

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<sub>4</sub>*

(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 <sub>6</sub> octahedron)	O–O (in the WO <sub>6</sub> 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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## 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<sub>3</sub> (Kay & Vousden, 1949; Evans, 1951), NaNbO<sub>3</sub> (Vousden, 1951*b*), CaTiO<sub>3</sub> (Bailey, 1952), and PbTiO<sub>3</sub> (Shirane, Pepinsky & Frazer, 1956). The purpose of this investigation was to determine the position of the ions in CdTiO<sub>3</sub> and NaTaO<sub>3</sub> 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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carbonate. The solvent was heated to about 900° C. in a small oxygen-coal-gas furnace and powdered cadmium titanate was added until no more would dissolve. Cooling in about an hour yielded clear, untwinned, orthogonal crystals of dimensions ~0.1 mm.

Sodium tantalate crystals were made by heating together 1.5 g. sodium carbonate, 2 g. sodium borate and 0.8 g. tantalum pentoxide for 12 hr. at 1250° C. in a platinum-wound electric furnace and allowing the furnace to cool in 6 hr. Colourless orthogonal crystals of side up to 1 mm. resulted. Many of the smaller crystals looked untwinned under the polarizing microscope but a large number of these had to be examined by X-rays before two truly untwinned crystals were found.

The chemical composition of the crystals was checked by superimposing on the same film a rotation photograph of the crystal and a powder photograph of cadmium titanate or sodium tantalate. All the reflexions from the crystal fell on the powder lines.

### 3. Unit cell

Working with powdered  $\text{CdTiO}_3$ , Megaw (1946b) showed that the structure is distorted from the ideal perovskite arrangement and that the true symmetry is orthorhombic. Megaw indexed the powder lines on the assumption that the cell is doubled along all three orthorhombic axes, and gave the unit cell as:

$$a = 10.695, \quad b = 7.615, \quad c = 10.834 \text{ \AA}.$$

Sets of 15° oscillation photographs were taken for each of these orthorhombic axes and doubling was in fact present only along the  $b$  axis. The true unit cell is thus:

$$a = 5.348, \quad b = 7.615, \quad c = 5.417 \text{ \AA}.$$

Fig. 1 shows the unit cell. Each of the eight small monoclinic cells contains one  $\text{CdTiO}_3$  unit; the orthorhombic cell thus has four such units.

The sodium tantalate unit cell is also an orthorhombic modification of the perovskite structure. Vousden (1951a) gave the unit cell as:

$$a = 5.4941, \quad b = 3.8754, \quad c = 5.5130 \text{ \AA}.$$

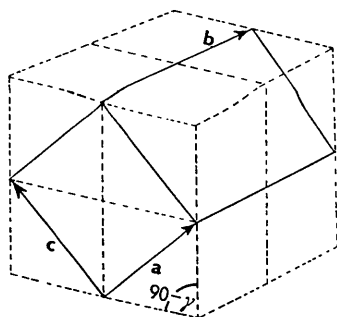


Fig. 1. Unit cells of both cadmium titanate and sodium tantalate (full-line) in relation to primitive pseudo-cubes (broken line).

Work on single crystals showed, however, that the cell is doubled along the  $b$  axis, giving  $b = 7.7508 \text{ \AA}$ . Thus the unit cell of sodium tantalate is also represented by Fig. 1.

### 4. Space-group determination of cadmium titanate

Photographs for intensity measurement were taken on a Weissenberg goniometer using the multiple-film technique. The layer-lines recorded were  $(hkl)$ ,  $(0kl)$  and  $(h0l)$ . The films were developed and printed using the Dawton (1938) technique. The intensities of the reflexions were measured on a photometer and were corrected for absorption, Lorentz, and polarization factors. Intensities for these layer lines were not put on a common scale.

