The Crystal Structure of GaNbO4*

By Bruno Morosin

Sandia Laboratory, Albuquerque, New Mexico, U.S.A.

and Abraham Rosenzweig

University of New Mexico, Albuquerque, New Mexico, U.S.A.

The crystal structure of gallium niobate has been determined by three-dimensional X-ray methods. Space group $C2$ was chosen as the one presenting the most general solution while still retaining the twofold axis established for related structures. The unit-cell dimensions are $a_0 = 12.660$, $b_0 = 3.7921$, $c_0 = 6.6147$, and $\beta = 107.90°$.

The gallium and niobium atoms occupy distorted octahedral sites similar to those found in titanium niobium oxides and in aluminum niobate.

An alternative centric interpretation is presented at the suggestion of the editor.

Introduction

The compound GaNbO4 was prepared at the Sandia Corporation Laboratories during a program of investigation of ferroelectric materials. At the time the compound was prepared, the only Group III niobates or tantalates of the RNbO4 type for which structural data were available were those of yttrium. Since some question exists as to the structures of these compounds it was hoped that an investigation of the gallium compound might shed some light on the nature of the yttrium compounds or that a new structure type might be found.

Prior to the final refinement of the structure by the present authors, the structure of AlNbO4 was published by Pedersen (1962). The structure determined by us for GaNbO4 is substantially in agreement with that reported by Pedersen; the major difference is the assignment of GaNbO4 to a non-centric space group, whereas Pedersen assigned AlNbO4 to a centric space group. Pedersen recognized, however, that his two-dimensional data were insufficent to determine the space group firmly.

Some further observations have also been made regarding the nature of the structure of aluminum and gallium niobate and its relationship to other structures, particularly to the titanium niobium oxides described by Wadsley (1961*a*, *b*).

Experimental

Crystals of gallium niobate were obtained by flame-fusion of an equimolar mixture of the two oxides (Phil-green, 1963). The fusion was allowed to crystallize on a platinum plate, yielding a radial aggregate of pris-matic or lath-shaped crystals. The crystals are transparent to translucent, of a very pale greenish tint, 3 mm in length and up to 0.5 mm in diameter.

Equi-inclination Weissenberg photographs were taken with Cu $K\alpha$ radiation. These were used for space group determination and the initial determination of the unit-cell dimensions. The final unit-cell dimensions, obtained by means of a modified Picker diffractometer, are as follows:

$$a_0 = 12.660 \pm 0.005 \text{ Å}$$
$$b_0 = 3.7921 \pm 0.0022$$
$$c_0 = 6.6147 \pm 0.0028$$
$$\beta = 107.90 \pm 0.02° .$$
$$(\lambda\text{Cu } K\alpha = 1.5418 \text{ Å})$$

The diffraction patterns were consistent with monoclinic symmetry and only reflections with $h+k$ odd were systematically absent. The space group is therefore $C2/m$, Cm, or $C2$. The crystals obtained were not of sufficiently good morphological development to aid in the assignment of the space group. A test for piezoelectric effect using the Geibe–Schiebe instrument and a very small sample yielded negative results.

The material available was not suitable for measurement of the specific gravity. With the assumption that this is a true compound rather than a disordered oxide of the RO2 type in which the metal sites are randomly occupied by Ga and Nb, an even number of empirical formulas per unit cell is required for a C-centered cell. The calculated density for four formulas per cell is 5.01 g.cm⁻³, which appears to be reasonable when compared with the density of 5.38 g.cm⁻³ for tetragonal YNbO4 (Barth, 1926). For two and six formulas per unit cell the densities are 2.50 and 7.51 g.cm⁻³, both of which seem unreasonable.

Intensity data for Mo $K\alpha$ radiation were collected by means of a General Electric XRD 5 diffractometer and single crystal orienter. Four hundred and twenty-

---

two reflections were observed and 76 were unobserved. The crystal used was a rectangular prism of dimensions $0.015 \times 0.023 \times 0.027$ cm. Lorentz–polarization factors and empirical absorption corrections, obtained by rotation of the crystal about the diffraction vector of several reflections, were applied. Structure factors were calculated using scattering factors for gallium and niobium according to Thomas & Umeda (1957), and for oxygen according to Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). All computations were carried out on a CDC-1604 computer.

Determination of structure

The corrected intensities were used in computing a three-dimensional Patterson function. Maxima in this function all had $v=0$ or $\frac{1}{2}$ (or nearly so), indicating that all atoms lay in planes approximately $b_0/2$ apart. A similar observation ($h0l$ and $h2l$ intensity distribution being similar) led Wadsley (1961) to the conclusion that the space group $A2/m$ was probable for $TiNb_2O_7$. Pedersen (1962) made the same observation and drew the same conclusion regarding $AlNbO_4$. It should be noted that b_0 for all these compounds is similar, about 3·8 Å. Since no positive evidence is available for establishing the space group as centric or non-centric, a non-centric space group was chosen as representing the more general case. If the structure is in fact centric, this should become apparent in that the atomic parameters should approach the centric positions upon refinement. In view of the establishment of the two-fold axes in $TiNb_2O_7$ and $AlNbO_4$, the space group $C2$ was chosen in preference to Cm.

