CHAPTER 5

RESULTS AND DISCUSSION

The final structure data for $CoWO_4$ are as follows: mono-clinic system; space group P2/c ; a = 4.678 $\pm$ 0.001 $\overset{o}{A}$, b = 5.684 $\pm$ 0.001 $\overset{o}{A}$, c = 4.949 $\pm$ 0.001 $\overset{o}{A}$, β = 90.04 $\pm$ 0.03^o; V = 131.61 $\overset{o}{A}^3$; D_m = 7.75 $\pm$ 0.02 $g.cm^{-3}$ at 28°C, D_x = 7.744 $g.cm^{-3}$ and Z = 2. The atomic coordinates and the thermal parameters are listed in Table 4.11.

5.1 Bond distances and bond angles

The bond distances and bond angles within 4 $\overset{o}{A}$ limit, were calculated by DISTAN program. The bond distances in $CoWO_4$ struc-ture are shown in Table 5.1.

Table 5.1 Bond distances and their standard deviations ($\overset{o}{A}$ units) in $CoWO_4$. Distances shorter than 4 $\overset{o}{A}$ are listed.

Bond	Distance	S.d.
W- 2O$_{II}$	1.814	.031
-2O$_I$	1.941	.023
-2O$_I$	2.059	.032

Table 5.1 (continued)

Bond	Distance	S.d.
W-2W	3.200	.005
$-2O_{II}$	3.289	.039
-2Co	3.520	.003
-2Co	3.522	.003
$-2O_I$	3.546	.024
-2Co	3.617	.009
$-2O_{II}$	3.727	.015
-2Co	3.745	.009
$-2O_{II}$	3.813	.040
$Co-2O_{II}$	2.091	.026
$-2O_I$	2.103	.029
$-2O_{II}$	2.108	.037
-2Co	3.098	.014
$-2O_I$	3.203	.034
$-2O_{II}$	3.410	.028
-2W	3.520	.003
-2W	3.522	.003
-2W	3.617	.009
$-2O_I$	3.730	.016
-2W	3.745	.009
$-2O_I$	3.836	.036

Table 5.1 (continued)

Bond	Distance	S.d.
Co-2O$_{II}$	3.959	.013
-2O$_{II}$	3.966	.020
O$_I$-W	1.941	.022
-W	2.059	.032
-Co	2.103	.029
-O$_I$	2.402	.039
-2O$_I$	2.700	.032
-O$_I$	2.700	.033
-O$_{II}$	2.706	.060
-O$_{II}$	2.830	.047
-O$_{II}$	2.876	.037
-O$_I$	2.942	.033
-O$_{II}$	3.000	.060
-O$_{II}$	3.059	.036
-O$_{II}$	3.094	.046
-O$_I$	3.192	.028
-Co	3.203	.034
-W	3.546	.024
-Co	3.730	.016
-O$_I$	3.763	.042
-Co	3.836	.036

Table 5.1 (continued)

Bond	Distance	S.d.
O_I-O_{II}	3.850	.045
-O_{II}	3.991	.044
O_{II}-W	1.814	.031
-Co	2.091	.025
-Co	2.108	.037
-O_{II}	2.698	.032
-O_I	2.706	.060
-O_{II}	2.823	.031
-O_I	2.830	.047
-$2O_{II}$	2.831	.044
-O_{II}	2.835	.050
-O_I	2.876	.036
-O_{II}	2.957	.048
-O_I	3.000	.060
-O_I	3.059	.035
-O_I	3.094	.046
-W	3.289	.038
-Co	3.410	.028
-W	3.727	.015
-W	3.813	.040
-O_I	3.850	.045

Table 5.1 (continued)

