Powder Diffraction Studies of Cu$_2$WO$_4$

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The crystal structure of copper(I) tungstate, Cu$_2$WO$_4$, has been investigated by X-ray and neutron powder diffraction methods. The cell dimensions are $a = 7.914$, $b = 8.205$, $c = 5.8578$ Å, $\alpha = 96.45$, $\beta = 93.97$ and $\gamma = 110.36°$. The structure has $P1$ symmetry, but only an approximate structure determination in space group $P\bar{1}$ could be made. The structure is built up of layers of WO$_6$ octahedra sharing edges and corners. The layers are held together by copper atoms.

Copper(I) tungstate, Cu$_2$WO$_4$, first synthesized by Haas and Kordes,[1] has been prepared from stoichiometric amounts of Cu, CuO and WO$_3$ under vacuum in a closed silica tube by the reaction

$$Cu + CuO + WO_3 \rightarrow Cu_2WO_4.$$

X-ray powder diffraction photographs of the reaction product were taken with a subtraction-geometry Guinier-Hägg camera. The diffraction pattern could not be indexed for any monoclinic or higher symmetry cell. The phase was therefore assumed to be triclinic and the unit cell volume was estimated from the relation[2]

$$V \approx 13.39 \cdot (d_{20})^3$$

where d_{20} is the interplanar spacing for the 20th observed diffraction line in the pattern.

From the value $d_{20} = 2.8432$ Å (see Table 1), the cell volume was estimated to be 308 Å^3. Since the true unit cell volume should not deviate more than 30 per cent from this value,[2] the upper limit was set at 400 Å^3 in the trial-and-error indexing

program TREOR.[3] Since the diffraction pattern was very dense, the normal procedure of adjusting the low-angle line positions by reference to higher-order lines could not be used. The first 25 lines could be completely indexed, however, with a De Wolff figure of merit[4] $M_{20} = 38$, on the basis of a triclinic cell: $a = 5.858$, $b = 7.912$, $c = 8.203$ Å, $\alpha = 69.64$, $\beta = 83.58$ and $\gamma = 94.01°$. A program for transformation to reduced and conventional unit cells (written by P.-E.W. and M.W.) was used to find the unit cell (data in Table 2). Since this cell is fairly small, $V = 351.9$ Å^3, we decided to try to determine the structure from powder diffraction data. We also considered it to be an interesting test case for the use of modern powder diffraction methods in structural studies of triclinic phases.

Structure determination

In order to compare powder diffraction data from Guinier-Hägg (GH) photographs measured with an LS18[5] line film scanner with powder diffractometer (PD) data obtained from a diffractometer using strictly monochromatized Cu$K\alpha_1$ radiation, data sets were collected by both techniques. GH data was collected at the Arrhenius Laboratory, Stockholm, and PD data was obtained from a *Compagnie Général de Radiologie* (C.G.R.) dif-

Table 1. Guinier-Hägg X-ray powder diffraction data for Cu$_2$WO$_4$.