The absence of Patterson function maxima of the type $0, v, \frac{1}{2}$ or $\frac{1}{2}, v, 0$ eliminates the twofold positions of $C2$ (or $C2/m$), and therefore the Ga and Nb must be in general positions if $C2$ is assumed. With this assumption the approximate parameters of Ga and Nb were determined from the Patterson function.

Oxygen parameters were obtained from a Fourier synthesis using phases calculated from the Ga and Nb parameters determined above. Refinement by several difference and differential syntheses (shifts $\leq 0.1\sigma$) yielded the parameters listed in Table 1 (y of niobium arbitrarily set to 0·0) with the estimated standard deviations in positional parameters calculated by the method of Cruickshank (1949). The final tabulation for observed and calculated structure factors is given in Table 2. The final R value was 0·080 using only

observed and unextinguished reflections. The value increases to 0·092 using all observed and unobserved reflections.

Discussion of the structure

An examination of the final parameters shows that all atoms have a y parameter close to zero. The y parameters of the gallium and two oxygen atoms, however, are more than ten standard deviations from zero. On this basis we conclude that the correct space group for $GaNbO_4$ is $C2$. It is likely that this is also true for $AlNbO_4$ and possibly for $TiNb_2O_7$. Both Pedersen and Wadsley consider this possibility, but defer a final conclusion because of their limited (two-dimensional) data. The low value of the thermal parameters, B, shown in Table 1 are consistent with those obtained in high refractory materials and with those observed for $BaTiO_3$ (Evans, 1961) and $NaNbO_4$ (Wood, Miller & Remeika, 1962).

Fig. 1 illustrates the structure of $GaNbO_4$ as viewed along b_0. The illustration is essentially that of Pedersen except that bonds rather than coordination groups are shown. The coordination about gallium and niobium is a highly distorted octahedral one. The bond lengths and bond angles are listed in Table 3. The distortion of the octahedra is clearly related to the sharing of octahedral edges. The O–O distance along shared edges varies from 2·50 to 2·70 Å, whereas the
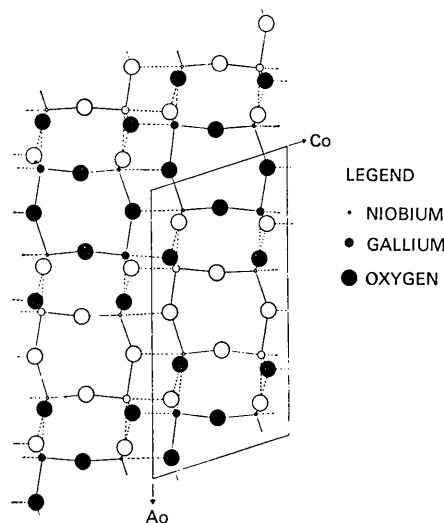
Fig. 1. The structure $GaNbO_4$ viewed down the b_0 axis. Filled circles indicate atoms situated near $y=0.0$. Open circles indicate atoms situated near $y=0.5$.

LEGEND

· NIOBIUM

• GALLIUM

● OXYGEN

Table 1. *Atomic positions and temperature factors*

	x	$10^{-5}\sigma(x)$	y	$10^{-5}\sigma(y)$	z	$10^{-5}\sigma(z)$	$B(\text{Å}^2)$
Ga	0·19711	7	0·00768	32	0·81355	16	0·073
Nb	0·10317	5	0·00000	22	0·23054	12	0·299
O(1)	0·25943	45	−0·00635	219	0·14614	108	0·300
O(2)	0·36246	46	0·00868	227	0·79903	112	0·402
O(3)	0·05483	43	0·02533	211	0·86090	104	0·174
O(4)	0·13734	46	−0·02390	226	0·51466	111	0·391

