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# The Crystal Structure of Magnesium Pyroborate

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The crystal structure of magnesium pyroborate has been studied, using rotation and Weissenberg photographs (Mo $K\alpha$, $\lambda = 0{\cdot}710$ Å), by the trial-and-error and Fourier-series (two-dimensional) methods. The unit cell has the dimensions $a = 12{\cdot}10 \pm 0{\cdot}05$, $b = 3{\cdot}12 \pm 0{\cdot}02$, $c = 9{\cdot}36 \pm 0{\cdot}05$ Å, $\beta = 104° \, 20' \pm 30'$, containing four molecules of $Mg_2B_2O_5$. The space group is $C_{2h}^5$–$P2_1/a$. The structure is composed of $B_2O_5$ (double-triangle) groups held together by magnesium atoms which are in the middle of distorted oxygen octahedra. The $B_2O_5$ group is almost identical in form with one recently found by Berger in cobalt pyroborate, which has a structure closely related to that of magnesium pyroborate. The possible explanation of the structure of $Mg_2B_2O_5$ as a polysynthetic structure has been envisaged, using the powder photographs of natural and artificial products.

## Introduction

As part of the program undertaken by Prof. T. Ito for the study of magnesium and other borates (Ito, 1950, p. 143; Takéuchi, Watanabé & Ito, 1950; Takéuchi, 1950) we have analysed the crystal structure of magnesium pyroborate. The material used for the study was not an artificial product but a possibly new mineral from the Suan mine, North Korea (Watanabé, 1937). It has the theoretical composition $Mg_2B_2O_5$ (MgO 46·63%, $B_2O_3$ 40·08%, CaO 5·06%, $SiO_2$ 0·60%, $Al_2O_3$ $Fe_2O_3$ 0·63%, $H_2O$ (+)0·90%, $H_2O$ (−)0·23%, $CO_2$ 5·06%, total 99·46%, analysis by N. Saito & N. Kokubu; after deduction of $CaCO_3$ and other impurities, MgO 53·8%, $B_2O_3$ 46·2% as against MgO 53·7%, $B_2O_3$ 46·3%, theoretical). Although the mineral as such will be described elsewhere in a detailed report by Dr Takéo Watanabé who kindly supplied the material and necessary information, we have been induced to give this prior account of our structural study by the publication (Berger, 1950) of the crystal structure of $Co_2B_2O_5$. The configurations of the $B_2O_5$ groups found in these closely related natural and artificial compounds are in form practically identical. The two structures, though worked out independently, show a striking similarity, so that we can very easily derive one from the other. Further, the structure of the mineral, together with that of its artificial counterpart, provides another example for the polysymmetric synthesis realized in nature (Ito, 1950).

## Unit cell and space group

For rotation and Weissenberg photographs Mo $K\alpha$ radiation ($\lambda = 0{\cdot}710$ Å) was used. The rotation photograph taken about the direction of elongation of a single crystal loosened from the fibrous aggregate indicates that this is the $b$ axis and that the crystal is monoclinic. The Weissenberg–Buerger photographs about the same axis give the constants

$$a = 12{\cdot}10 \pm 0{\cdot}05,\ b = 3{\cdot}12 \pm 0{\cdot}02,\ c = 9{\cdot}36 \pm 0{\cdot}05 \text{ Å},$$
$$\beta = 104° \, 20' \pm 30',$$

with the axial ratio

$$a:b:c = 3{\cdot}880:1:3{\cdot}000 .$$

There are four molecules of $Mg_2B_2O_5$ in the unit cell, the specific gravity calculated being 2·89 against 2·91 measured. The space group is $C_{2h}^5$–$P2_1/a$, ($h0l$) and ($0k0$) reflexions being absent respectively when $h$ and $k$ are odd.

## Analysis

In analysis we have proceeded in the same way as in working out the similar compounds (Takéuchi *et al.*, 1950). The very short $b$ length suggests that the unit cell contains along this direction virtually a

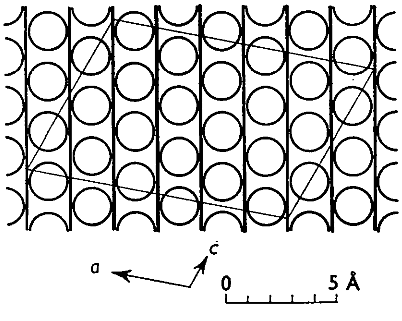

Fig. 1. A hexagonal close-packed layer of oxygen atoms in which the $a$ and $c$ axes are so placed as to make ($60\bar{2}$) reflexion strong, the third axis being perpendicular to the layer. The traces of ($60\bar{2}$) are shown as a system of parallel lines.

single layer of oxygen atoms. Therefore, we can simulate the unit cell by putting a layer of hexagonally closest-packed oxygen atoms (radius 1·33 Å) parallel to (010) and by taking the other crystallographic axes in such directions that a very strong (60$\bar{2}$) reflexion, as observed, would occur (Fig. 1). This ideal unit cell has the dimensions $a = 13{\cdot}94$, $b = 2{\cdot}66$, $c = 9{\cdot}12$ Å, $\beta = 110°$, and contains the same number (twenty) of oxygen atoms as the actual cell. The observed ($h$00) and (00$l$) spectra enable us further to select in this arrangement one out of several possible sets of positions for magnesium with a six-fold coordination. With the positions of oxygen and magnesium atoms thus approximately fixed, and assuming the usual triangular coordination for boron, the final structure was achieved by the trial-and-error method followed by the refinement of $x$ and $z$ parameters of certain atoms by the Fourier synthesis.

In contrast to the readiness and accuracy with which the atoms have been located in the $x$ and $z$ directions, the $y$ parameters are rather difficult (apart from the geometrical considerations) to obtain even roughly on account of the above-mentioned very short $b$ length with the consequent lack of reflexions with $k > 2$. In order to find these parameters we first took into account, not the individual reflexions, but the general trends of ($hnl$) spectra as revealed in the $b(n)$ Weissenberg–Buerger photographs (Takéuchi *et al.*, 1950). These show that a similarity in intensity distribution exists between ($h0l$) and ($h2l$) spectra except for a few ($h2l$) reflexions with $h$ odd. The structure amplitude for the assigned space group is such that this can occur only when almost all atoms in the cell have $b = \frac{1}{4}$ or $\frac{3}{4}$. We made these the starting points for the determination of the $b$ parameters of atoms.

Since the preliminary analysis revealed that there is in the structure a $B_2O_5$ group which was of a new type at the time of this study, and since its mode of grouping, as may easily be seen, varies visibly with the positions of oxygen atoms, especially the one at the centre of the group, we were very careful in determining these positions, taking into account various eventualities in bond lengths and angles. The final parameters (Table 1) explain best the experimental data (Table 2).

