

CHAPTER 4

DETERMINATION OF THE STRUCTURE

The CoWO_4 compound is composed of cobalt, tungsten and oxygen which atomic numbers are 27, 74 and 8 respectively. Since the atomic number of tungsten is much larger than those of cobalt and oxygen, the structure can be determined by heavy atom method.

Numerical computations were made on a CDC 3100 computer. All programs are written in FORTRAN IV*. The details of the programs used are listed in Table 4.1. Computations with these programs were carried out at the Bangkok Data Center Co. Ltd. .

Table 4.1 Programs used in performing the crystallographic calculations on a CDC 3100 computer.

Program	Calculation	Authors
FFCRL	Film factors	R. Liminga, Institute of Chemistry, University of Uppsala, Uppsala, Sweden.

* The programs were obtained from Institute of Chemistry, University of Uppsala, Sweden. They were modified to use with CDC 3100 computer at Bangkok Data Center Co., Ltd. by R. Liminga and Crystallography Group, Faculty of Science, Chulalongkorn University.

Table 4.1 (continued)

Program	Calculation	Authors
LPARL	Lorentz-polarization and absorption corrections for cylindrical or spherical crystals	Idem.
ABSOT	Lorentz-polarization and absorption corrections for crystals of other shapes	J.O. Thomas, Institute of Chemistry, University of Uppsala, Sweden. Original version by P. Coppens, L. Leiserowitz and D. Rabinovich.
XSFRL	Interpolation of the X-ray scattering factors	R. Liminga, Institute of Chemistry, University of Uppsala, Sweden.
SFCRL	Structure factor calculations. The temperature factor may be isotropic and/or anisotropic. The anomalous dispersion correction terms may be included.	Idem.
EXPRL	Expansion of reflection data for Fourier summations	Idem.
FORRE	Fourier series summations	Idem.

Table 4.1 (continued)

Program	Calculation	Authors
LSQRL	Full matrix least squares refinements	Idem. Based on the program UPALS by J-O Lundgren.
DISTAN	Calculation of interatomic distances and angles	Idem.

4.1 Intensity data reduction

From two sets of Weissenberg intensity data of b and c rotation axes, the FFCRL and LPARL programs were applied to each set separately. The observed structure factor amplitudes were obtained, 458 reflections of hnl , $hn\bar{l}$, $n = 0$ to 2 and 92 reflections of $hk0$. The observed $\bar{h}nl$ reflections were changed to $hn\bar{l}$ by symmetry $2/m$, otherwise the indices will be changed to $hn\bar{l}$ by the program EXPRL. The linear absorption coefficient of $CoWO_4$ for MoK α radiation is 526 cm^{-1} . The values of the absorption correction factors, A^* , were taken from the International Table vol. II p.295. They are listed in Table 4.2.

Table 4.2(a) The absorption correction factors, A^* , for b rotation axis.

layer	radius, r $\times 10^3$ cm.	μr	A^* for Bragg's angle				
			0°	22.5°	45°	67.5°	90°
0	1.66	0.87	4.14	3.96	3.53	3.17	3.03
1	1.66	0.87	4.14	3.96	3.53	3.17	3.03
2	1.67	0.88	4.20	4.01	3.57	3.20	3.05

Table 4.2(b) The absorption correction factors, A^* , for c rotation axis.

layer	radius, r $\times 10^3$ cm.	μr	A^* for Bragg's angle				
			0°	22.5°	45°	67.5°	90°
0	0.89	0.47	2.19	2.17	2.09	2.01	1.98

The hnl , $hn\bar{l}$ with $n = 0$ to 2 reflections were used for the Patterson function and F_0 synthesis. For least squares refinements, the $h0l$ and $h0\bar{l}$ reflections corrected by ABSOT program for Lorentz-polarization and absorption factors were used together with $hk0$ data.

Before proceeding with the structure factor calculations by SFCRL program, the X-ray scattering factors must be interpolated by XSFRL program. Atomic scattering factors were taken from Acta Cryst., 17, 1041 - 1042 (1964)., those for tungsten and cobalt atoms were corrected for anomalous dispersion, taking the anomalous dispersion terms from Acta Cryst., 18, 20 (1965).

4.2 Determination of the heavy atom by using Patterson function

Since CoWO_4 crystallizes in monoclinic system, space group $P2/c$, a unit cell consisted of two atoms of tungsten, two cobalt atoms and eight oxygen atoms. It is impossible to locate tungsten and cobalt atoms in 4(g) general positions (Table 4.3). It is also impossible to locate them in special positions 2(a), 2(b), 2(c) and 2(d) because these positions require special condition $hkl : l = 2n$ which does not occur in this case. However, they may be located in special positions 2(f) or 2(e) which need the same conditions as general positions.

The equivalent positions for special position 2(f) are $\pm (\frac{1}{2}, y, \frac{1}{4})$ and for special position 2(e) are $\pm (0, y, \frac{1}{4})$. The Harker vectors are shown in Table 4.4. In this case the heavy atom vectors must be located in the Harker section $P(0vw)$.

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Table 4.3 The space group $P2/c$ (16).