(hkl)	2θ$_o$(°)	2θ$_c$(°)	d$_o$(Å)	10³I$_o$/I$_{max}$	(hkl)	2θ$_o$(°)	2θ$_c$(°)	d$_o$(Å)	10³I$_o$/I$_{max}$
(010)	11.587	11.619	7.6308	170	(1̄22)	40.004	40.002	2.2520	190
(110)	11.969	12.001	7.3883	19	(2̄1̄2)	40.419	40.418	2.2298	22
(1̄10)	13.354	13.384	6.6248	347	(2̄2̄2)	40.999	40.984	2.1996	58
(001)	15.291	15.314	5.7899	313	(022)	41.879	41.881	2.1554	246
(01̄1)	17.832	17.849	4.9702	332	(310)	42.517	42.503	2.1245	17
(1̄01)	18.337	18.356	4.8342	374	(3̄11)	43.212	43.194	2.0919	76
(110)	19.521	19.531	4.5438	19	(3̄3̄1)	43.611	43.596	2.0737	143
[(101)		20.584			(03̄2)	43.894	43.885	2.0610	55
(011)	20.600	20.588	4.3081	120	(3̄12)	44.807	44.806	2.0211	66
[(1̄11)		20.618			(2̄40)	45.090	45.073	2.0091	50
(2̄10)	22.712	22.711	3.9121	210	(2̄32)	45.698	45.690	1.9838	41
(020)	23.362	23.361	3.8047	204	(4̄10)	46.351	46.324	1.9573	88
(02̄1)	26.075	26.070	3.4146	130	(2̄22)	46.757	46.748	1.9413	22
[(111)	26.821	26.797	3.3213	404	(1̄1̄3)	48.238	48.245	1.8851	55
[(2̄11)		26.868			(31̄2)	48.453	48.455	1.8772	43
(2̄20)	26.960	26.955	3.3045	109	(3̄40)	48.884	48.876	1.8616	78
(2̄01)	27.124	27.123	3.2849	28	(3̄1̄2)	49.470	49.472	1.8409	195
[(21̄1)		28.132			(103)	50.256	50.271	1.8140	39
[(1̄21)	28.142	28.141	3.1683	362	(230)	50.449	50.431	1.8075	273
(021)	29.913	29.912	2.9846	670	(1̄23)	50.596	50.598	1.8026	42
(201)	30.234	30.218	2.9537	114	(2̄13)	51.798	51.816	1.7636	22
(210)	30.494	30.491	2.9291	607	(3̄41)	52.402	52.400	1.7447	108
[(22̄1)	30.842	30.837	2.8968	1000	(2̄42)	53.047	53.044	1.7249	67
[(002)		30.910			(401)	53.945	53.922	1.6983	71
[(01̄2)	31.439	31.437	2.8432	565	(113)	54.575	54.559	1.6802	303
[(2̄21)		31.451			(231)	55.619	55.602	1.6511	134
(1̄21)	31.539	31.515	2.8344	42	(132)	56.918	56.910	1.6165	97
(1̄02)	31.882	31.888	2.8047	701	(3̄13)	57.059	57.076	1.6128	80
(2̄11)	32.120	32.111	2.7845	246	(2̄33)	57.876	57.883	1.5920	105
(1̄30)	32.948	32.936	2.7163	96	(2̄42)	58.178	58.186	1.5844	26
(11̄2)	33.540	33.530	2.6697	73	(1̄42)	58.740	58.734	1.5706	245
(1̄1̄2)	34.002	33.991	2.6345	43	(141)	58.921	58.933	1.5662	56
[(3̄10)		34.068			(4̄32)	59.899	59.901	1.5429	83
[(1̄12)	34.090	34.102	2.6279	25	(3̄1̄3)	60.021	60.027	1.5401	63
(102)	34.612	34.597	2.5895	35	(5̄11)	60.156	60.126	1.5370	62
[(012)	34.757	34.740	2.5790	42	(05̄1)	60.558	60.561	1.5277	183
[(131)		34.826			(050)	60.824	60.812	1.5217	34
(121)	36.099	36.092	2.4861	31	(213)	61.322	61.336	1.5107	21
(300)	36.544	36.554	2.4569	698	(2̄41)	61.803	61.830	1.4999	134
(2̄02)	37.205	37.206	2.4147	42	(5̄21)	61.848	61.877	1.4989	106
(1̄31)	38.133	38.127	2.3581	463	(1̄33)	62.082	62.072	1.4938	79
(3̄21)	38.686	38.679	2.3256	362	(2̄52)	62.419	62.427	1.4866	91
(2̄31)	39.387	39.364	2.2858	79	(5̄01)	63.227	63.224	1.4695	59
(112)	39.497	39.489	2.2797	66	(3̄33)	63.336	63.352	1.4672	98
(220)	39.684	39.660	2.2694	88	(04̄3)	63.440	63.451	1.4651	114

