i	$1-x$	y	z
ii	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$

* Indicates atoms of adjacent cells.

---

† A list of $|F_o|$ and F_c is available from the authors.

Table 5. *Interatomic angles, with standard deviations in parentheses, in* $Cu(OH)_4O_2$, SO_4 *and* CO_3

Symmetry references as for Table 4.

OH(1)—Cu–OH(3)	96·9 (1·3)°	O(1)—S(1)–O(2)	106·7 (2·3)°
OH(1)—Cu–OH(3^{ii})	83·8 (1·3)	O(1)—S(1)–O(3)	112·1 (2·1) (×2)
OH(1)—Cu–O(4)	82·9 (1·2)	O(2)—S(1)–O(3)	110·3 (2·0) (×2)
OH(1)—Cu–O(4^{ii})	97·2 (1·2)	O(3)—S(1)–O(3^{i})	105·6 (1·9)
OH(2)—Cu–OH(3)	83·0 (1·4)		
OH(2)—Cu–OH(3^{ii})	96·3 (1·4)	O(4)—S(2)–O(5)*	107·5 (1·5)
OH(2)—Cu–O(4)	96·0 (1·4)	O(4)—S(2)–O(6)	111·3 (2·5)
OH(2)—Cu–O(4^{ii})	83·9 (1·3)	O(4)—S(2)–O(7)	109·5 (2·1)
OH(3)—Cu–O(4)	101·5 (1·3)	O(5)*–S(2)–O(6)	108·6 (2·2)
OH(3)—Cu–O(4^{ii})	81·6 (1·4)	O(5)*–S(2)–O(7)	111·3 (2·2)
OH(3^{ii})–Cu–O(4)	82·0 (1·3)	O(6)—S(2)–O(7)	108·7 (1·9)
OH(3^{ii})–Cu–O(4^{ii})	94·8 (1·3)		
OH(1)—Cu–OH(2)	178·9 (1·9)	O(8)—C—O(9)*	121·7 (2·4) (×2)
OH(3)—Cu–OH(3^{ii})	176·4 (1·5)	O(8)—C—O(8^{i})	114·5 (5·1)
O(4)—Cu–O(4^{ii})	176·9 (1·7)		

There are three independent lead atoms Pb(1), Pb(2) and Pb(3), the first of which lies on the mirror plane. Pb(1)–O distances inspection shows nine values ranging from 2·45 to 3·17 Å, with a mean value of 2·81 Å. Four of these distances are significantly shorter than the above average and they refer to oxygen atoms arranged to one side of Pb(1). In this Pb(1)O_4 group the mean Pb–O distance is 2·50 Å.

Pb(2) lies at the top of a four-sided pyramid the basis of which is made by one oxygen atom, namely O(8), and three hydroxyl groups. Pb(2)–OH distances in this pyramid range from 2·34 to 2·54 Å, while Pb(2)–O(8) is 2·60 Å. Four additional oxygen atoms, farther from Pb(2) than the previous ones, complete the environment of this lead atom. The splitting of the Pb(2)–O distances into two different groups is pretty evident; indeed all the oxygen atoms of the second set are almost equidistant from Pb(2) (from 2·88 to 2·91 Å). On the whole Pb(2) is surrounded (see Fig. 2) by eight anions to form a polyhedron which resembles a trigonal prism with additional atoms above two prism faces; a ninth oxygen atom, O(9) very distant at 3·55 Å from Pb(2), lies above the third face. Similar polyhedra for Pb^{II} have already been found, for instance, in rathite I (Marumo & Novacki, 1965) and in diaboleite (Rouse, 1971*a*).

A one-sided coordination also affects Pb(3), which lies at the top of a trigonal distorted pyramid of composition $Pb(OH)_2O$ with a mean lead–oxygen distance of 2·37 Å. As for Pb(1) and Pb(2), more oxygen atoms (five in this instance) surround Pb(3) at greater distances, which range widely between 2·66–3·10 Å.

Apart from some minor differences, the three lead atoms show on the whole a similar crystal-chemical behaviour, mainly with regard to the one-sided coordination and the wide range of Pb–O distances. As depicted by Sahl (1970), this trend is quite frequently found in oxygenated Pb^{II} compounds. The short Pb–O bonds and the pyramidal configuration are usually referred to a considerable degree of covalent character in the metal–oxygen bonds (Bouvaist & Weigel, 1970; Prewitt, Kirchner & Preisinger, 1967; Rouse, 1971*a*). Actually in caledonite also many Pb–O distances are shorter than those expected for an ionic bond (Shannon & Prewitt, 1969). Finally it can be noted that, as in many other structures, the Pb–OH distances fall in the 'short distances' group: Pb(2)–OH av. = 2·42, Pb(3)–OH av. = 2·37 Å; these values compare favourably with those found *e.g.* by Bachmann & Zemann (1961) in linarite (Pb–OH = 2·38 Å), and Rouse (1971*b*) in quenselite (Pb–OH av. = 2·48 Å).

