Marsh, R. E. (1952). *Acta Cryst.* **5**, 458.
Marsh, R. E. & McCullough, J. D. (1951). *J. Amer. Chem. Soc.* **73**, 1106.
Marsh, R. E., Pauling, L. & McCullough, J. D. (1953). *Acta Cryst.* **6**, 71.
Pauling, L. (1945). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.
Sparks, R. A., Prosen, R. J., Kruse, F. H. & Trueblood, K. N. (1956). *Acta Cryst.* **9**, 350.
Trueblood, K. N. (1956). *Acta Cryst.* **9**, 359.

Acta Cryst. (1957). **10**, 209

The Structure of $NiWO_4$

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The structure of $NiWO_4$ has been determined, using the Fourier difference method to locate the oxygen atoms. The structure is based on a distorted hexagonal close packing of oxygen atoms with Ni and W atoms each occupying one-fourth of the octahedral interstices. The Ni and W atoms lie off the centers of their respective octahedra by 0·13 Å and 0·30 Å.

1. Introduction

$NiWO_4$ is a member of the isomorphous series of tungstates of small cations which also includes $MgWO_4$, $MnWO_4$, $FeWO_4$, $CoWO_4$ and $ZnWO_4$. The structure of $MgWO_4$, with the exception of oxygen positions, was determined by Broch (1929). The unit cell is monoclinic (space group $P2/c$; $a = 4{\cdot}68$, $b = 5{\cdot}66$, $c = 4{\cdot}92$ Å, $\beta = 89°\,40'$) and contains two formula units. Atomic coordinates are:

$2\,\mathrm{Mg}$ in (e): $\pm(\frac{1}{2}, y_{\mathrm{Mg}}, \frac{1}{4})$,
$2\,\mathrm{W}$ in (f): $\pm(0, y_{\mathrm{W}}, \frac{1}{4})$,
$4\,\mathrm{O_I}$ in (g): $\pm(x_1, y_1, z_1;\ x_1, \bar{y}_1, z_1+\frac{1}{2})$,
$4\,\mathrm{O_{II}}$ in (g): $\pm(x_2, y_2, z_2;\ x_2, \bar{y}_2, z_2+\frac{1}{2})$,

with $y_{\mathrm{Mg}} = 0{\cdot}68$ and $y_{\mathrm{W}} = 0{\cdot}18$. It is suggested in *Strukturbericht* (1928–32) that the oxygen parameters are: $x_1 = 0{\cdot}20$, $y_1 = -0{\cdot}04$, $z_1 = 0{\cdot}10$, $x_2 = 0{\cdot}20$, $y_2 = 0{\cdot}40$, and $z_2 = 0{\cdot}40$. The structure as proposed in *Strukturbericht* is shown in Fig. 1.

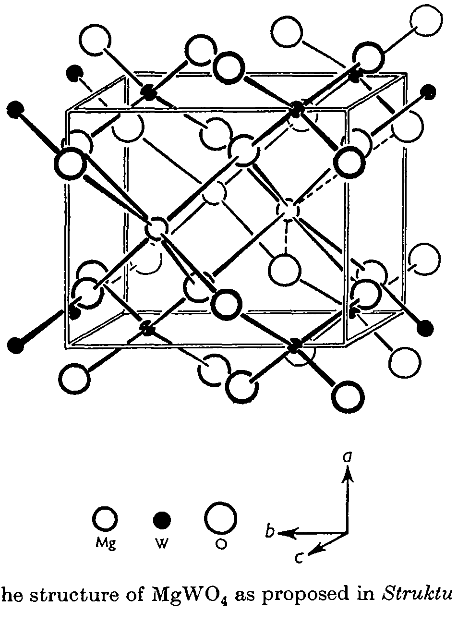

Fig. 1. The structure of $MgWO_4$ as proposed in *Strukturbericht.*

There are two objections to this structure. First, six of the eight oxygens surrounding Mg are assigned to a highly distorted MgO_6 octahedron. The remaining two oxygens, shown by broken lines in Fig. 1, are not considered a part of the coordination group although they lie just as close to Mg (2·27 Å and 3·01 Å) as do two of those in the octahedron. Second, the proposed oxygen parameters appear to be based largely on the assumption that W is surrounded by an oxygen tetrahedron. Since octahedral coordination is known to exist, as in WO_3 for example, this assumption is questionable.