Table 1. *Coordinates of atoms*

| | $x/a$ | $y/b$ | $z/c$ | No. of equivalent points |
|---|---|---|---|---|
| $O_I$ | 0·187 | 0·81 | 0·320 | 4 |
| $O_{II}$ | 0·390 | 0·80 | 0·438 | 4 |
| $O_{III}$ | 0·315 | 0·50 | 0·199 | 4 |
| $O_{IV}$ | 0·006 | 0·25 | 0·245 | 4 |
| $O_V$ | 0·387 | 0·31 | 0·000 | 4 |
| $Mg_I$ | 0·147 | 0·31 | 0·135 | 4 |
| $Mg_{II}$ | 0·061 | 0·75 | 0·412 | 4 |
| $B_I$ | 0·298 | 0·71 | 0·321 | 4 |
| $B_{II}$ | 0·408 | 0·35 | 0·146 | 4 |

## Description of structure

The structure of $Mg_2B_2O_5$ is shown in Fig. 2, projected on (010), and the corresponding Fourier projection of electron density in Fig. 3. The structure is composed of the double-triangular groups, $B_2O_5$, linked together by magnesium atoms. The $B_2O_5$ group (Fig. 4) does not have all its oxygen atoms in a plane, the angle between the two slanting planar $BO_3$ groups

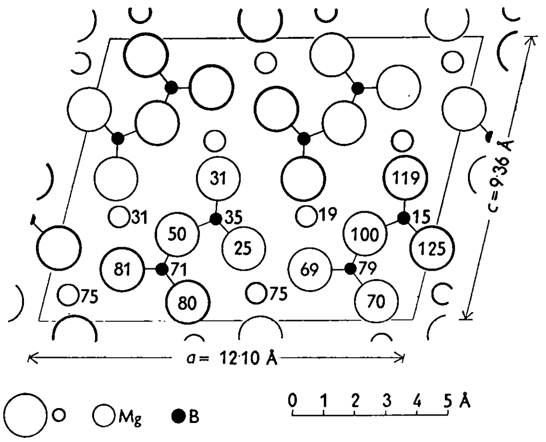

Fig. 2. The structure of $Mg_2B_2O_5$, projected on (010). Numbers give the height of atoms in the unit cell as a percentage of the $b$ translation. The B–O bonds are indicated.

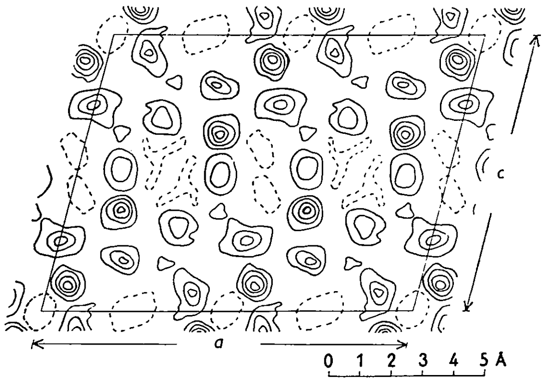

Fig. 3. The $xz$ Fourier projection of electron density of $Mg_2B_2O_5$. Contours at intervals of 2 e.Å$^{-2}$, the zero-electron lines being broken.

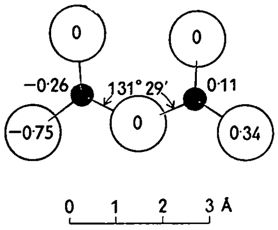

Fig. 4. The $B_2O_5$ group in $Mg_2B_2O_5$. Large open circles represent oxygen and small black circles boron atoms. The height of atoms from the plane of the figure is given in Ångström units.

Table 2. *Observed and calculated intensities of reflexions*

Intensities estimated visually. Intensities observed were converted to the absolute values by scaling them by the calculated $F$ value of the most strong ($60\bar{2}$) reflexion and by multiplying by the Lorentz and polarization factors, no other correction being made. In calculation, the atomic $f$ values given in *International Tables* were used.