Bond	Distance	S.d.
O_{II}-Co	3.959	.013
-Co	3.966	.020
-O_I	3.991	.044

5.2 Discussion

By considering the arrangement of oxygen atoms in Fig. 5.1, it can be seen that the atoms in the second layer are above the hollows in the first layer. The atoms in the third and fourth layers are vertically above the atoms in the first and second layers respectively and so on. The sequence of layer stacking can be summarized as ABABAB... . However, the arrangement is slightly distorted. Therefore, the structure of $CoWO_4$ is based on a distorted hexagonal close packing of oxygen atoms with Co and W atoms each occupying one-fourth of the octahedral holes. The CoO_6 and WO_6 octahedra are joined by corners and the similar octahedra of CoO_6 and WO_6 are joined by edges. The system of CoO_6 and WO_6 octahedra is shown in Fig. 5.2.
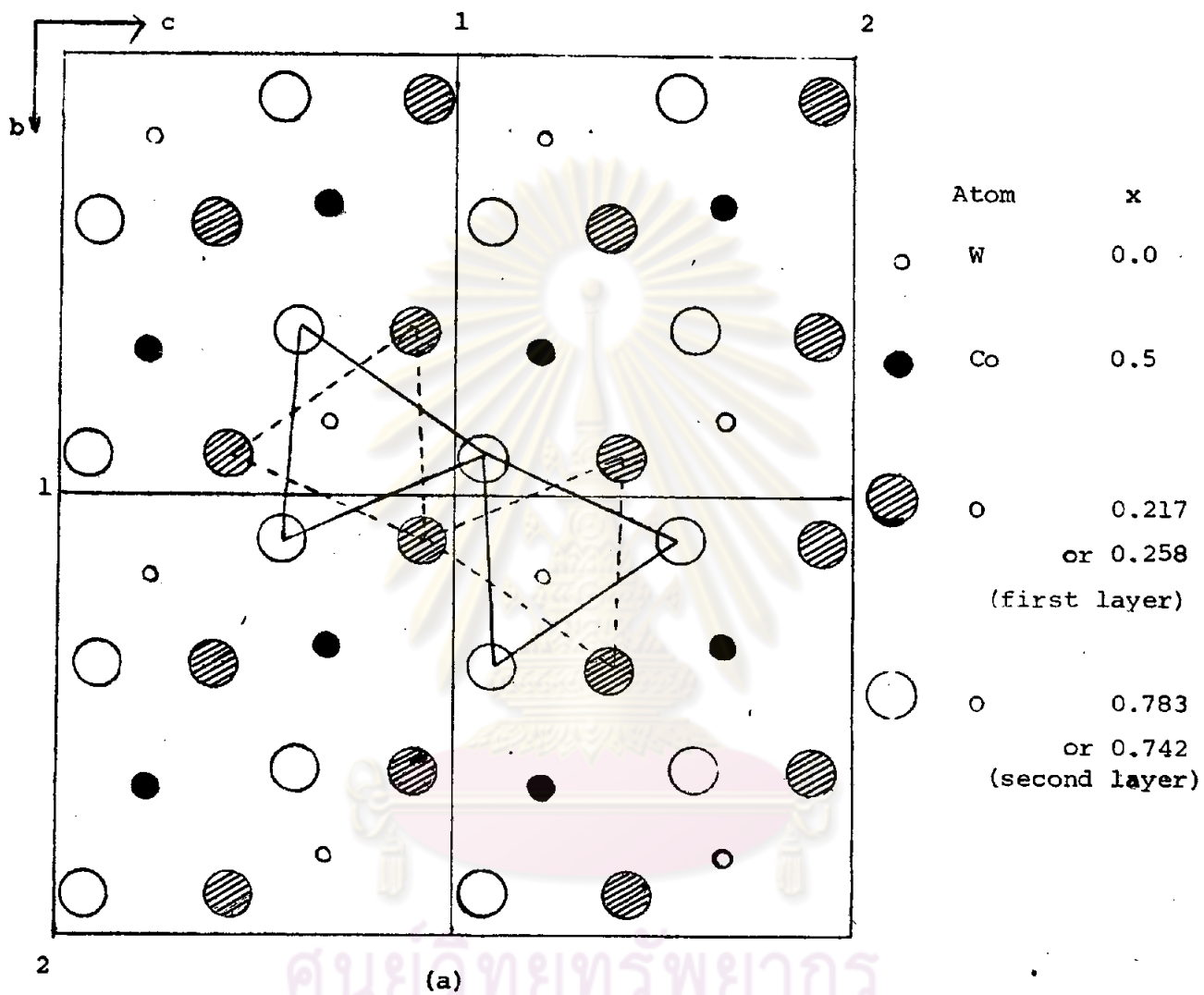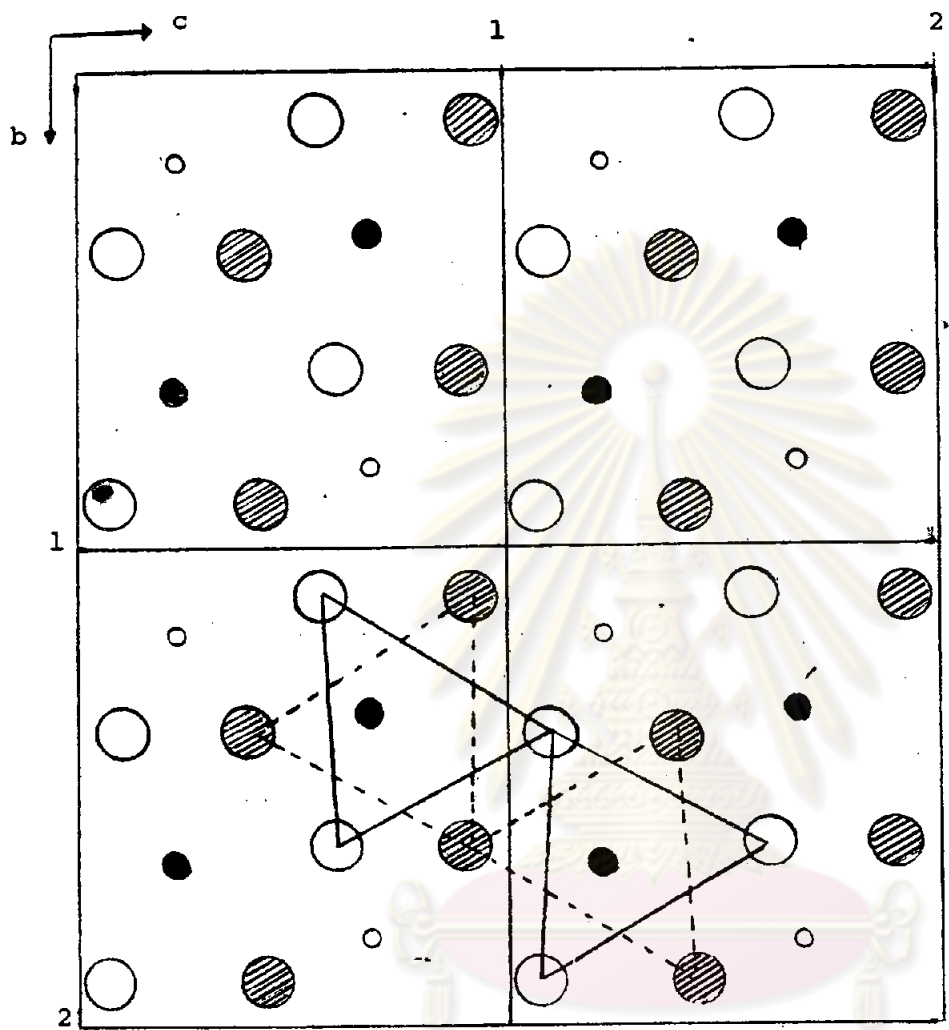
Fig. 5.1 The structure of $CoWO_4$ projected on (100)

