The crystal structure of paramelaconite, Cu_4O_3

M. O'Keeffe[1] AND J.-O. Bovin

Inorganic Chemistry 2, Chemical Centre
P. O. Box 740, S-220 07 Lund, Sweden

Abstract

The structure of paramelaconite, ideal composition Cu_4O_3, has been solved utilizing 113 independent reflections, $R = 0.035$. The space group is $I4_1/amd$; $a = 5.837$, $c = 9.932$ A. The structure contains interpenetrating rods of Cu^+–O (Cu^+ forming two colinear bonds with oxygen) and Cu^{2+}–O (Cu^{2+} forming four bonds to oxygen atoms at the corners of a rectangle). The structure is simply related to those of cuprite and tenorite.

Introduction

Paramelaconite is an oxide of copper intermediate between Cu_2O and CuO. It was first described by Koenig (1891), and more completely by Frondel (1941). Frondel's analysis gave the composition $CuO_{0.884}$. He determined the space group of the crystal to be $I4_1/amd$ but did not resolve the structure. Authentic specimens are rare.[2] However, of the two magnificent examples (those examined by Frondel) from the Copper Queen mine, Bisbee, Arizona, one is in the Smithsonian Institution and one in the American Museum of Natural History. A fragment from the Smithsonian Institution specimen, #112878 (shown on the left in Fig. 1 of Frondel's paper), was kindly made available to us by J. S. White, Associate Curator.

Experimental

A powder pattern of a crushed fragment was taken with a Guinier-Hägg focussing camera, with KCl ($a = 6.2929$ A) as an internal standard. This revealed the presence of some tenorite in addition to lines ascribed to paramelaconite. The paramelaconite lines could be indexed with a tetragonal cell with $a = 5.837$ and $c = 9.932$ A (Table 1). We did not observe the 110 reflection (not allowed in $I4_1/amd$) with $d = 4.027$ A, reported by Frondel (1941); it is possible

that this is a transcription error for $d = 5.027$ close to $d = 5.032$ A calculated for 101.

The chip selected for structure analysis was an irregular tetrahedron bounded approximately by (100), (010), (00$\bar{1}$), and ($\bar{1}\bar{1}3$), and measuring $0.25 \times 0.27 \times 0.17$ mm along a, b and c respectively. Data were collected using an automatic four-circle diffractometer, CAD4 using graphite-monochromatized $MoK\alpha$ radiation ($\lambda = 0.70930$ A) and a take-off angle of 6°. The ω-2θ scan technique was used with $\Delta\omega = 1.1° + 1.0°\tan\theta$. A minimum net count of 3000 for each reflection was attained within the maximum measuring time of 5 min. One octant of reciprocal space (including dependent reflections hkl, khl) out to $\theta = 35°$ was examined. After every 40 measurements three standards were checked. For all three standards during the course of the experiment $R(= \Sigma|I_0 - I_m|/\Sigma I_0) \leq 0.008$ (I_m is the mean of all observations), so no scaling was necessary. Intensities less than three standard deviations (estimated from counting statistics) were rejected as unobserved. The reflections were corrected for polarisation and absorption. The range of transmission factors was 0.16–0.24 ($\mu = 259$ cm^{-1}). The absorption correction was checked by comparing the deviation between dependent reflections (hkl and khl) which fell from 25 percent before correction for absorption to less than 10 percent after correction. 113 independent reflections were used in the subsequent refinement of the structure. The unit-cell dimensions were determined from a least squares refinement of twenty θ-values, ranging from 6.4° to 25°, collected from the single crystal on the automatic diffractometer using $MoK\alpha$ radiation. Crystallographic data are given in Table 2.

---

[1] Permanent address: Chemistry Department, Arizona State University, Tempe, Arizona 85281

[2] We have examined a number of samples purported to be paramelaconite, all of which proved to be aggregates of cuprite and tenorite. However specimens have been reported from Algomah mine, Ontonagon County, Michigan by Williams (1962).