| *hkl* | $F_o$ | $F_c$ |
|---|---|---|
| 003 | 0 | 0 |
| 004 | 4 | −16 |
| 005 | 48 | 51 |
| 006 | 2 | 16 |
| 007 | 34 | 51 |
| 008 | 3 | 9 |
| 009 | 5 | 17 |
| 0,0,10 | 0 | 6 |
| 0,0,11 | 25 | −40 |
| 0,0,12 | 0 | 11 |
| | | |
| $20\bar{8}$ | 40 | 39 |
| $20\bar{7}$ | 10 | −19 |
| $20\bar{6}$ | 65 | 77 |
| $20\bar{5}$ | 0 | 0 |
| $20\bar{4}$ | 22 | 44 |
| 203 | 20 | −38 |
| 204 | 0 | − 5 |
| 205 | 70 | 69 |
| 206 | 13 | −18 |
| 207 | 23 | 33 |
| 208 | 0 | 6 |
| | | |
| $40\bar{8}$ | 0 | − 4 |
| $40\bar{7}$ | 70 | −60 |
| $40\bar{6}$ | 8 | 10 |
| $40\bar{5}$ | 0 | 17 |
| $40\bar{4}$ | 0 | − 4 |
| $40\bar{3}$ | 9 | 28 |
| $40\bar{2}$ | 72 | −79 |
| 401 | 36 | −42 |
| 402 | 16 | −32 |
| 403 | 7 | 12 |
| 404 | 48 | 63 |
| 405 | 15 | −29 |
| 406 | 65 | −59 |
| 407 | 0 | −15 |
| | | |
| $60\bar{7}$ | 18 | −28 |
| $60\bar{6}$ | 16 | 28 |
| $60\bar{5}$ | 0 | 0 |
| $60\bar{4}$ | 11 | −13 |
| $60\bar{3}$ | 9 | 12 |
| $60\bar{2}$ | 137 | −137 |
| $60\bar{1}$ | 36 | 38 |
| 600 | 10 | 34 |
| 601 | 23 | 24 |
| 602 | 0 | 1 |
| 603 | 20 | −39 |
| 604 | 2 | 19 |
| 605 | 43 | −54 |
| 606 | 0 | 1 |
| 607 | 0 | − 4 |
| 608 | 0 | − 6 |
| | | |
| $80\bar{8}$ | 27 | 49 |
| $80\bar{7}$ | 6 | 7 |
| $80\bar{6}$ | 15 | −22 |
| $80\bar{5}$ | 14 | −30 |
| $80\bar{4}$ | 0 | − 3 |
| $80\bar{3}$ | 0 | 19 |
| $80\bar{2}$ | 20 | 25 |
| $80\bar{1}$ | 62 | 81 |
| 800 | 6 | − 8 |
| 801 | 7 | 1 |
| 802 | 0 | − 5 |
| 803 | 18 | −26 |
| 804 | 30 | 23 |
| 805 | 0 | − 3 |
| 806 | 14 | 24 |
| 807 | 10 | 17 |
| 10,0,$\bar{8}$ | 31 | 21 |
| 10,0,$\bar{7}$ | 0 | 12 |
| 10,0,$\bar{6}$ | 0 | 19 |
| 10,0,$\bar{5}$ | 0 | 4 |
| 10.0,$\bar{4}$ | 26 | 36 |
| 10,0,$\bar{3}$ | 0 | − 2 |
| 10,0,$\bar{2}$ | 13 | 21 |
| 10,0,$\bar{1}$ | 0 | − 7 |
| 10,0,0 | 0 | − 1 |
| 10,0,1 | 11 | 24 |
| 10,0,2 | 41 | −59 |
| 10,0,3 | 27 | 33 |
| 10,0,4 | 25 | 37 |
| 10,0,5 | 0 | 6 |
| 10,0,6 | 0 | 1 |
| 10,0,7 | 5 | −12 |
| 10,0,8 | 0 | 2 |
| | | |
| 12,0,$\bar{8}$ | 4 | −24 |
| 12,0,$\bar{7}$ | 0 | − 7 |
| 12,0,$\bar{6}$ | 0 | − 9 |
| 12,0,$\bar{5}$ | 17 | 3 |
| 12,0,$\bar{4}$ | 21 | 33 |
| 12,0,$\bar{3}$ | 50 | −57 |
| 12,0,$\bar{2}$ | 10 | −14 |
| 12,0,$\bar{1}$ | 18 | −21 |
| 12,0,0 | 0 | − 2 |
| 12,0,1 | 17 | 30 |
| 12,0,2 | 0 | − 4 |
| 12,0,3 | 9 | 19 |
| 12,0,4 | 25 | −40 |
| 12,0,5 | 0 | − 5 |
| 12,0,6 | 0 | − 3 |
| 12,0,7 | 5 | −14 |
| 12.0,8 | 0 | 9 |
| | | |
| 14,0,$\overline{11}$ | 20 | −24 |
| 14,0,$\overline{10}$ | 0 | − 9 |
| 14,0,$\bar{9}$ | 0 | 9 |
| 14,0,$\bar{8}$ | 0 | 12 |
| 14,0,$\bar{7}$ | 0 | 8 |
| 14,0,$\bar{6}$ | 0 | − 7 |
| 14,0,$\bar{5}$ | 0 | − 9 |
| 14,0,$\bar{4}$ | 19 | 20 |
| 14,0,$\bar{3}$ | 25 | 28 |
| 14,0,$\bar{2}$ | 0 | 16 |
| 14,0,$\bar{1}$ | 0 | −12 |
| 14,0,0 | 0 | − 5 |
| 14,0,1 | 0 | 3 |
| 14,0,2 | 10 | −22 |
| 14,0,3 | 0 | 1 |
| 14,0,4 | 15 | −23 |
| 14,0,5 | 0 | − 9 |
| 14,0,6 | 0 | − 9 |
| 14,0,7 | 0 | 4 |
| 14,0,8 | 18 | 21 |
| | | |
| 16,0,$\overline{10}$ | 25 | 39 |
| 16,0,$\bar{9}$ | 0 | 12 |
| 16,0,$\bar{8}$ | 0 | 1 |
| 16,0,$\bar{7}$ | 0 | − 2 |
| 16,0,$\bar{6}$ | 20 | −30 |
| 16,0,$\bar{5}$ | 0 | 19 |
| 16,0,$\bar{4}$ | 0 | 4 |
| 16,0,$\bar{3}$ | 0 | 14 |
| 16,0,$\bar{2}$ | 0 | 9 |
| 16,0,$\bar{1}$ | 0 | 5 |
| 16,0,0 | 0 | 12 |
| 16,0,1 | 21 | −30 |
| 16,0,2 | 0 | −12 |
| 16,0,3 | 0 | 5 |
| 16,0,4 | 15 | 23 |
| 16,0,5 | 0 | 9 |
| 16,0,6 | 0 | −11 |
| 16,0,7 | 0 | − 2 |
| 16,0,8 | 0 | 1 |
| | | |
| 18,0,$\bar{8}$ | 0 | 6 |
| 18,0,$\bar{7}$ | 20 | 17 |
| 18,0,$\bar{6}$ | 0 | 9 |
| 18,0,$\bar{5}$ | 25 | 31 |
| 18,0,$\bar{4}$ | 5 | 10 |
| 18,0,$\bar{3}$ | 0 | 9 |
| 18,0,$\bar{2}$ | 0 | − 6 |
| 18,0,$\bar{1}$ | 0 | − 8 |
| 18,0,0 | 0 | 15 |
| 18,0,1 | 0 | 10 |
| 18,0,2 | 15 | 29 |
| 18,0,3 | 0 | 10 |
| 18,0,4 | 0 | 1 |
| 18,0,5 | 0 | 12 |
| 18,0,6 | 0 | −13 |
| 18,0,7 | 0 | 9 |
| | | |
| 510 | 20 | 14 |
| 610 | 49 | −47 |
| 710 | 30 | −22 |
| 810 | 38 | 29 |
| 910 | 0 | − 8 |
| 10,1,0 | 34 | 30 |
| 11,1,0 | 0 | 11 |
| 12,1,0 | 22 | 20 |
| 13,1,0 | 0 | 2 |
| 14,1,0 | 19 | 23 |
| 15,1,0 | 0 | 0 |
| | | |
| 013 | 58 | −50 |
| 014 | 22 | 20 |
| 015 | 31 | −27 |
| 016 | 17 | −18 |
| 017 | 0 | − 7 |
| 018 | 0 | 0 |
| 019 | 62 | 63 |
| 0,1,10 | 0 | 0 |
| | | |
| $11\bar{8}$ | 0 | − 3 |
| $11\bar{7}$ | 0 | 0 |
| $11\bar{6}$ | 0 | − 8 |
| $11\bar{5}$ | 0 | 0 |
| $11\bar{4}$ | 0 | 4 |
| 116 | 0 | 0 |
| 117 | 0 | − 5 |
| 118 | 0 | − 8 |
| | | |
| $21\bar{8}$ | 28 | −29 |
| $21\bar{7}$ | 0 | 0 |
| $21\bar{6}$ | 24 | 16 |
| $21\bar{5}$ | 38 | 31 |