Number of positions	Wyckoff notation	point symmetry	Coordinates of equivalent positions	Conditions limiting possible reflections
4	g	1	$x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{x}, y, \frac{1}{2} - z;$ $x, \bar{y}, \frac{1}{2} + z$	General hkl : no conditions $h0l$: $l = 2n$ $0k0$: no conditions Special: as above, plus
2	f	2	$\frac{1}{2}, y, \frac{1}{4}; \frac{1}{2}, \bar{y}, \frac{3}{4}$	no extra conditions hkl : $l = 2n$
2	e	2	$0, y, \frac{1}{4}; 0, \bar{y}, \frac{3}{4}$	
2	d	$\bar{1}$	$\frac{1}{2}, 0, 0; \frac{1}{2}, 0, \frac{1}{2}$	
2	c	$\bar{1}$	$0, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}$	
2	b	$\bar{1}$	$\frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	
2	a	$\bar{1}$	$0, 0, 0; 0, 0, \frac{1}{2}$	

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Table 4.4(a) The Harker vectors for special position 2(e).

special position 2(e)	Harker vectors	
$0, y, \frac{1}{4}$	$0, 0, 0$	$0, -2y, \frac{1}{2}$
$0, -y, \frac{3}{4}$	$0, 2y, -\frac{1}{2}$	$0, 0, 0$

Table 4.4(b) The Harker vectors for special position 2(f).

special position 2(f)	Harker vectors	
$\frac{1}{2}, y, \frac{1}{4}$	$0, 0, 0$	$0, -2y, \frac{1}{2}$
$\frac{1}{2}, -y, \frac{3}{4}$	$0, 2y, -\frac{1}{2}$	$0, 0, 0$

The Patterson section $P(0vw)$ was evaluated by EXPRL and FORRL programs using only the reflections of hnl and $h\bar{n}l$, $n = 0$ to 2. The calculation was performed at section $u = 0$, $v = 0-0.5$ and $w = 0-0.5$. The Patterson map is shown in Fig.4.1.

According to the program, the height of the origin peak is normalized to 999, the expected peak heights for the various Patterson maxima can be approximately determined. The Patterson's peak height maxima for a pair of atoms are proportional to the products of the atomic numbers of the atoms they join. The approximated peak height maxima in the Patterson map between two atoms are listed in Table 4.5.