Table 2. *Observed and calculated structure factors for* GaNbO4
The plus sign before the observed values should be interpreted as 'less than'.

```
H  10FO 10FC  10A 10B        H  10FO 10FC  10A 10B        H  10FO 10FC  10A 10B        H  10FO 10FC  10A 10B        H  10FO 10FC  10A 10B

   K=0 L=0                      K+3 L--1                   7  359  367 -363  48        15  658  600 -599 -23        10 +115   24  -24   0
2  666  630 -630   0         1  +96   92   80 -46        9  389  365 -365  12        17  640  655  655  10        12  368  304 -304   0
4  926 1094-1094   0         3  746  845  845 -33       11 +124   71  -66 -26                                     14  943  902  902   0
6  556  601 -601   0         5  264  229  229  -9       13 1063 1067 1066  25           K-2 L- -4                 16 +140   48  -48   0
8  145   12   12   0         7 1346 1550-1548 -80                                     2  229  199  199  -4
10 1140 1173 1173   0        9  248  197  193  42          K-2 L-3                    4 1561 1756-1756 -16           K-1 L- -6
12  447  411 -411   0       11  308  313  305 -69       0 1774 1492-1491 -66         6  689  594  588  81         1  461  386 -385 -14
14  574  522 -522   0       13  581  550  549  28       2 1434 1321 1321   5         8  466  460  460 -17         3  702  682  682   9
16 +136   36   36   0                                   4  836  856  856   8        10  542  513  513   4         5 1061 1037 1035  53
                              K 4 L--1                   6  730  705 -705 -14        12 +121   89   52  72         7  898  853 -853 -38
   K 1 L-0                   2  226  274  265 -71        8  261  266 -248  96        14 1010  992 -990 -68         9  413  423 -423   6
1 1513 1700 1700  21         4  794  863  863  12       10  304  308 -305 -41        16 +140  164  164   5        11  158  150 -150  -9
3  955 1149-1149  18         6  839 1070-1066 -98       12  667  658  658  14                                     13  364  315  315 -11
5  269  390 -386  54         8  473  479 -479   4                                      K-3 L- -4                 15  794  757  757   0
7  741  800 -797 -75        10  435  422  421  27          K 3 L-3                    1  849  881  881  26
9  639  753  752 -13                                    1  304  289 -282 -64         3  810  863 -863 -21           K-2 L- -6
11  835  811  810  18         K 5 L--1                   3 1489 1363 1363  30         5  799  799 -799  27         2  199  109 -106 -26
13  975 -951 -951 -27        1 +135   84   57 -61       5  254  239 -234 -48         7  757  713  710  56         4 1150 1212 1209  84
15 +132   51  -49  13        3  531  566  566 -23       7  305  317 -298 106         9  350  333  329 -45         6  166  166 -166  -4
                             5 +138  151  151   1       9  327  309 +308  31        11  619  570  560 109         8  689  705 -704 -38
   K-2 L-0                                              11 +140   94  -67 -66        13  792  742 -741 -34        10 +124   36  -14  33
0 2151 2714 2712  91          K 0 L 2                                                                            12  309  278 -272 -57
2  480  447 -447  -2         0 2011 2116-2116   0          K 4 L-3                      K-4 L -4                 14  887  834  834   5
4  711  821 -820  42         2  502  332  332   0       0  865  963 -958 -95         2 +126  158  157   7
6  428  483 -483   7         4  111  164  164   0       2  810  912  911  17         4 1097 1245-1244 -39           K-3 L- -6
8 +100  111  -15 -110        6 1553 1491 1491   0       4  543  606  605  13         6  449  416  400 115         1  373  329 -327 -34
10 1049 1076 1075  45        8  +97   59  -59   0       6  502  535 -535 -29         8  356  319  318 -27         3  565  543  543  18
12  408  368 -366 -43       10 1238 1274-1274   0                                   10  433  385  385   4         5  849  857  848 125
14  525  482 -482  -1       12  236  231  231   0          K 0 L -3                                              7  752  727 -721 -92
                            14  200  165  165   0       2  391  491 -491   0           K-0 L 5                    9  361  339 -338  20
   K 3 L-0                                              4  702  638 -638   0         0 1233 1111 1111   0        11 +137  120 -118 -24
1  803 1039 1038  39          K 1 L 2                    6  996 1065 1065   0         2 1256 1238-1238   0
3  740  801 -801  -1         1  503  589 -588  28       8  907  888  888   0         4  459  469 -469   0           K-4 L- -6
5  191  279 -256 109         3  424  382  379  44      10  951  895 -895   0         6 +115    0    0   0         2 +140  116 -107 -45
7  607  615 -597 -147        5  228  310  310  -1      12 +108   33  -33   0         8  418  391  391   0         4  876  942  933 126
9  623  623  622 -24         7 1379 1429 1329  30      14  258  241 -241   0        10  704  724  724   0         6 +141  131 -130  -9
11  694  677  676  43        9 1100 1120-1120 -13      16  418  370  370   0
13  733  803 -800 -70       11  581  565 -565   7                                      K-1 L 5                      K-0 L-7
                            13  277  292  292  -5          K 1 L- -3                 1 +100  145 -144 -17         0  847  691 -691   0
   K 4 L 0                                              1  879 1018-1018   1         3 1162 1144-1144 -36         2  830  733  733   0
0 1750 1596 1592 117          K 2 L 2                    3  403  544 -544 -18         5  240  200  200  12         4  358  300  300   0
2  262  283 -281 -29         0 1821 1641-1637 -116      5  433  292 -283 -73         7  256  248 -247 -19         6  264  255  255   0
4  488  526 -524  46         2  380  275  258  97       7 1411 1595 1594  66         9  897  908  908   9