Table 2 (*cont.*)

| *hkl* | $F_o$ | $F_c$ |
|---|---|---|
| $21\bar{4}$ | 72 | 72 |
| 213 | 100 | −102 |
| 214 | 19 | −11 |
| 215 | 39 | −29 |
| 216 | 0 | − 8 |
| 217 | 18 | 19 |
| 218 | 14 | −11 |
| $31\bar{8}$ | 0 | 9 |
| $31\bar{7}$ | 0 | 6 |
| $31\bar{6}$ | 0 | 0 |
| $31\bar{5}$ | 11 | −19 |
| $31\bar{4}$ | 0 | − 5 |
| $31\bar{3}$ | 0 | − 4 |
| 313 | 19 | −18 |
| 314 | 0 | − 7 |
| 315 | 0 | −11 |
| 316 | 0 | 0 |
| 317 | 0 | 9 |
| 318 | 0 | 8 |
| $41\bar{8}$ | 17 | − 9 |
| $41\bar{7}$ | 20 | 26 |
| $41\bar{6}$ | 0 | − 1 |
| $41\bar{5}$ | 80 | 74 |
| $41\bar{4}$ | 51 | −47 |
| $41\bar{3}$ | 26 | −20 |
| $41\bar{2}$ | 0 | 0 |
| 411 | 20 | −16 |
| 412 | 72 | −73 |
| 413 | 11 | 6 |
| 414 | 32 | 30 |
| 415 | 29 | 28 |
| 416 | 25 | 27 |
| 417 | 20 | −30 |
| 418 | 5 | − 5 |
| $51\bar{8}$ | 0 | − 7 |
| $51\bar{7}$ | 17 | −10 |
| $51\bar{6}$ | 0 | − 6 |
| $51\bar{5}$ | 0 | − 6 |
| $51\bar{4}$ | 0 | − 5 |
| $51\bar{3}$ | 0 | 0 |
| $51\bar{2}$ | 12 | 10 |
| $51\bar{1}$ | 12 | 10 |
| 511 | 26 | −20 |
| 512 | 0 | − 8 |
| 513 | 18 | −10 |
| 514 | 0 | 3 |
| 515 | 0 | 5 |
| 516 | 0 | 0 |
| 517 | 0 | 2 |
| 518 | 0 | 1 |
| $61\bar{8}$ | 0 | − 6 |
| $61\bar{7}$ | 0 | − 4 |
| $61\bar{6}$ | 17 | −19 |
| $61\bar{5}$ | 19 | 15 |
| $61\bar{4}$ | 129 | −127 |
| $61\bar{3}$ | 0 | − 8 |
| $61\bar{2}$ | 20 | 16 |
| $61\bar{1}$ | 29 | 20 |
| 611 | 70 | 62 |
| 612 | 0 | − 9 |
| 613 | 39 | 39 |
| 614 | 0 | 6 |
| 615 | 0 | 9 |
| 616 | 0 | 15 |
| 617 | 45 | −44 |
| 618 | 0 | 0 |
| $71\bar{8}$ | 0 | 0 |
| $71\bar{7}$ | 0 | − 8 |
| $71\bar{6}$ | 0 | − 3 |
| $71\bar{5}$ | 0 | − 4 |
| $71\bar{4}$ | 25 | 24 |
| $71\bar{3}$ | 0 | 5 |
| $71\bar{2}$ | 0 | − 8 |
| $71\bar{1}$ | 0 | − 5 |
| 711 | 0 | 4 |
| 712 | 0 | 9 |
| 713 | 0 | 6 |
| 714 | 0 | 0 |
| 715 | 0 | 0 |
| 716 | 0 | 1 |
| 717 | 0 | − 2 |
| 718 | 0 | − 1 |
| $81\bar{8}$ | 0 | − 1 |
| $81\bar{7}$ | 40 | −32 |
| $81\bar{6}$ | 38 | −31 |
| $81\bar{5}$ | 0 | 0 |
| $81\bar{4}$ | 16 | 6 |
| $81\bar{3}$ | 43 | 36 |
| $81\bar{2}$ | 0 | − 8 |
| $81\bar{1}$ | 30 | −28 |
| 811 | 80 | 79 |
| 812 | 33 | −16 |
| 813 | 17 | −12 |
| 814 | 14 | −10 |
| 815 | 9 | − 4 |
| 816 | 0 | 9 |
| 817 | 0 | − 3 |
| 818 | 40 | 38 |
| $91\bar{8}$ | 0 | 9 |
| $91\bar{7}$ | 0 | 11 |
| $91\bar{6}$ | 27 | 22 |
| $91\bar{5}$ | 0 | 2 |
| $91\bar{4}$ | 0 | − 5 |
| $91\bar{3}$ | 0 | − 9 |
| $91\bar{2}$ | 0 | 3 |
| $91\bar{1}$ | 0 | 8 |
| 911 | 12 | 9 |
| 912 | 0 | 2 |
| 913 | 0 | 0 |
| 914 | 0 | 0 |
| 915 | 0 | − 9 |
| 916 | 0 | − 9 |
| 917 | 0 | 0 |
| 918 | 0 | 8 |
| $10,1,\bar{8}$ | 0 | 5 |
| $10,1,\bar{7}$ | 48 | −42 |
| $10,1,\bar{6}$ | 50 | 47 |
| $10,1,\bar{5}$ | 0 | − 5 |
| $10,1,\bar{4}$ | 0 | − 6 |
| $10,1,\bar{3}$ | 0 | 0 |
| $10,1,\bar{2}$ | 16 | 18 |
| $10,1,\bar{1}$ | 12 | −17 |
| 10,1,1 | 26 | 29 |
| 10,1,2 | 33 | −32 |
| 10,1,3 | 25 | −21 |
| 10,1,4 | 24 | −29 |
| 10,1,5 | 20 | 23 |
| 10,1,6 | 0 | − 5 |
| 10,1,7 | 10 | 8 |
| 10,1,8 | 0 | 0 |
| $11,1,\bar{8}$ | 0 | 1 |
| $11,1,\bar{7}$ | 0 | − 4 |
| $11,1,\bar{6}$ | 0 | 0 |
| $11,1,\bar{5}$ | 0 | 0 |
| $11,1,\bar{4}$ | 0 | 0 |
| $11,1,\bar{3}$ | 0 | − 2 |
| $11,1,\bar{2}$ | 0 | − 9 |
| $11,1,\bar{1}$ | 0 | 3 |
| 11,1,1 | 0 | 5 |
| 11,1,2 | 0 | − 2 |
| 11,1,3 | 0 | − 9 |
| 11,1,4 | 0 | 0 |
| 11,1,5 | 0 | 0 |
| 11,1,6 | 0 | 6 |
| 11,1,7 | 0 | 0 |
| 11,1,8 | 0 | − 1 |
| $12,1,\bar{8}$ | 0 | 19 |
| $12,1,\bar{7}$ | 0 | 4 |
| $12,1,\bar{6}$ | 40 | 41 |
| $12,1,\bar{5}$ | 12 | −19 |
| $12,1,\bar{4}$ | 0 | − 8 |
| $12,1,\bar{3}$ | 10 | − 2 |
| $12,1,\bar{2}$ | 17 | −11 |
| $12,1,\bar{1}$ | 65 | 58 |
| 12,1,1 | 26 | −27 |
| 12,1,2 | 0 | 11 |
| 12,1,3 | 0 | − 4 |
| 12,1,4 | 0 | 0 |
| 12,1,5 | 0 | 16 |
| 12,1,6 | 40 | −35 |
| 12,1,7 | 0 | −11 |
| 12,1,8 | 0 | −19 |
| 520 | 21 | 22 |
| 620 | 21 | 22 |
| 720 | 0 | 1 |
| 820 | 0 | 8 |
| 920 | 0 | 4 |
| 10,2,0 | 0 | −11 |
| 11,2,0 | 0 | 2 |
| 12,2,0 | 0 | 6 |
| 13,2,0 | 0 | − 4 |
| 14,2,0 | 25 | −23 |
| 024 | 0 | 9 |
| 025 | 0 | −16 |
| 026 | 0 | 15 |
| 027 | 36 | −38 |
| 028 | 0 | 0 |
| 029 | 0 | −12 |
| 0,2,10 | 0 | 2 |
| $12\bar{8}$ | 0 | 5 |
| $12\bar{7}$ | 0 | −14 |
| $12\bar{6}$ | 0 | 8 |
| $12\bar{5}$ | 0 | − 6 |
| $12\bar{4}$ | 28 | −23 |
| 125 | 35 | −34 |
| 126 | 0 | − 4 |
| 127 | 0 | 0 |
| 128 | 0 | 3 |
| $22\bar{8}$ | 24 | −12 |
| $22\bar{7}$ | 0 | 7 |
| $22\bar{6}$ | 36 | 33 |
| $22\bar{5}$ | 0 | 0 |
| $22\bar{4}$ | 0 | 5 |
| 223 | 29 | 20 |
| 224 | 7 | 3 |
| 225 | 44 | −42 |
| 226 | 20 | 18 |