Systematic absences were observed for  $(hkl)$  with  $h+k$  odd and for  $(0kl)$  with  $l$  odd. There were no extra systematic absences for  $(h0l)$ ; it follows that there can be no systematic absences for  $(hkl)$ . If, in addition to the glide planes indicated by these absences, there are mirror planes perpendicular to the  $b$  axis, the space group will be No. 62,  $Pcmn$ . On the other hand, if these mirror planes do not exist, the space group will be No. 33,  $Pc2_1n$ .

The unit cell contains 4  $\text{CdTiO}_3$ .

The positions of the undisplaced ions in the unit cell are shown in Table 1.

Table 1. Positions of undisplaced ions

Cd	$0, \frac{1}{2}, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
Ti	$\frac{1}{2}, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}; 0, 0, \frac{1}{2}$
O (group 1)	$0, \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, 0$
O (group 2)	$\frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
O (group 3)	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}$

Since the ionic displacements from these positions cannot be very great, the symmetry elements of the two space groups can immediately be placed relative to this undisplaced array. The positions of the symmetry elements in  $Pc2_1n$  are:

$hk0$  glide in  $x, y, \frac{1}{4}; x, y, \frac{3}{4}$ .

$0kl$  glide in  $\frac{1}{4}, y, z; \frac{3}{4}, y, z$ .

Screw diads in  $0, y, 0; \frac{1}{2}, y, 0; 0, y, \frac{1}{2}; \frac{1}{2}, y, \frac{1}{2}$ .

In  $Pcmn$ , however, with the undisplaced atomic coordinates already fixed, there are two ways of placing the mirror planes so that they go through either the cadmium or titanium ions. These will be named  $Pcmn(1)$  and  $Pcmn(2)$  respectively. In  $Pc2_1n$  and  $Pcmn(2)$  the choice of origin relative to the symmetry elements is that given in the *International Tables*: thus, in  $Pcmn(2)$   $(0, 0, 0)$  is at a centre of symmetry. In  $Pcmn(1)$ , however, the origin is chosen so as to put the symmetry centre at  $(0, \frac{1}{4}, 0)$ .

It is worth considering the differences between these arrangements. In  $Pcmn(1)$  the cadmiums are on symmetry centres with no unknown parameters. The titaniums are on mirror planes with  $x$  and  $z$  parameters

only. In  $Pcmn(2)$  these are reversed: titaniums are on symmetry centres, cadmiums on mirror planes. The remaining arrangement,  $Pc2_1n$ , is polar and allows arbitrary parameters  $x, y$  and  $z$  for both cations.

A set of relationships between the ionic displacements in each of the three space groups may be deduced from the symmetry. The twelve oxygen ions divide into three groups of four ions with related displacements. Let the atoms in positions  $X_i, Y_i, Z_i$  in the first column of Table 1 have displacements of  $x_i, y_i, z_i$ , where subscript  $i$  denotes Cd, Ti, O1, O2, O3, and all coordinates are expressed as a fraction of the cell edge. Then, for example, in the space group  $Pc2_1n$  the oxygen atoms of group 1 have the displacements shown in Table 2.

Table 2. Displacements of O (group 1) atoms

Undisplaced positions	$0, \frac{1}{2}, \frac{1}{2}$	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, 0$	$\frac{1}{2}, \frac{1}{2}, 0$
Displacements	$\begin{cases} x_{O1} = -x_{O1} = -x_{O1} = x_{O1} \\ y_{O1} = y_{O1} = y_{O1} = y_{O1} \\ z_{O1} = -z_{O1} = z_{O1} = -z_{O1} \end{cases}$			

To determine which of the space groups is correct, and to evaluate the magnitude of the displacements of the ions, necessitates an examination of the intensities of the reflexions. The reflexions which are most sensitive to the ion displacements are clearly those which are produced solely by those displacements. Assuming for the moment that all the ionic displacements are zero then there will be lattice points at  $0, \frac{1}{2}, 0$  and  $\frac{1}{2}, 0, \frac{1}{2}$  as well as at  $0, 0, 0$ . It follows that reflexions with  $k$  odd or  $(h+l)$  odd would be absent. Hence, since these reflexions in fact appear, they must be due to ionic displacements only. These superlattice reflexions are:

$$\begin{aligned} (0kl): & \quad k \text{ odd, } l \text{ even;} \\ (hk0): & \quad h \text{ odd, } k \text{ odd;} \\ (h0l): & \quad h \text{ odd, } l \text{ even;} \\ (h0l): & \quad h \text{ even, } l \text{ odd.} \end{aligned}$$