With Broch's results on $MgWO_4$ as a starting point, the Fourier difference technique has been applied to the location of the oxygens in $NiWO_4$. The resulting oxygen positions give a structure which is not subject to the first of the aforementioned objections, and which contains WO_6 instead of WO_4 groups.

2. Experimental

Single crystals of $NiWO_4$ were grown from a melt of Na_2WO_4, $NiCl_2$, and NaCl in the ratio 1:2:2 by weight. This mixture was held at 900° C. for 2 hr. and then cooled slowly. Small dark brown, acicular crystals of $NiWO_4$, with the needle axis along c, were washed from the solidified melt with water.

Cell dimensions, as measured from a combination of powder and back-reflection single-crystal photographs, using Ni-filtered Cu $K\alpha$ radiation, are:

$$a = 4{\cdot}60\pm0{\cdot}015, \quad b = 5{\cdot}66\pm0{\cdot}02, \quad c = 4{\cdot}91\pm0{\cdot}015 \text{ Å}, \quad \beta = 90^\circ\, 5'\pm5' .$$

Intensity data were recorded for projections of the structure on (001) and (100). Multiple-film Weissenberg photographs taken with Ni-filtered Cu $K\alpha$ radiation were used for the $hk0$ data, and the $0kl$ data were obtained from precession photographs taken with unfiltered Mo $K\alpha$ radiation. The crystals used for intensity photographs were approximately cylindrical with lengths of 0·5 mm. and diameters of 0·16 mm. (for $hk0$) and 0·10 mm. (for $0kl$). Intensities were measured by visual comparison with a scale of known relative intensities, and magnitudes of structure factors ($|F_o|$) were derived from the intensities (I) by application of the usual relation,

$$|F_o| = K\sqrt{\frac{I}{(LP)A}} ,$$

where K is a scale factor necessary to place I on an absolute basis, (LP) is the Lorentz–polarization correction, and A is an absorption correction. The absorption correction was important for both projections ($\mu r_{hk0} = 7{\cdot}22$, $\mu r_{0kl} = 2{\cdot}86$), and was determined by the method of Claassen (1930) from plots of the values given in the *Internationale Tabellen* (1935). It is realized that this method is not strictly applicable to precession photographs but it was considered to be a close enough approximation for present purposes.

3. Structure determination

(*a*) *The* (001) *Projection*

The expression for the structure factor for $hk0$ reflections is

$$\begin{aligned} F_c(hk0) &= 2f_{\mathrm{W}} \exp\,[-B_{\mathrm{W}}S^2] \cos ky_{\mathrm{W}} \\ &\quad + 2(-1)^h f_{\mathrm{Ni}} \exp\,[-B_{\mathrm{Ni}}S^2] \cos ky_{\mathrm{Ni}} \\ &\quad + 4f_{\mathrm{O}} \exp\,[-B_{\mathrm{O}}S^2]\,(\cos hx_1 \cos ky_1 + \cos hx_2 \cos ky_2) , \end{aligned}$$

where B_{W}, B_{Ni}, and B_{O} are the temperature factors associated with the individual atoms and $S^2 = (\sin^2\theta)/\lambda^2$. The atomic scattering factors f_{Ni} and f_{O} were those given by Viervoll & Ögrim (1949), and f_{W} was that given by the *Internationale Tabellen* (1935).