Table 1. Powder data for a mixture of paramelaconite and tenorite

| Present work | | | | | Frondel (1941) | | Tenorite** | |
I/I_1	d(obs)	d(calc)***	h k l		I	d(obs)	I/I_1	d
8	5.014	5.032	1 0 1					
			1 1 0*		vw	4.027		
10	3.151	3.174	1 1 2		vw	3.115		
20	2.929	2.912	2 0 0		w	2.888		
15	2.875	2.880	1 0 3					
12	2.757						12	2.751
51	2.528	2.525	2 1 1				49	2.530
							100	2.523
78	2.508	2.516	2 0 2		vs	2.490		
54	2.475	2.483	0 0 4		w	2.464		
59	2.328						96	2.323
27	2.313						30	2.312
71	2.057	2.064	2 2 0		m	2.050		
14	2.047	2.050	2 1 3					
5	1.900	1.909	3 0 1					
31	1.886	1.891	2 0 4		vw	1.874		
37	1.869						25	1.866
22	1.712						8	1.714
100	1.582	1.587	2 2 4		s	1.575		
34	1.508						20	1.505
95	1.455	1.459	4 0 0		m	1.449		
10	1.450	1.454	3 2 3					
92	1.436	1.440	2 0 6		m	1.430		
17	1.419						12	1.418
36	1.409						15	1.410
39	1.377						19	1.375
17	1.305						7	1.304
24	1.267						6	1.265
85	1.259	1.262	4 2 2				7	1.262
78	1.255	1.258	4 0 4		s	1.251		
22	1.238	1.241	0 0 8		w	1.233		

*   *not allowed in $I4_1/amd$*

**   *Joint Committee of Powder Diffraction Standards, 5-0661*

*** *indexed with the tetragonal unit cell: a=5.837 and c=9.932 Å*

Table 2. Crystallographic data

Space group:	$I4_1/amd$ (no 141)
Unit cell:	a = 5.837(1) Å
	c = 9.932(2) Å
Cell volume:	338 Å^3
Cell content:	4[Cu_4O_3]
Formula weight:	302.18
Density, 25°C:	D_m* = 5.83 g cm^{-3}
	D_m** = 6.04 g cm^{-3}
	D_x = 5.93 g cm^{-3}
μ (Mo$K\alpha$)	259 cm^{-1}

*   *Koenig (1891)*

** *Frondel (1941)*

isotropic temperature factors and a scale factor converged to $R = 0.06$.

On the basis of chemical analysis and measured density, Frondel (1941) proposed a unit-cell content of $Cu_{16}O_{14}$; accordingly, the possibility of partial occupancy by oxygen of positions 4a, 4b, and 8e was investigated. Least-squares refinement led to the 4b sites being empty and the 8e and 4b sites completely occupied, so that unit-cell content is $Cu_{16}O_{12}$ (i.e. Cu_4O_3). The difference between this formula and that determined by analysis must surely be due to the presence of admixed CuO in analyzed samples. The calculated density (Table 2) is bracketed by two experimental values.

A final refinement was carried out with anisotropic thermal vibration factors for the copper atoms, and scattering factors for Cu^{2+}, Cu^+ and O^- were taken from the *International Tables for X-ray Crystallography* (vol. IV, 1974). The secondary extinction coefficient (Coppens and Hamilton, 1970) was also refined. The function minimised was $\Sigma w_i (|F_0| - |F_c|)^2$ with weights $w^{-1} = \delta^2(|F_0|) + (0.004 \cdot |F_0|)^2$. In the last

Solution and refinement of the structure

Systematic absences confirmed the space group $I4_1/amd$. A three-dimensional Patterson synthesis led directly to placing copper atoms in 8c and 8d and oxygen in 4a and 8e: 0 1/4 z etc. with z = 0.12. A preliminary full-matrix least-squares refinement with

Table 3. Atom coordinates and thermal vibration parameters ($\beta_{ij} \times 10^4$)*

		x	y	z	B(Å^2)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	8c	0	0	0	-	66(6)	93(6)	21(2)	0	0	-23(4)
Cu(2)	8d	0	0	1/2	-	55(5)	38(5)	3(1)			1(3)
O(1)	8e	0	1/4	0.1173(9)	0.8(2)						
O(2)	4a	0	1/4	3/8	0.7(3)						

* *Estimated standard errors in parentheses refer to the last digit. The atoms designated are followed by the Wykoff notation for the equipoint of $I4_1/amd$. The form of the anisotropic temperature factor is* $\exp(-\beta_{11} h^2 - \beta_{22} k^2 - \beta_{33} l^2 - 2\beta_{12} hk - 2\beta_{13} hl - 2\beta_{23} kl)$.

cycle all atom parameters changed by less than 0.02 standard deviations. The extinction coefficient was $4.2(6) \cdot 10^2$ and the final agreement indices R_w ($= [\Sigma w_i (|F_o| - |F_c|)^2 / \Sigma w_i |F_o|^2]^{1/2}) = 0.039$, $R = 0.035$ and $S = ([\Sigma w_i (|F_o| - |F_c|)^2 / (m - n)]^{1/2} = 3.9$. The positional and thermal parameters are given in Table 3, and observed and calculated structure amplitudes

compared in Table 4. Distances and bond angles are presented in Table 5.