Since the coordinates of the  $i$ th atom are  $(X_i + x_i), (Y_i + y_i), (Z_i + z_i)$ , the intensity of a reflexion  $(hkl)$  is given by

$$|F_{hkl}|^2 = [\sum_i f_i \cos(\varphi_i + \Delta_i)]^2 + [\sum_i f_i \sin(\varphi_i + \Delta_i)]^2, \quad (1)$$

where

$$\begin{aligned} \varphi_i &= 2\pi(hX_i + kY_i + lZ_i), \\ \Delta_i &= 2\pi(hx_i + ky_i + lz_i). \end{aligned}$$

This may be expanded in terms of  $\cos \varphi_i, \sin \varphi_i, \cos \Delta_i$  and  $\sin \Delta_i$ . Since the coordinates  $X_i, Y_i, Z_i$  are all multiples of  $\frac{1}{2}$ , all factors  $\cos \varphi_i$  and  $\sin \varphi_i$  are  $\pm 1$  or  $0$ ; hence the expression can be much simplified.

Summation over  $i$  involves (i) summation over sets of atoms related by symmetry, e.g. over all oxygen atoms of group 1; (ii) summation over the five sets of atoms in Table 1. In performing summation (i) we use the relations between displacements such as those illustrated in Table 2. The results may be expressed in terms of the atoms in the first column of

Table 1, which are taken as prototypes of the set. Since some terms constantly recur, it is convenient to use an abbreviated notation, e.g.

$$\begin{aligned} 2f_{Cd} \{\sin 2\pi(hx_{Cd} + ky_{Cd}) - \sin 2\pi(hx_{Cd} - ky_{Cd})\} &= S_{Cd}^-(hk), \\ 2f_{O} \{\cos 2\pi(ky_{O2} + lz_{O2}) + \cos 2\pi(ky_{O2} - lz_{O2})\} &= C_{O2}^+(kl). \end{aligned}$$

Here  $x_{Cd}, y_{Cd}, z_{Cd}$  are the displacements of the cadmium atom from  $(0, \frac{1}{2}, 0)$ ;  $x_{O2}, y_{O2}, z_{O2}$  are the displacement of a group (2) oxygen atom from  $(\frac{1}{2}, 0, \frac{1}{2})$ . The indices  $(hk)$  or  $(kl)$  are omitted from the symbol where the content makes it clear what they should be.

## 5. Elimination of the space group $Pcmn(1)$

Since  $Pc2_1n$  is polar and  $Pcmn$  is non-polar, physical methods of determining which was correct were tried. Unfortunately, no apparatus for piezoelectric detection was available and tests for pyroelectric effect were inconclusive.

The space group  $Pcmn(1)$  is, however, readily eliminated by considering the reflexions of class  $(0kl)$ ,  $k$  odd,  $l$  even. The structure factor equations are:

$$Pcmn(1): |F_{0kl}|^2 = [4f_{Ti}^{0kl} \sin 2\pi lz_{\frac{1}{2}, 0, 0}]^2, \quad (2)$$

$$Pcmn(2): |F_{0kl}|^2 = [S_{Cd}^- + S_{O1}^{\pm} (C_{O2}^- - C_{O3}^-)]^2, \quad (3)$$

with the positive sign for  $(k+l) = 4n+1$  and the negative sign for  $(k+l) = 4n+3$ .

$$\begin{aligned} Pc2_1n: |F_{0kl}|^2 &= [\pm S_{Cd}^- + C_{Ti}^{\pm} S_{O1}^{\pm} (C_{O2}^- - C_{O3}^-)]^2 \\ &+ [\pm C_{Cd}^- + S_{Ti}^{\pm} C_{O1}^{\pm} (S_{O2}^- - S_{O3}^-)]^2, \quad (4) \end{aligned}$$

where the signs depend upon whether  $(k+l) = (4n+1)$  or  $(4n+3)$ .