The initial step in the determination of atomic coordinates in the (001) projection was the evaluation of F_c, using Broch's metal atom positions in $MgWO_4$ and neglecting the oxygen contribution. Following the assignment of the sign of each F_c to the corresponding $|F_o|$, a scale factor and a crystal temperature factor were determined from a Wilson (1942) plot. Calculations for an electron-density difference map were made with the aid of Beevers–Lipson strips; from the map a correction was made in the Ni position and individual temperature factors were assigned to Ni and W. These corrections resulted in an improvement in the disagreement index from 0·21 to 0·17. The second difference map contained peaks which could be definitely associated with oxygen atoms. These oxygen positions were entered in the third cycle of calculations and the refinement by means of difference maps was carried through several more cycles. The final values of observed and calculated $hk0$ structure factors are given in Table 1. $F_{\mathrm{Ni+W}}$ is the structure factor calculated from Ni and W contributions only and F_c is the total structure factor. The disagreement index associated with $F_{\mathrm{Ni+W}}$ is 0·127; that associated with F_c is 0·091. The oxygen peaks are shown in the difference map of Fig. 2, which was plotted from the $F_o - F_{\mathrm{Ni+W}}$ data of Table 1.

Table 1. *The hk*0 *structure factors for* $NiWO_4$

$hk0$	$\lvert F_o\rvert$	$F_{\mathrm{Ni+W}}$	F_c	$F_o - F_{\mathrm{Ni+W}}$	$F_o - F_c$
010	42·7	32·2	34·1	10·5	8·6
020	88·8	−89·8	−83·6	1·0	−5·2
030	75·1	−69·4	−65·3	−5·7	−9·8
040	65·9	−36·8	−58·4	−29·1	−7·5
050	54·1	54·9	53·2	−0·8	0·9
060	61·0	63·9	59·0	−2·9	2·0
070	16·2	− 8·9	−12·2	−7·3	−4·0
100	88·9	87·7	90·1	1·2	−1·2
110	78·2	80·6	85·5	−2·4	−7·3
120	52·0	−58·9	−58·1	6·9	6·1
130	98·0	−125·6	−127·4	27·6	29·4
140	< 11·4	−0·4	−1·1	—	—
150	61·3	57·4	55·5	3·9	5·8
160	40·6	41·5	40·9	−0·9	−0·3
170	7·0	6·7	6·9	0·3	0·1
200	105·0	148·9	111·2	−43·9	−6·2
210	32·6	27·3	26·8	5·3	5·8
220	75·1	−73·5	−77·4	−1·6	2·3
230	61·3	−62·5	−65·7	1·2	4·4
240	14·1	−30·7	−14·0	16·6	−0·1
250	48·0	49·3	50·5	−1·3	−2·5
260	63·5	57·6	61·7	5·9	1·8
300	67·7	66·2	63·1	1·5	4·6
310	51·9	52·8	46·0	−0·9	5·9
320	54·0	−45·0	−46·1	−9·0	−7·9
330	71·7	−90·9	−87·6	19·2	15·9
340	< 9·5	−2·8	−1·4	—	—
350	52·0	46·1	50·1	5·9	1·9
360	40·4	36·5	38·0	3·9	2·4
400	90·9	89·7	104·4	1·2	−13·5
410	23·7	21·5	20·9	2·2	2·8
420	50·0	−47·5	−45·8	−2·5	−4·2
430	43·8	−47·9	−45·9	4·1	2·1
440	32·8	−19·8	−29·3	−13·0	−3·5
450	37·0	38·1	37·9	−1·1	−0·9
500	49·1	46·8	49·0	2·3	0·1
510	39·2	30·6	35·8	8·6	3·4
520	32·6	−30·8	−29·9	−1·8	−2·7
530	61·3	−57·7	−60·7	−3·6	−0·6