Discussion of the structure

The chemical formula of paramelaconite is $Cu_2^+ Cu_2^{2+} O_3$. It is clear from the interatomic distances and angles (Table 5) that Cu(1) is cuprous copper

Table 4. Observed and calculated structure amplitudes

h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$
2	0	0	144,13	148,55	4	3	5	13,79	12,76
4	0	0	592,56	607,72	2	1	5	33,07	22,97
6	0	0	40,24	46,23	6	0	6	282,79	283,45
2	2	0	525,07	552,18	1	1	6	30,14	31,79
4	2	0	59,03	64,93	0	2	6	569,03	543,80
6	2	0	271,66	274,65	6	4	6	220,05	222,37
4	4	0	422,34	414,66	2	4	6	388,82	377,70
6	4	0	33,48	34,38	3	5	6	21,66	13,35
8	4	0	202,77	199,51	2	8	6	176,27	181,67
6	6	0	183,34	166,86	1	8	7	26,80	29,08
0	8	0	249,25	244,68	1	4	7	35,59	36,45
2	8	0	24,84	25,80	3	4	7	24,57	22,11
1	8	1	25,70	24,55	5	4	7	30,52	33,44
5	4	1	16,48	16,13	5	2	7	17,01	15,84
3	4	1	24,78	24,26	2	1	7	22,76	15,74
1	4	1	22,83	26,54	0	1	7	44,52	43,68
8	3	1	18,51	23,55	3	0	7	23,92	22,08
3	2	1	16,16	16,32	5	0	7	35,46	36,72
1	2	1	14,94	26,15	6	0	8	32,19	29,48
3	0	1	23,59	25,30	2	0	8	52,99	52,50
1	0	1	30,82	33,24	0	0	8	560,98	545,72
6	0	2	323,73	332,70	3	1	8	14,68	12,85
7	1	2	14,80	13,05	6	2	8	205,88	209,13
3	1	2	35,35	33,09	2	2	8	376,99	360,29
1	1	2	47,23	47,44	6	4	8	25,33	24,47
0	2	2	730,40	726,94	4	4	8	304,87	297,37
4	2	2	462,95	465,59	2	4	8	37,21	37,11
8	2	2	198,62	201,37	0	4	8	401,63	388,58
3	3	2	27,15	27,88	0	8	8	190,40	197,18
6	4	2	254,79	252,63	1	6	9	19,28	18,44
3	5	2	16,68	12,38	3	4	9	22,69	25,18
2	3	3	38,02	34,95	0	3	9	18,46	26,32
6	3	3	27,23	28,96	2	1	9	16,50	17,49
7	2	3	22,39	20,80	6	0	10	228,01	220,23
3	2	3	34,89	34,96	2	0	10	363,82	358,70
2	1	3	37,76	36,66	3	3	10	17,56	24,19
6	1	3	26,09	28,18	6	4	10	182,49	181,11
3	0	3	32,47	31,07	2	4	10	284,06	274,56
1	0	3	41,08	42,35	3	6	11	34,27	34,25
0	0	4	626,44	601,28	2	3	11	40,59	41,61
2	0	4	105,50	102,07	5	2	11	21,82	14,61
8	0	4	167,86	177,20	6	1	11	23,99	27,88
8	2	4	24,32	26,78	2	1	11	34,22	31,63
4	2	4	56,08	56,02	4	0	12	219,14	219,31
2	2	4	653,12	659,19	2	0	12	27,32	29,59
8	4	4	144,01	144,08	0	0	12	265,12	277,90
6	4	4	26,76	30,20	2	2	12	305,79	301,25
4	4	4	291,38	293,18	4	4	12	187,96	178,94
0	4	4	395,57	407,77	2	5	13	23,23	27,52
6	6	4	211,95	208,19	3	4	13	25,16	26,17
4	6	4	29,47	30,19	0	3	13	25,49	28,49
2	6	4	324,30	327,08	1	2	13	18,30	22,61
0	6	4	28,50	37,39	1	0	13	20,09	16,98
1	6	5	20,79	23,58	2	0	14	221,76	238,00
5	6	5	21,54	22,44	0	2	14	223,78	237,83
8	3	5	18,42	16,34	0	3	15	21,77	23,92
					1	0	15	38,35	38,63