    (a) showing WO_6 octahedra.

    (b) showing CoO_6 octahedra.

Atom	x
W	0.0
Co	0.5
⊙	0.217 or 0.258 (first layer)
⊙	0.783 or 0.742 (second layer)

(b)
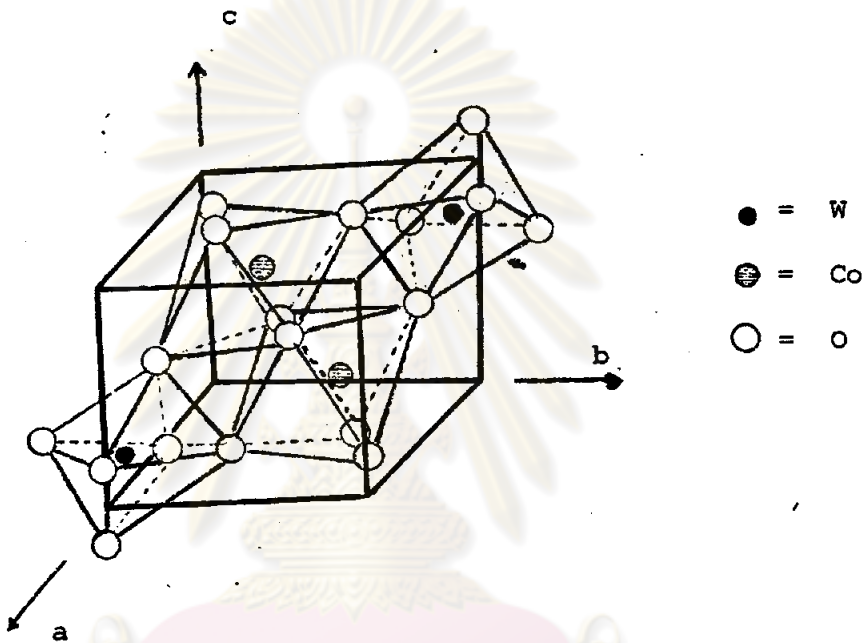
Fig. 5.2 CoO_6 and WO_6 octahedra in $CoWO_4$.

The tungsten atom is surrounded by six oxygen atoms (Fig. 5.3 (a)). The coordinates of these atoms are listed in Table 5.2(a). The cobalt atom is also surrounded by six oxygen atoms as shown in Fig. 5.3(b). The coordinates of these atoms are listed in Table 5.2(b). For the neighbours of an oxygen atom, in addition to being contact with six oxygen nearest neighbours in one distorted layer, it is in contact with three oxygen atoms in the layer above and three in the layer below along a, so that it has twelve nearest neighbours, i.e. a coordination number of twelve, as shown in Fig. 5.3(c). The coordinates of these atoms are listed in Table 5.2(c). Interatomic distances of atoms in Fig. 5.3 are given in Table 5.3. Interatomic angles are given in Table 5.4.

Table 5.2(a) The coordinates of atoms in Fig. 5.3(a).
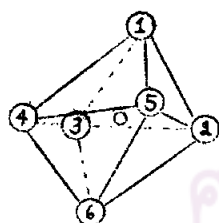
o = W

◯ = O

Fig. 5.3(a) The WO_6 octahedron in $CoWO_4$.

Atom	x	y	z
W	0.0	0.1785	0.25
O_1	-0.217	0.0947	0.570
O_2	-0.258	0.3794	0.102
O_3	-0.217	-0.0947	0.070
O_4	0.217	-0.0947	0.430
O_5	0.258	0.3794	0.398
O_6	0.217	0.0947	-0.070

Table 5.2 (b)   The coordinates of

atoms in Fig. 5.3(b).
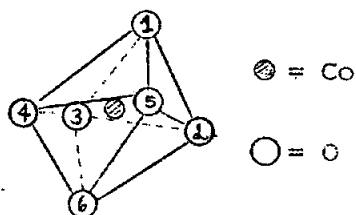
Fig. 5.3(b)   The CoO_6 octa-

hedron in $CoWO_4$.

Atom	x	y	z
Co	0.5	0.6644	0.25
O_1	0.742	0.6206	0.602
O_2	0.217	0.9053	0.430
O_3	0.258	0.3794	0.398
O_4	0.742	0.3794	0.102
O_5	0.783	0.9053	0.070
O_6	0.258	0.6206	-0.102

Table 5.2(c)   The coordinates of

atoms in Fig. 5.3(c).
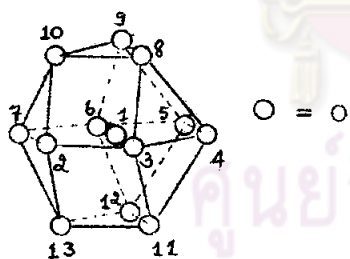
Fig. 5.3(c)   The polyhedron

of the twelve

oxygen neighbours

of an oxygen

atom.

