Acta Cryst. (1965). **19**, 169

Double Oxides Containing Niobium or Tantalum. I. Systems Including Alkali Metals

By C. D. Whiston* and A. J. Smith

Department of Chemistry, The University, Sheffield 10, *England*

(*Received* 1 *October* 1964)

The binary systems $A_2O-B_2O_5$ (A = Li, Na, or K; B = Nb or Ta) and two phases in the system $Cs_2O-Nb_2O_5$ have been studied. One new intermediate phase, $Li_2Ta_4O_{11}$, has been found, and unit-cell data are reported for most of the 22 double oxides which were observed. These do not include the well-known ABO_3 compounds. Two superstructures of the tetragonal bronze type, with unit cells of three and nine times the 'ideal' cell, are among those found.

Introduction

Mixed oxide systems involving niobium or tantalum have received attention from a number of investigators in recent years. For convenience in presentation, the results of previous studies are summarized under the separate systems.

Each system was first surveyed by firing mixtures of various proportions of alkali metal carbonate and niobium or tantalum pentoxide in air at temperatures usually between 800° and 1000 °C. Examination of the products of these solid-state reactions by X-ray powder diffraction procedures served to determine the compositions of the intermediate phases formed in the system. In a few cases the powder patterns were indexed. When this was not possible, the compositions corresponding to single-phase products were either heated a little above their melting points and cooled slowly, or heated below their melting points for extended periods of time, in attempts to grow single crystals suitable for X-ray studies. These firings were usually carried out in platinum or iridium boats. Powder patterns from the crystals so obtained were compared with those found in the original survey in order to confirm that the crystals had the composition assigned to them.

Nickel-filtered copper radiation was used throughout for the X-ray work, and the wavelengths were taken to be $K\alpha_1 = 1{\cdot}54051$, $K\alpha_2 = 1{\cdot}54432$, and $K\alpha_m = 1{\cdot}54178$ Å. Cell constants were determined, wherever possible, from powder data by a Nelson–Riley extrapolation procedure using the least-squares Mercury computer program of Wait (1961), or from Weissenberg α_1/α_2 spot separations by the method of Main & Woolfson (1963). Where limits of error are quoted they are the standard deviations obtained by one or other of these procedures; otherwise lattice parameters should be taken to be correct to within about $\pm 0{\cdot}3\%$.

The compositions of the phases detected in the powder survey were deduced initially from compositions of starting mixtures (Johnson Matthey 'Specpure' materials were used whenever possible) and observed weight losses. The difficulty of attacking the compounds to form a suitable solution proved a serious obstacle to chemical analysis, and a few revisions of these initial compositions are noted below. The compound of composition ABO_3 was observed in each of the systems here reported, but these compounds are well known and were not further studied. Fuller details of all experimental conditions used are given by Whiston (1963).

We have examined the systems Li_2O, Na_2O, and K_2O with Nb_2O_5 and Ta_2O_5 (except for the alkali-rich end of the $K_2O–Nb_2O_5$ system). The phases observed are listed in Tables 1 and 2; unit-cell data are presented for those listed in bold type. In addition, we have studied $Cs_4Nb_{30}O_{77}$ and $Cs_5Nb_{13}O_{35}$, and report unit cells for both of them.

Table 1. *Niobium compounds observed*

$Li_2Nb_{24}O_{61}$	**$Na_2Nb_{24}O_{61}$**	
		$K_6Nb_{44}O_{113}$
	$Na_2Nb_8O_{21}$	**'$K_2Nb_8O_{21}$'**
$LiNb_3O_8$		**KNb_3O_8**
		$\left\{\begin{array}{l}\textbf{K}_4\textbf{Nb}_6\textbf{O}_{17}\ \textbf{(high temp.)}\\ K_4Nb_6O_{17}\ \text{(low temp.)}\end{array}\right\}$
		$K_{12}Nb_{14}O_{41}$
($LiNbO_3$)	($NaNbO_3$)	($KNbO_3$)
Li_3NbO_4	**Na_3NbO_4**	