Table 5. Interatomic distances (A) and angles (°)

Distances[*]			Angles[*]	
The Cu$^+$-oxygen rod.				
Cu(1) - O(1)	(2x)	1.867(6)	O(1) - Cu(1) - O(1)	180.0
O(1) - O(1)		3.735(11)	Cu(1) - O(1) - Cu(1)	102.8(4)
The Cu^{2+}-oxygen rod.				
Cu(2) - O(2)	(2x)	1.916(1)	O(1) - Cu(2) - O(1)	180.0
Cu(2) - O(1)	(2x)	1.966(6)	O(2) - Cu(2) - O(2)	180.0
O(1) - O(2)	(2x)	2.559(9)	O(1) - Cu(2) - O(2)	97.5(2)
O(1) - O(2)	(2x)	2.920(1)	O(1) - Cu(2) - O(2)	82.5(2)
The O(1) - Cu tetrahedron.				
O(1) - Cu(1)	(2x)	1.867(6)	Cu(1) - O(1) - Cu(1)	102.8(4)
O(1) - Cu(2)	(2x)	1.966(6)	Cu(1) - O(1) - Cu(2)	114.7(1)
Cu(1) - Cu(2)	(2x)	2.919(1)	Cu(2) - O(1) - Cu(2)	95.8(4)
Cu(1) - Cu(2)	(2x)	3.229(1)		
The O(2) - Cu tetrahedron.				
O(2) - Cu(2)	(4x)	1.916(1)	Cu(2) - O(2) - Cu(2)	99.2(1)
Cu(2) - Cu(2)		2.919(1)	Cu(2) - O(2) - Cu(2)	114.8(1)
Cu(2) - Cu(2)		3.229(1)	Cu(2) - O(2) - Cu(2)	99.2(1)

Standard deviations are given in parentheses.
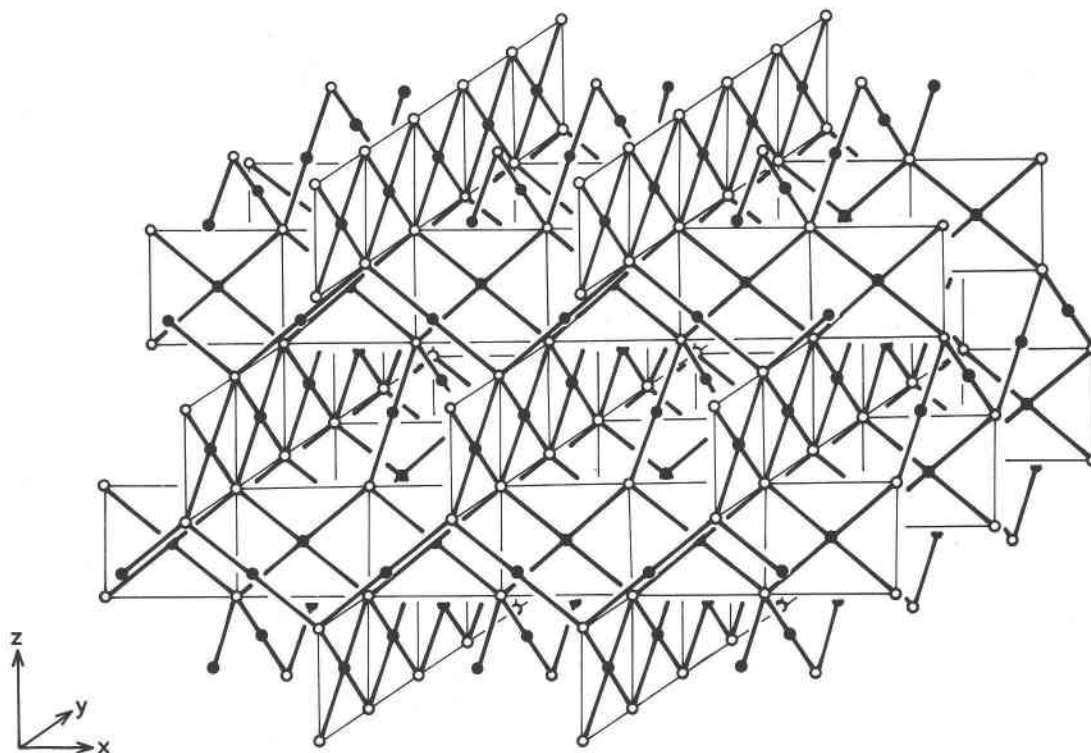
Fig 1. The Cu$_4$O$_3$ structure. Open circles are oxygen atoms and filled circles are copper atoms. See also Fig 3.
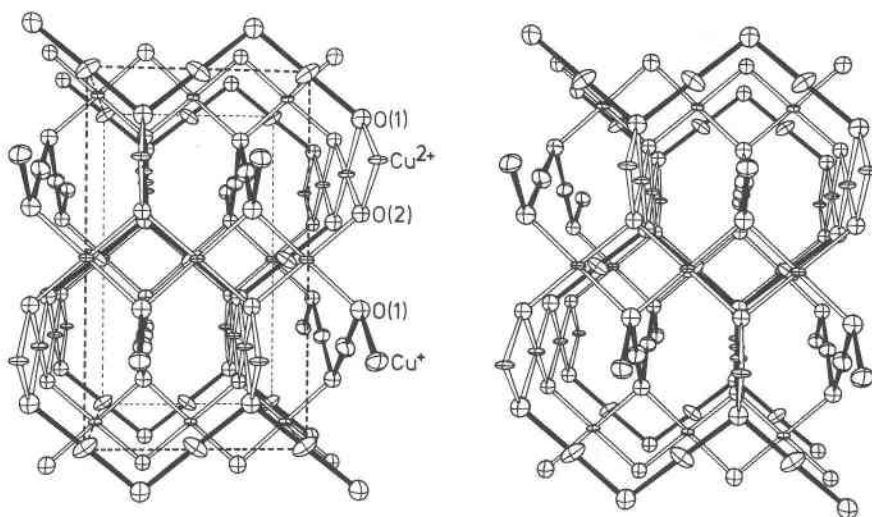
Fig 2. Stereo view down the *a* axis of the structure of paramelaconite, Cu_4O_3.

