atom. The odd H atom would then be located in special position at $\frac{1}{2},0,0$.

K at 0,0,0 is surrounded by four atoms O(1), and two of each of the oxygen atoms O(2), O(3), O(4) and O(5). Its
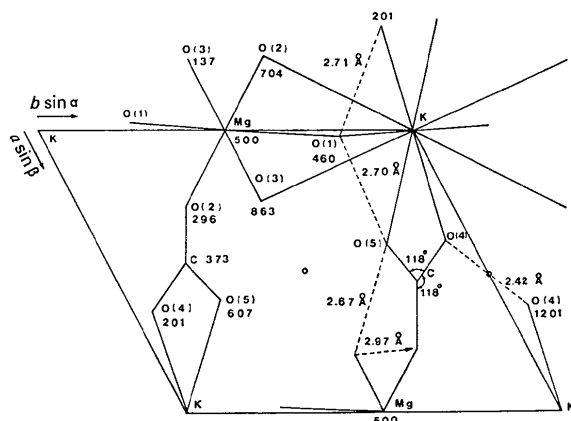

Fig. 1. The crystal structure of KHCO₃.MgCO₃.4H₂O projected along the c axis; z coordinates are given in fractions multiplied by 1000. Probable hydrogen bonds are marked with dotted lines.

polyhedron shares edges O(1)–O(1') with the K ions at 0,0,1 and 0,0,$\bar{1}$, and edges O(2)–O(3) with Mg ions at $0,\frac{1}{2},\frac{1}{2}$ and $0, -\frac{1}{2}, -\frac{1}{2}$. It links the carbonate groups in subsequent cells along the c axis through O(4) in the cell below and O(5) in the cell shown in the Figure.

A list of calculated and observed structure factors is available upon request from the Laboratory for Crystallography of the University of Amsterdam, 126 Nieuwe Prinsengracht, Amsterdam C, Netherlands. Interatomic distances are given in Table 2.

References

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The Crystal Structure of Nesquehonite, MgCO₃.3H₂O

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Nesquehonite is monoclinic; $a=7\cdot705$, $b=5\cdot367$, $c=12\cdot121$ Å, $\beta=90°\cdot45$. Space group $P2_1/n$, $Z=4$. The Mg ions are surrounded by strongly deformed oxygen octahedra, sharing an edge with a carbonate group, and a corner with another Mg octahedron. This leads to infinite strings along the b axis.

The crystal structure of nesquehonite was studied about 20 years ago (Kinsolving, MacGillavry & Pepinsky, 1950). It was then established that all available crystals are strongly twinned on (001); resolution of the two orientations was obtained by means of a specially constructed Weissenberg camera with a ratio of film-holder shift to crystal rotation twice as large as usual. Although a trial structure was set up at the time, no information about this was given in the short communication referred to above. Correspondence with Professor Pepinsky revealed that the old data could not easily be traced. In view of our general interest in hydrated magnesium carbonates we decided, with Pepinsky's permission, to take up the structure determination again.

Crystals of nesquehonite were prepared synthetically by the method of Menzel & Brückner (1930). Clear, thin needles were obtained of a size suitable for structure determination. Among these needles we never

found an untwinned specimen, so we had to work with what was probably a multiple twin.

Cell constants

These were determined from Weissenberg diagrams $h0l$ and $hk0$, taken with Cu $K\alpha$ radiation and calibrated with Al powder lines. They agree with the older data:

Present results	Kinsolving *et al.*
$a=7\cdot7053$ (11) Å	$a=7\cdot68$ Å
$b=5\cdot3673$ (6)	$b=5\cdot39$
$c=12\cdot1212$ (11)	$c=12\cdot00$
$\beta=90\cdot451$ (13)°	$\beta=90\cdot45°$

$Z=4$, X-ray density $1\cdot85$ g.cm^{-3}. The needles are elongated along the b axis. Space group $P2_1/n$.

Intensities of reflexions

Owing to the twinning low θ reflexions hkl and $hk\bar{l}$ coincide; at higher θ the deviation of β from 90° is

large enough to separate reflexions from the two orientations of the twin. It was found that better separation was obtained with a Rimsky retigraph than with the conventional Weissenberg camera. The $h0l$ to $h5l$ and $hk0$ to $hk3$ reciprocal planes were recorded on the retigraph using Cu $K\alpha$ radiation. Afterwards a Weissenberg camera with a shift of 2 mm per 2° rotation became available. This permitted the observation of a few more reflexions separately, as in the work by Kinsolving *et al.* (1950). The reciprocal planes $h0l$ to $h4l$ were measured, giving 595 independent reflexions.

