the abscissa at some point $x$. The half-curves so obtained were weighed with a chemical balance and, after several cuttings and weighings, two half-curves with equal weight were obtained. After the balance had been effected, the distance between the cut edge and a fiducial mark on the tracing was measured. This value constituted the $X$ coordinate for the median.

The standard deviation was determined from the $X$ coordinates of a given diffraction line and, as before, $\pm 3\sigma$ was taken as the value beyond which the number of observations having this error would be negligible.

The results are presented in Table 2.

Table 2. *Photometric estimation of centers of diffraction lines*

| | $\sigma$ (cm.) | $B=RW$ (cm.) | $r=3\sigma/B$ |
|---|---|---|---|
| Coarse film, sharp line | 0·0018 | 0·034 | 1/6 |
| Coarse film, broad line | 0·0034 | 0·17 | 1/18 |
| Fine film, broad line | 0·0026 | 0·18 | 1/23 |

The general tendency for increased relative accuracy for wider lines is again apparent. However, it is surprising that, for lines broader than those evaluated visually, the accuracy is lower. It seems that the discriminating ability of the eye makes it superior to the microphotometer for the usual range of line width.

In a more accurate method of objective evaluation, one would first have computed, by the method of least squares, the best-fitting curve corresponding to each microphotometer tracing and then have determined the median. However, this procedure appears too cumbersome for routine use.

It is doubtful whether the present choice of exposure time and background density are the most favorable. Only further investigations can answer the question.

### 3. Conclusions

The minimum width of a diffraction line depends on the spectral impurity of the incident characteristic radiation. It has been shown that at large diffraction angles, 80° or more, the spectral width will predominate over the geometrical width.

Such a diffraction line, produced with a smooth intensity distribution, will appear irregular when recorded on film because of the fluctuations in density caused by the film grain. The limit of accuracy of lattice-parameter determination is reached because of the error of determination of the intensity maximum of a wide line photographically recorded. Objective and subjective measurements of the error in determination of the line center lead to a relative error $|\delta d/d| \approx 3\times10^{-5}$, *due to the spectral width alone*, in agreement with the best reported accuracy.

The authors wish to thank Dr C. S. Barrett for a critical review of this paper.

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*Acta Cryst.* (1949). **2**, 104

# The Crystal Structure of Groutite, $HMnO_2$

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The crystal structure of groutite, a new modification of $HMnO_2$, has been determined. The dimensions of the orthorhombic unit cell are $a=4{\cdot}58$ A., $b=10{\cdot}76$ A., and $c=2{\cdot}89$ A., and the space group is $D_{2h}^{16}$–$Pbnm$. The atomic arrangement is very nearly identical with that of diaspore.

## Introduction

The crystallography of groutite, which has been reported by Gruner (1947), indicates that it is a member of the diaspore–goethite group. In a preliminary X-ray diffraction study the size of the unit cell was indicated as $a=4{\cdot}56$ A., $b=10{\cdot}70$ A., and $c=2{\cdot}85$ A. or possibly twice the last value. Since manganite does not show the same structure as the isoformular aluminum and iron minerals, boehmite and lepidocrocite, it was thought advisable to make a determination of the unit cell, space group, and structure of groutite in order to make certain of its identification as a member of the diaspore–goethite group.

## The unit cell and space group

A crystal with no dimension larger than 0·3 mm. was selected. The Laue symmetry *mmm* was verified, and the unit-cell values $a=4{\cdot}58$ A., $b=10{\cdot}76$ A., and

$c = 2{\cdot}89$ A. were determined from oscillation and rotation photographs about [100], [010], and [001] taken with Cu $K\alpha$ and Mo $K\alpha$ radiation. The unit cell was further checked by the indexing of a Laue photograph taken with the X-ray beam at an angle of about 6° from the $c$ axis; 59 first-order reflections were observed, all consistent with the unit cell. These values are in satisfactory agreement with those obtained by Gruner, and no doubling of the $c$ axis was indicated.

The reflections on a rotation photograph taken with Mo $K\alpha$ radiation about $b$, the asymmetric Laue photograph, and zero-level Weissenberg photographs taken with Mo $K\alpha$ radiation about $a$ and $b$ indicated the extinctions* of $0kl$ when $k$ is odd and of $h0l$ when $h+l$ is odd. These extinctions are consistent with the space group $D_{2h}^{16}$–$Pbnm$. Since a qualitative test† showed no piezoelectricity, this space group was then assumed to be correct. The two Weissenberg photographs provided a further check on the unit-cell dimensions.

### The atomic arrangement

The intensities of the reflections on the $b$-axis photograph taken with Mo $K\alpha$ radiation were estimated with the aid of an intensity standard prepared by controlled exposures for varying length of time to an X-ray beam the size of the diffraction spots. After correction for Lorentz, polarization, and multiplicity factors the structure factors $F_{\text{obs.}}$ listed in Table 1 were obtained. The absolute scale of $F_{\text{obs.}}$ was established by comparison with $F_{\text{calc.}}$ by the method of least squares.

