

## THE CRYSTAL STRUCTURE OF HYDRODRESSERITE, $\text{BaAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}$

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### ABSTRACT

The crystal structure of hydrodresserite,  $\text{BaAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ , from the Francon quarry in Montreal (Quebec), has been refined to  $R=2.37\%$  from 4544 unique reflections measured twice on a four-circle diffractometer with  $\text{MoK}\alpha$  radiation. The structure is triclinic,  $P\bar{1}$  with  $a$  9.7545(5),  $b$  10.4069(5),  $c$  5.6322(3) Å,  $\alpha$  95.695(5),  $\beta$  92.273(5),  $\gamma$  115.643(4)°. Barium is co-ordinated by nine oxygen atoms, at distances ranging from 2.741(3) to 3.103(2) Å. Aluminum co-ordination is distorted octahedral, with four hydroxyl groups in a square, and two carbonate oxygen atoms *trans* to each other. Carbonate ions bind the aluminum atoms into *zig-zag* ribbons. The metal co-ordination is very similar to that found in dundasite (Cocco *et al.* 1972). All hydrogen atoms were located and their positions refined, indicating hydrodresserite to be a hydroxy-carbonate. An extensive network of hydrogen bonds (interhydroxyl, hydroxyl-water and water-carbonate oxygen) holds the elements of the structure together. The O-H bond lengths in hydroxyl and water are significantly different.

**Keywords:** hydrodresserite, barium dialuminum hydroxy-carbonate, structural refinement to 2.37%, all hydrogens located and refined, dundasite-like metal co-ordination.

### SOMMAIRE

La structure cristalline de l'hydrodressérite  $\text{BaAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}$  a été affinée ( $R=2.37\%$ ) sur un cristal provenant de la carrière Francon à Montréal (Québec), à partir de 4544 réflexions uniques mesurées deux fois sur un diffractomètre à quatre cercles avec rayonnement  $\text{MoK}\alpha$ . La structure est triclinique,  $P\bar{1}$ , avec  $a$  9.7545(5),  $b$  10.4069(5),  $c$  5.6322(3) Å,  $\alpha$  95.695(5),  $\beta$  92.273(5),  $\gamma$  115.643(4)°. Le baryum est coordonné par neuf atomes d'oxygène à des distances variant de 2.741(3) à 3.103(2) Å. La coordinence de l'aluminium représente un octaèdre déformé, avec quatre groupes hydroxyle en carré et deux atomes d'oxygène de carbonate en position *trans*. Les ions de carbonate lient les atomes d'aluminium en rubans disposés en zigzag. La coordinence des métaux est fort semblable à celle que l'on trouve dans la dundasite (Cocco *et al.* 1972). Tous les atomes d'hydro-

gène ont été localisés, et leurs positions affinées: on conclut que l'hydrodressérite est un hydroxy-carbonate. Tout un réseau de liaisons hydrogènes (entre hydroxyles, hydroxyle et eau, eau et oxygène de carbonate) assure la stabilité de la structure. Les longueurs de liaison O-H diffèrent notablement dans l'eau et les groupes hydroxyles.

**Mots-clés:** hydrodressérite, hydroxy-carbonate d'aluminium et de baryum, affinement structural à 2.37%, localisation et affinement de tous les atomes d'hydrogène, coordinence des métaux comme dans la dundasite.

### INTRODUCTION

The mineral *hydrodresserite*,  $\text{BaAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ , found in the Francon limestone quarry, quartier St-Michel, Montreal, Quebec, was described by Jambor *et al.* (1977b). Hydrodresserite is unstable under normal laboratory conditions, and dehydrates to dresserite (a monohydrate), in some cases *via* an intermediate phase (possibly the dihydrate). The infrared absorption investigation of dresserite and hydrodresserite (Farrell 1977) suggested that the formula for the latter should be written  $\text{BaAl}_2\text{O}_2(\text{OH})_2(\text{HCO}_3)_2 \cdot 3\text{H}_2\text{O}$  based upon the strong hydrogen-bond frequencies, which produced bicarbonate-like spectral behavior. To resolve this problem of formulation, a crystal-structure investigation was undertaken to find the positions, and hence the functions, of all hydrogen atoms in the structure. The structural relationship of hydrodresserite to dresserite will be discussed when the latter structure has been solved.