(*b*) *The* (100) *projection*

The expression for $0kl$ structure factors is

$$\begin{aligned} F_c(0kl) &= 2(-1)^l\{f_{\mathrm{W}} \exp\,[-B_{\mathrm{W}}S^2] \cos\,(ky_{\mathrm{W}} - \tfrac{1}{4}l) \\ &\quad + f_{\mathrm{Ni}} \exp\,[-B_{\mathrm{Ni}}S^2] \cos\,(ky_{\mathrm{Ni}} - \tfrac{1}{4}l)\} \\ &\quad + 4f_{\mathrm{O}} \exp\,[-B_{\mathrm{O}}S^2]\,\{\cos\,(lz_1 + \tfrac{1}{4}l) \cos\,(ky_1 - \tfrac{1}{4}l) \\ &\quad + \cos\,(lz_2 + \tfrac{1}{4}l) \cos\,(ky_2 - \tfrac{1}{4}l)\} . \end{aligned}$$

Coordinates in the (100) projection were determined by essentially the same procedure as that followed in

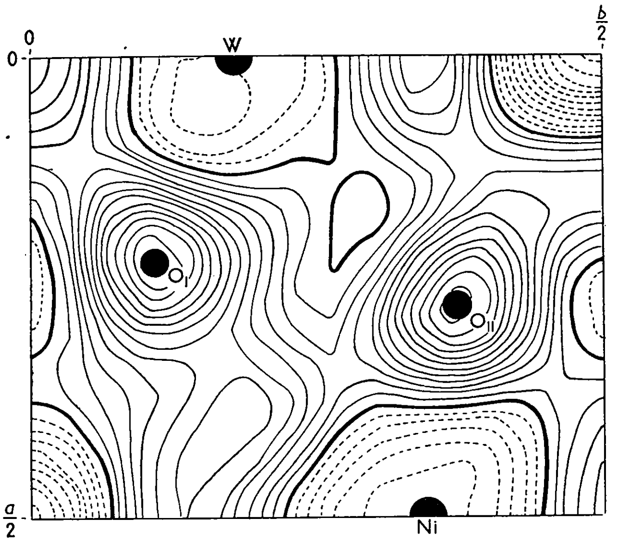

Fig. 2. The $F_o - F_{\text{Ni+W}}$ synthesis on (001). Zero contour shown by heavy solid lines, positive regions by light solid lines and negative regions by broken lines. Contours are at intervals of 1·1 e.Å^{-2}.

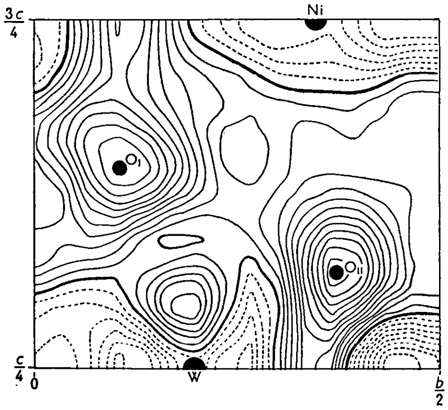

Fig. 3. The $F_o - F_{\text{Ni+W}}$ synthesis on (100). Zero contour shown by heavy solid lines, positive regions by light solid lines and negative regions by broken lines. Contours are at intervals of 1·1 e.Å^{-2}.

the (001) projection, with the exception that the first cycle of calculations made use of Ni and W parameters obtained from the (001) projection. Final values of observed and calculated $0kl$ structure factors are given in Table 2. The disagreement index omitting oxygens is 0·134; including oxygens it is 0·110. The oxygen peaks are shown in Fig. 3, which was plotted from the $F_o - F_{\text{Ni+W}}$ data of Table 2.

(c) *Final atomic coordinates*

The projections of the structure on (100) and (001) leave four possible combinations for the oxygen coordinates. They are:

	(1)	(2)	(3)	(4)
x_1	0·22	0·22	0·22	0·22
y_1	0·11	0·11	0·11	0·11
z_1	0·96	0·54	0·96	0·54
x_2	0·26	0·26	0·26	0·26
y_2	0·38	0·38	0·38	0·38
z_2	0·39	0·39	0·11	0·11

Of these four combinations, 2 and 3 may be eliminated immediately because they both require unreasonably short O–O distances (~ 1·7 Å). The choice between (1) and (4) is possible in principle from a comparison of the intensities of $h0l$ and $h0\bar{l}$ reflections. However, since β is not detectably different from 90° in $NiWO_4$, $h0l$ and $h0\bar{l}$ reflections cannot be indexed unambiguously and combinations (1) and (4) give experimentally indistinguishable structures. If $\beta \equiv 90°$ the two structures are equivalent.