Now Table 3 shows that the intensities of the  $(0kl)$  reflexions are strongly dependent upon whether  $(k+l)$  is  $(4n+1)$  or  $(4n+3)$ . As the structure-factor equation for  $Pcmn(1)$  is independent of this criterion,  $Pcmn(1)$  cannot be the correct space group.

It is not possible to eliminate either of the other space groups so easily. However, the ion shifts permitted by the two space groups are very similar except that  $Pcmn(2)$  imposes certain restrictions on the displacements. If, therefore, the space group is assumed to be  $Pc2_1n$  and the true space group is  $Pcmn(2)$  this will reveal itself by the fact that the titanium shifts will be zero, as will the  $y$  shifts of the cadmium and oxygen (group 1) ions. Also the shifts of the group 2 and group 3 oxygen ions will be equal in magnitude.

## 6. Reflexions $(h0l)$ , $h$ odd, $l$ even, and $(h0l)$ , $h$ even, $l$ odd

The structure-factor equations for these reflexions are:

$h$  even,  $l$  odd:

$$|F_{h0l}|^2 = [C_{Cd}^- + C_{Ti}^- - C_{O1}^{\pm} (S_{O2}^+ + S_{O3}^+)]^2; \quad (5)$$

$h$  odd,  $l$  even:

$$|F_{h0l}|^2 = [C_{Cd}^- - C_{Ti}^- + C_{O1}^{\pm} (S_{O2}^- + S_{O3}^-)]^2. \quad (6)$$

Table 3. *Intensities of cadmium titanate*

<i>hkl</i>	$ F_o $	$ F_c $	<i>hkl</i>	$ F_o $	$ F_c $	<i>hkl</i>	$ F_o $	$ F_c $
201	7.6	7.8	130	11.7	10.7	012	21.1	17.8
401	6.8	7.3	150	7.5	8.4	032	24.0	23.0
601	< 3.0	3.6	170	3.9	3.5	052	10.0	11.8
203	3.5	3.5	310	< 3.0	1.2	072	13.0	14.8
403	< 3.0	0.1	330	5.6	7.0	092	7.6	9.2
603	6.3	5.4	350	< 3.0	1.8	014	30.0	25.7
102	4.4	8.6	370	3.6	3.8	034	19.9	16.6
104	8.2	8.4	390	< 3.0	2.0	054	24.9	24.4
106	< 3.0	2.5	510	6.2	4.9	074	12.5	12.5
302	6.4	4.6	530	5.5	4.7	094	12.9	14.4
304	< 3.0	1.8	550	6.1	4.9	0,11,4	10.0	13.2
306	4.8	4.8	570	4.5	4.2	016	19.9	19.6
502	3.3	1.6	590	3.0	3.8	036	23.0	22.6
504	4.0	2.5	710	8.3	6.7	056	13.6	17.1
506	3.6	2.9	730	5.7	4.1	076	16.6	19.1
702	< 3.0	0.7	750	8.5	7.9	096	10.5	15.8
704	4.8	4.5	770	4.9	4.5	018	13.5	19.0
706	< 3.0	2.4	790	5.5	5.2	038	11.1	18.3
			910	5.4	5.1	058	12.1	18.6
			930	7.8	8.1			
			950	3.0	3.2			
			970	6.6	7.1			
			11,1,0	4.6	6.1			

The positive sign applies for  $(h+l) = (4n+3)$  and the negative sign for  $(h+l) = (4n+1)$ .