All structure-factor calculations were made with the use of atomic scattering factors (*Internationale Tabellen*...(1935, vol. 2, p. 571)) with no correction for temperature vibrations. The $\text{Mn}^{+3}$ scattering factor was assumed to be the same as that for Mn except for a smooth extrapolation to atomic number 22 in the region $0 \leqslant \sin\theta < 0{\cdot}15$. In a preliminary calculation the atomic parameters found for diaspore were used. The agreement between observed and calculated structure factors indicated that groutite was isostructural with diaspore. Some improvement in the agreement was obtained by a change in the $y$ parameter of the $\text{Mn}^{+3}$ ion from 0·146 to 0·140. It was not thought worth while to investigate further variations, especially of the para-

Table 1. *Comparison of observed and calculated structure factors*

| *hkl* | $F_{\text{obs.}}$ | $F_{\text{calc.}}$ | *hkl* | $F_{\text{obs.}}$ | $F_{\text{calc.}}$ | *hkl* | $F_{\text{obs.}}$ | $F_{\text{calc.}}$ | *hkl* | $F_{\text{obs.}}$ | $F_{\text{calc.}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 002 | 85 | −82 | 220 | <11 | −10 | 043 | <25 | −15 | 162 | <15 | 8 |
| 101 | 23 | 16 | 221 | 60 | −70 | 140 | 50 | −46 | 260 | 28 | 26 |
| 103 | <19 | −9 | 222 | <20 | 7 | 141 | 23 | −24 | 261 | 23 | 19 |
| 200 | 24 | 25 | 223 | 36 | 44 | 142 | 26 | 25 | 262 | 12 | −21 |
| 202 | 20 | −25 | 320 | 42 | 33 | 143 | <11 | 8 | 360 | 36 | −28 |
| 301 | 38 | 36 | 321 | 18 | −21 | 240 | 50 | −61 | 361 | 27 | 21 |
| 400 | 27* | 44 | 322 | 30 | −27 | 241 | 21 | 20 | 362 | 19 | 24 |
| 402 | 22 | −36 | 420 | <17 | −11 | 242 | 28 | 46 | 460 | <23 | 15 |
| 501 | 36 | 33 | 421 | <17 | −20 | 340 | <25 | 7 | 461 | 25 | 33 |
|  |  |  | 422 | <18 | 7 | 341 | 37 | −29 |  |  |  |
| 110 | 54 | 56 | 520 | 35 | 37 | 342 | <17 | − 3 | 170 | 39 | 53 |
| 111 | 54 | −51 | 521 | <18 | −0·1 | 440 | <24 | −22 | 171 | <12 | 8 |
| 112 | 31 | −36 | 522 | 30 | 36 | 441 | <10 | 7 | 172 | 33 | −42 |
| 113 | 32 | 32 | 620 | <29 | − 2 | 442 | <18 | 20 | 270 | <11 | − 3 |
| 210 | <18 | 23 |  |  |  | 540 | <28 | −21 | 271 | 23 | 16 |
| 211 | 34 | 25 | 130 | 54 | −58 |  |  |  | 272 | <15 | 7 |
| 212 | <20 | −12 | 131 | 25 | −26 | 150 | 28 | −22 | 370 | 36 | 42 |
| 213 | <19 | −16 | 132 | 36 | 41 | 151 | 59 | 58 | 371 | <15 | − 8 |
| 310 | <24 | 20 | 133 | <17 | 17 | 152 | 18 | 16 | 372 | 31 | −32 |
| 311 | 30 | −30 | 230 | <11 | 9 | 153 | 28 | −39 | 470 | <23 | 4 |
| 312 | <17 | 16 | 231 | 37 | −22 | 250 | 38 | −32 | 471 | 34 | 38 |
| 410 | 44 | 36 | 232 | <15 | − 8 | 251 | 9 | − 4 |  |  |  |
| 411 | <17 | 14 | 233 | <21 | 15 | 252 | 24 | 24 | 081 | 38 | −34 |
| 412 | 34 | −30 | 330 | 44 | −46 | 350 | <14 | − 1 | 082 | 29 | −18 |
| 510 | <26 | 17 | 331 | 32 | −25 | 351 | <22 | −30 | 180 | <26 | − 6 |
| 511 | <19 | −15 | 332 | 29 | 34 | 352 | <17 | 7 | 181 | <10 | 8 |
|  |  |  | 430 | 24 | 22 | 450 | 29 | −26 | 182 | <15 | − 3 |
| 021 | 39 | −45 | 431 | 29 | −32 | 451 | <17 | −14 | 280 | 38 | 46 |
| 022 | <14 | 10 | 432 | 21 | −18 |  |  |  | 281 | 20 | −27 |
| 023 | 29 | 33 | 530 | <26 | − 7 | 061 | 58 | 72 | 282 | 28 | −37 |
| 120 | 25 | 18 | 531 | <18 | −0·04 | 062 | 18 | −26 | 380 | 22 | 28 |
| 121 | 24 | 29 |  |  |  | 063 | 35 | −48 | 381 | <12 | 8 |
| 122 | <18 | −12 | 041 | 30 | 24 | 160 | 12 | −11 | 480 | <23 | 10 |
| 123 | <18 | −11 | 042 | 47 | 40 | 161 | <11 | 2 |  |  |  |

* The white radiation background was high compared with the intensity of this diffraction.