Intensities were estimated visually by comparison with an intensity scale, taking account of spot size. When they did not coincide, $I(hkl)$ and $I(hk\bar{l})$ were estimated separately on both sides of the twinning plane. It was found that the two orientations are not present in the same amount, the ratio being approximately 43:57. In principle, it should then be possible to determine the intensities $I(hkl)$ and $I(hk\bar{l})$ by measuring the coinciding spots on both sides (left and right) of the twinning plane. If x is the fraction of the left-hand orientation and $(1-x)$ that of the right-hand one, then

$$I(\text{left}) = xI(hkl) + (1-x)I(hk\bar{l});$$
$$I(\text{right}) = xI(hk\bar{l}) + (1-x)I(hkl).$$

It is seen that the ratio of $I(\text{left})$ to $I(\text{right})$ depends both on x and on the difference of $I(hkl)$ and $I(hk\bar{l})$. If the latter are about equal and x is not far from 0·5, then $I(\text{left})$ and $I(\text{right})$ will be approximately the same. Probably both conditions apply so that all we could do was assign half of a coinciding spot to $I(hkl)$ and the other half to $I(hk\bar{l})$. In this way, the already strong structural pseudosymmetry may have become enhanced in the result of the structure determination. The structure was solved from the three-dimensional Patterson function which shows large values in the planes $u=0$ and $u=\frac{1}{2}$ only, and some lower maxima in the planes $u=\frac{1}{4}$ and $u=\frac{3}{4}$. It is clear that most atoms lie in sheets $(100)_{1/4}$ and $(100)_{3/4}$. The position of Mg and its octahedral surrounding could be established, and from a subsequent Fourier synthesis the last oxygen atoms and the carbon atom were found. The structure was refined by a least-squares block-diagonal programme with anisotropic thermal parameters to a final value $R=12\cdot4\%$. A difference Fourier synthesis terminated

at $\sin\theta/\lambda=0\cdot45$ gave no clear indications for hydrogen atom positions, probably due to the uncertain intensities of the low-order reflexions which could not be measured separately for the two twin orientations. Also, the rather large value of the residual R appears to be mainly due to the inevitably inaccurate values of the visually estimated intensities; in general the trend in intensity ratios of subsequent reflexions is very well accounted for by the F_{calc} values. In particular, this holds for the ratios $I(hkl)/I(hk\bar{l})$. However, the absolute values of F_{obs} and F_{calc} differ in general rather more than is usual with counter-determined intensities. Among the very weak reflexions only four have $F_{calc} < \frac{1}{2}F_{obs}$; among the medium and strong reflexions there are no cases of particularly bad agreement.

Coordinate and thermal parameters are given in Table 1. Calculated and observed structure factors are available on request from the Laboratory of Crystallography. Interatomic distances and valence angles are given in Table 2.
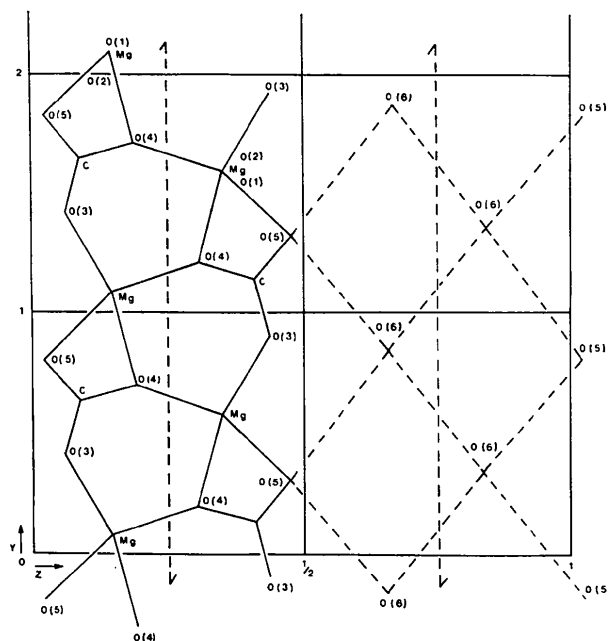

Fig. 1. Crystal structure of nesquehonite. Only the atoms near the plane $x=\frac{1}{4}$ are shown, in projection along the x axis. O(1) and O(2) are almost directly above and below the Mg ions, at $x\simeq\frac{1}{4}$ and 0 respectively.

Table 1. *Atomic coordinates and thermal parameters of nesquehonite* $MgCO_3.3H_2O$

The temperature factor is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{13}hl)]$. All values $\times 10^5$.