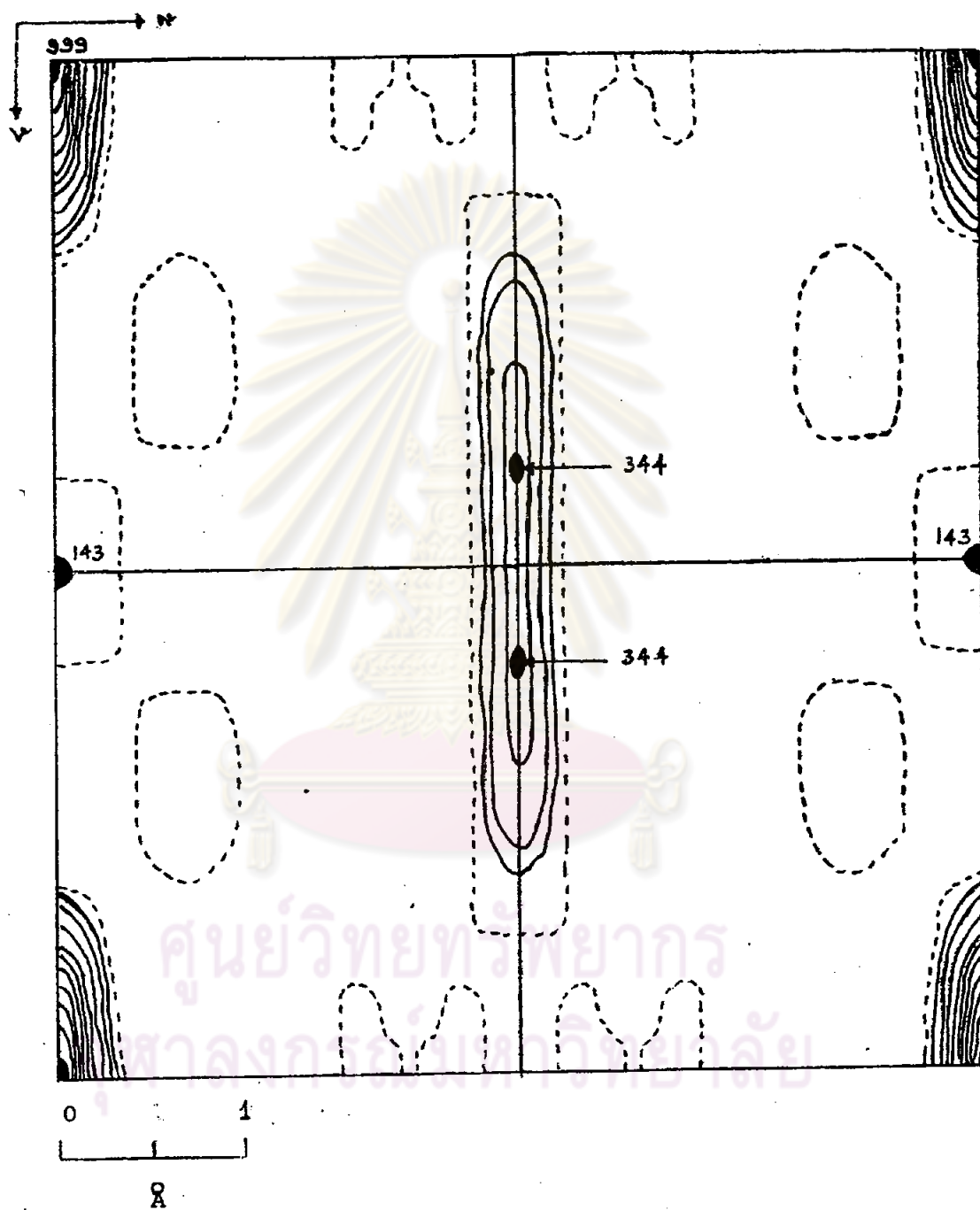


Fig. 4.1 The Patterson section $P(Ovw)$ of $CoWO_4$.

Table 4.5 The approximated peak height maxima in Patterson map of CoWO_4 .

Type of atoms	The approximated peak height maxima
origin peak	999
W-W	423
W-Co	154
W-O	46
Co-Co	56
Co-O	17
O-O	5

From the Patterson map, there was only one peak that should correspond to tungsten-tungsten peak. This was the peak of height 344 and coordinate $(0, 0.40, \frac{1}{2})$. If we generated by symmetry, there was also a peak at $(0, 0.40, -\frac{1}{2})$ which corresponded to tungsten-tungsten peak. Therefore,

$$\begin{aligned} 2y &= 0.40 \\ y &= 0.20. \end{aligned}$$

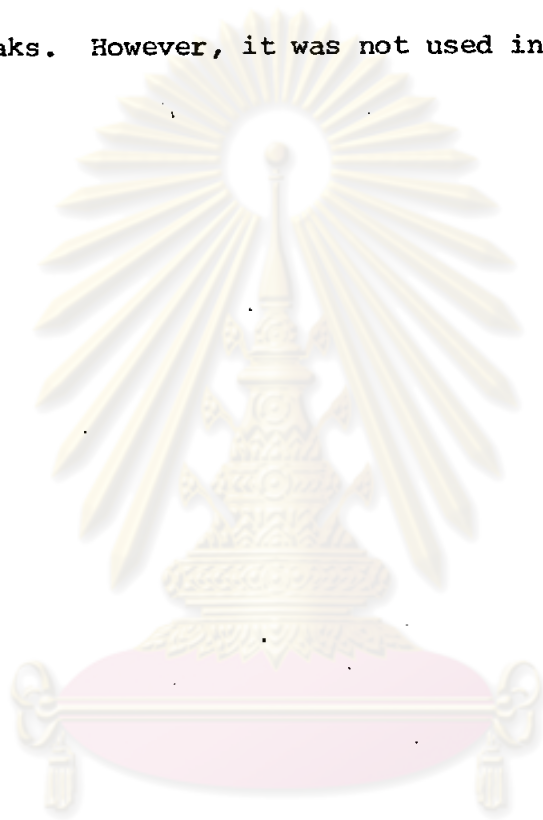
Atomic coordinates of tungsten atom should be at position

$$\begin{aligned} 2(e) &= \pm (0, 0.20, 0.25), \text{ or} \\ 2(f) &= \pm (0.5, 0.20, 0.25) \end{aligned}$$

The 2(e) position was arbitrarily chosen. Therefore, the co-

ordinates of tungsten atoms obtained from the Patterson map were $\pm(0, 0.20, 0.25)$. Hence the cobalt atoms should be located in 2(f) position, i.e. at $\pm(\frac{1}{2}, y, 0.25)$.

There was also a peak of 143 height at $(0, 0.5, 0)$ which might be the $O_{\text{I}}-O_{\text{II}}$ peaks. However, it was not used in the calculation.



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4.3 Determination of other atoms by the F_o synthesis

Fourier calculations using the observed structure factor amplitudes with the calculated phases as the coefficients are called the F_o synthesis. This can be expressed in the form

$$\rho_o(xyz) = \frac{1}{V} \sum_{hkl} A_{oc} \cos 2\pi(hx+ky+lz) + \frac{1}{V} \sum_{hkl} B_{oc} \sin 2\pi(hx+ky+lz) \quad \dots\dots\dots 4.1$$

$$\text{where } \begin{cases} A_{oc}(hkl) = |F_o(hkl)| \cos \alpha_c(hkl) \\ B_{oc}(hkl) = |F_o(hkl)| \sin \alpha_c(hkl) \end{cases}$$

$$\begin{cases} \cos \alpha_c(hkl) = A_c(hkl) / |F_c(hkl)| \\ \sin \alpha_c(hkl) = B_c(hkl) / |F_c(hkl)| \end{cases}$$

$$\begin{cases} A_c(hkl) = \sum_n f_n \cos 2\pi(hx_n+ky_n+lz_n) \\ B_c(hkl) = \sum_n f_n \sin 2\pi(hx_n+ky_n+lz_n) \end{cases}$$

$$|F_c(hkl)| = \sqrt{A_c^2(hkl) + B_c^2(hkl)}$$

Since the CoWO_4 crystal has a center of symmetry, eq. 4.1 gives

$B_c = 0$ and

$$\rho_o(xyz) = \frac{1}{V} \sum_{hkl} A_{oc} \cos 2\pi(hx+ky+lz) \quad \dots\dots\dots 4.2$$

The sequence of finding the positions of other atoms by F_o synthesis are as follows:

1. The structure factors F_c were calculated by program SFCRL using only the positions of tungsten atoms in the calculation. The individual temperature factor was assigned to be 1.0. The scale factors for each layer were 1.0. The first structure factor calculation yielded the R value of 0.42.