An examination of the  $|F_o|$  values of Table 3 reveals the following facts: First, in the reflexions having  $h$  or  $l$  equal to 1 or 3, reflexions  $(h0l)$  have roughly the same intensity as reflexions  $(l0h)$ ; thus the titanium and group 1 oxygen displacements do not affect the intensities of this group of reflexions greatly. In fact, as will be shown later, the  $z$  displacement of the titanium is large but the term  $C_{\bar{Ti}}$  is still small since it vanishes if  $x_{Ti}$  vanishes. Secondly, there is a dependence upon whether  $(h+l) = (4n+3)$  or  $(4n+1)$ . This means that the cadmium term and oxygen (groups 2, 3) terms must be non-zero.

Now consider absences in reflexion class  $(h0l)$ ,  $h$  odd,  $l$  even. For  $h > 5$  the absent reflexions have  $(h+l) = (4n+1)$ , for  $h = 5$  there are no absences, and for  $h < 5$  the absent reflexions have  $(h+l) = (4n+3)$ . It follows that either the cadmium or oxygen (groups 2, 3) terms change sign at  $h = 5$ . The cadmium displacements are too small to cause a sign change but if we put  $x_{O2} = x_{O3} = 0.05$  we obtain the desired result. The  $z$  displacement must also be  $\sim 0.05$  to give good agreement between observed and calculated intensities.

It is now necessary to decide the signs of these displacements. Putting  $x_{\frac{1}{2},0,\frac{1}{2}} = -x_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$  or  $z_{\frac{1}{2},0,\frac{1}{2}} = -z_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$  results in the terms containing oxygen (groups 2, 3) in equations (5) and (6) becoming zero and this is impossible, as pointed out above. We are thus left with the following cases:

- 1  $\begin{cases} x_{\frac{1}{2},0,\frac{1}{2}} \text{ positive, } x_{\frac{1}{2},\frac{1}{2},\frac{1}{2}} \text{ positive,} \\ z_{\frac{1}{2},0,\frac{1}{2}} \text{ negative, } z_{\frac{1}{2},\frac{1}{2},\frac{1}{2}} \text{ negative;} \end{cases}$
- 2  $\begin{cases} x_{\frac{1}{2},0,\frac{1}{2}} \text{ positive, } x_{\frac{1}{2},\frac{1}{2},\frac{1}{2}} \text{ positive,} \\ z_{\frac{1}{2},0,\frac{1}{2}} \text{ positive, } z_{\frac{1}{2},\frac{1}{2},\frac{1}{2}} \text{ positive.} \end{cases}$

To see which of these is the more probable we can consider the interionic distances. The sum of the Goldschmidt radii for  $Ti^{+4}$  and  $O^{-2}$  is 1.96 Å. In the first case the Ti-O distance shortens to 1.52 Å for two of the oxygen ions and no displacement of the titanium ion can make both these distances much greater. On the other hand, the signs given in the second case make all the O2,3-Ti distances about 1.9 Å. It is therefore by far the more likely arrangement. This argument was checked after the displacement of the titanium ion had been deduced and was found to hold good.

Various values were tried for the cadmium displacements and the following values were found to give the best results for the  $(h0l)$  reflexions:

$$x_{Cd} = 0.008; z_{Cd} = 0.015 \text{ (signs not determined).}$$

$$x_{O2} = x_{O3} = +0.05; z_{O2} = z_{O3} = +0.06.$$

## 7. Reflexions $(h k 0)$ , $h$ odd, $k$ odd

The structure-factor equation for this class of reflexion is:

$$|F_{h k 0}|^2 = [-C_{\bar{Ti}} \pm S_{Cd}^+ + S_{O1}^+ \pm (S_{O2}^- - S_{O3}^-)]^2 + [-S_{Ti}^+ \pm C_{Cd}^- + C_{O1}^- \pm (S_{O2}^+ - S_{O3}^+)]^2. \quad (7)$$

Examination of the  $|F_o|$  values in Table 3 shows that the (130) reflexion is strong and that the reflexions with  $h = 1$  fall off rapidly in intensity. It is likely that this effect is caused by the oxygen displacements since the atomic scattering factor of oxygen falls off rapidly as  $\sin \theta/\lambda$  increases. In order to make the effect of the O2,3 displacements great at low angles it is necessary to put  $y_{O2} \approx -0.03$  and  $y_{O3} \approx +0.07$ . Table 3 shows that  $(h k 0)$  reflexions with  $h = 3$  or 5 are stronger when  $(h+k) = (4n+2)$  than when  $(h+k) = 4n$ , whereas those with  $h = 7$  and 9 are stronger when