Atom	x	y	z
O_1	0.742	0.3794	0.102
O_2	0.742	0.6206	0.602
O_3	0.783	0.9053	0.070
O_4	0.742	0.6206	-0.398
O_5	0.783	0.0947	-0.430
O_6	0.783	-0.0947	0.070
O_7	0.783	0.0947	0.570
O_8	0.258	0.6206	-0.102
O_9	0.217	0.0947	-0.070
O_{10}	0.258	0.3794	0.398
O_{11}	1.258	0.6206	-0.102
O_{12}	1.217	0.0947	-0.070
O_{13}	1.258	0.3794	0.398

Table 5.3(a)   Interatomic distances of WO_6 octahedron, shorter

than 4 Å, in Fig. 5.3(a).

Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å
$W - O_1$	1.9406	$O_1 - O_2$	2.8296	$O_2 - O_6$	2.8759
$- O_2$	1.8140	$- O_3$	2.6999	$O_3 - O_4$	2.7002
$- O_3$	2.0590	$- O_4$	2.4021	$- O_6$	2.4021
$- O_4$	2.0590	$- O_5$	2.8759	$O_4 - O_5$	2.7057
$- O_5$	1.8140	$O_2 - O_3$	2.7057	$- O_6$	2.6999
$- O_6$	1.9406	$- O_5$	2.8227	$O_5 - O_6$	2.8296

Table 5.3(b)   Interatomic distances of CoO_6 octahedron, shorter

than 4Å in Fig. 5.3(b).

Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å
$Co - O_1$	2.0912	$O_1 - O_2$	3.0593	$O_2 - O_6$	3.0944
$- O_2$	2.1034	$- O_3$	2.3345	$O_3 - O_4$	2.6976
$- O_3$	2.1079	$- O_4$	2.8311	$- O_6$	2.8311
$- O_4$	2.1079	$- O_5$	3.0944	$O_4 - O_5$	3.0001
$- O_5$	2.1034	$O_2 - O_3$	3.0001	$- O_6$	2.8345
$- O_6$	2.0912	$- O_5$	3.1924	$O_5 - O_6$	3.0593

Table 5.3(c)   Interatomic distances of distorted hexagonal close packing surrounded an oxygen atom in Fig. 5.3(c). Distances shorter than 4 Å are listed.

Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å
O_1 - O_2	2.8311	O_2 - O_3	3.0944	O_5 - O_{12}	2.7002
- O_3	3.0001	- O_7	3.0001	O_6 - O_7	2.6999
- O_4	2.8311	- O_{10}	2.8345	- O_9	2.9418
- O_5	3.0944	- O_{13}	2.9566	- O_{12}	2.4021
- O_6	2.7057	O_3 - O_4	2.8296	O_7 - O_{10}	3.0593
- O_7	2.8296	- O_8	3.0593	- O_{13}	2.8759
- O_8	2.8345	- O_{11}	2.8759	O_8 - O_9	3.0001
- O_9	3.0593	O_4 - O_5	3.0001	- O_{10}	2.8311
- O_{10}	2.6976	- O_8	2.6976	O_9 - O_{10}	2.8296
- O_{11}	2.9566	- O_{11}	2.8227	O_{11} - O_{12}	3.0001
- O_{12}	2.8759	O_5 - O_6	2.6999	- O_{13}	2.8311
- O_{13}	2.8227	O_9	3.1924	O_{12} - O_{13}	2.8296

Table 5.4(a)   Interatomic angles of WO$_6$ octahedron in Fig. 5.3(a).