2. The F_0 synthesis was then performed by EXPRL and FORRL programs and taking the phases from calculated structure factor based only on the positions of two tungsten atoms. Since the cobalt atoms should be located in the special position 2(f), the electron density section on (001) was performed at $z = 0.25$. The F_0 synthesis was prepared only in one asymmetric unit which was one-fourth of the cell volume, i.e. $x = 0-0.5$, $y = 0-1.0$. This map is shown in Fig. 4.2.

The maximum electron density is proportional to the atomic number of the atom. For CoWO_4 the atomic number 74 corresponds to peak of height 999, therefore the atomic number 27 and 8 will approximately correspond to peaks of height 365 and 108 respectively.

From the F_0 map, better coordinates of tungsten atoms and the two cobalt atoms were obtained. The shifted atomic positions were determined by the Booth's method.

Table 4.6 $\Delta\rho$ as a function of x coordinate in the Booth's method.

x	0	1	2
$\Delta\rho$	0	ρ_1	ρ_2

$$\rho_1 \geq \rho_2 \geq 0$$

From Table 4.6 the highest peak obtained from the electron density map is at the point $x = 1$. $\Delta\rho$ is the difference between electron density of each point and that of the lowest point, i.e. at

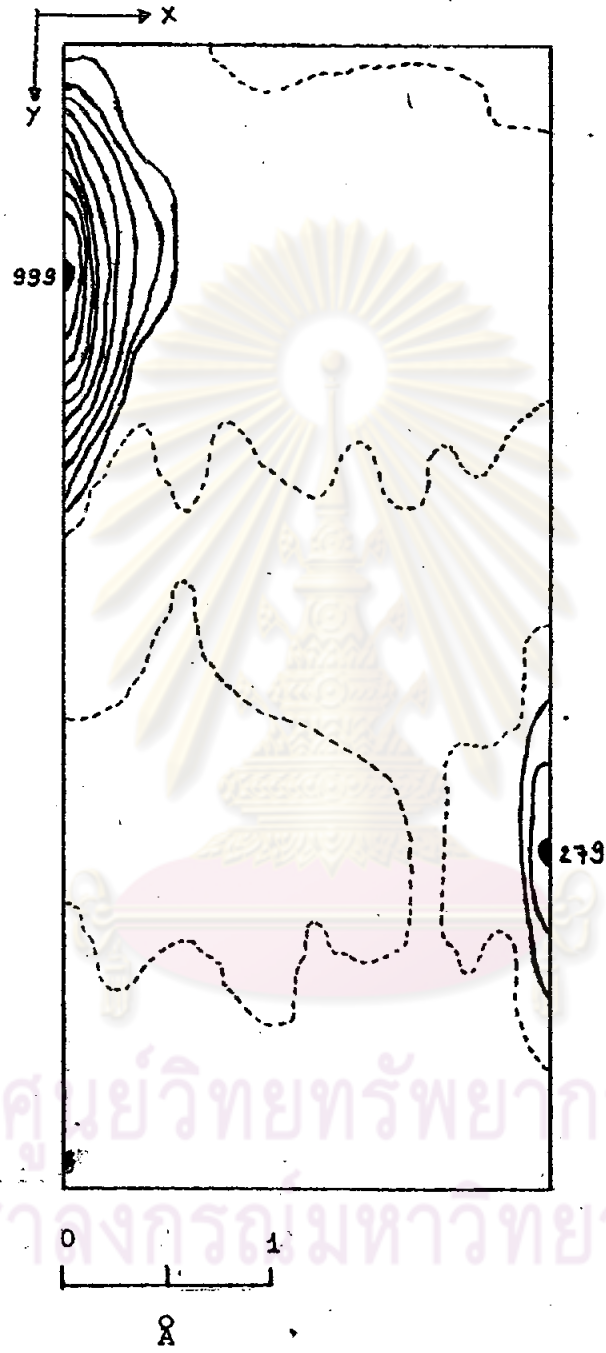


Fig. 4.2 The electron density section
at $z = 0.25$.