6  317  328 -327  19         4  +91  128  125  28       9   97   42  -42   5                                      K-1 L-7
8 -129  154  -38 -149        6 1178 1239 1239  33      11  849  826 -826  -3           K 2 L 5                    1  419  380  378  34
10  830  854  851  72        8 +109   53  -52   4      13  123   73   69  22         0 1059  990  987  77         3  624  542  542 -13
                            10 1130 1147-1146 -30      15  145  158 -158  -7         2 1118 1102-1098 -94         5 +135  104  103 -12
   K 5 L 0                   12  202  224  218  50      17  974  952  952   8         4  425  422 -412 -17
1  559  663  662  44                                                                6 +124    9    7   5           K-2 L-7
3  474  550 -550 -22          K 3 L 2                      K 2 L- -3                 8  396  357  357 -16         0  723  631 -631   9
5  165  198 -154 124         1  362  450 -447  55       2  272  374 -374  13                                     2  717  671  669  42
                             3  277  276  266  74       4  549  544 -537 -83           K-3 L-5                    4  327  274  269 -51
   K=0 L 1                    5  206  250  250 -17       6  846  881  881  -2         1 +121  111 -105 -38
0  749  787  787   0         7 1047 1079 1076  76       8  819  804  800  83         3  931  938 -934 -83           K 3 L-7
2  990 1108-1108   0         9  932  919 -914 -36      10  867  819 -818 -42         5  186  178  175  35         1  317  329  317  87
4  986 1072-1072   0        11  466  457 -457  17      12 +118   74  -42  61         7  193  207 -201 -50
6 1553 1564 1564   0                                   14  239  219 -219  -2                                       K-0 L- -7
8  162  199  199   0          K 4 L 2                   16  390  344  344  -9           K 4 L 5                   2  887  783 -783   0
10 +103   31  -31   0        0 1312 1110-1102 -132                                   0  739  766  757 113         4  981  929  929   0
12  504  481  481   0        2  209  220  181 126         K-3 L- -3                 2  824  847 -836 -139        6 +115   20   20   0
14  910  793 -793   0        4 -124   71   70   9       1  633  709 -709   2                                     8  543  477  477   0
16  788  772  772   0        6  812  871  870  47       3  304  357 -357 -14           K-0 L- -5                10  794  739 -739   0
                             8 -136   45  -41  16       5  279  257 -213 -143        2  549  587  587   0        12  678  617 -617   0
   K=1 L 1                                              7 1190 1250 1242 137         4  153  120 -120   0        14  618  575  575   0
1  440  343  322 118          K 5 L 2                    9  119   65  -65   4         6  112  165 -165   0
3 1067 1248-1248 -30         1  268  317 -310  63      11  715  686 -686  -7         8 1083 1054-1054   0           K 1 L= -7
5  130  103  101  22         3 +140  199  184   4      13 +134   80   56  57        10 1159 1106 1106   0         1 1357 1227-1227  -2
7 1071 1139 1139  23                                                               12  390  380  380   0         3  262  202  201  20
9  226  159 -156 -27          K 0 L -2                     K 4 L- -3                14  391  348 -348   0         5  553  520  520 -14
11  211  166  166   0        2  108   96   96   0       2  201  231 -228  39        16  377  332 -332   0         7  330  330  -8
13 1197 1201-1201 -25        4 1434 1432 1432   0       4  405  409 -395 -102                                    9 +123   19    9  16
15 +136  149  149   4        6  616  455 -455   0       6  635  620  620  -4           K-1 L- -5                11 1172 1157-1156 -45
                             8  251  136  136   0       8  623  628  618  13         1 1073 1039 1038  37        13  238  236  236  11
   K 2 L 1                   10 1107 1137-1137   0      10  662  652 -649 -68         3  118  171  168 -28
0  481  575  563 114        12  190  151  151   0                                   5  223  137  131  35           K-2 L- -7
2  700  847 -845  48        14 1090 1086 1086   0         K 5 L- -3                  7 1027 1020-1020   5         2  797  713 -713  24
4  906  941 -939 -61        16 +132  117 -117   0       1  423  466 -466   1         9  163  129 -129   7         4  877  833  832  29
6 1218 1303 1298 113                                    3  237  227 -227  -2        11 1362 1384 1384   8         6 +125   64   19 -60
8  172  196  192 -39          K 1 L -2                                             13  433  371 -369 -36         8  484  446  445  28
10 +114   41  -20 -35        1 1298 1379-1376 -92         K 0 L-4                   15  287  270 -269 -17        10  737  674 -673 -19
12  476  434  434  -7        3  801  867  866  32       0  897  824  824   0                                    12  616  573 -570 -55
14  750  728 -727 -34        5  418  505  503 -44       2  254  274  274   0           K 2 L= -5
                             7  +83   24  -15 -18       4  +96  106 -106   0         2  491  511  511 -11           K-3 L- -7
   K 3 L 1                    9  351  393 -393  10       6 1261 1296-1296   0         4  138  120 -118 -18         1 1116 1034-1034 -11
1  264  281  207 190        11 1157 1166-1166  -3       8  439  391  391   c         6  145  182 -166  73         3  225  177  169  93
3  897 1032-1030 -67        13 1247 1259 1259  37      10  803  788  788   0         8  966  939 -939  -1         5  461  426  424 -36
5 +105  100   91  43        15  438  414  414  -7      12 +136   61  -61   0        10 1040  994  994  27         7  311  280  279 -21
7  879  899  897  48        17  257  237 -237  -2                                  12  386  348  345 -46         9 +139   50   26  43
9  144  138 -121 -67                                      K-1 L-4                  14  342  317 -316 -24