In order to resolve this ambiguity, crystals of $MgWO_4$, which has a monoclinic angle detectably

Table 2. *0kl structure factors for* $NiWO_4$

$0kl$	$\|F_o\|$	$F_{\text{Ni+W}}$	F_c	$F_o - F_{\text{Ni+W}}$	$F_o - F_c$
002	110·2	−153·0	−130·0	42·8	19·8
004	80·9	98·2	95·2	−17·3	−14·3
006	55·9	−60·6	−62·8	4·7	−6·9
010	40·9	30·4	33·0	10·5	7·9
011	80·3	−79·9	−87·8	−0·4	7·5
012	29·3	−27·0	−16·3	−2·3	−13·0
013	61·8	62·2	59·0	−0·4	2·8
014	30·2	20·8	30·9	9·4	−0·7
015	39·1	−43·2	−38·4	4·1	−0·7
016	17·7	−15·2	−12·4	−2·5	−5·3
020	87·0	−90·3	−84·7	3·3	−2·3
021	94·9	−124·2	−106·6	29·3	11·7
022	83·2	72·1	75·8	11·1	7·4
023	99·0	89·7	107·1	9·3	−8·1
024	55·5	−51·8	−50·4	−3·7	−5·1
025	51·3	−57·6	−53·7	6·3	2·4
026	30·6	33·6	33·9	−3·0	−3·3
030	67·9	−69·2	−63·7	1·3	−4·2
031	36·9	32·5	29·1	4·4	7·8
032	61·4	62·5	60·2	−1·1	1·2
033	28·3	−24·7	−25·0	−3·6	−3·3
034	46·7	−47·5	−53·8	0·8	−7·1
035	20·5	16·6	22·3	3·9	−1·8
036	27·1	35·0	32·7	−7·9	−5·6
040	66·1	−34·7	−56·0	−31·4	−10·1
041	97·5	93·1	94·1	4·4	3·4
042	28·9	31·1	21·3	−2·2	7·6
043	73·5	−77·6	−75·3	4·1	1·8
044	22·5	−21·2	−18·8	−1·3	−3·7
045	49·7	55·0	57·4	−5·3	−7·7
050	58·2	56·3	53·7	1·9	4·5
051	32·8	23·3	26·7	9·5	6·1
052	54·0	−51·1	−56·5	−2·9	2·5
053	20·8	−20·8	−17·2	0·0	−3·6
054	34·5	40·4	34·0	−5·9	0·5
055	13·0	17·5	16·2	−4·5	−3·2
060	67·2	64·1	59·8	3·1	7·4
061	32·8	−21·4	−26·3	−11·4	−6·5
062	64·1	−58·8	−64·5	−5·3	0·4
063	17·7	19·0	12·1	−1·3	5·6
064	46·2	46·0	43·9	0·2	2·3
070	22·8	−12·3	−16·7	−10·5	−6·1
071	47·9	−44·0	−43·1	−3·9	−4·8
072	14·4	11·0	9·7	3·4	4·7
073	44·1	38·7	38·6	5·4	5·5

different from 90°, were grown by the same procedure as that used for $NiWO_4$ and oscillation photographs were taken to record the 102, $10\bar{2}$, 302, and $30\bar{2}$ reflections*. These reflections were chosen because they contain large oxygen contributions. Relative intensities were found to be:

$$I(10\bar{2}) > I(102), \quad I(302) > I(30\bar{2})\,.$$

These results are consistent with intensities calculated from combination (1) and inconsistent with those calculated from (4).