$x = 0$. The electron density is assumed to be given by the equation

$$\rho = ax^2 + bx \quad \dots\dots\dots 4.3$$

Substituting the value of x corresponding to ρ_1 and ρ_2 from Table 4.6, eq. 4.3 gives

$$a = \frac{\rho_2 - 2\rho_1}{2} \quad \dots\dots\dots 4.4$$

$$b = \frac{-(\rho_2 - 4\rho_1)}{2} \quad \dots\dots\dots 4.5$$

The position of the maximum electron density is obtained by differentiating eq. 4.3 and equating the result to zero.

$$\begin{aligned} x_m &= -\frac{b}{2a} \\ &= \frac{\rho_2 - 4\rho_1}{2\rho_2 - 4\rho_1} \\ &= \frac{(\rho_2/\rho_1) - 4}{(2\rho_2/\rho_1) - 4} \quad \dots\dots\dots 4.6 \end{aligned}$$

where x_m is the distance to be shifted from $x = 0$. The y and z coordinates are also calculated by the same procedure as the x -coordinate.

The coordinates of tungsten and cobalt obtained from the first F_o map are listed in Table 4.7.

Table 4.7 The coordinates of tungsten and cobalt atoms obtained from the first electron density map.

atom	peak height	atomic coordinates
W	999	0, 0.202, 0.25
Co	279	0.5, 0.692, 0.25

3. The new structure factors were calculated including both new positions of tungsten and cobalt atoms in Table 4.7. The individual temperature factor for tungsten atom was 1.0 and for cobalt atoms was 2.0. The scale factors for each layer were also 1.0. At this point the R index was 0.38. The second electron density map was then prepared and this gave new positions of tungsten and cobalt atoms as listed in Table 4.8.

Table 4.8 The coordinates of tungsten and cobalt atoms obtained from the second electron density map.

atom	peak height	atomic coordinates
W	999	0, 0.201, 0.25
Co	280	0.5, 0.688, 0.25

Since the shift in coordinates was very little, there was no need to calculate an electron density map again.

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4.4 Determination of oxygen atoms by ΔF -synthesis

4.4.1 ΔF -synthesis 001 projection

The $hk0$ reflections were used in the calculations. These reflections were divided into two groups: (1) reflections with $\sin\theta/\lambda > 0.40$; (2) reflections with $\sin\theta/\lambda < 0.40$. Reflections in group (1) will be the most sensitive to change in atomic positions; group (2) are susceptible to such effects as extinction, absorption errors (due to deviations from assumed cross-section of the crystal) ⁽¹⁷⁾.

Although the CoWO_4 crystal used was flat needle-shaped, it was approximated to be cylinder. Hence the absorption corrections might not be exactly correct. Furthermore, before determination of oxygen coordinates the positions of tungsten and cobalt atoms were improved by difference syntheses, (001) projection. Therefore, only 79 reflections of group (1) were used.

To improve the positions of tungsten and cobalt atoms, the structure factors were first calculated using the positions of tungsten and cobalt atoms taken from Table 4.8. The scale factor was 1.28. Structure factors based on these positions resulted in R index of 0.53. The ΔF -synthesis was then calculated by programs EXPRL and FORRL. The calculation was performed at $x = 0-0.5$ and $y = 0-1.0$. The atomic coordinates were shifted by the Booth's method.

Three cycles of structure factor and difference Fourier calculations yielded the lowest R index of 0.34. The corresponding coordinates of tungsten and cobalt atoms were $\pm(0, 0.177, 0.25)$ and $\pm(0.5, 0.663, 0.25)$ respectively. The ΔF -map based on these coordinates is shown in Fig. 4.3.

4.4.2 ΔF -synthesis on(010) projection

As described in section 2.5 that the most valuable reflections for the use in the difference syntheses are those for which $|F_o|$ is smaller than $|F_c|$. The h0l reflections of CoWO_4 , when $\sin\theta/\lambda < 0.75$ $|F_o|$ is smaller than $|F_c|$, therefore only 26 reflections which $\sin\theta/\lambda < 0.75$ were used in the calculations.

The electron density difference map was made by the same procedure as in (001) projection except that the calculation was performed at $x = 0-0.5$, and $z = 0-0.5$. The atomic positions of tungsten and cobalt used in the structure factor calculations were $\pm(0, 0.177, 0.25)$ and $\pm(0.5, 0.663, 0.25)$ respectively. The scale factor used was 1.63. The calculation yielded the R value of 0.28. This map is shown in Fig. 4.4 .

4.4.3 Final oxygen coordinates

The projection of the difference maps on (001) and (010), as in Figs. 4.3 and 4.4 respectively, gave twelve possible