Table 2. *Tantalum compounds observed*

		KTa_5O_{13}
$Li_2Ta_8O_{21}$	**$Na_2Ta_8O_{21}$**	
$Li_2Ta_4O_{11}$	**$Na_2Ta_4O_{11}$**	**$K_2Ta_4O_{11}$**
($LiTaO_3$)	($NaTaO_3$)	($KTaO_3$)
Li_3TaO_4	**Na_3TaO_4**	K_3TaO_4

The system $Li_2O–Nb_2O_5$

Li_3NbO_4 was prepared by Lapitskii & Simanov (1954), who found it to be cubic with $a = 8{\cdot}405$ Å. Recently Blasse (1963) has reported the structure based on that of rock salt and given $a = 8{\cdot}433$ Å.

Reisman & Holtzberg (1958*b*) reported the compounds $Li_2Nb_{28}O_{71}$ (m.p. 1268 °C) and $Li_2Nb_8O_{21}$ (m.p. 1231 °C) also.

---

* Present address: Stewarts and Lloyds, Ltd, Corby, Northants, England.

We obtained products corresponding to each of these phases. Li_3NbO_4 was formed at 1000 °C and gave the pattern of a body-centred cubic lattice with $a=8{\cdot}4300\pm0{\cdot}0008$ Å. The density was observed to be 3·8 g.cm^{-3} (calculated for $Z=8$, 3·9). At higher temperatures (1300 to 1400 °C) this compound decomposed yielding $LiNbO_3$ (and presumably Li_2O).

'$Li_2Nb_8O_{21}$' was obtained at 1230 °C, in the form of colourless squarish plates, together with a few acicular crystals of $LiNbO_3$. The primitive monoclinic cell was found to have

$$a=7{\cdot}435,\ b=5{\cdot}618,\ c=7{\cdot}079\ \text{Å};\ \beta=101{\cdot}0^\circ.$$

The observed density was 4·75 g.cm^{-3}. (Reisman & Holtzberg found 4·784.) But that calculated for the formula $Li_2Nb_8O_{21}$ and $Z=1$ was 6·3 g.cm^{-3}. The true unit-cell content is thought to be $Li_2Nb_6O_{16}$, which gives a calculated density of 4·79 g.cm^{-3}. On further heating at high temperature this compound decomposed to give $LiNbO_3$ and Nb_2O_5.

'$Li_2Nb_{28}O_{71}$' was obtained in the form of pale yellow crystals on heating an appropriate starting mixture at 1250 °C for a week. The lattice was found to be primitive monoclinic with

$$a=44{\cdot}79,\ b=3{\cdot}807,\ c=28{\cdot}38\ \text{Å};\ \beta=106{\cdot}5^\circ.$$

The density measured (4·6 g.cm^{-3}) agrees with that of Reisman & Holtzberg, but not with any calculated for the above formula (5·4 g.cm^{-3} for $Z=4$) and we consider that the true composition of the phase is $Li_2Nb_{24}O_{61}$. This gives a calculated density of 4·6 g.cm^{-3} for $Z=4$.

The system Na_2O–Nb_2O_5

In addition to $NaNbO_3$, the compound Na_3NbO_4 has long been known but its structure has not been previously reported on. An alkali-rich phase, Na_5NbO_5, was reported by Spitzyn & Lapitskii (1955) and Lapitskii (1958) but does not seem to have been observed by other workers. The complete system has been studied by Reisman & Holtzberg (1958*a*) and by Shafer & Roy (1959), but the two sets of results do not wholly agree. Both groups of investigators found the first two phases mentioned above and also one of composition $Na_2Nb_8O_{21}$. Reisman & Holtzberg gave the unit cell of this last as orthorhombic with $a=12{\cdot}39$, $b=36{\cdot}98$ and $c=3{\cdot}97$ Å. They also reported one other niobium-rich phase, to which they assigned the composition $Na_2Nb_{28}O_{71}$, whereas Shafer & Roy reported two niobium-rich phases, given as $NaNb_7O_{18}$ (stable only above 990 °C) and $Na_2Nb_{20}O_{51}$. Andersson (1963) has also studied two niobium-rich phases.