The Cu atom is bonded to four hydroxyl groups arranged at the corners of a slightly irregular square; the four Cu–OH distances are equivalent within the standard deviations and lead to an average value of 1·99 Å. Two more ligands (oxygen atoms belonging to sulphate groups) at greater distances (2·37 and 2·44 Å) complete the usual pseudo-octahedron.

The sulphate groups show a slightly distorted tetrahedral configuration with average S–O distances of 1·49 Å both in S(1) and S(2) polyhedra.

In the CO_3 group, halved by the mirror plane, the two independent C–O distances, as well as the two O–C–O angles, are equivalent within the standard deviations, which are quite large. However the O(8)–C–O(8′) angle notably deviates from the standard value. On the other hand the O–O–O angles in CO_3 are distorted (61 and 58°) but not in such an anomalous way. Therefore the above angular irregularity is mainly due to the C atom, lying off the plane of the oxygen atoms. Unfortunately the carbon position is clearly affected by large errors and no conclusion is possible as regards the actual distortion in the CO_3 group.

Consideration of the distances between the hydroxyl groups and surrounding oxygen atoms allowed the location of the three hydrogen bonds (see Table 4 for O–O distances).

Taking into account Pb–O bonds of up to 3·20 Å it follows that the oxygen atoms, except O(8) and O(9), have a fourfold environment; O(8) and O(9), belonging to the carbonate group, are surrounded by three and two cations respectively. This is shown in the following scheme.

OH(1) binds	**1Cu***		+**1Pb(2)**	+**1Pb(3)**		
OH(2)	**1Cu**		+**1Pb(2)**	+**1Pb(3)**		
OH(3)	**2Cu**		+**1Pb(2)**			
O(1)		1Pb(1)	+2Pb(2)		+1S(1)	
O(2)		**1Pb(1)**	+2Pb(2)		+1S(1)	
O(3)		1Pb(1)			+1S(1)	(+2H bonds)
O(4)	2Cu			+1Pb(3)	+1S(2)	
O(5)				2Pb(3)	+1S(2)	(+1H bond)
O(6)		1Pb(1)	+1Pb(2)	+1Pb(3)	+1S(2)	
O(7)		**1Pb(1)**	+1Pb(2)	+1Pb(3)	+1S(2)	
O(8)			**1Pb(2)**	+**1Pb(3)**	+1C	
O(9)		**1Pb(1)**			+1C	

* Bold Cu and Pb refer to 'short distances'.

The main structural features of caledonite are the following: Cu polyhedra are linked to each other by the sharing of the OH(3)–O(4) edge to form chains (two in the unit cell) running along the screw axes at $x=\frac{1}{4},\frac{3}{4}$; $y=\frac{1}{2}$; the repeat unit of the chain is $^{\infty}_{1}[Cu(OH)_3O]^{3-}$. The half cell between these two chains is filled by a group built up of 5Pb polyhedra linked to each other in such a way as to form empty space where one CO_3 and three SO_4 groups are situated. The latter give rise to further connexions among the Pb polyhedra, within the same group, and between Pb polyhedra and Cu chains. Connexions between different groups of Pb polyhedra are given by the Cu chains and the S(2) sulphate tetrahedra. H bonds give further strength to the structure.

The perfect cleavage {100} ({010} in Richmond's setting) occurs parallel to the Cu polyhedra chains and breaks only some of the Pb–O bonds.

References

Bachmann, H. G. & Zemann, J. (1961). *Acta Cryst.* **14**, 747–753.

Berg, G. (1901). *Mineral. Petrog. Mitt.* **20**, 390–398.

Bouvaist, J. & Weigel, D. (1970). *Acta Cryst.* A**26**, 501–510.

Brooke, H. J. (1820). *Edinburgh Phil. J.* **3**, 117.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Marumo, F. & Novacki, W. (1965). *Z. Kristallogr.* **122**, 433–456.

Palache, C., Berman, H. & Frondel, C. (1951). *Dana's System of Mineralogy*, Vol. II, pp. 630-632. New York: John Wiley.

Palache, C. & Richmond, W. E. (1939). *Amer. Min.* **24**, 441–445.

Prewitt, C. T., Kirchner, E. & Preisinger, A. (1967). *Z. Kristallogr.* **124**, 115–130.

Richmond, W. E. (1939). See Palache, C. & Richmond, W. E. (1939).

Rouse, R. C. (1971*a*). *Z. Kristallogr.* **134**, 69–80.

Rouse, R. C. (1971*b*). *Z. Kristallogr.* **134**, 321–332.

Sahl, K. (1970). In *Handbook of Geochemistry*. Vol. II/2, 82 A-1-82 A-6. Heidelberg: Springer-Verlag.

Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* B**25**, 925–946.