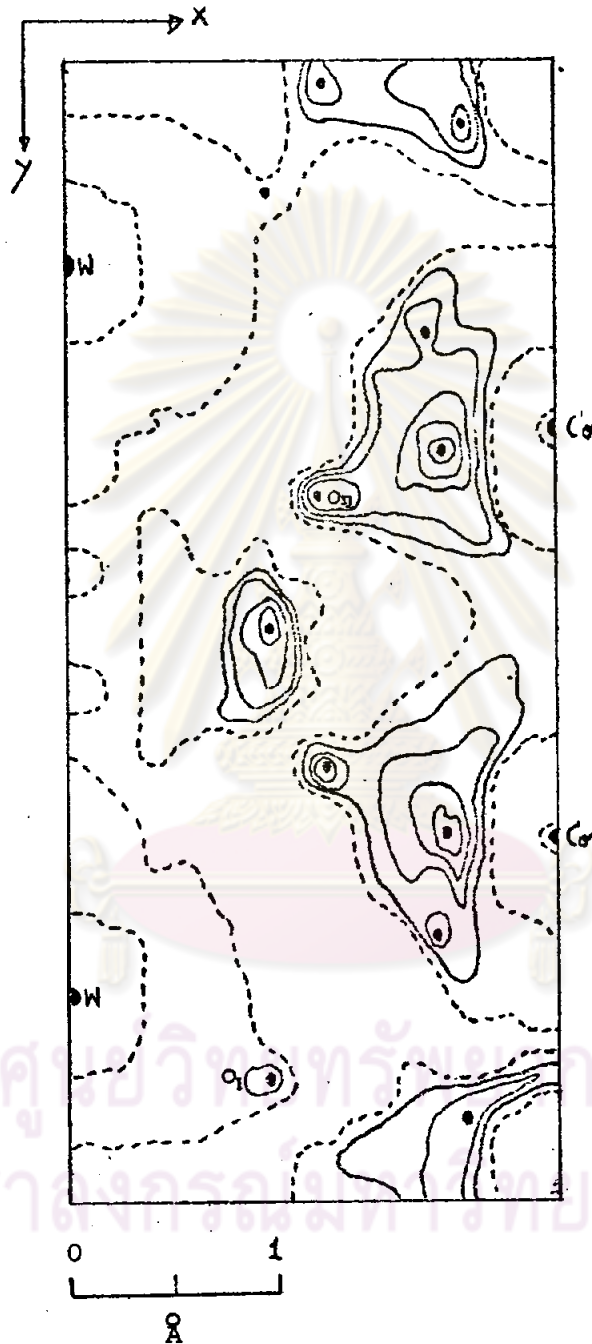


Fig. 4.3 The electron density difference map on (001) projection. Zero contour shown by broken lines, positive regions by full lines. Contours are at intervals of $0.4 \text{ e.}\text{\AA}^{-3}$.

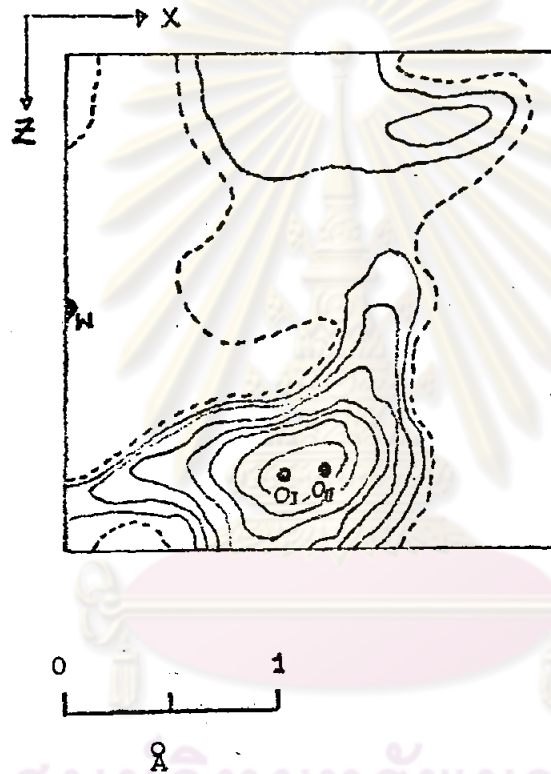


Fig. 4.4 The electron density difference map on (010) projection. Zero contour shown by broken lines, positive regions by full lines. Contours are at intervals of 0.4 e.Å^{-3} .

coordinates of oxygen atoms. They are listed in Table 4.9.

Table 4.9 The twelve possible coordinates of oxygen atoms obtained from electron density difference maps on (001) and (010) projections.

Number	Coordinates
1	0.22, 0.12, 0.42
2	0.22, 0.90, 0.42
3	0.22, 0.50, 0.42
4	0.26, 0.38, 0.42
5	0.26, 0.63, 0.42
6	0.26, 0.02, 0.42
7	0.36, 0.24, 0.10
8	0.37, 0.78, 0.10
9	0.39, 0.34, 0.09
10	0.39, 0.68, 0.09
11	0.40, 0.06, 0.09
12	0.40, 0.94, 0.09

Of these twelve coordinates, only two coordinates, number 2 and 4, can be used. The others were eliminated because they gave unreasonably short W-O, Co-O or O-O distances. Since the ionic radii of W^{6+} , Co^{2+} and O^{2-} are about 0.34, 0.72 and 1.45 Å respectively, bond distances of W-O, Co-O and O-O should

therefore be larger than 1.79, 2.17 and 2.90 Å respectively.

The atomic coordinates for CoWO_4 are listed in Table 4.10.

Table 4.10 The atomic coordinates for CoWO_4 .

atom	x	y	z
W	0	0.177	0.25
Co	0.5	0.663	0.25
O _I	0.22	0.90	0.42
O _{II}	0.26	0.38	0.42

4.5 Least squares refinement

The structure was finally refined by the full matrix least squares method using LSQRL program with the Cruickshank⁽⁸⁾ weight scheme. The individual isotropic temperature factors were assigned as 1.0 for tungsten, 2.0 for cobalt and 1.0 for oxygens. The refinement was separated into three steps.