$(h+k) = 4n$  than when  $(h+k) = (4n+2)$ . The O2,3 terms in equation (7) are dependent upon  $h$  and change sign according to whether  $h = (4n+1)$  or  $(4n+3)$ . In order to account for the above effect there must be an additional reversal of sign when  $h = 7$  and 9. This is precisely the effect of putting  $x_{O2} = x_{O3} = 0.05$ ,  $y_{O2} = -0.03$ ,  $y_{O3} = +0.07$ .

### 8. Reflexions $(0kl)$ , $h$ odd, $k$ odd

For this class of reflexions we have:

$$|F_{0kl}|^2 = [\pm S_{Cd} + C_{Ti} \pm S_{O1} \pm (C_{O2} - C_{O3})]^2 + [\pm C_{Cd} + S_{Ti} \pm C_{O1} \pm (S_{O2} - S_{O3})]^2 \quad (8)$$

In order to obtain good correlation between the observed and calculated intensities of this class it is necessary that there should be a large  $z$  displacement of the titanium ions. This displacement and the lack of equality between the  $y$  displacements of the group 2 and group 3 oxygen ions means that the space group cannot be  $Pcmn$ . Hence the displacements in the  $y$  directions of the various ion groups are polar and independent of one another. It follows that the  $y$  displacements of any one group of ions can be fixed in an arbitrary manner. Thus the  $y$  displacements of the cadmium ions will be taken as zero and the other  $y$  displacements calculated in relationship to this. Best results with this class of reflexions are obtained with  $y_{Ti} = 0$ ,  $z_{Ti} = -0.065$ .

Having found the signs and approximate magnitudes of the most important displacements, it becomes a simple matter to try various values of those displacements which have so far been ignored to see which make the most improvement in  $|F_c|$ . The effect of making slight changes on the other displacements can also be tried.

The final calculated positions of the various ions

Table 4. Ion positions in cadmium titanate

	Ion positions				Estimated error
Cd	$x: 0+0.006$	$0-0.006$	$\frac{1}{2}+0.006$	$\frac{1}{2}-0.006$	$\pm 0.002$
	$y: \frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	
	$z: 0+0.016$	$0-0.016$	$\frac{1}{2}-0.016$	$\frac{1}{2}+0.016$	$\pm 0.002$
Ti	$x: \frac{1}{2}+0.005$	$\frac{1}{2}-0.005$	$0+0.005$	$0-0.005$	$\pm 0.005$
	$y: 0$	$\frac{1}{2}$	$\frac{1}{2}$	$0$	
	$z: 0-0.065$	$0+0.065$	$\frac{1}{2}+0.065$	$\frac{1}{2}-0.065$	$\pm 0.010$
O1	$x: 0-0.03$	$0+0.03$	$\frac{1}{2}+0.03$	$\frac{1}{2}-0.03$	$\pm 0.015$
	$y: \frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\pm 0.025$
	$z: \frac{1}{2}+0.05$	$\frac{1}{2}-0.05$	$0+0.05$	$0-0.05$	$\pm 0.015$
O2	$x: \frac{1}{2}+0.05$	$\frac{1}{2}-0.05$	$\frac{1}{2}-0.05$	$\frac{1}{2}+0.05$	$\pm 0.005$
	$y: 0-0.03$	$0-0.03$	$\frac{1}{2}-0.03$	$\frac{1}{2}-0.03$	$\pm 0.015$
	$z: \frac{1}{2}+0.06$	$\frac{1}{2}+0.06$	$\frac{1}{2}-0.06$	$\frac{1}{2}-0.06$	$\pm 0.015$
O3	$x: \frac{1}{2}+0.05$	$\frac{1}{2}-0.05$	$\frac{1}{2}-0.05$	$\frac{1}{2}+0.05$	$\pm 0.005$
	$y: \frac{1}{2}+0.07$	$\frac{1}{2}+0.07$	$0+0.07$	$0+0.07$	$\pm 0.015$
	$z: \frac{1}{2}+0.06$	$\frac{1}{2}+0.06$	$\frac{1}{2}-0.06$	$\frac{1}{2}-0.06$	$\pm 0.015$