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* The presence of a very faint (302) reflection ($F_{\text{obs}} = 5$) was observed on the $b$-axis photograph. By use of short-range oscillation and stationary-crystal photographs with Mo $K\alpha$ radiation it was demonstrated that both (211) and (221) were reflecting simultaneously with (302). It was further shown that (302) was not present on a third-level Weissenberg photograph about the $a$ axis. This exception to the space group is therefore due to two successive Bragg reflections within the crystal; this is the *Umweganregung* phenomenon described by Renninger (1937), and observed in other crystals by Davisson and Haworth (1944), and by Pabst (1939).

† This test was carried out with the use of a Giebe-Scheibe type of apparatus somewhat modified from that described by Stokes (1947). This apparatus was constructed by Mr William J. Dulmage.

meters of the oxygen ions which scatter comparatively poorly. The atomic positions are

$$x, y, \tfrac{1}{4};\ \bar{x}, \bar{y}, \tfrac{3}{4};\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{3}{4};\ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{4},$$

with the parameters

| | $x$ | $y$ |
|---|---|---|
| $Mn^{+3}$ | −0·036 | 0·140 |
| $O_{I}^{-2}$ | 0·27 | −0·20 |
| $O_{II}^{-2}$ | −0·21 | −0·05 |

The values of $F_{\text{calc.}}$ in Table 1, obtained from these parameters, are in satisfactory agreement with $F_{\text{obs.}}$.

### Discussion

The average $Mn^{+3}$–$O^{-2}$ distance is 2·06 A., in satisfactory agreement with the sum of radii, 2·02 A. (Pauling (1940, p. 350)). The average $O^{-2}$–$O^{-2}$ distance is 2·9 A., again in agreement with the expected value, 2·80 A. (Pauling (1940, p. 350)).

Gruner (1947) has discussed the diaspore–goethite–groutite series and the boehmite–lepidocrocite–manganite series on the basis of unit-cell volumes. The member of each dimorph with the smaller cell volume is observed to be the more stable, presumably because the coulomb energy is greater for smaller inter-atomic distances. It may be of interest to add a possible explanation for the deviation of manganite from the second series, inasmuch as its true unit cell has about twice the $a$ value and one-half of the $b$ value of boehmite. The electronic configuration of $Mn^{+3}$ is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$. Hund's rule places the four $3d$ electrons unpaired in four of the five $3d$ orbitals, leaving one $3d$ orbital unoccupied. The $Mn^{+3}$ ion could then form partially ionic, partially covalent bonds of intermediate type; the covalent part would be of the square, coplanar $dsp^2$ type. It seems very likely that this is the case, because the structure of manganite (Buerger, 1936) actually has four oxygen ions surrounding a manganese ion at distances of 1·85 to 1·92 A. in a nearly square configuration, while the two other oxygen ions of the octahedron are at a distance of 2·30 A. Bonding of this type is not possible for the $Fe^{+3}$ ion because each of the $3d$ orbitals is occupied by an unpaired electron, and none is available for covalent contribution. In $Al^{+3}$ the $3d$ orbitals are at much too high an energy level to be useful in this way.

While it is possible that this phenomenon contributes also to the stability of manganite as compared with groutite, it is also possible that such distortions of the oxygen octahedra occur in groutite as well. Again, because of the low scattering power of $O^{-2}$ compared with that of $Mn^{+3}$, we did not think it profitable to try to refine the oxygen parameters in order to investigate this possibility.

We are very much indebted to Prof. John W. Gruner, who suggested that we undertake this problem, for supplying us with the groutite crystals. We wish to thank the Graduate School of the University of Minnesota for a grant in aid of this research.

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# Die Absorption der Röntgenstrahlen in Kristallen im Interferenzfall

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Experiments by Borrmann show that the absorption of the primary X-ray in a perfect crystal is affected, and sometimes reduced, by the presence of diffracted rays. The paper discusses the case where both the primary and the diffracted rays leave the crystal slab by the same face; the change of absorption of the primary ray is calculated according to the dynamical theory of X-ray diffraction and is found to be in general agreement with Borrmann's observations.

## 1. Problemstellung

Die dynamische Theorie der Röntgenstrahlinterferenzen dürfte im Allgemeinen ziemlich abgeschlossen sein; eine Folgerung aus ihr ist jedoch noch nie völlig durchdiskutiert worden, nämlich wie die Strahlen im Fall einer Interferenz absorbiert werden. Zwar weiss man lange, dass in diesem Falle der gewöhnliche Absorptionskoeffizient gleich dem Brechungsindex seine Bedeutung verliert. Die *Wellenfelder*, welche dabei an die Stelle der einfachen ebenen Welle treten, erleiden grundsätzlich eine ganz andere Absorption. Nun ruft eine ebene Welle, wenn sie auf einen Kristall trifft, in