At first the 92 observed $hk0$ reflections were used to refine atomic positions of tungsten and cobalt atoms and the scale factor of $hk0$ reflections. Three cycles of refinement led to the value of $R = 0.35$.

Next step, the atomic positions of all atoms were refined. The observed $hk0$, $h01$ and $h0\bar{1}$ reflections were used. The observed $F(h01)$ and $F(h0\bar{1})$ were obtained from Lorentz-polarization and absorption corrections by ABSOT program as mentioned in section 4.1. The scale factors k_1 for $hk0$ and k_2 for $h01$ and $h0\bar{1}$, were refined in every refinement. All 229 reflections were used for the first 3 cycles. The R index obtained was 0.36. Only 148 reflections ($0.5 < y_o/y_c < 2.0$) were next used to refine for 3 cycles. The R value was reduced to 0.26.

The last step, the atomic positions and the individual isotropic temperature factors for all atoms were refined and also scale factors. In the first 6 cycles of the refinement of this step, all reflections were used. This led to the R value of 0.11. The 200 and 002 reflections showed obvious extinction effects. The observed structure factors of 070 and $110\bar{2}$ reflections were much different from the calculated values, these reflections are too weak and might cause marked errors in the measurement of the intensity. These reflections should be omitted. The refinement was converged in the next four cycles. The R value was 0.09. The final parameters are listed in Table 4.11. The observed and calculated structure factors are listed in Tables 4.12 and 4.13.

Table 4.11 The final atomic coordinates, thermal parameters and their standard deviations.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	$B \text{ \AA}^2$	$\sigma(B) \text{ \AA}^2$
2W in 2(e)	0.0	-	0.1785	0.0007	0.25	-	0.10	0.02
2Co in 2(f)	0.5	-	0.6644	0.0023	0.25	-	0.52	0.06
4O _I in 4(g)	0.217	0.004	0.9053	0.0075	0.430	0.005	-0.35	0.15
4O _{II} in 4(g)	0.258	0.006	0.3794	0.0083	0.398	0.006	-0.13	0.20

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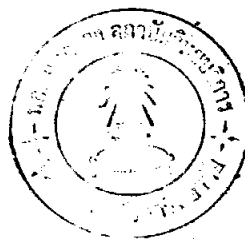


Table 4.12 Observed and calculated structure factors for $l = 0$.

h	k	$ F_o $	$ F_c $	h	k	$ F_o $	$ F_c $
2	0	80.56	140.98	2	1	31.27	30.42
3	0	51.27	68.71	3	1	43.09	57.12
4	0	106.61	128.33	4	1	27.35	25.44
5	0	63.94	62.43	5	1	48.29	49.31
6	0	74.36	81.35	6	1	26.02	23.39
7	0	46.37	45.40	1	2	57.59	55.34
8	0	70.59	67.30	2	2	73.01	90.58
9	0	38.87	40.38	3	2	45.04	49.15
10	0	55.89	48.29	4	2	64.67	64.61
11	0	31.82	29.39	5	2	37.57	37.50
12	0	35.32	37.30	6	2	61.62	50.55
0	2	88.19	94.52	7	2	37.82	32.59
0	3	67.72	69.20	8	2	40.17	37.70
0	4	64.34	52.58	10	2	25.27	28.43
0	5	63.52	58.12	1	3	119.78	144.41
0	6	92.26	88.49	2	3	66.72	71.75
0	8	74.74	60.33	3	3	93.84	116.73
0	9	35.62	34.00	4	3	53.32	56.74
0	11	51.59	47.57	5	3	76.11	91.96
0	14	37.49	39.42	6	3	55.34	51.29
1	1	69.19	84.20	7	3	68.62	67.10

Table 4.12 (continued)

h	k	$ F_o $	$ F_c $	h	k	$ F_o $	$ F_c $
8	3	39.69	37.86	7	6	37.07	38.48
9	3	56.22	54.21	8	6	45.67	48.53
10	3	32.07	34.04	10	6	36.22	37.44
11	3	41.67	39.14	1	8	59.64	52.29
4	4	42.34	35.18	2	8	78.86	65.14
1	5	81.44	78.96	3	8	55.64	48.10
2	5	61.64	57.11	4	8	62.47	51.55
3	5	85.76	74.06	5	8	52.87	43.26
4	5	55.47	49.30	6	8	54.42	49.56
5	5	58.77	53.60	7	8	38.72	35.26
6	5	39.22	39.39	8	8	40.12	36.01
7	5	55.79	50.63	10	8	29.00	34.12
8	5	35.37	35.49	1	9	60.97	56.41
11	5	33.20	33.05	2	9	28.67	31.74
12	5	20.72	26.97	3	9	60.69	54.69
1	6	54.47	50.52	5	9	45.02	43.60
2	6	94.21	92.91	7	9	43.57	42.16
3	6	58.84	50.03	1	11	56.67	49.13
4	6	81.26	72.23	2	11	44.27	36.63
5	6	42.59	39.02	3	11	51.69	43.92
6	6	67.59	62.92	4	11	44.97	42.16