We found no evidence of a phase of composition Na_5NbO_5 although suitable starting mixtures were fired under a variety of conditions. Na_3NbO_4 and $NaNbO_3$ were observed in the products.

Pale yellow hygroscopic crystals of Na_3NbO_4 were obtained at 990 °C. The crystal lattice was *C*-centred monoclinic with

$$a=12{\cdot}23,\ b=12{\cdot}85,\ c=5{\cdot}782\ \text{Å};\ \beta=121{\cdot}5^\circ.$$

The space groups permitted by the observed absences are $C2$, Cm, and $C2/m$. The density gives $Z=6$ (ϱ_{obs} 2·5: ϱ_{calc} 2·9 g.cm^{-3}). The substance reacted with water yielding $NaNbO_3$.

$Na_2Nb_8O_{21}$ yielded crystals at 1300 °C. The unit-cell dimensions were found to be

$$a=12{\cdot}45,\ b=36{\cdot}97,\ c=3{\cdot}910\ \text{Å},$$

in agreement with the results of Reisman & Holtzberg quoted above and with those of Andersson. Because of similarities of the powder pattern and the cell dimensions with those of other materials studied, this phase is believed to have a structure closely related to that of the tetragonal bronzes, but with the basic bronze unit tripled in the [010] direction. The number ratio of small cations (Nb) to anions is not correct for the ideal tetragonal bronze structure (for which it should be 1:3), and therefore anion vacancies or interstitial niobium cations must be present. Anion vacancies, giving a cell content of $30\times Na_{0\cdot25}NbO_{2\cdot625}$, result in too low a density, *viz.* 3·9 g.cm^{-3}, that observed being 4·6 g.cm^{-3}. (Reisman & Holtzberg gave the observed density as 4·62 g.cm^{-3}.) Much better agreement is obtained by postulating an intact oxygen lattice with extra niobium ions in interstitial positions or in those large-cation positions which are not occupied by sodium. $30\times Na_{0\cdot286}Nb_{1\cdot143}O_3$ per unit cell gives a density of 4·5 g.cm^{-3}. Ordering of the 'extra' niobium ions or of the vacancies in the sodium lattice is presumed to be the cause of the tripling of the unit cell. Only rather small changes from the observed composition and density are required to give the formula $Na_{10}Nb_{34}O_{90}$ with just one third of the sodium positions occupied. It is hoped to discuss the structures of this compound and of related phases in a later paper in more detail.

Attempts to grow crystals of the niobium-rich phase at temperatures below its melting-point resulted in solid solutions of sodium oxide in niobium pentoxide. The parameters of the monoclinic cell are compared with the ranges of recentlyreported values for high-temperature Nb_2O_5:

$a=20{\cdot}78$ Å	20·93 to 21·34 Å
$b=3{\cdot}783$	3·816 to 3·835
$c=20{\cdot}06$	19·33 to 19·63
$\beta=124{\cdot}0^\circ$	119·8 to 120·5°

But by slow cooling of a melt, colourless platy crystals of the desired double oxide were obtained. They showed a monoclinic lattice with

$$a=22{\cdot}33,\ b=3{\cdot}821,\ c=14{\cdot}88\ \text{Å};\ \beta=95{\cdot}0^\circ.$$

The observed density, 4·4 g.cm^{-3}, does not agree with 5·1 calculated for $Na_2Nb_{28}O_{71}$ per unit cell (formula of Reisman & Holtzberg), nor with 3·6 for $Na_2Nb_{20}O_{51}$ (Shafer & Roy), but it does agree well with that calculated for $Na_2Nb_{24}O_{61}$, *viz.* 4·4 g.cm^{-3}. Reisman & Holtzberg observed a density of 4·43 g.cm^{-3} for their product.

This unit cell is very similar to a quarter of that of the corresponding lithium compound and the structures are thought to be closely related.

As expected, we did not observe the $NaNb_7O_{18}$ phase of Shafer & Roy as we collected no X-ray data above room temperature.