and Cu(2) is cupric copper. Thus Cu(1) has two O(1) nearest neighbors forming colinear bonds of length 1.87 A, as found in cuprite, Cu_2O (in which the bond length is 1.85 A). Likewise Cu(2), surrounded by four oxygen atoms in a plane (almost at the corners of a square), is clearly Cu^{2+}—the bond lengths [1.92 A(2×), 1.97 A(2×)] and angles being very close to those observed in tenorite, CuO [bond lengths 1.95 A(2×), 1.96 A(2×), Åsbrink and Norrby, 1970]. In fact, the structure of paramelaconite is simply and elegantly related to the structures both of cuprite and of tenorite.

The structure is illustrated in Figures 1 and 2. It is composed of two kinds of rod[3] of atoms running through the structure parallel to [100] and [010]. The two kinds of rod are illustrated in Figure 3, and are (a) zig-zag strings of $O-Cu^+-O-Cu^+$, and (b) strings of $Cu^{2+}O_4$ rectangles joined by sharing opposite edges. The packing of each kind of rod is as in the body-centered tetragonal cylinder packing shown in Figure 4, which also has symmetry $I4_1/amd$ (O'Keeffe and Andersson, 1977).

───────────

[3] We use the term rod in the general sense of a figure with a singular axis but without singular points or planes (Shubnikov and Kopstik, 1974).
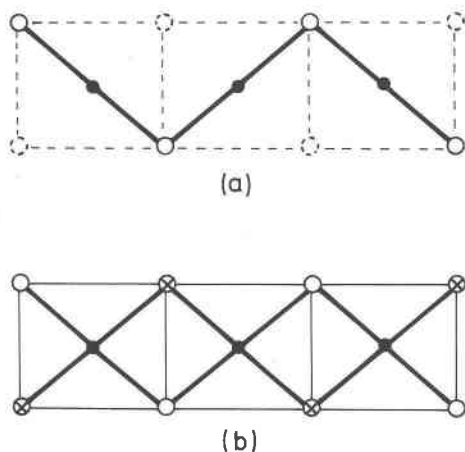

(a)

(b)

Fig 3. (a) The Cu^+-O rod. Filled circles Cu(1), open circles O(1). The broken circles are the $4b$ positions of $I4_1/amd$. (b) The $Cu^{2+}-O$ rod. Filled circles Cu(2), open circles O(1), circled cross O(2).
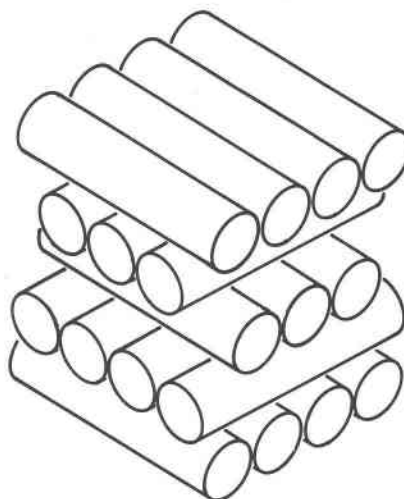

Fig 4. Body-centered tetragonal cylinder packing with symmetry $I4_1/amd$.