fractometer set-up at *Laboratoire de Crystallochimie, Université de Rennes.*

At a preliminary stage of the investigation we believed that the structure could be solved and completely refined in space group P1̄. Unfortunately, as we later found out, the structure could not be rigorously refined in P1̄, and refinements in P1 using powder data failed because the number of parameters was too large.
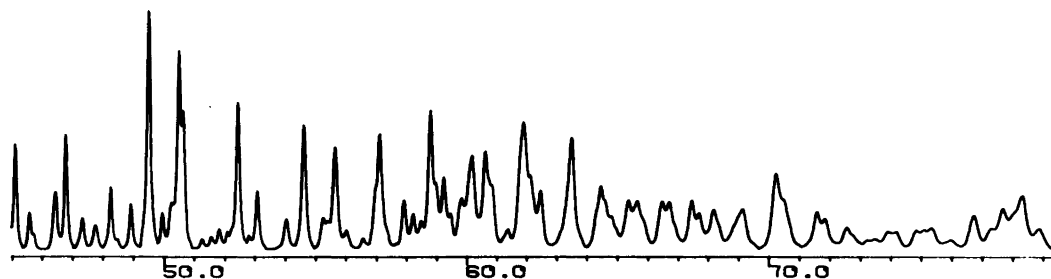
The GH data were used to determine the ap-
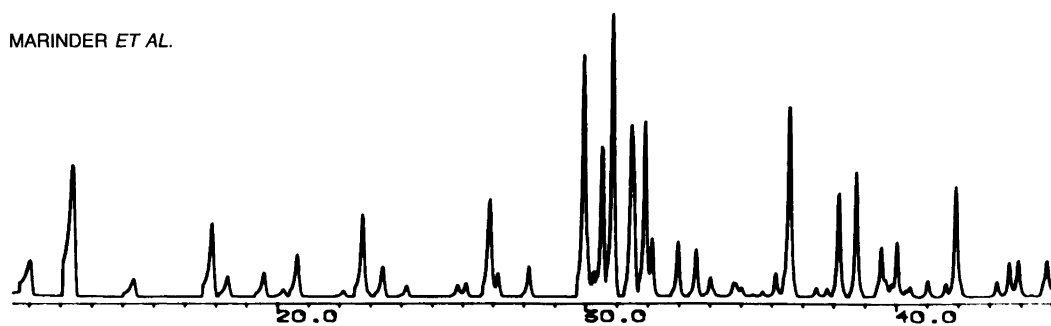
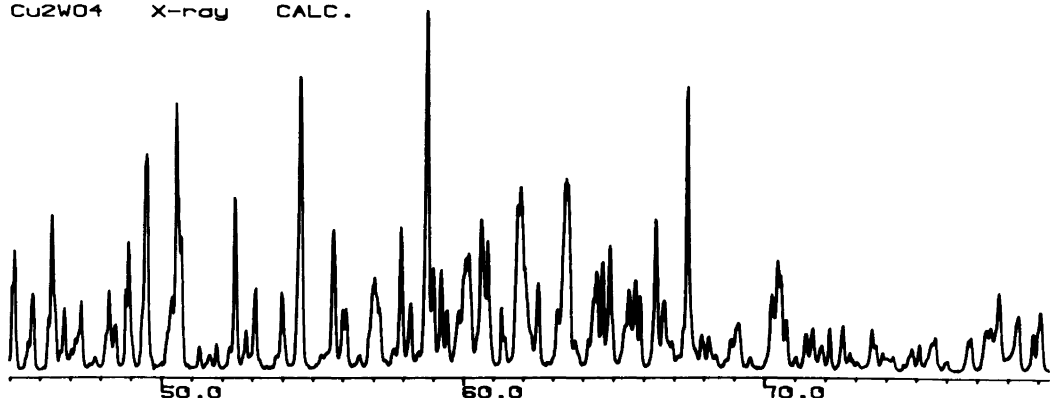Cu2WO4   X-ray   CALC.
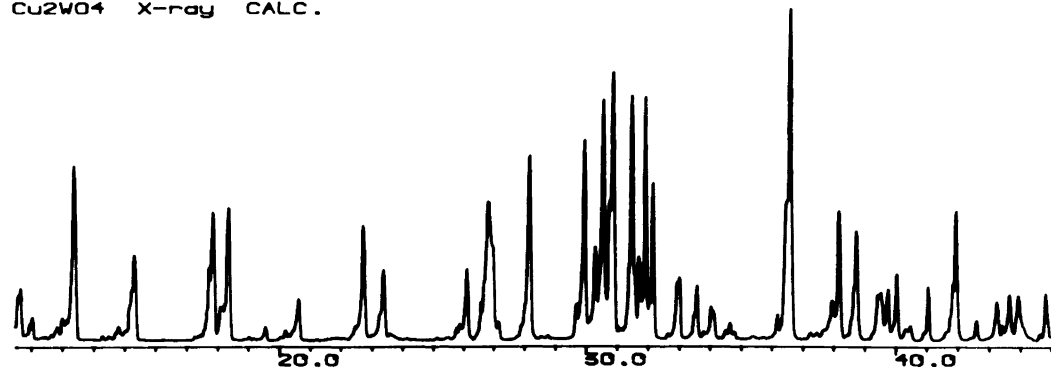
Cu2WO4   X-ray   OBS.