The system K_2O–Nb_2O_5

Phases reported in the literature for this system are summarized in Table 3. We obtained products corresponding to phases 1 to 5 in this Table (and 6 also, though this was not studied). The alkali-rich compositions proved too hygroscopic for ready examination.

The metastable phase $K_{12}Nb_{14}O_{41}$ was obtained in the form of large thin colourless plates, by quenching of melts. There was extensive twinning but an orthorhombic cell was found having

$$a=8{\cdot}81,\ b=21{\cdot}55,\ c=3{\cdot}76\ \text{Å}.$$

Powder patterns of KNb_3O_8 and $K_4Nb_6O_{17}$ showed the existence of two different phases having these compositions. Melts of each of them yielded crystals on slow cooling from 1200 °C, the former platy and the latter acicular. The unit cells found from the crystals were both tetragonal (tetragonal bronze type) the former composition showing superlattice reflexions.

$$\begin{aligned} KNb_3O_8\ a&=37{\cdot}71\pm0{\cdot}03\ \text{Å}\\ c&=3{\cdot}939\pm0{\cdot}005\\ \varrho_{\text{obs.}}&=4{\cdot}5\ \text{g.cm}^{-3}\\ \text{‘}K_4Nb_6O_{17}\text{’}\ a&=12{\cdot}525\pm0{\cdot}002\ \text{Å}\\ c&=\ 3{\cdot}763\pm0{\cdot}001\\ \varrho_{\text{obs.}}&=4{\cdot}4\ \text{g.cm}^{-3} \end{aligned}$$

The powder patterns of both the crystalline materials were indistinguishable from that previously obtained for KNb_3O_8. The density of the material with the multiple cell agrees better with that calculated for interstitial cations (4·5 g.cm^{-3}) than with the value for anion vacancies (4·0 g.cm^{-3}). The material with the ‘ideal’ tetragonal bronze cell cannot be given a composition with certainty on the present data, but is probably a polymorph of KNb_3O_8, loss of potash having occurred on crystallization. The powder pattern of $K_4Nb_6O_{17}$ obtained below its melting point, the only product which can definitely be assigned to this composition, was not indexed.

Platy crystals of ‘$K_2Nb_8O_{21}$’ were obtained on cooling a melt from 1400 °C. The primitive tetragonal cell had

$$a=27{\cdot}41,\ c=3{\cdot}955\ \text{Å}.$$

The observed density was 4·43 g.cm^{-3} whereas that calculated for eight times the above formula is 5·17 g.cm^{-3}. The formula is probably wrong.

$K_6Nb_{44}O_{113}$ was obtained as a distinct phase in powder work only: the powder diffraction pattern was complex and was not indexed. The only crystals which could be grown were monoclinic with

$$a=19{\cdot}83,\ b=3{\cdot}899,\ c=19{\cdot}03\ \text{Å};\ \beta=115.0^\circ,$$

and were considered to be solid solutions of potassium oxide in high-temperature niobium pentoxide.

The system Cs_2O–Nb_2O_5

Reisman & Mineo (1961) investigated this system and reported five intermediate phases of compositions $CsNbO_3$, $Cs_4Nb_6O_{17}$, $Cs_2Nb_4O_{11}$, $Cs_4Nb_{30}O_{77}$, and approximately $Cs_5Nb_{13}O_{35}$. They gave no unit-cell data.

We prepared samples of the last two of these phases. A melt of $Cs_4Nb_{30}O_{77}$ was slowly cooled from 1430 °C to give pale yellow rod-shaped crystals with a primitive tetragonal cell having

$$a=27{\cdot}21,\ c=3{\cdot}975\ \text{Å}.$$

The structure is clearly related to that of ‘$K_2Nb_8O_{21}$’ (*vide supra*).