11 -130  138  138   5         K-3 L--2                   1  +89  153  136 -70                                      K-0 L- -8
13 1026 1010-1008 -65        1 1087 1015-1003 -157      3  249  192  191  22           K-3 L= -5                 0 +130   53  -53   0
                             3  721  773  770  73       5  599  593 -593   1         1  864  872  868  84         2 1097  994  994   0
   K 4 L 1                    5  329  393  383 -85       7  817  813 -813 -21         3 +117  105   78 -70         4 +141   87  -87   0
0  299  372  354 114         7 +109   39  -24 -31       9  881  971  971  32         5  131  124   82  92
2  470  564 -561  54         9  328  321 -320  28      11 +132  128  128   2         7  846  821 -821   6           K-1 L-8
4  657  722 -718 -83        11  964  934 -934 -17                                   9 +126   99  -98  13         1  553  446  446   6
6  883  940  927 150        13 1045 1043 1038  92         K 2 L-4                  11 1173 1139 1139  25         3  653  693  693  29
8 +132  166  154 -62                                    0  729  713  711 -53        13  344  326 -313 -92
10 -139   48   -8 -47         K-4 L--2                   2  237  244  239 -49                                      K-2 L-8
                             2 +118   53   51 -16       4 +107   85  -60  60           K-4 L- -5                 0 +138   74  -56 -48
   K 5 L-1                    4  802  873  871  58       6 1064 1172-1170 -72        2  384  374  374 -22
1 +135  242  146 193         6  257  256 -206 -151      8  358  350  347  39         4 +133  110 -107 -25           K-0 L- -8
3  608  761 -757 -79         8 +128   82   71  41      10  727  723  721  44         6  181  174 -137 107         2 +127   66  -66   0
5 +141   81   64  49        10  760  765 -765   3                                   8  757  720 -720 -13         4  741  683 -683   0
                                                          K-3 L-4                                              6  234  254 -254   0
   K=0 L--1                   K 5 L- -2                  1 +113  194  126 -147          K=0 L-6                  8 1082 1079 1079   0
2  483  579  579   0         1  701  719 -700 -163      3  201  209  202  51         0  150   62   62   0        10  309  318 -318   0
4 1633 1703 1703   0         3  522  591  584  88       5  478  491 -491   3         2 1059  963 -963   0        12 +137  110 -110   0
6 1991 2095-2095   0         5  281  286  269 -97       7  649  687 -685 -53         4 +118   99  -99   0
8  760  806 -806   0                                    9  721  824  820  28         6 1086 1118 1118   0           K-1 L- -8
10  660  629  629   0         K=0 L- -3                                             8  247  289 -289   0         1 +131   12   -5 -11
12  297  317  317   0        0 2316 1971-1971   0         K-4 L-4                                               3 +128  301 -300  22
14  616  579  579   0        2 1717 1636 1636   0       2  475  524  520 -62           K-1 L-6                  5  968  920 -920 -28
16  646  625 -625   C        4 1000 1020 1020   0       4 +130  191  177 -72         1 +111  127 -124  25        7  784  764  764   3
                             6  837  796 -796   0       6  149   91   -7  91         3  951  902 -902 -16         9  597  554  554 -16
   K-1 L--1                   8  268  286 -286   0       8  848  919 -913 -111        5  836  812  812   0        11  605  528 -528  -8
1   75   65   63 -15        10  334  318 -318   0                                   7  448  397  397 -21
3 1005 1230 1230 -28        12  672  716  716   0         K=0 L= -4                  9  441  454 -454 -11           K-2 L- -8
5  469  388  387 -14        14  413  417  417   0       2  267  225  225   0                                    2 +135   66  -60  27
7 1952 2167-2167 -35                                    4 2111 2113-2113   0           K-2 L-6                  4  688  623 -623   0
9  297  203  202  14         K-1 L--3                   6  868  739  739   0         0 +117   51   41  30         6  261  232 -230 -30
11  375  401  399 -29        1  549  448 -447 -29       8  544  543  543   0         2  922  857 -857  -1         8 1021  995  995  -6
13  697  668  668  12        3 1593 1803 1803   6      10  595  581  581   0         4 +127   92  -87 -31        10  329  299 -295 -46
15 +129   33    8  32        5  327  268 -268 -17      12  126   49   49   0         6  952 1028 1028  16
                                                       14 1099 1076-1076   0                                      K-0 L- -9
   K=2 L- -1                                           16  191  173  173   0           K-3 L-6                  2  803  681  681   0
2  309  427  425 -46                                                               1 +130  123 -106  64         4  843  781  781   0
4 1118 1299 1299 -19                                       K-1 L- -4                3  771  748 -747 -43         6  337  244 -244   0
6 1345 1621-1619 -75                                    1 1127 1159 1159   4         5  699  695  695   1         8 +139  102 -102   0
8  659  680 -680   3                                    3 1075 1129-1129  -6
10  567  557  556  15                                   5 1036 1072-1072  16           K=0 L- -6                  K-1 L- -9
12  284  283  274 -70                                   7  996  941  941  23         2  144   98  -98   0         3 +140   55  -55  -8
14  559  540  533  82                                   9  412  460  460 -16         4 1261 1350 1350   0         5  786  760 -759 -33
                                                       11  770  672  670  46         6  265  188 -188   0         7 +140   85  -83  18
                                                       13  938  889 -889 -13         8  779  767 -767   0
```