Cu2WO4   X-ray   CALC.

Cu2WO4   X-ray   OBS.

Fig. 1. Observed and calculated X-ray diffraction intensities for Cu_2WO_4 as a function of 2θ. Powder diffractometer data. Calculated data in $P\bar{1}$.

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proximate arrangement of the metal atoms in the structure, since the line half-widths in question were less than the corresponding line widths for the PD data. A Patterson function, computed from relatively well-resolved reflections, was used to derive the tungsten and the majority of the copper positions in space group $P\bar{1}$.

The θ dependence of $H(2\theta)$ (= Full Width at Half Maximum, FWHM) could be written as

$$H^2(2\theta) = 0.1700 \cdot \tan^2\theta - 0.1324 \cdot \tan\theta + 0.0276$$

for the GH data and as

$$H^2(2\theta) = 0.3340 \cdot \tan^2\theta - 0.2265 \cdot \tan\theta + 0.0487$$

for the PD data. Thus the PD lines were almost twice as broad as the GH lines. It should be noted, however, that half-widths for the PD data are strongly dependent on the slits used. The half-widths may therefore be considerably re-duced at the cost of longer measuring times. Fur-thermore, no significant differences were found between the quality of the Rietveld refinements with GH and with PD data. The better defined shapes of the PD peaks may well compensate for their larger half-widths. Since only the metal atom positions could be refined in space group $P\bar{1}$, the two data sets could not be compared accurately. Trial refinements of the tungsten posi-tions in space group $P1$ revealed small, but sig-nificant deviations from centrosymmetry. Since the number of metal atom coordinates to be re-fined increases from 18 to 33 on reduction of the symmetry, and since the deviation from centro-symmetry is small, it was impossible to make con-vergent refinements in $P1$, regardless of the data set used, even by introducing constraints. Fur-thermore, oxygen atom positions could only be deduced from geometrical considerations, be-cause of the large difference in scattering power between tungsten and oxygen.
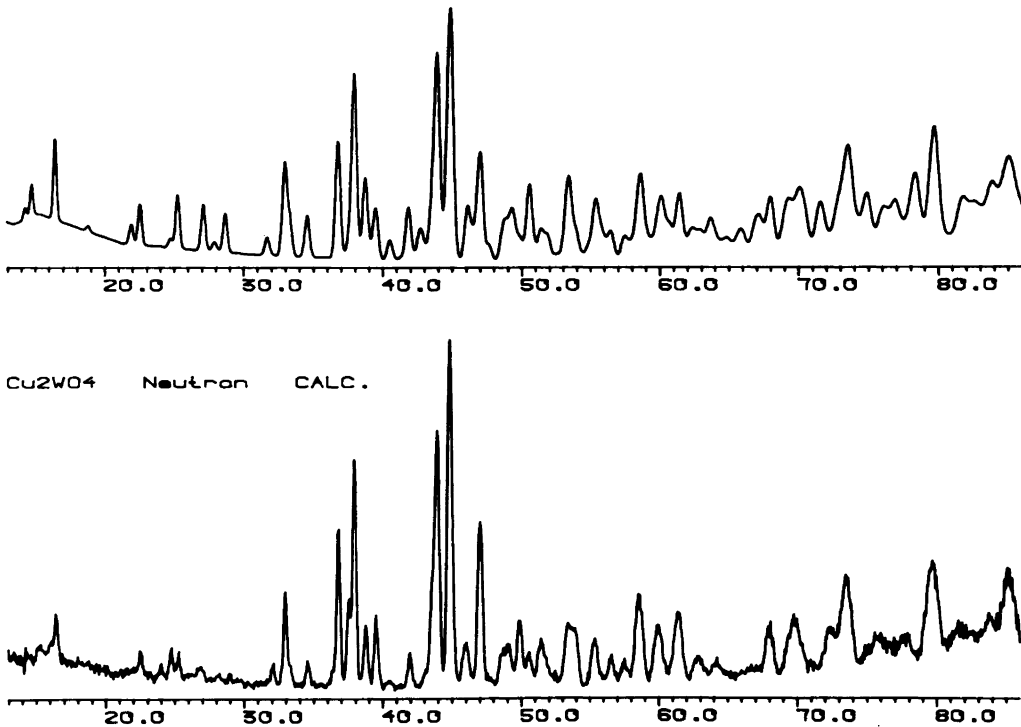