Making use of the results from $MgWO_4$, the final parameters for $NiWO_4$ are listed in Table 3. In this table parameters obtained in the two projections and the averages are listed separately. An anisotropic temperature factor given by

$$B_{\mathrm{Ni}} = \frac{(4\sin^2\theta)/\lambda^2}{1/(a^2B_a)+1/(b^2B_b)}$$

was applied to Ni in the final cycle of calculations for the (001) projection.

Table 3. *Final parameters for* $NiWO_4$

	(001) projection	(100) projection	Averages
y_{W}	0·179	0·180	0·180
y_{Ni}	0·653	0·653	0·653
x_1	0·223	—	0·22
y_1	0·107	0·104	0·11
z_1	—	0·963	0·96
x_2	0·263	—	0·26
y_2	0·378	0·374	0·38
z_2	—	0·392	0·39
B_{W}	1·0 Å^2	1·0 Å^2	—
B_{Ni}	B_a = 2·5 Å^2 B_b = 2·2 Å^2	2·0 Å^2	—
B_{O}	1·0 Å^2	1·0 Å^2	—

4. Discussion of results

A rigorous computation of the errors in atomic coordinates was not carried out. It appears from the agreement between the y coordinates observed in the two projections that y_{W} and y_{Ni} are accurate to at least ±0·001 of a cell division (~ 0·005 Å) and that the oxygen coordinates are correct to within ±0·01 of a cell division (~ 0·05 Å).

The final difference maps indicate that some further improvement could be made in Ni and W temperature factors. In particular, an anisotropic temperature factor is needed for W in the (100) projection. However, it is felt that further refinement along these lines would add little to the objective of the analysis, i.e. the location of oxygens. The temperature factors for Ni and W are quite large in view of the fact that $NiWO_4$ melts at 1390±10° C. The reason for such large values of B_{W} and B_{Ni} might lie in some disorder due to departures from strict stoichiometry.

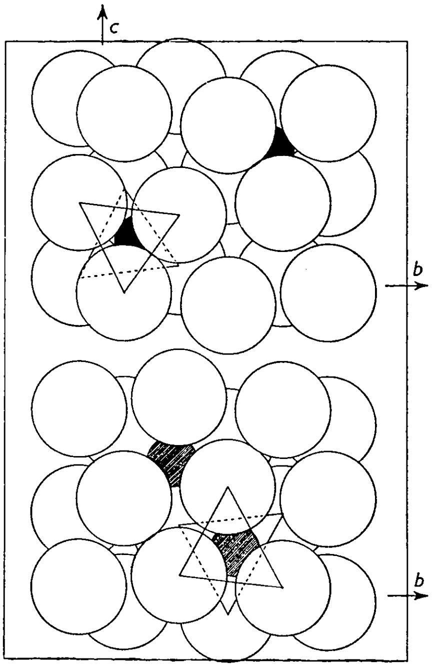

Fig. 4. The structure of $NiWO_4$ projected on (100). Large open circles: oxygen; small filled circles: tungsten; small shaded circles: nickel.

Top: layer centered on plane at $x = 0$. Bottom: layer centered on plane at $x = \frac{1}{2}$.

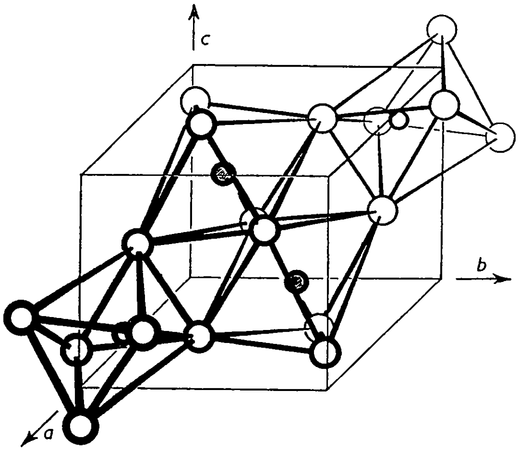

Fig. 5. WO_6 and NiO_6 octahedra in $NiWO_4$. Large open circles: oxygen; small open circles: tungsten; small shaded circles: nickel.