O–O distance for adjacent oxygens on unshared edges varies from 2·73–3·26 Å. Although the average bond angle involving two adjacent oxygens and either metal is very close to the undistorted octahedral value of 90°, the range is from 72·7° to 108·6°.

It is interesting to note that for both gallium and niobium the four shortest metal–oxygen bonds (first four distances in Table 3) form a distorted tetrahedron. For both metals the average bond angle (first six bond angles in Table 3) for this distorted tetrahedral group
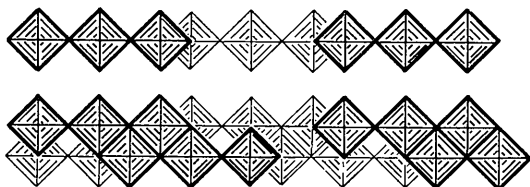

Fig. 2. Upper part of the figure illustrates a unit of the hypothetical R_3O_8 structure formed by fusing together the blocks of octahedra. Each hatched square represents an octahedron in projection as viewed down a corner; the lighter lines indicate blocks diplaced downwards by half an octahedral diagonal. Two of these R_3O_8 units can be joined together (by translating the lower unit sideways by $1\frac{1}{2}$ octahedral diagonals) to form the double octahedral sheet.

is within a few degrees of the tetrahedral angle, but one of the six angles in each case is very large (about 149°). In Fig. 1, the longer metal–oxygen bonds are shown by broken lines. Tetrahedrally coordinated niobium is reported by Komkov (1959) in fergusonite (natural $YNbO_4$). The crystals display an excellent cleavage parallel to (001) and a good cleavage parallel to (100). Both cleavages involve rupturing of the longer, and thus weaker, metal-oxygen bonds.

Another interesting feature of the structure is the rather large void centered at $x=0$, $y=\frac{1}{2}$, $z=\frac{1}{2}$. The shortest distance between this point and a neighboring oxygen position is 2·62 Å. An ion with a radius somewhat greater than 1 Å could be easily accommodated in this void. No structures analagous to that of $GaNbO_4$ with the void occupied are known to the authors.

Wadsley (1961b) proposes a structural scheme for a series of disordered titanium niobium oxides of composition $R_{3n}O_{8n-3}$. This series includes both known and hypothetical members. The structures are formed from units consisting of three octahedra forming a short chain by sharing of corners. These units are linked into 'single' or 'double' layers in the manner shown in Fig. 2 by edge and corner sharing. The several mem-

Table 3. *Interatomic separations and angles*

Ga–O(4a)	1·891 Å	Nb–O(4a)	1·797 Å
Ga–O(3a)	1·918	Nb–O(3e)	1·906
Ga–O(1b)	1·922	Nb–O(2c)	1·937
Ga–O(1c)	2·021	Nb–O(2b)	2·000
Ga–O(1d)	2·097	Nb–O(1a)	2·215
Ga–O(2a)	2·125	Nb–O(3f)	2·333
O(2a)–O(1c)	2·498	O(3e)–O(3f)	2·631
O(1a)–O(2c)	2·498	O(1d)–O(1b)	2·666
O(2a)–O(1b)	2·583	O(1d)–O(1c)	2·666
O(1a)–O(2b)	2·583	O(3a)–O(1d)	2·698
O(4a)–O(2c)	2·730	O(3e)–O(2c)	2·934
O(3a)–O(4a)	2·800	O(3a)–O(1c)	2·959
O(3f)–O(2b)	2·840	O(4a)–O(1b)	2·965
O(4a)–O(1c)	2·879	O(2a)–O(1d)	2·969
O(4a)–O(3e)	2·894	O(3e)–O(2b)	3·096
O(2a)–O(4a)	2·895	O(3a)–O(1c)	3·109
O(4a)–O(2b)	2·896	O(1a)–O(4a)	3·264
O(3f)–O(2c)	2·924		
O(3a)–Ga–O(4a)	94·51°	O(4a)–Nb–O(2c)	93·89°
O(4a)–Ga–O(1c)	94·71	O(4a)–Nb–O(2b)	99·28
O(3a)–Ga–O(1b)	100·78	O(3e)–Nb–O(2b)	99·55
O(4a)–Ga–O(1b)	102·22	O(4a)–Nb–O(3e)	102·78
O(3a)–Ga–O(1c)	104·06	O(3e)–Nb–O(2c)	104·85
O(1c)–Ga–O(1b)	148·60	O(2b)–Nb–O(2c)	148·80
O(2a)–Ga–O(1b)	76·12	O(1a)–Nb–O(3f)	72·73
O(2a)–Ga–O(1c)	77·03	O(1a)–Nb–O(2b)	73·64
O(1d)–Ga–O(1c)	80·66	O(1a)–Nb–O(2c)	75·39
O(1d)–Ga–O(1b)	83·06	O(3e)–Nb–O(3f)	75·98
O(3a)–Ga–O(1d)	84·21	O(3f)–Nb–O(2c)	81·53
O(2a)–Ga–O(1d)	89·38	O(3f)–Nb–O(2b)	85·90
O(2a)–Ga–O(4a)	92·07	O(4a)–Nb–O(1a)	108·46

In parenthesis for each oxygen atom are letters which refer to the following symmetry operations:

a x, y, z
b $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$
c $\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$
d $x, y, 1+z$
e $-x, -y, 1-z$
f $x, y, -1+z$

bers of the series may now be formed by corner-sharing between successive single and double layers in the appropriate ratio. A structure consisting of purely single layers has the composition R_3O_8 (not a part of the series).