Table 2 (*cont.*)

| *hkl* | $F_o$ | $F_c$ |
|---|---|---|
| 227 | 20 | −19 |
| 228 | 0 | 3 |
| $32\bar{8}$ | 0 | 8 |
| $32\bar{7}$ | 14 | 14 |
| $32\bar{6}$ | 0 | −10 |
| $32\bar{5}$ | 0 | 10 |
| $32\bar{4}$ | 7 | 5 |
| 323 | 0 | − 7 |
| 324 | 0 | − 3 |
| 325 | 26 | 25 |
| 326 | 0 | 13 |
| 327 | 0 | 12 |
| 328 | 0 | − 3 |
| $42\bar{8}$ | 0 | 0 |
| $42\bar{7}$ | 41 | 49 |
| $42\bar{6}$ | 0 | − 5 |
| $42\bar{5}$ | 0 | − 9 |
| $42\bar{4}$ | 0 | 14 |
| $42\bar{3}$ | 31 | −29 |
| $42\bar{2}$ | 61 | 54 |
| 421 | 0 | 0 |
| 422 | 0 | − 1 |
| 423 | 0 | − 4 |
| 424 | 32 | −25 |
| 425 | 19 | 20 |
| 426 | 36 | 30 |
| 427 | 0 | 6 |
| $52\bar{8}$ | 0 | − 5 |
| $52\bar{7}$ | 17 | −21 |
| $52\bar{6}$ | 0 | 2 |
| $52\bar{5}$ | 0 | 2 |
| $52\bar{4}$ | 0 | 9 |
| $52\bar{3}$ | 7 | 7 |
| $52\bar{2}$ | 20 | 12 |
| $52\bar{1}$ | 16 | −16 |
| 521 | 0 | − 4 |
| 522 | 0 | 12 |
| 523 | 0 | 11 |
| 524 | 0 | 9 |
| 525 | 0 | 7 |
| 526 | 0 | − 8 |
| 527 | 0 | − 7 |
| 528 | 0 | −10 |
| $62\bar{8}$ | 24 | −20 |
| $62\bar{7}$ | 0 | − 8 |
| $62\bar{6}$ | 24 | −21 |
| $62\bar{5}$ | 0 | 0 |
| $62\bar{4}$ | 0 | 9 |
| $62\bar{3}$ | 0 | −10 |
| $62\bar{2}$ | 68 | 60 |
| $62\bar{1}$ | 34 | −34 |
| 621 | 0 | 0 |
| 622 | 0 | − 9 |
| 623 | 0 | 4 |
| 624 | 0 | − 6 |
| 625 | 42 | 44 |
| 626 | 0 | 0 |
| 627 | 0 | 3 |
| 628 | 0 | 5 |
| $72\bar{8}$ | 0 | − 7 |
| $72\bar{7}$ | 0 | − 2 |
| $72\bar{6}$ | 0 | 13 |
| $72\bar{5}$ | 0 | 0 |
| $72\bar{4}$ | 0 | 0 |
| $72\bar{3}$ | 21 | −11 |
| $72\bar{2}$ | 28 | −30 |
| $72\bar{1}$ | 14 | −11 |
| 721 | 0 | 0 |
| 722 | 0 | − 2 |
| 723 | 0 | 7 |
| 724 | 0 | − 8 |
| 725 | 0 | − 9 |
| 726 | 0 | 0 |
| 727 | 0 | −11 |
| 728 | 0 | 4 |
| $82\bar{8}$ | 21 | −26 |
| $82\bar{7}$ | 0 | 11 |
| $82\bar{6}$ | 0 | 5 |
| $82\bar{5}$ | 0 | 3 |
| $82\bar{4}$ | 14 | −13 |
| $82\bar{3}$ | 17 | 15 |
| $82\bar{2}$ | 0 | 6 |
| $82\bar{1}$ | 49 | −51 |
| 821 | 10 | −13 |
| 822 | 26 | 28 |
| 823 | 24 | 29 |
| 824 | 37 | −36 |
| 825 | 0 | − 7 |
| 826 | 16 | −23 |
| 827 | 0 | 2 |
| 828 | 0 | 1 |
| $92\bar{8}$ | 0 | 14 |
| $92\bar{7}$ | 0 | 14 |
| $92\bar{6}$ | 0 | − 9 |
| $92\bar{5}$ | 0 | − 4 |
| $92\bar{4}$ | 20 | −18 |
| $92\bar{3}$ | 0 | 0 |
| $92\bar{2}$ | 0 | 0 |
| $92\bar{1}$ | 14 | 20 |
| 921 | 0 | 5 |
| 922 | 0 | 15 |
| 923 | 19 | −17 |
| 924 | 0 | − 6 |
| 925 | 0 | 0 |
| 926 | 0 | 9 |
| 927 | 0 | 6 |
| 928 | 0 | 8 |
| $10,2,\bar{8}$ | 0 | 6 |
| $10,2,\bar{7}$ | 0 | 14 |
| $10,2,\bar{6}$ | 0 | 3 |
| $10,2,\bar{5}$ | 0 | 11 |
| $10,2,\bar{4}$ | 41 | −43 |
| $10,2,\bar{3}$ | 0 | − 9 |
| $10,2,\bar{2}$ | 0 | −13 |
| $10,2,\bar{1}$ | 0 | 15 |
| 10,2,1 | 0 | 6 |
| 10,2,2 | 0 | 15 |
| 10,2,3 | 18 | −26 |
| 10,2,4 | 4 | −14 |
| 10,2,5 | 0 | 1 |
| 10,2,6 | 0 | −10 |
| 10,2,7 | 0 | 2 |
| 10,2,8 | 0 | 4 |