The composition $Cs_5Nb_{13}O_{35}$ yielded colourless plates on cooling from 1420 °C. Most of the crystals were multiply twinned but the unit cell was determined to be monoclinic with

$$a=15{\cdot}17,\ b=7{\cdot}500,\ c=6{\cdot}683\ \text{Å};\ \beta=106{\cdot}0^\circ.$$

The system Li_2O–Ta_2O_5

By means of powder patterns, Reisman (1962) observed three phases in this system, Li_3TaO_4, $LiTaO_3$, and $LiTa_3O_8$, of which the first two had been studied previously. Li_3TaO_4 was reported by Lapitskii & Simanov (1954) to be cubic with $a=4{\cdot}203$ Å.

We prepared powder samples of Li_3TaO_4 at 900 °C but could not index the complicated powder pattern; it certainly was not cubic.

Table 3. *Literature on potassium niobium oxides*

	K:Nb	Formula	Melting point	Reference
(1)	3:22	$K_6Nb_{44}O_{113}$	1279 °C, incongruent	R & H
(2)	1:4	$K_2Nb_8O_{21}$		G
(3)	1:3	KNb_3O_8	1234 °C, incongruent	R & H
(4)	2:3	$K_4Nb_6O_{17}$	1163 °C, congruent	R & H
(5)	6:7	$K_{12}Nb_{14}O_{41}$		RHB
(6)	1:1	$KNbO_3$		
(7)	2:1	$K_4Nb_2O_7$		G
(8)	3:1	K_3NbO_4	*ca.* 950 °C, congruent	R & H

R & H – Reisman & Holtzberg (1955): RHB – Reisman, Holtzberg & Berkenblit (1959): G – Guerchais (1962).

On the tantalum-rich side we found two distinct intermediate phases of different compositions, one of which was formed at 900 °C and the other at 1400 °C. Study of the weight losses from mixtures of various initial compositions led to the following formulae and reaction scheme:

$$2Li_2CO_3+4Ta_2O_5 \xrightarrow{900^\circ} 2Li_2Ta_4O_{11} \xrightarrow{1400^\circ} Li_2Ta_8O_{21}+Li_2O$$

$$Li_2CO_3+4Ta_2O_5 \xrightarrow{900^\circ} Li_2Ta_4O_{11}+2Ta_2O_5 \xrightarrow{1400^\circ} Li_2Ta_8O_{21}.$$

The two new phases were identified by their powder patterns. This scheme also accords with Reisman's not having observed $Li_2Ta_4O_{11}$ in his studies, which were conducted at 1350 °C; presumably his $LiTa_3O_8$ is the same as our $Li_2Ta_8O_{21}$. Attempts to grow crystals of this high-temperature phase led to a solid solution of lithium oxide in tantala, the orthorhombic cell of which may be compared with that given by Harvey & Wilman (1961) for low-temperature Ta_2O_5.

Solid solution	Ta_2O_5
$a=$ 6·132 Å	$a=$ 6·2 Å
$b=$69·61	$b=$69·6
$c=$ 3·783	$c=$ 3·9

The system Na_2O–Ta_2O_5

The results of X-ray powder studies by King, Schultz, Durbin & Duckworth (1956) and by Reisman (1962) are summarized in Table 4. King *et al.* considered the tantalum-rich phases, which they prepared from melts, to be members of a solid solution range, whereas Reisman thought them to be distinct compounds, related structurally to the tetragonal bronzes.

Table 4. *Literature on sodium tantalum oxides*

		King *et al.*	Reisman
(1)	Na_3TaO_4	Hex. $a=$16·40 Å $c=$16·81 Å	
(2)	$NaTaO_3$		
(3)	$Na_2Ta_4O_{11}$	Tetr. $a=$7·806 Å $c=$7·66 Å	Ortho. $a=$6·00 Å $b=2\times$3·83 Å $c=$5·08 Å isostructural $K_2Ta_4O_{11}$
(4)	$NaTa_3O_8$	Tetr. $a=$7·795 Å $c=$7·60 Å	Ortho. $a=2\times$3·87 Å $b=2\times$5·97 Å $c=$5·97 Å

We obtained Na_3TaO_4 both by heating sodium carbonate and tantalum pentoxide at 800 °C and by fusing tantala with an excess of sodium hydroxide. The line positions on the powder pattern were indistinguishable from those for Na_3NbO_4 (though relative intensities differed) and crystals grown in the presence of an excess of sodium carbonate at 1000 °C confirmed the identity of the cell dimensions of the two substances within experimental error.