Table 6. The structures of Cu_2O, Cu_4O_3, and "CuO" (PdO) referred to a common tetragonal cell

| | c/a | equipoints of $I4_1/amd$ | | | | |
		4a	4b	8c	8d	8e
Cu_2O*	1.414			Cu^+	Cu^+	O, $z = 1/8$
Cu_4O_3	1.702	O		Cu^+	Cu^{2+}	O, $z = 0.117$
"CuO"**	1.754	O	O	Cu^{2+}	Cu^{2+}	O, $z = 1/8$

* symmetry $Pn3m$
** with structure of PdO, symmetry $P4_2/mmc$

Reference to Figure 3(a) shows that addition of oxygen atoms at sites shown by broken circles (corresponding to the $4b$ positions) converts a rod of Cu^+ and oxygen into a rod identical to the rod of Cu^{2+} and oxygen. The structure would then be that of PdO or, with a small topological distortion (Wells, 1976), that of CuO. Conversely, removing the O(2) atoms (in position $4a$) from the rods of Figure 3(b) would convert them into the Cu^+–oxygen rods of Figure 3(a), and the resulting structure is topologically the same as that of Cu_2O [to make it exactly that of Cu_2O would require changing c/a from 1.70 to $\sqrt{2}$ and changing the z parameter of O(1) from 0.117 to 1/8]. Thus the paramelaconite structure can be described either as derived from the CuO (PdO) structure by ordered removal of oxygen atoms or as derived from the Cu_2O structure by ordered insertion of oxygen atoms. These relationships are summarized in Table 6 by referring all three structures to a common tetragonal cell.

The paramelaconite structure is closely related to that of $SrCu_2O_2$ (Teske and Müller-Buschbaum, 1970), which has the same symmetry and similar cell dimensions. The Cu^+–O rods are identical in the two compounds, and Sr replaces the O(2) of paramelaconite.

An alternative and complementary way of describing the structures of the copper oxides is to note that the copper arrangement approximates that of cubic close packing (it is exactly that in the cuprite) and oxygen is in the tetrahedral interstices of that packing. The observed structures represent ways in which oxygen can be inserted so that Cu^+ has two colinear bonds and Cu^{2+} forms four directed bonds to the corners of a rectangle. It is an intriguing topological problem to determine whether other ways of doing this are possible—we think not. This description allows us to understand the magnitude of the axial ratio in paramelaconite ($c/a = 1.702$) as a compromise between that for tetrahedral bonds from oxygen ($c/a = 2$) and square coordination for Cu^{2+} ($c/a = \sqrt{2}$).

References

Äsbrink, S. and L. J. Norrby (1970) A refinement of the crystal structure of copper(II) oxide with a discussion of some exceptional e.s.d.'s Acta Crystallogr., B26, 8–15.
Coppens, P. and W. C. Hamilton (1970) Anisotropic extinction corrections in the Zachariasen approximation. Acta Crystallogr., A26, 71–83.
Frondel, C. (1941) Paramelaconite: a tetragonal oxide of copper. Am. Mineral., 26, 657–672.
Koenig, G. A. (1891) On paramelaconite, and the associated minerals. Proc. Acad. Nat. Sci. Philadelphia, 284.
O'Keeffe, M. and S. Andersson (1977) Rod packings and crystal chemistry. Acta Crystallogr., A33, 914–923.
Shubnikov, A. V. and V. A. Kopstik (1974) Symmetry in Science and Art. Plenum Press, New York.
Teske, C. L. and H. Müller-Buschbaum (1970) Zur Kenntnis von $SrCu_2O_2$. Z. Anorg. Allgem. Chem., 379, 113–124.
Wells, A. F. (1976) Structural Inorganic Chemistry, 4th ed. Oxford University Press.
Williams, S. A. (1962) Paramelaconite and associated minerals from the Algomah mine, Ontonagon County, Michigan. Am. Mineral. 47, 778–9.