The composition, $GaNbO_4$ or R_2O_4, does not appear in Wadsley's proposed series. The configuration of shared octahedra in $GaNbO_4$, however, bears a strong resemblance to part of Wadsley's double layers. A structural scheme is here proposed which will include a compound of the R_2O_4 type with a structure corresponding to that of $GaNbO_4$. This scheme differs from Wadsley's in that the fundamental unit consists of two rather than three octahedra. The series of composition $R_{4n}O_{10n-4}$ is formed, then, by assembling the units into single and double layers and linking these in appropriate sequence as shown in Fig. 3. A structure consisting of single layers alone would have the composition R_2O_5, again not fitting into the series. If $n=2$, we have R_8O_{16} consisting only of double layers. If we consider this to be an ordered structure involving two metals we can write $Ga_4Nb_4O_{16}$, the unit-cell contents for the present compound. Other members of the series would be:

$$n=3 \qquad R_{12}O_{26},$$
$$n=4 \qquad R_{16}O_{36}, \quad etc.$$
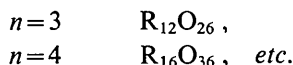
The compound R_4O_6, for $n=1$, cannot be made by any combination of double and single layers. No structures of this type corresponding to these compounds are known to us.

Wadsley proposes both a monoclinic and orthorhombic structure in his series with $n=6$. This compound has the composition R_2O_5. In the scheme proposed here the single-layer structure has the composition R_2O_5 and would be orthorhombic, C-centered, with dimensions near $a_0=12\cdot4$, $b_0=3\cdot7$, $c_0=4\cdot2$ Å. No detailed structures for Nb_2O_5 or Ta_2O_5 have been reported, but several reported cell dimensions are related to these values or to simple multiples or fractions thereof (Lapitskii, Simanov, Semenenko & Yarembash, 1954; Simanov, Lapitskii & Artamonova, 1954).

APPENDIX

The referee has objected to our choice of the noncentric space group, especially since the difference of the y coordinates from zero between a centric and noncentric space group would probably be strongly correlated with thermal displacements parallel to b_0 (i.e., the B_{22} term using anisotropic thermal parameters). We have refined, with several cycles of differential synthesis, the positional and anisotropic thermal parameters for a centric model. The final R value of $0\cdot078$ using only observed reflections ($0\cdot092$ for all reflections) was not significantly different from that obtained with the noncentric case. These centric parameters are presented in Table 4*.

Table 4. *Atomic positions and anisotropic temperature factors for centric interpretation*

	x	z	B_{11}	B_{22}	B_{33}	B_{13}
Ga	0·19712	0·81359	0·084	0·303	0·044	0·082
Nb	0·10320	0·23062	0·302	0·449	0·237	0·058
O(1)	0·25941	0·14594	0·312	0·331	0·294	−0·012
O(2)	0·36252	0·79879	0·487	0·082	0·295	−0·047
O(3)	0·05492	0·86129	0·164	0·799	0·325	0·190
O(4)	0·13705	0·51397	0·567	1·319	0·104	0·011

The editor has pointed out that a y coordinate of $0\cdot025$, representing a displacement of the oxygen atoms from the symmetry plane by about $0\cdot1$ Å, is essentially indistinguishable from a y coordinate of zero and a B_{22} term of such a magnitude as to give an extra $0\cdot1$ Å r.m.s. thermal displacement along b. This appears to be the case for oxygen atoms O(3) and O(4). The average of the difference between the r.m.s. displacements along b_0 and the next largest principal axis for these atoms is $0\cdot06$ Å. This perhaps would be predictable since these oxygen atoms do not have any constraining bonds directed along b_0 whereas O(1) and O(2) do. In addition the anisotropic thermal parameters for O(1) and O(2) are in general agreement with their respective regular and irregular arrangement of nearest neighbors. Similarly the differences of the r.m.s. displacement along b_0 and the next largest principal axis for the Ga atom corresponds very closely to the $0\cdot03$ Å displacement from the symmetry plane obtained in the noncentric refinement.

A satisfactory solution for our intensity data may be obtained either with the centric space group with anisotropic refinement of thermal parameters or with the noncentric space group and isotropic thermal para-

Fig. 3. The hypothetical R_2O_4 structure is formed with two octahedra compared with three for R_3O_8 (Fig. 2). Two of these R_2O_4 units (top of figure) can be joined together by translation of the lower unit sideways by $\frac{1}{2}$ octahedral diagonals to form the double layer R_8O_{16} (lower figure) of which $GaNbO_4$ is a member.