Fig. 2. Observed and calculated neutron diffraction intensities for Cu_2WO_4 as a function of 2θ. Calculated data in $P\bar{1}$.
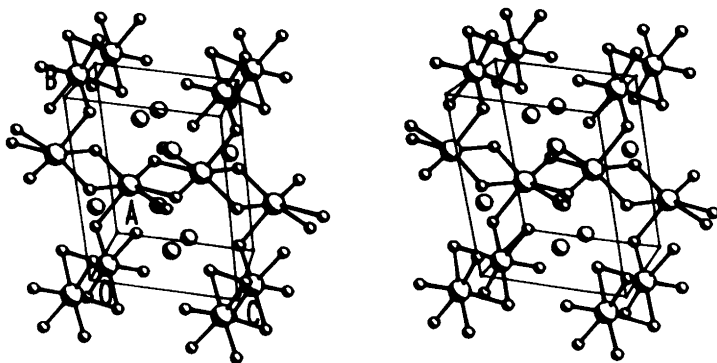
Fig. 3. Stereo view of Cu_2WO_4 (approximately) along *a*. Large spheres = W, medium size spheres = Cu and small spheres = O.

In order to verify the assumed oxygen atom positions by a Rietveld refinement, a neutron diffraction diagram was recorded with the OPUS III diffractometer at the JEEP II reactor, Kjeller, Norway. The instrument has a multi-detector system consisting of 5 He^3 detectors spaced $10°$ apart. The neutron wavelength was 1.877 Å. The neutron scattering amplitudes, $b_{Cu} = 0.76 \cdot 10^{-2}$, $b_W = 0.48 \cdot 10^{-2}$ and $b_O = 0.58 \cdot 10^{-2}$ pm, were taken from a compilation by Bacon.[6]

In a cyclic procedure, the metal coordinates were refined with the X-ray data, and the oxygen positions with the neutron data. The *R*-values reported in Table 2 were obtained from the final refinement cycles in which all parameter shifts were less than 20 % of the corresponding standard deviations. The high *R*-values, especially for the X-ray data, are partly due to the fact that the space group *P*1̄ was used. Observed and calculated diffraction patterns for the X-ray (PD) and neutron data, respectively, are shown in Figs. 1 and 2. Considering the agreement between observed and calculated patterns – only very few lines show drastic differences between observed and calculated intensities – it may be concluded that the deviation of the structure from centrosymmetry is small. The general picture of the structure derived in space group *P*1̄ (Fig. 3) should therefore be an acceptable model. The coordinates obtained are listed in Table 3.

Discussion

The structure is built up of layers, parallel to the (11̄0) planes, of WO_6 octahedra sharing edges and corners. The layers are held together by the copper atoms. A chain of edge-sharing octahedra

parallel to the *c* axis passes through the centre of the unit cell. Edge-sharing WO_6 doublets connect the chains by corner-sharing. The vectors between the tungsten atoms in the doublets are approximately parallel to the *a* axis (see Fig. 3). The structure contains an unusual kind of network of WO_6 octahedra which it was not possible to analyse accurately, however, since it could only be centrosymmetrically refined. Nevertheless, it seems likely that the WO_6 doublet in the *a* axis direction is relatively well determined, whereas the description of the WO_6 octahedra in the chain is more strongly affected by the incorrect space

Table 2. Crystal data.