The structure as determined in the present study is shown in Fig. 4 and 5. It is based on a distorted hexagonal close packing of O atoms with Ni and W atoms each occupying one-fourth of the octahedral interstices (Fig. 4). The system of NiO_6 and WO_6 octahedra is shown in Fig. 5. Like octahedra are joined by edges, and different octahedra by corners.

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* These reflections are indexed according to the modern convention of $\beta > 90°$; i.e. $\beta = 90° 20'$, rather than 89° 40′ as given by Broch.

The structure differs from that proposed in *Strukturbericht* (1928–32) principally in the octahedral as opposed to tetrahedral coordination of O about W. It also has a more regular coordination of O about Ni. Interatomic distances are given in Table 4.

Table 4. *Interatomic distances in* $NiWO_4$

(Numbers in parentheses indicate multiplicity)

Ni–O	W–O
2·13 Å (2)	1·79 Å (2)
2·09 Å (2)	1·79 Å (2)
2·02 Å (2)	2·19 Å (2)
2·08 Å (average)	1·92 Å (average)
O–O (in the NiO_6 octahedron)	O–O (in the WO_6 octahedron)
2·93 Å (2)	2·93 Å (2)
2·92 Å (2)	2·80 Å (2)
2·81 Å (2)	2·89 Å (2)
2·81 Å (2)	2·76 Å (2)
3·20 Å (2)	2·61 Å (2)
3·30 Å (1)	2·60 Å (1)
2·60 Å (1)	3·30 Å (1)
2·94 Å (average)	2·82 Å (average)

An interesting feature of the structure is the position of the metal atom in relation to that of the center of charge of its surrounding oxygen octahedron. It is found that the metal atoms lie off center of their respective octahedra in a direction parallel to the *b* axis by 0·30 Å for W and 0·13 Å for Ni. Since the two like atoms in a unit cell are related by a center of symmetry, they are off center in opposite senses in a manner characteristic of an antiferroelectric. Thus far, attempts to discover a transition to a para- or ferroelectric structure have been unsuccessful.

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References

Broch, E. K. (1929). *Skr. norske VidenskAkad. Mat. Nat. Klasse*, No. 8.

Claassen, A. (1930). *Phil. Mag.* **2**, 57.

Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.

Strukturbericht (1928–32), vol. 2, p. 85.

Viervoll, H. & Ögrim, O. (1949). *Acta Cryst.* **2**, 277.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Acta Cryst. (1957). **10**, 213

The Structure of Cadmium Titanate and Sodium Tantalate

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Crystals of cadmium titanate and sodium tantalate grown from solution were found to have a distorted perovskite-type structure. The displacements of the ions from their ideal perovskite positions were calculated by a 'trial and error' method.

1. Introduction

It has been realized for a number of years that homopolar bonding must play an important part in the phenomenon of ferroelectricity (Megaw, 1946*a*; Vousden, 1951*a*, *b*) and Megaw (1952) has put forward a qualitative theory for barium titanate and associated materials. Later she widened the scope of the theory to include other types of ferroelectrics (Megaw, 1954). This theory suffers from the scarcity of knowledge about the actual ion positions in the unit cell. It needs an accurate knowledge of all the ion positions, and in most cases the displacements from the ideal perovskite structure are not known, or are not all known. The only perovskite-type materials for which the ionic displacements are known are $BaTiO_3$ (Kay & Vousden, 1949; Evans, 1951), $NaNbO_3$ (Vousden, 1951*b*), $CaTiO_3$ (Bailey, 1952), and $PbTiO_3$ (Shirane, Pepinsky & Frazer, 1956). The purpose of this investigation was to determine the position of the ions in $CdTiO_3$ and $NaTaO_3$ and hence to see to what extent homopolar bonding occurs and to attempt to explain the properties of these materials in terms of their bonding.

2. Crystal growth

Crystals were grown from solution. For cadmium titanate the solvent was two parts by weight sodium chloride, two parts sodium borate and one part sodium

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