amounting to 22° 19′ and the B–O–B angle to 131° 29′.* Magnesium has a sixfold coordination, being surrounded by a distorted octahedron of six oxygen atoms of which two come from a $B_2O_5$ group and the remaining four one each from four other similar groups. Further, an $MgO_6$ octahedron has four of its eight O–O edges shared by the neighbouring similar octahedra so that we may conceive a band of oxygen and magnesium atoms stretched indefinitely parallel to (201). An oxygen atom is either between one boron and three magnesium atoms ($O_I$, $O_{II}$ and $O_{IV}$), between one boron and two magnesium atoms ($O_V$),

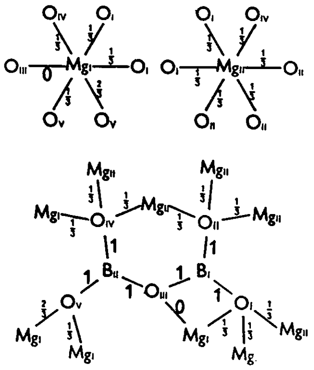

Fig. 5. The electrostatic balance of bonds in the structure of $Mg_2B_2O_5$.

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* It is interesting to note that in the majority of borates the B–O–B angle does not vary much:

| Substance | B–O–B angle | Type of group |
|---|---|---|
| $CaB_2O_4$ | 130° 13′† | $BO_2$ chain (Zachariasen, 1931) |
| $K_2B_3O_6$ | 126° 30′ | $B_3O_6$ ring (Zachariasen, 1937*a*) |
| $KH_2(H_3O)_2B_5O_{10}$ | 126° 30′† | $B_5O_{10}$ group (Zachariasen, 1937*b*) |
| $CoB_2O_5$ | 153° | $B_2O_5$ double-triangle (Berger, 1950) |

† Calculated by the present writer.

or between two boron and one magnesium atoms ($O_{III}$). The balance of valency is illustrated in Fig. 5, and the interatomic distances are given in Table 3.

Table 3. *Interatomic distances in* $Mg_2B_2O_5$

| Atom | Neighbour | Distance (Å) |
|---|---|---|
| $B_{I}$ | $O_{I}$ | 1·35 |
| | $O_{II}$ | 1·38 |
| | $O_{III}$ | 1·38 |
| $B_{II}$ | $O_{III}$ | 1·37 |
| | $O_{IV}$ | 1·33 |
| | $O_{V}$ | 1·33 |
| $Mg_{I}$ | $O_{III}$ | 2·09 |
| | $O_{IV'}$ | 2·19 |
| | $O_{I}$ | 2·29 |
| | $O_{I}$* | 2·29 |
| | $O_{V'}$ | 2·03 |
| | $O_{V'}$* | 2·03 |
| $Mg_{II}$ | $O_{I}$ | 1·95 |
| | $O_{II}$* | 2·43 |
| | $O_{IV'}$ | 2·19 |
| | $O_{IV'}$* | 2·19 |
| | $O_{II'}$ | 1·96 |
| | $O_{II'}$* | 2·19 |

$O_{I}$–$O_{II}$ 2·41, $O_{I}$–$O_{III}$ 2·36, $O_{II}$–$O_{III}$ 2·38, $O_{III}$–$O_{IV}$ 2·33, $O_{III}$–$O_{V}$ 2·34, $O_{IV}$–$O_{V}$ 2·40 Å.

* Primes denote equivalent atoms and asterisks those of the neighbouring cell.

## Polymorphism of $Mg_2B_2O_5$

The structures of cobalt and magnesium pyroborates are very similar, both containing $B_2O_5$ groups of the same type. The unit cells compare as follows:

| $Co_2B_2O_5$<br>(Berger, 1950)<br>Triclinic | | $Mg_2B_2O_5$<br>Monoclinic | |
|---|---|---|---|
| $a$ | 3·16 Å | $b$ | 3·12 Å |
| $b$ | 5·94 Å | $\frac{1}{2}a$ | 6·05 Å |
| $c$ | 8·95 Å | $c$ | 9·36 Å |
| $\alpha$ | 103° 54′ | $\beta$ | 104° 24′ |
| $\beta$ | 91° | | |
| $\gamma$ | 92° | | |

The structure of $Mg_2B_2O_5$ as worked out by us may be obtained from that of $Co_2B_2O_5$ of Berger by the replacement of cobalt by magnesium atoms, followed by a multiple twinning. In the polysymmetric synthesis the domain of operation may be a submultiple as well as a multiple of a unit cell (Ito, 1950, p. 2). Now, we divide the unit cell of $Co_2B_2O_5$ into two by (100) planes passing through the points $\frac{1}{4}, 0, 0$ and $\frac{3}{4}, 0, 0$ and subject them to the glide planes across the same planes with a glide $b$ (Fig. 6(*a*)). The new unit cell has about the dimensions of that of $Mg_2B_2O_5$ (Fig. 6(*b*); note that $a$ and $b$ are interchanged), and the space group and structure (with cobalt replaced by magnesium) are the same.