$a = 7.914(1)$ Å	$\alpha = 96.45(2)°$
$b = 8.205(2)$ Å	$\beta = 93.97(2)°$
$c = 5.8578(8)$ Å	$\gamma = 110.36(2)°$
$M_{20} = 36$	
$F_{30} = 53(0.012,47)$	
$V = 351.9$ Å^3 $V_{est} = 308$ Å^3	
$D_x = 7.076$ g cm^{-3}	
$F_w = 374.9$ $Z = 4$	

Rietveld refinements in space group *P*1̄

	X-ray data(PD)	Neutron data
2θ-step/°	0.02	0.05
2θ-max/°	79	86
λ/Å	1.5405986	1.877
Refl.	420	283
Param.	25	31
R_P	49	34
R_{wp}	56	34
R_{Bragg}	34	14
R_F	16.2	6.6

Table 3. Fractional atomic coordinates in Cu_2WO_4, with e.s.d.'s (as calculated from Rietveld refinements in space group $P\bar{1}$) in parentheses.

Atom	x	y	z
W1	0.520(2)	0.434(2)	0.241(3)
W2	0.219(2)	0.031(2)	0.081(3)
Cu1	0.115(5)	0.200(5)	0.561(7)
Cu2	0.526(4)	0.169(4)	0.617(6)
Cu3	0.073(5)	0.407(5)	0.094(6)
Cu4	0.861(4)	0.243(4)	0.361(5)
O1	0.284(4)	0.440(3)	0.013(4)
O2	0.592(4)	0.301(3)	0.470(5)
O3	0.440(4)	0.186(4)	0.982(6)
O4	0.650(4)	0.558(4)	0.412(4)
O5	0.055(4)	0.132(4)	0.821(5)
O6	0.326(4)	0.988(4)	0.308(5)
O7	0.220(3)	0.243(3)	0.314(5)
O8	0.228(4)	0.819(3)	0.904(5)

group symmetry. The centrosymmetrically re-fined WO_6 doublet converges to rather regular octahedra with W−O bond lengths ranging from 1.66 to 2.34 Å and 12 bond angles, O−W−O, va-rying between 83 and 103°. The corresponding variation in distances is 1.42 to 2.53 Å, and in angles 73 to 134°, for the WO_6 octahedra in the chain. In $Li_2W_2O_7$,[7] the W−O bond lengths vary from 1.74 to 2.30 Å, in fairly good agreement with the WO_6 doublet data for the present struc-ture. A found W−O bond length of 1.42 Å is probably much too small to be accurate.

The W···W distances found between edge-sharing octahedra are 3.17(2) and 3.19(3) Å in the chain and 3.37(2) Å in the doublet. Three Cu···Cu distances of less than 2.8 Å were found in the structure, namely 2.42(5), 2.51(5) and 2.51(7) Å. These values should be treated with caution. The copper atoms are also surrounded by four oxygen atoms within a distance of 3.0 Å. No regular coordination squares or tetrahedra have been identified, however.

We have attempted to refine the structure with strong constraints placed on the metal−oxygen distances, using the X-ray Rietveld system (XRS-82) developed by Baerlocher.[9] Refinements of this type failed to yield acceptable models for the copper coordination, however.

An error in the refinement program used (DBW 2.9[8]), which resulted in too small Bragg R-values unless the background was subtracted prior to the refinements, had to be corrected. Some confusingly small Bragg R-values, probably due to this error, have been reported previously in the literature.

References

1. Haas, H. and Kordes, E. *Z. Kristallogr. 129* (1969) 252.
2. Smith, G. S. *J. Appl. Crystallogr. 10* (1977) 252.
3. Werner, P.-E., Eriksson, L. and Westdahl, M. *J. Appl. Crystallogr. 18* (1985) 367.
4. De Wolff, P. M. *J. Appl. Crystallogr. 1* (1968) 108.
5. Johansson, K.-E., Palm, T. and Werner, P.-E. *J. Phys. E 13* (1980) 1289.
6. Bacon, G. E. In: Yelon, W. B., Ed., *Neutron Diffraction Newsletter,* Columbia 1977.
7. Okada, K., Morikawa, H., Marumo, F. and Iwai, S. *Acta Crystallogr., Sect. B 31* (1975) 1451.
8. Wiles, D. B. and Young, R. A. *J. Appl. Crystallogr. 14* (1981) 149.
9. Baerlocher, Ch. *The X-ray Rietveld System,* Institute für Kristallographie und Petrographie, ETH, Zürich 1982.