$$a=12·23,\ b=12·85,\ c=5·732\ \text{Å};\ \beta=121·5^\circ.$$

The observed density, 3·8 g.cm^{-3}, confirmed that $Z=6$ (calculated density: 4·0 g.cm^{-3}). The above cell may be approximated by King's hexagonal one in the orientation $[100]_h=[110]_m$, $[010]_h=[001]_m$, $[001]_h=[1\bar{1}0]_m$. Na_3TaO_4 was found to be hygroscopic, being transformed in time to $NaTaO_3$ by atmospheric moisture. $NaTaO_3$ was also the product of heating the substance to 1400 °C.

We obtained two quite distinct powder patterns from products of compositions $Na_2Ta_4O_{11}$ and $Na_2Ta_8O_{21}$ prepared at 1000 °C. The latter was of the tetragonal bronze type, and the former could be indexed (except for a few weak lines) on the basis of a tetragonal cell having

$$a=7·860\pm0·001,\ c=7·152\pm0·003\ \text{Å}.$$

The observed density, 7·2 g.cm^{-3}, agreed well with that (7·1 g.cm^{-3}) calculated for $Z=2$. This compound decomposed at 1400 °C with loss of sodium oxide to form the other (tetragonal bronze) phase. Thus it should have escaped observation by King *et al.*

Crystals of the bronze-type phase, $Na_2Ta_8O_{21}$, could be grown slowly at 1500 °C or from a melt at 1650 °C, but had to be cooled rapidly to room temperature to avoid decomposition to tantalum pentoxide. Consequently only rather small and badly twinned crystals were available, but these served to confirm the tetragonal bronze cell with approximate dimensions

$$a=12·5,\ c=3·92\ \text{Å}.$$

By analogy with other systems (see, for example, K_2O–Nb_2O_5 above) a bronze-type phase with a tripled *a* dimension may also be expected. This may then represent the other of the two phases reported by King *et al.*

The system K_2O–Ta_2O_5

Reisman, Holtzberg, Berkenblit & Berry (1956) identified four intermediate phases in this system: KTa_5O_{15}, $K_2Ta_4O_{11}$, $KTaO_3$, and K_3TaO_4. The structure of $KTaO_3$ is well known, and Sawaguchi (1964) has reported the tetragonal bronze structure for $K_2Ta_4O_{11}$, with a range of composition.

An unindexed powder pattern confirmed the compound K_3TaO_4 but no crystals of this moisture-sensitive phase could be prepared. It is not isostructural with Na_3TaO_4.

Colourless acicular crystals of $K_2Ta_4O_{11}$ were formed on heating the reactant mixture at 1500 °C. The powder pattern of this substance showed it to have the tetragonal bronze structure, and examination of the single crystals showed that the *a* dimension was tripled (Sawaguchi, using powder patterns, did not observe the tripling).

$$a=37·29,\ c=3·878\ \text{Å}.$$

The observed density of 7·1 g.cm^{-3} agrees with that calculated for interstitial cations, *i.e.* $90\times K_{0·545}$

$Ta_{1\cdot091}O_3$ per unit cell, *viz.* 7·4 g.cm^{-3}, rather than with that for anion vacancies.

We obtained powder patterns of KTa_5O_{13} which we could not index, but attempts to grow crystals by cooling melts from 1700 °C in iridium led to solid solutions of potassium oxide in high-temperature tantala.

This work was carried out under a research contract for the United Kingdom Atomic Energy Authority and we wish to thank the Director of the Atomic Energy Research Establishment, Harwell for permission to publish these results.

References

Andersson, S. (1963). *Acta Cryst.* **16**, A 21.

Blasse, G. (1963). *Z. anorg. Chem.* **326**, 44.

Guerchais, J. E. (1962). *Bull. Soc. chim. Fr.*, p. 103.

Harvey, J. & Wilman, H. (1961). *Acta Cryst.* **14**, 1278.