Bond	Angle	Bond	Angle	Bond	Angle
O$_1$- W - O$_2$	97.75	O$_2$- O$_1$- O$_5$	59.30	O$_1$- O$_4$- O$_5$	68.23
O$_3$	84.86	O$_3$- O$_1$- O$_4$	63.59	- O$_6$	94.88
- O$_4$	73.76	- O$_5$	87.29	O$_3$- O$_4$- O$_5$	90.84
- O$_5$	99.93	O$_4$- O$_1$- O$_5$	60.90	- O$_6$	52.83
- O$_6$	151.69	O$_1$- O$_2$- O$_3$	58.34	O$_5$- O$_4$- O$_6$	63.13
O$_2$- W - O$_3$	88.39	- O$_5$	61.17	O$_1$- O$_5$- O$_2$	59.53
- O$_4$	167.61	- O$_6$	82.54	- O$_4$	50.87
- O$_5$	102.16	O$_3$- O$_2$- O$_5$	88.27	- O$_6$	82.54
- O$_6$	99.93	- O$_6$	50.87	O$_2$- O$_5$- O$_4$	88.27
O$_3$- W - O$_4$	81.95	O$_5$- O$_2$- O$_6$	59.53	- O$_6$	61.17
- O$_5$	167.61	O$_1$- O$_3$- O$_2$	63.13	O$_4$- O$_5$- O$_6$	58.34
- O$_6$	73.76	- O$_4$	52.83	O$_2$- O$_6$- O$_3$	60.90
O$_4$- W - O$_5$	88.39	- O$_6$	94.88	- O$_4$	87.29
- O$_6$	84.36	O$_2$- O$_3$- O$_4$	90.84	- O$_5$	59.30
O$_5$- W - O$_6$	97.75	- O$_6$	68.23	O$_3$- O$_6$- O$_4$	63.59
O$_2$- O$_1$- O$_3$	58.54	O$_4$- O$_3$- O$_6$	63.58	- O$_5$	94.43
- O$_4$	94.43	O$_1$- O$_4$- O$_3$	63.58	O$_4$- O$_6$- O$_5$	58.54

Table 5.4(b)   Interatomic angles of CoO_6 octahedron in Fig. 5.3(b).

Bond	Angle	Bond	Angle	Bond	Angle
O_1-Co - O_2	93.66	O_2- O_1 - O_5	62.50	O_1- O_4 - O_5	64.02
- O_3	84.91	O_3- O_1 - O_4	56.87	- O_6	94.30
- O_4	84.78	- O_5	90.00	O_3- O_4 - O_5	94.73
- O_5	95.07	O_4- O_1 - O_5	60.64	- O_6	61.50
- O_6	166.58	O_1- O_2 - O_3	55.77	O_5- O_4 - O_6	63.17
O_2- Co - O_3	90.86	- O_5	59.29	O_1- O_5 - O_2	58.21
- O_4	170.39	- O_6	84.91	- O_4	55.33
- O_5	98.73	O_3- O_2 - O_5	85.27	- O_6	84.91
- O_6	95.07	- O_6	55.33	O_2- O_5 - O_4	85.27
O_3- Co - O_4	79.56	O_5- O_2 - O_6	58.21	- O_6	59.29
- O_5	170.39	O_1- O_3 - O_2	63.17	O_4- O_5 - O_6	55.77
- O_6	84.78	- O_4	61.50	O_2- O_6 - O_3	60.64
O_4- Co - O_5	90.86	- O_6	94.30	- O_4	90.00
- O_6	84.91	O_2- O_3 - O_4	94.73	- O_5	62.50
O_5- Co - O_6	93.66	- O_6	64.02	O_3- O_6 - O_4	56.87
O_2- O_1 - O_3	61.06	O_4- O_3 - O_6	61.63	- O_5	90.78
- O_4	90.78	O_1 O_4 - O_3	61.63	O_4- O_6 - O_5	61.06

Table 5.4(c)   Interatomic angles of distorted hexagonal close pack-
ing of oxygen atoms surrounded an oxygen atom in Fig.
5.3(c).