are shown in Table 4; the errors indicated were arrived at by considering the effect of a small change in the ion displacements. If a small change in the displacement of one ion has a large effect on the calculated  $F$  values, then the probable error is likely to be small. Conversely, if the effect of the change is small the probable error is large. Since the analysis was performed by 'trial and error' methods the errors will not be independent. The values of  $|F_c|$  which these displacements give are listed in Table 3. The reliability factor  $\Sigma|F_o| - \Sigma|F_c| \div \Sigma|F_c|$  is 0.17 for the  $(0kl)$ , 0.14 for  $(hk0)$  and 0.20 for  $(h0l)$  reflexions. Fig. 2(a) shows the displacements of the ions.

### 9. The structure of sodium tantalate

The systematic absences for sodium tantalate were the same as for cadmium titanate; thus the possible space

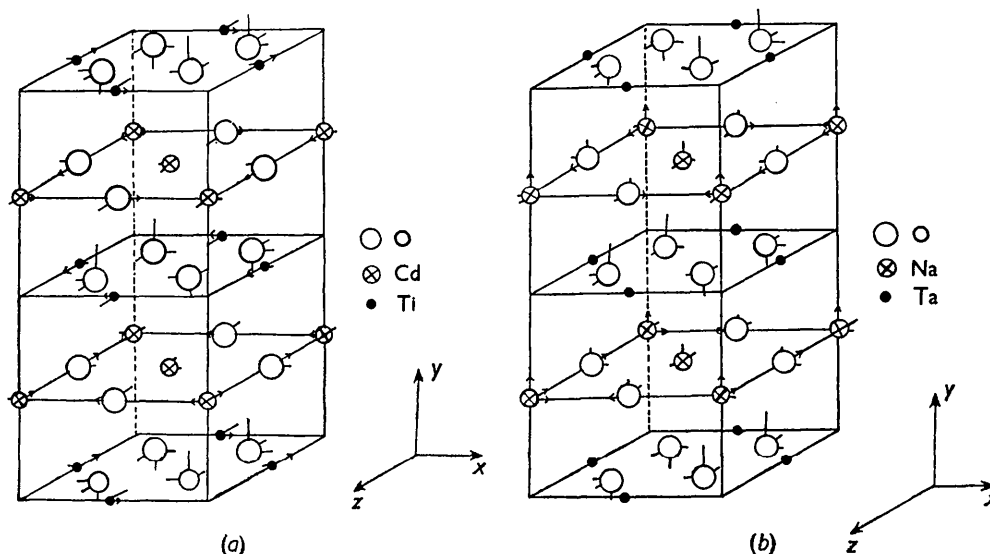


Fig. 2. Ionic displacements (a) in cadmium titanate, (b) in sodium tantalate.

Table 5. *Intensities of sodium tantalate*

<i>hkl</i>	$ F_o $	$ F_c $	<i>hkl</i>	$ F_o $	$ F_c $	<i>hkl</i>	$ F_o $	$ F_c $
130	13.8	12.0	012	< 2.0	0.9	102	8.5	7.2
150	5.9	6.7	014	3.9	6.8	104	6.0	6.4
170	6.8	6.0	016	< 2.0	1.7	302	3.7	3.3
310	9.1	5.8	032	7.3	6.2	304	2.2	3.7
330	< 2.0	1.4	034	< 2.0	0.8	201	8.9	6.4
350	7.1	6.5	036	3.5	5.4	401	5.7	6.8
370	< 2.0	1.5	052	< 2.0	1.6	203	3.4	4.3
390	4.3	4.3	054	4.1	5.3	403	3.5	2.5
510	< 2.0	2.5	056	< 2.0	1.6			
530	2.4	4.0	072	4.1	3.3			
			074	< 2.0	1.7			
			076	3.0	5.0			