King, B. W., Schultz, J. S., Durbin, E. A. & Duckworth, W. H. (1956). United States Atomic Energy Commission. Report BMI – 1106.

Lapitskii, A. V. (1958). *Vestnik Moskov. Univ., Ser. Mat. Mekh. Astron. Fiz. Khim.* **13**, 121.

Lapitskii, A. V. & Simanov, Yu. P. (1954). *Vestnik Moskov. Univ.* **9**, No. 2, *Ser. Fiz. Mat. i Estestven. Nauk No.* 1, 69.

Main, P. & Woolfson, M. M. (1963). *Acta Cryst.* **16**, 731.

Reisman, A. (1962). *J. Phys. Chem.* **66**, 15.

Reisman, A. & Holtzberg, F. (1955). *J. Amer. Chem. Soc.* **77**, 2115.

Reisman, A. & Holtzberg, F. (1958*a*). *J. Amer. Chem. Soc.* **80**, 37.

Reisman, A. & Holtzberg, F. (1958*b*). *J. Amer. Chem. Soc.* **80**, 6503.

Reisman, A., Holtzberg, F. & Berkenblit, M. (1959). *J. Amer. Chem. Soc.* **81**, 1292.

Reisman, A., Holtzberg, F., Berkenblit, M. & Berry, M. (1956). *J. Amer. Chem. Soc.* **78**, 4514.

Reisman, A. & Mineo, J. (1961). *J. Phys. Chem.* **65**, 996.

Sawaguchi, E., & Kikuchi, A. (1964). *J. Phys. Soc. Japan*, **19**, 579.

Shafer, M. W. & Roy, R. (1959). *J. Amer. Ceram. Soc.* **42**, 482.

Spitzyn, V. & Lapitskii, A. V. (1955). *J. Gen. Chem. U.S.S.R.* **23**, 101.

Wait, E. (1961). United Kingdom Atomic Energy Authority Report AERE – R3598.

Whiston, C. D. (1963). *Ph. D. Thesis*, University of Sheffield.

Acta Cryst. (1965). **19**, 173

Computational Aspects of Space-Group Symmetry

By M. Wells

Electronic Computing Laboratory, The University, Leeds 2, *England*

(*Received* 24 *July* 1964)

Some well-known results which are often used in the analysis of X-ray diffraction data are derived, and some new results proved. Algorithms are given which allow these results to be used on a computer.

Introduction

In recent papers Jeffery (1963) and Bienenstock & Ewald (1962) have studied the symmetry of reciprocal space; earlier work by Buerger (1949), Waser (1955) and Trueblood (1956) has dealt with other aspects of the effects of symmetry on X-ray diffraction. In this paper, an attempt is made to develop a systematic approach to the problems arising in programming a digital computer for the three basic calculations of crystallography, *i.e.* structure factors, Fourier synthesis and least squares. Some of the results have been derived by earlier workers; some, to the best of the writer's knowledge, have never been derived at all, although they are in common use; still others are new. In each case, algorithms for application of the results are given, in ALGOL 60 reference language (Naur, 1963).

Notation

We shall denote a group by a script capital, *e. g.* $\mathcal{G}, \mathcal{H}$, and particular elements of a group by upper case letters, possibly with a suffix, *e.g.* G, H_i. Since the groups with which we are concerned are all groups of symmetry operations, it is convenient to describe them in terms of matrices; in particular a bold-faced $\mathbf{R}$ denotes a 3×3 rotation matrix each of whose elements is either $+1$, 0 or -1, and $\mathbf{t}$ denotes a 3×1 matrix (column vector) whose elements are all multiples of $\frac{1}{12}$ and lie in the range 0 to <1. The inverse of $\mathbf{R}$ is written $\mathbf{R}^{-1}$ and its transpose as $\mathbf{R}^t$.

The action of any crystallographic symmetry operator G, on a vector $\mathbf{r}$ can be defined as

$$G\mathbf{r}=\mathbf{R}\mathbf{r}+\mathbf{t} \qquad (1\cdot1)$$