Although we know as yet no triclinic $Mg_2B_2O_5$ which, corresponding to $Co_2B_2O_5$, constitutes the building unit of monoclinic $Mg_2B_2O_5$, the existence of such may certainly be expected in view of the similar parts played by cobalt and magnesium in crystal chemistry (Berger, 1949). Actually Watanabé obtained synthetically a compound of the composition $Mg_2B_2O_5$, of which the powder pattern, compared with that of the natural crystal, reveals certain visible differences though with the nearly same main

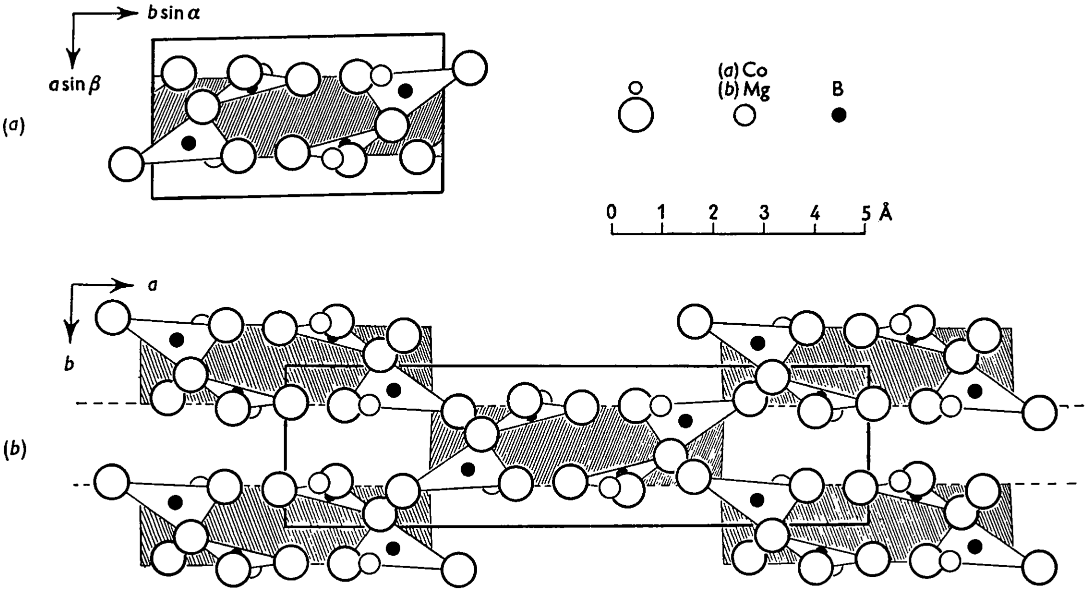

Fig. 6. The relationship of the structures of cobalt and magnesium pyroborates, both being projected on a plane normal to the $c$ axis. Notation as in Fig. 2. (Some of boron atoms are displaced from the actual positions so as to be seen. The height of atoms are not given.) The $B_2O_5$ double-triangles, instead of B–O bonds, are traced. (*a*) $Co_2B_2O_5$. (*b*) $Mg_2B_2O_5$. The corresponding portions of the two structures are shaded. Broken lines in (*b*) indicate the traces of glide planes, $(010)_{\frac{1}{4}}$ and $(010)_{\frac{3}{4}}$.

Table 4. *Powder photographs of natural and artificial* $Mg_2B_2O_5$

Camera radius 28·65 mm. Co $K\alpha$ ($\lambda$=1·79 Å).

$$Q=4\sin^2\theta/\lambda^2=h^2a^{*2}+k^2b^{*2}+l^2c^{*2}+2klb^*c^*\cos\alpha^*+2lha^*c^*\cos\beta^*+2hka^*b^*\cos\gamma^*$$

Natural

| | |
|---|---|
| $a$ | 12·10 Å |
| $b$ | 3·12 Å |
| $c$ | 9·36 Å |
| $\beta$ | 104·3° |

| $hkl$ | $Q_o$ | $Q_c$ | $I_o$ |
|---|---|---|---|
| 201 | 0·0500 | 0·0486 | *m*− |
| $20\bar{2}$ | 0·0601 | 0·0588 | *s* |
| 202 | 0·0952 | 0·0942 | *s* |
| $40\bar{2}$ | 0·1255 | 0·1239 | *s* |
| 012 | 0·1520 | 0·1513 | *vs* |
| $20\underline{3}$ | 0·1645 | 0·1642 | *m* |
| $20\bar{4}$ | 0·1859 | 0·1856 | *w* |
| 212 | 0·2026 | 0·1989 | *w* |
| 013 | 0·2173 | 0·2142 | *w* |
| $60\bar{2}$ | 0·2481 | 0·2439 | *vs* |
| 213 | 0·2712 | 0·2689 | *m* |
| $41\underline{2}$ | 0·2979 | 0·2974 | *m* |
| $41\bar{4}$ | 0·3387 | 0·3344 | *mw* |
| 610 | 0·3498 | 0·3496 | *mw* |
| 611 | 0·3920 | 0·3890 | *m*− |
| 020 | 0·4074 | 0·4108 | *m*+ |
| 220 | 0·4386 | 0·4382 | *m* |
| $61\bar{4}$ | 0·4418 | 0·4402 | *m* |
| 222 | 0·4895 | 0·4862 | *w* |
| $42\bar{2}$ | 0·5361 | 0·5327 | *w* |
| $81\bar{3}$ | 0·5472 | 0·5421 | *w* |
| 811 | 0·5947 | 0·5902 | *w*+ |
| $62\bar{2}$ | 0·6484 | 0·6517 | *w* |
| 406 | 0·6598 | 0·6569 | *w*+ |
| $62\bar{4}$ | 0·7503 | 0·7483 | *w* |
| 027 | 0·9987 | 1·0029 | *w*+ |