groups were the same. The superlattice reflexions were very weak and fell off rapidly at high angles. Now for  $\sin \theta/\lambda \geq 0.5$  we have  $f_{Ta} \geq 10f_{Na}$  and  $f_{Ta} \geq 15f_O$ . It follows that the tantalum displacements must be zero or very small. Calculation shows that the tantalum displacements cannot be greater than 0.002.

The structure determination was carried out on similar lines to that of cadmium titanate. The accuracy of the final result is limited by the fact that the observed number of superlattice reflexions was small and some of these were so faint that their intensities could not be reliably measured. Additional information was given by the fact that ten reflexions were too faint to be seen although they had indices which are lower than those of spots which were present.

Table 5 shows the correlation between  $|F_o|$  and  $|F_c|$  for sodium tantalate and Table 6 gives the displaced

Table 6. *Ion positions in sodium tantalate*

Ion positions				
Na	$x:$	0-0.01	0+0.01	$\frac{1}{2}$ -0.01
	$y:$	$\frac{1}{2}$ +0.03	$\frac{1}{2}$ +0.03	$\frac{1}{2}$ +0.03
	$z:$	0+0.02	0-0.02	$\frac{1}{2}$ -0.02
Ta*	$x:$	$\frac{1}{2}$	$\frac{1}{2}$	0
	$y:$	0	$\frac{1}{2}$	0
	$z:$	0	0	$\frac{1}{2}$
O1	$x:$	0-0.02	0+0.02	$\frac{1}{2}$ +0.02
	$y:$	$\frac{1}{2}$ +0.01	$\frac{1}{2}$ +0.01	$\frac{1}{2}$ +0.01
	$z:$	$\frac{1}{2}$ +0.02	$\frac{1}{2}$ -0.02	0+0.02
O2	$x:$	$\frac{1}{2}$ +0.04	$\frac{1}{2}$ -0.04	$\frac{1}{2}$ +0.04
	$y:$	0-0.03	0-0.03	$\frac{1}{2}$ -0.03
	$z:$	$\frac{1}{2}$ +0.04	$\frac{1}{2}$ +0.04	$\frac{1}{2}$ -0.04
O3	$x:$	$\frac{1}{2}$ +0.04	$\frac{1}{2}$ -0.04	$\frac{1}{2}$ +0.04
	$y:$	$\frac{1}{2}$ +0.06	$\frac{1}{2}$ +0.06	0+0.06
	$z:$	$\frac{1}{2}$ +0.04	$\frac{1}{2}$ +0.04	$\frac{1}{2}$ -0.04

\* All positions  $\pm 0.002$ .

positions of the ions. Taking slightly different positions for some of the ions does not greatly affect the values of  $|F_c|$ . In particular, the reduction of  $y_{O1}$  to zero results in only slight deterioration of the correlation between  $|F_o|$  and  $|F_c|$ . However, although this dis-

placement is not accurately calculable by these X-ray measurements the bonding will be different if it is in fact zero. This point will be further discussed in a later paper on the bonding and properties of cadmium titanate and sodium tantalate. The reliability factor is 0.22 in the case of sodium tantalate. Fig. 2(b) shows the ionic displacements.

### 10. Summary

The purpose of these structure determinations was to try to find correlation between the properties of the materials and their bonding. Thus any use of inter-ionic distances or of bonding considerations in the analysis would tend to invalidate arguments about the bonding which are based on the structure determination. The only occasion in which interionic distances were used was in deciding the relative signs of the  $x$  and  $z$  displacements of the group 2 and 3 oxygen ions. In this case the only alternative to the configuration chosen would have given impossibly small distances between the oxygen and titanium ions. Hence the structures determined may be used to determine the bonding in the crystals.

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