Table 4.12 (continued)

h	k	$ F_o $	$ F_c $	h	k	$ F_o $	$ F_c $
5	11	48.74	44.17	2	12	33.75	33.54
6	11	30.82	31.87	2	14	31.22	33.22
7	11	41.17	33.03	4	14	32.97	36.15
8	11	26.92	31.03				

Table 4.13 Observed and calculated structure factors for $k = 0$.

h	l	$ F_o $	$ F_c $	h	l	$ F_o $	$ F_c $
2	0	115.64	140.98	12	0	31.80	37.30
3	0	69.74	68.71	0	2	105.40	154.18
4	0	122.03	128.33	0	-2	128.85	154.18
5	0	67.44	62.43	0	4	108.77	116.09
6	0	81.61	81.35	0	-4	113.66	116.09
7	0	50.64	45.40	0	6	104.76	97.99
8	0	68.94	67.30	0	-6	100.78	97.99
9	0	42.68	40.38	0	8	76.28	66.54
10	0	50.31	48.29	0	-8	75.36	66.54
11	0	28.99	29.39	0	10	58.53	51.06

Table 4.13 (continued)

n	l	$ F_o $	$ F_c $	n	l	$ F_o $	$ F_c $
0	-10	59.81	51.06	10	2	46.41	46.32
0	12	45.50	43.67	10	-2	43.78	48.67
0	-12	44.55	43.67	11	2	28.85	32.08
1	2	48.71	59.39	12	2	32.64	39.16
1	-2	109.61	95.33	12	-2	32.20	38.53
2	2	123.34	150.29	1	4	80.44	75.40
2	-2	139.04	154.03	1	-4	54.70	56.80
3	2	86.94	81.44	2	4	121.81	120.67
3	-2	58.24	60.05	2	-4	118.59	116.76
4	2	102.97	108.69	3	4	53.97	53.65
4	-2	90.63	104.54	3	-4	79.34	66.99
5	2	44.29	49.30	4	4	86.10	86.42
5	-2	67.55	61.00	4	-4	107.68	92.14
6	2	83.43	82.81	5	4	63.90	56.38
6	-2	91.61	86.68	5	-4	52.36	48.23
7	2	56.49	52.34	6	4	86.75	79.76
7	-2	40.09	45.44	6	-4	79.38	73.56
8	2	66.96	63.63	7	4	41.66	40.64
8	-2	62.04	60.32	7	-4	47.54	44.89
9	2	37.86	33.63	8	4	53.67	51.94
9	-2	36.22	37.20	8	-4	58.75	58.06

Table 4.13 (continued)

h	l	$ F_o $	$ F_c $	h	l	$ F_o $	$ F_c $
9	4	36.07	35.90	7	-6	39.11	37.39
9	-4	32.06	35.15	8	6	55.13	54.84
10	4	46.23	49.20	8	-6	54.92	49.50
10	-4	41.19	44.11	9	6	35.45	36.27
11	4	27.68	29.41	9	-6	31.77	31.87
11	-4	19.69	27.08	10	6	35.75	37.68
12	4	26.14	32.83	10	-6	39.80	42.94
12	-4	26.47	35.94	11	6	19.40	23.05
1	6	60.90	56.11	11	-6	21.18	28.37
1	-6	59.41	55.10	1	8	43.85	39.67
2	6	82.56	78.81	1	-8	56.23	48.30
2	-6	83.03	81.10	2	8	73.68	67.97
3	6	53.13	48.92	2	-8	76.60	68.44
3	-6	55.68	50.42	3	8	56.23	48.44
4	6	87.01	82.19	3	-8	43.41	40.52
4	-6	87.38	78.33	4	8	69.01	58.96
5	6	52.18	48.48	4	-8	66.53	58.27
5	-6	57.25	46.23	5	8	40.46	31.24
6	6	62.62	56.42	5	-8	42.46	37.91
6	-6	59.08	61.37	6	8	54.11	50.94
7	6	41.70	34.10	6	-8	55.65	51.78

Table 4.13 (continued)

h	l	$ F_o $	$ F_c $	h	l	$ F_o $	$ F_c $
8	8	43.05	44.71	6	10	48.93	47.89
8	-8	43.45	44.20	6	-10	38.81	40.76
9	8	19.97	23.00	7	10	20.34	26.32
9	-8	18.84	26.56	7	-10	25.01	26.51
10	8	27.17	33.13	8	10	27.31	30.14
10	-8	29.76	33.14	8	-10	35.20	37.80
1	10	41.19	39.49	1	12	32.79	29.52
1	-10	39.91	33.46	1	-12	30.42	30.48
2	10	64.34	54.62	2	12	40.86	36.64
2	-10	55.83	51.67	2	-12	42.17	39.89
3	10	32.53	30.81	4	12	39.21	42.81
3	-10	35.78	35.71	4	-12	37.90	36.71
4	10	41.77	42.60	5	12	23.37	29.50
4	-10	52.14	48.15	5	-12	23.51	27.86
5	10	31.07	34.97	6	12	26.29	29.65
5	-10	26.07	32.12	6	-12	33.37	37.73