* A table of observed and calculated structure factors has not been included for the centric refinement. Values are not significantly different from those listed in Table 2. Interatomic separations are essentially the same as Table 3 with approximate averages to be taken between atoms related by the symmetry operations (b) and (c).

meters. We believe that where there are two solutions possible, it is preferable to choose the more general case, *i.e.* the noncentric interpretation.

References

BARTH, T. (1926). *Norsk Geol. Tidskr.* **9**, 23.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOP-STRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 154.

EVANS, H. T. (1961). *Acta Cryst.* **14**, 1019.

KOMKOV, A. I. (1959). *Kristallografiya*, **4**, No. 6, 836.

LAPITSKII, A. V., SIMANOV, V. P., SEMENENKO, K. N. & YAREMBASH, E. I., (1954). *Vestnik Moskov. Univ.* **9**, No. 3, Ser. Fiz.-Mat. i Estestven. Nauk, No. 2, 85.

PEDERSEN, B. F. (1962). *Acta Chim. Scand.* **16**, 421.

PHILGREEN, F. A. (1964). *J. Amer. Ceram. Soc.* **47**, No. 1, 49.

SIMANOV, Y. P., LAPITSKII, A. V. & ARTAMONOVA, E. P. (1954). *Vestnik Moskov. Univ.* **9**, No. 9, Ser. Fiz.-Mat. i Estestven. Nauk, No. 6, 109.

THOMAS, L. K. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

WADSLEY, A. D. (1961*a*). *Acta Cryst.* **14**, 660.

WADSLEY, A. D. (1961*b*). *Acta Cryst.* **14**, 664.

WOOD, E. A., MILLER, R. C. & REMEIKA, J. P. (1962). *Acta Cryst.* **15**, 1273.

The Crystal Structure of NaCl . 5⅐NH₃ and NaBr . 5⅐NH₃

BY IVAR OLOVSSON

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structures of NaCl . 5⅐NH₃ and NaBr . 5⅐NH₃ have been determined from single-crystal X-ray data, collected in a low-temperature Weissenberg camera with Cu K radiation. Both compounds are trigonal, space group $R\bar{3}$, with 21 formula units in a hexagonal cell for which the measured dimensions are:

$$\text{NaCl . } 5\tfrac{1}{7}\text{NH}_3 : a = 23\cdot67, c = 9\cdot25 \text{ Å } (t = -58 \text{ °C}) ;$$
$$\text{NaBr . } 5\tfrac{1}{7}\text{NH}_3 : a = 24\cdot34, c = 9\cdot46 \text{ Å } (t = -35 \text{ °C}) .$$

The ammonia molecules and halide ions together form a roughly cubic close-packed arrangement, the sodium ions occupying certain of the octahedral interstices, so that only ammonia molecules are closest neighbours. The octahedra, which enclose some of the sodium ions, share two corners with adjacent octahedra; in this case the effective coordination of the sodium is only fivefold, the sixth ammonia molecule lying at a greater distance.

Introduction

The present investigation forms part of a series of structure determinations of some ammines formed with salts of the alkali metals and ammonium. The structures of NH₄ . 3NH₃ (X = Cl, Br, I) and NH₄I . 4NH₃ have been reported earlier (Olovsson, 1960 *a, b*)

In the systems NaX–NH₃ (X = F, Cl, Br, I) the following compounds have been reported: NaCl . 2·5NH₃ (Friedrichs, 1921), NaCl . 5NH₃ (Joannis, 1891; Biltz & Hansen, 1923; Biltz, 1923; Patscheke, 1933), NaBr . 5·25NH₃ and NaBr . 5·75NH₃ (Biltz & Hansen, 1923; Biltz, 1923), NaI . 4NH₃ (Picon, 1919; Leonard, Lippincott, Nelson & Sellers, 1955), NaI . 4·5NH₃ and NaI . 6NH₃ (Biltz & Hansen, 1923; Biltz, 1923). A phase with the composition NaCl . 2·5NH₃ does not exist according to later investigations (Biltz & Hansen, 1923). The phase reported as NaI . 4NH₃ has the composition NaI . 4·5NH₃ according to Biltz & Hansen (1923). The structures of the ammines of sodium iodide are currently being investigated in this laboratory.

In this paper the structures of the compounds formulated above as NaCl . 5NH₃ and NaBr . 5·25NH₃ are reported. The X-ray crystallographic investigation shows that these compounds are isomorphous and have the exact composition NaCl . 5⅐NH₃ and NaBr . 5⅐NH₃, respectively. This point is further discussed below. For covenience these compounds are called 'pentammines' in the following text, although it should be kept in mind that this designation is not altogether adequate.

Experimental

The solubility curve of sodium chloride in ammonia is shown in Fig. 1. The values were taken from the work by Patscheke (1933) (*cf.* also Patscheke & Tanne, 1935), but the results of Guyer, Bieler & Schmid (1934) and Distanov (1938) are very similar. The curves give the composition of the solution in equili-