|	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{13}$
Mg	25174 (29)	8872 (61)	15050 (22)	493 (38)	1310 (143)	237 (16)	−46 (96)	−47 (66)	150 (35)
O(1)	52473 (67)	9140 (144)	15257 (54)	471 (86)	3222 (381)	411 (43)	−229 (235)	−98 (197)	304 (89)
O(2)	98257 (68)	9667 (153)	14691 (52)	593 (93)	4240 (421)	318 (41)	257 (371)	5 (214)	45 (91)
O(3)	26062 (80)	40719 (134)	6257 (58)	1245 (110)	838 (336)	454 (46)	293 (244)	−44 (170)	273 (102)
O(4)	24408 (62)	20582 (134)	30895 (48)	747 (90)	1108 (300)	322 (37)	−79 (209)	−187 (146)	254 (82)
O(5)	25134 (67)	81598 (142)	2076 (48)	831 (92)	1911 (322)	251 (36)	−97 (215)	−75 (142)	61 (81)
O(6)	27989 (87)	34792 (167)	83847 (61)	1428 (119)	2616 (396)	373 (45)	146 (286)	122 (192)	328 (108)
C	24393 (87)	13607 (196)	40940 (63)	432 (106)	2413 (451)	218 (45)	−1 (280)	−72 (208)	15 (103)
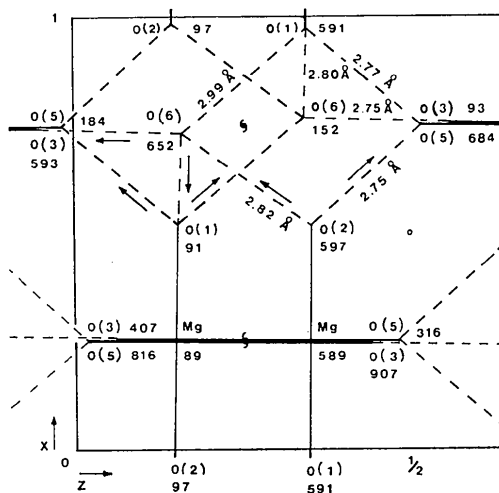
Fig. 2. Hydrogen bridges in nesquehonite. The structure is projected along the y axis. The nearly flat $MgCO_3$ ribbons are presented as heavy lines parallel to the z axis. Numbers near the atoms give their y coordinates. O(4), which lies in the ribbon and does not take part in the hydrogen bonding, is not shown in the Figure.

Table 2. *Interatomic distances and angles in nesquehonite*

Mg–O(1)	2·106 (6) Å		C–O(3)	1·275 (13) Å
Mg–O(2)	2·075 (6)		C–O(4)	1·273 (10)
Mg–O(3)	2·016 (8)		C–O(5)	1·284 (12)
Mg–O(4)	2·022 (7)		O(3)–C–O(4)	122·6 (9)°
Mg–O(4′)	2·113 (8)		O(4)–C–O(5)	114·1 (9)
Mg–O(5)	2·148 (7)		O(5)–C–O(3)	123·3 (8)

O(4)–Mg–O(5)	60·5°
O(5)–Mg–O(3)	117
O(3)–Mg–O(4′)	102
O(4′)–Mg–O(4)	95

All other O–Mg–O angles are $90 \pm 4°$.

The structure

As far as the senior author remembers, the structure is the same as that found 20 years ago. Fig. 1 shows the atoms in or near the pseudo-mirror plane $x = \frac{1}{2}$. Mg and carbonate ions are linked to a flat infinite ribbon along the b axis, which is the fibre axis of the crystal. The octahedral coordination of Mg is completed by O(1) and O(2), not drawn, which lie practically on top and below the Mg ions with x coordinates near 0 and $\frac{1}{2}$, see Table 1. The octahedron is strongly deformed because Mg shares an edge O(4)–O(5) with the carbon-

ate ion. This sharing also deforms the carbonate ion, as seen from the angles in Table 2. The ribbon occupies only half of the cell section $(100)_{1/4}$, namely that between $z = 0$ and $\frac{1}{2}$. The other half of the section is occupied solely by two water molecules O(6). These O(6) and the neighbouring O(5) atoms form a zigzag ribbon of deformed squares, about $3·5 \times 3·5$ Å, sharing edges, as indicated in Fig. 1. In the section $(100)_{3/4}$ the inverted ribbon of squares lies on top of the $MgCO_3$ ribbon, and *vice versa*, so that the oxygen atoms O(1) and O(2) at $x \simeq \frac{1}{2}$ come almost directly under the centres of these squares. This is seen in Fig. 2. The y values of only one of each of the b-translated O(6) atoms, forming one of the diagonals of the squares, are given in Fig. 2. Although the hydrogen atoms could not be found from the difference Fourier synthesis they are expected to be located somewhere on hydrogen bonds, identified by the shortest $O \cdots O$ distances. This hydrogen bond system is shown in Fig. 2, projected along the b axis. Arrows indicate possible directions $OH \cdots O$. The structure has strong pseudo-mirror symmetry with respect to (100), see Fig. 2. Remarkably enough, this is not the twinning plane. With $P2_1/n$ and m on the x axis, the twinning plane (001) is a pseudo-glide plane b. This glide plane is visible in Fig. 1; it cuts the z axis at $z = \frac{1}{4}$. The deviations from the twin symmetry $Pmnb$ are the following:

1. $\beta = 90·45°$ instead of 90°
2. x coordinates of Mg, O(3), O(4), O(5), O(6) and C deviate slightly from $\frac{1}{4}$, causing a slight puckering of the ribbons.
3. The atoms O(1) and O(2) are not completely symmetrically located with respect to the planes $(100)_{1/4}$ and $(100)_{3/4}$.

At the contact plane (001) of the two twin orientations, the deviations 2 and 3 are probably smoothed out.

References

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