Bond	Angle	Bond	Angle	Bond	Angle
$O_2 - O_1 - O_3$	64.02	$O_4 - O_5 - O_9$	85.27	$O_{10} - O_9 - O_6$	87.49
$- O_7$	64.01	$- O_{12}$	90.76	$- O_8$	58.02
$O_3 - O_1 - O_4$	57.97	$O_6 - O_5 - O_9$	59.20	$O_2 - O_{10} - O_7$	61.06
$O_4 - O_1 - O_5$	60.64	$- O_{12}$	52.83	$- O_8$	94.30
$O_5 - O_1 - O_6$	54.99	$O_5 - O_6 - O_9$	66.77	$O_9 - O_{10} - O_7$	88.89
$O_6 - O_1 - O_7$	58.34	$- O_{12}$	63.59	$- O_8$	64.01
$O_3 - O_2 - O_{10}$	90.00	$O_7 - O_6 - O_9$	93.92	$O_3 - O_{11} - O_4$	59.53
$- O_{13}$	84.32	$- O_{12}$	94.88	$- O_{13}$	90.78
$O_7 - O_2 - O_{10}$	63.17	$O_2 - O_7 - O_{10}$	55.77	$O_{12} - O_{11} - O_4$	88.44
$- O_{13}$	57.73	$- O_{13}$	60.38	$- O_{13}$	57.97
$O_2 - O_3 - O_8$	84.91	$O_6 - O_7 - O_{10}$	117.75	$O_5 - O_{12} - O_6$	63.58
$- O_{11}$	90.42	$- O_{13}$	119.76	$- O_{11}$	90.76
$O_4 - O_3 - O_8$	54.36	$O_3 - O_8 - O_4$	58.48	$O_{13} - O_{12} - O_6$	94.43
$- O_{11}$	59.30	$- O_{10}$	90.78	$- O_{11}$	58.02
$O_3 - O_4 - O_8$	67.17	$O_9 - O_8 - O_4$	94.73	$O_2 - O_{13} - O_7$	61.89
$- O_{11}$	61.17	$- O_{10}$	57.97	$- O_{11}$	94.19
$O_5 - O_4 - O_8$	94.73	$O_5 - O_9 - O_6$	52.03	$O_{12} - O_{13} - O_7$	82.54
$- O_{11}$	88.44	$- O_8$	85.27	$- O_{11}$	64.01

In the isomorphous series of small cations which includes $NiWO_4$ $CoWO_4$, $MgWO_4$, $MnWO_4$, $FeWO_4$ and $ZnWO_4$, the structure of $NiWO_4$ has been determined by Keeling[2]. The structure of $CoWO_4$ determined in the present study is very similar to that of $NiWO_4$. The compound $CoWO_4$ crystallizes with the same space group symmetry as $NiWO_4$ and the atoms are situated in the same type of crystallographic position. The structure of $CoWO_4$ and $NiWO_4$ are both based on a distorted hexagonal close packing of oxygen atoms with Co or Ni and W atoms each occupying one-fourth of the octahedral holes. The distances between a cobalt atom and six oxygen neighbours are nearly equal and also for nickel atom, but the octahedral group around a tungsten atom of both $CoWO_4$ and $NiWO_4$ is considerably distorted. The structure data for $CoWO_4$ and $NiWO_4$ are compared in Table 5.5.

The structure of $CoWO_4$ obtained thus confirms that the space group is P2/c and the x coordinate of tungsten atom is 0.0. The individual temperature factors of oxygen atoms obtained from the least squares refinement were negative values. This effect can be ascribed to the influence of the absorption, since the crystal used for hk0 data was a flat needle-shaped but for absorption correction it was approximated to be cylinder. Furthermore, it is probably related to a systematic error in the intensity measurement. However, the full matrix least squares refinement converged satisfactorily and gave the R value of 0.09.

Table 5.5 Comparison of the structure data between $CoWO_4$ and $NiWO_4$. Standard deviations are shown in parentheses.

Atom	x	y	z	B $\overset{o}{A}^2$	a $\overset{o}{A}$	b $\overset{o}{A}$	c $\overset{o}{A}$	β degree
$CoWO_4$					4.678(1)	5.684(1)	4.949(1)	90.04(3)
Co	0.5	0.6644(23)	0.25	0.52(6)				
W	0.0	0.1785(7)	0.25	0.10(2)				
O_I	0.217(4)	0.9053(75)	0.230(5)	-0.35(15)				
O_{II}	0.258(6)	0.3794(83)	0.398(6)	-0.13(20)				
$NiWO_4$								
Ni	0.5	0.653	0.25	2.0	4.600(15)	5.66(2)	4.910(15)	90.08(8)
W	0.0	0.180	0.25	1.0				
O_I	0.22	0.11	0.96	1.0				
O_{II}	0.26	0.38	0.39	1.0				

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