Artificial

| | |
|---|---|
| $a$ | 3·12 Å |
| $b$ | 5·93 Å |
| $c$ | 9·03 Å |
| $\alpha$ | 103·9° |
| $\beta$ | 90·9° |
| $\gamma$ | 92·0° |

| $hkl$ | $Q_o$ | $Q_c$ | $I_o$ |
|---|---|---|---|
| 011 | 0·0520 | 0·0527 | *m* |
| $01\bar{2}$ | 0·0630 | 0·0632 | *s* |
| 012 | 0·1020 | 0·1012 | *s* |
| $02\bar{2}$ | 0·1331 | 0·1348 | *s* |
| $10\bar{2}$ | 0·1495 | 0·1493 | *s* |
| 102 | 0·1560 | 0·1565 | *vs* |
| 013 | 0·1761 | 0·1758 | *vw* |
| $\bar{1}12$ | 0·1948 | 0·1939 | *m*− |
| $10\bar{3}$ | 0·2127 | 0·2125 | *m*− |
| $\bar{1}21$ | 0·2434 | 0·2427 | *s* |
| $03\bar{2}$ | 0·2652 | 0·2668 | *vs* |
| $\bar{1}13$ | 0·2764 | 0·2766 | *m*− |
| 113 | 0·2880 | 0·2866 | *s* |
| $\bar{1}14$ (?) | 0·3365 | 0·3386 | *vw* |
| $\bar{1}23$ | 0·3829 | 0·3832 | *vw* |
| 200 | 0·4039 | 0·4036 | *m*+ |
| $2\bar{1}0$ | 0·4243 | 0·4246 | *m*+ |
| $2\bar{1}1$ | 0·4310 | 0·4317 | *m*+ |
| $20\bar{2}$ | 0·4462 | 0·4464 | *vw* |
| $12\underline{4}$ | 0·5231 | 0·5221 | *m*− |
| $22\bar{2}$ | 0·5490 | 0·5497 | *m*− |
| 221 | 0·5700 | 0·5688 | *w*+ |
| 133 | 0·5888 | 0·5880 | *w*+ |
| $\bar{1}41$ | 0·6138 | 0·6148 | *vw* |
| $20\underline{4}$ | 0·6250 | 0·6260 | *vw* |
| $2\bar{3}0$ | 0·6473 | 0·6476 | *vw* |
| 026 | 0·7031 | 0·7028 | *m* |
| 231 | 0·7482 | 0·7483 | *vw* |
| $20\bar{7}$ | 1·0150 | 1·0153 | *m* |

features. Comparing line by line we have succeeded in indexing completely the powder photographs of both of them. The result is given in Table 4 and shows that the artificial compound, as anticipated, is triclinic with the lattice constants nearly identical with those of $Co_2B_2O_5$. That $Mg_2B_2O_5$ is dimorphous and the monoclinic form is a multiple twin of the triclinic one may be considered established.

Actually, the twinning operation is described by the matrix $\frac{\bar{2}}{57}\ 1\ \frac{\bar{1}}{57}/\frac{1}{2}\ 0\ 0/0\ 0\ 1$. The atomic parameters of the monoclinic structure are then converted into those of the triclinic one by a simple transformation (Table 5). Further, the $F$ values calculated on the basis of these new parameters check well with

Table 5. *Coordinates of atoms of* $Mg_2B_2O_5$, *artificial.*

The coordinates $m', n', p'$ of the triclinic crystal are derived from the coordinates $m, n, p$ of the monoclinic crystal by the formulae: $m' = n-\frac{1}{2}$, $n' = 2m+2n/57-\frac{1}{2}$, $p' = n/57+p$. The origin of the triclinic cell is placed at $\frac{1}{2}$, $\frac{1}{2}$, 0 of the monoclinic cell.

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| $O_1$ | 0·81 | 0·374 | 0·320 |
| $O_2$ | 0·80 | 0·780 | 0·438 |
| $O_3$ | 0·50 | 0·630 | 0·199 |
| $O_4$ | 0·25 | 0·012 | 0·245 |
| $O_5$ | 0·31 | 0·774 | 0·000 |
| $Mg_1$ | 0·31 | 0·294 | 0·135 |
| $Mg_2$ | 0·75 | 0·122 | 0·412 |
| $B_1$ | 0·71 | 0·596 | 0·321 |
| $B_2$ | 0·35 | 0·816 | 0·146 |

Table 6. *Calculated and observed intensities of* $Mg_2B_2O_5$, *artificial*

Intensities estimated visually in the powder photograph (Co $K\alpha$)

| *hkl* | $I_o$ | $F_c$ | *hkl* | $I_o$ | $F_c$ | *hkl* | $I_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|
| 011 | *m* | −25 | $03\bar{2}$ | *s* | −63 | $22\bar{2}$ | *m*− | 22 |
| $01\bar{2}$ | *s* | 13 | $\bar{1}13$ | *m*− | −15 | 221 | *w*+ | −12 |
| 012 | *s* | 14 | 113 | *s* | 52 | 133 | *w*+ | −17 |
| $02\bar{2}$ | *s* | −35 | $\bar{1}14$ | *vw* | −1 | $\bar{1}41$ | *vw* | 5 |
| $10\bar{2}$ | *s* | 59 | $\bar{1}23$ | *vw* | − 5 | 204 | *vw* | 6 |
| 102 | *vs* | −50 | 200 | *m*+ | −44 | $2\bar{3}0$ | *vw* | − 9 |
| 013 | *vw* | − 3 | $2\bar{1}0$ | *m*+ | −20 | 026 | *m* | −30 |
| $\bar{1}12$ | *m*− | −21 | $2\bar{1}1$ | *m*+ | 25 | 231 | *vw* | − 1 |
| $10\bar{3}$ | *m*− | −10 | $20\bar{2}$ | *vw* | − 9 | $20\bar{7}$ | *m* | −24 |
| $\bar{1}21$ | *s* | −20 | 124 | *m*− | −15 | | | |

the intensities of reflexions observed in the powder photograph of the artificial (triclinic) crystal (Table 6), supporting our statement.

In conclusion the writer wishes to express his sincere thanks to Prof. Ito for suggestion and guidance throughout the work.

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# The Structure of Synthetic Polypeptides. I. The Transform of Atoms on a Helix

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(*Received* 16 *February* 1952)

The formulæ are given for the Fourier transforms of a number of helical structures; namely, a thin helical wire, a set of identical atoms spaced at regular intervals on a helix, and the general case of a group of atoms repeated by the operation of a non-integer screw. General predictions are made concerning the intensities of the X-ray diffraction pattern of the synthetic polypeptide poly-$\gamma$-methyl-L-glutamate, assuming that its structure is based on the $\alpha$-helix suggested by Pauling & Corey.

## 1. Introduction

The following calculations were undertaken because of current interest in the structures of certain synthetic polypeptides. The preliminary X-ray data for these polypeptides have been described by Bamford, Hanby & Happey (1951) and their infra-red behaviour by Ambrose & Elliott (1951). Pauling & Corey (1951) have interpreted the structures of the two polypeptides which have so far given the best X-ray diffraction pictures, namely poly-$\gamma$-methyl-L-glutamate and poly-$\gamma$-benzyl-L-glutamate, in terms of the $\alpha$-helix described by Pauling, Corey & Branson (1951). In this structure the residues repeat along the helix with a spacing of about 1·5 Å in the chain direction, and Perutz (1951) has found that a strong meridional reflexion of spacing 1·5 Å is given by poly-$\gamma$-benzyl-

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