### EXPERIMENTAL

The type material from the National Mineral Collection, Geological Survey of Canada (No. 13936), was used in the crystal-structure determination. Hydrodresserite occurs as compact groups of fibrous crystals that radiate from a point to form hemispheres. With care, these can be separated into individual laths that usually

have intergrowths of smaller crystals nearest the focal point of the hemisphere. One such lath was isolated, and the end with adhering and intergrown crystals was dissolved in acid. The crystal was then mounted by this end with epoxy resin, in the extremity of a very fine glass tube. The specimen selected is an acicular platelet,  $0.5 \times 0.076 \times 0.020$  mm, elongate [001], terminated (102) with prominent {010} and narrow {210}. These forms, described by Jambor *et al.* (1977b), were confirmed when the crystal was mounted on a 4-circle diffractometer.

After precise measurement of its geometry, the crystal was coated with a transparent acrylic spray to minimize the reported dehydration to dresserite. The cell dimensions were obtained from a least-squares refinement (Busing 1970) of the fitted  $2\theta$ ,  $\omega$ , and  $\chi$  values for 60 reflections in the range  $45^\circ < 2\theta < 52^\circ$ . The values, which are in good agreement with (though more precise than) those given by Jambor *et al.* (1977b), are set out in Table 1.

Intensity data were collected with graphite-monochromated  $\text{MoK}\alpha$  radiation using a  $\theta - 2\theta$  scan at a rate of  $2^\circ/\text{min}$  in  $2\theta$  and a peak width of  $1.7^\circ$  plus the  $\alpha_1 - \alpha_2$  dispersion. Backgrounds were counted for 20 seconds on either side of the intensity peak. Three standards were measured every 50 reflections to monitor crystal alignment and decomposition as well as instrumental instability; no systematic deviation of intensities was noted. The complete reciprocal sphere of intensity data, to a limit of  $2\theta = 60^\circ$ , was collected in two halves; these were kept separate (not averaged) in the event the space group should turn out to be  $P1$  rather than  $P\bar{1}$ .

Absorption corrections were applied to the intensity data using a Gaussian integration procedure (Gabe & O'Byrne 1970) and a grid of  $10 \times 10 \times 10$  points. The absorption-correction factors varied between 1.09 and 1.27. Data re-

TABLE 2. STATISTICS ON NORMALIZED STRUCTURE FACTORS, (E)

| QUANTITY                     | CALCULATED    | THEORETICAL |          |
|------------------------------|---------------|-------------|----------|
|                              |               | CENTRIC     | ACENTRIC |
| Average $ E $                | 0.872         | 0.798       | 0.886    |
| Average $ E^2-1 $            | 0.748         | 0.968       | 0.736    |
| Average $ E^2-1 ^{1/2}$      | 0.992         | 2.000       | 1.000    |
| Average $ E^2-1 ^{3/2}$      | 1.746         | 8.000       | 2.000    |
| Number and % of reflections: | OBSERVED      |             |          |
| $ E  > 3.0$                  | 0.00 (0)      | 0.27        | 0.01     |
| $ E  > 2.5$                  | 0.03 (1)      | 1.24        | 0.19     |
| $ E  > 2.0$                  | 1.37 (41)     | 4.55        | 1.83     |
| $ E  > 1.8$                  | 3.21 (96)     | 7.19        | 3.92     |
| $ E  > 1.6$                  | 7.33 (219)    | 10.96       | 7.73     |
| $ E  > 1.4$                  | 14.45 (432)   | 16.15       | 14.09    |
| $ E  > 1.2$                  | 26.63 (796)   | 23.01       | 23.69    |
| $ E  > 1.0$                  | 40.55 (1212)  | 31.73       | 36.79    |
| $ E  > 0.0$                  | 100.00 (2989) | 100.00      | 100.00   |

hkℓ hemisphere of  $\text{MoK}\alpha$  data to  $2\theta = 60^\circ$ .

duction was completed with the application of Lorentz and polarization factors to the intensities, and a set of normalized structure-factors ( $E_s$ ) was obtained using the program NORMSF in the XRAY-76 system (Stewart *et al.* 1976). Comparison of the magnitude distribution of the  $E_s$  with the theoretical distributions for centrosymmetric and non-centrosymmetric structures showed there was excellent agreement with the latter theoretical distribution (Table 2). The space group was therefore taken as  $P1$ . The structure was solved in this space group with the application of Patterson and Fourier methods to locate the 36 non-hydrogen atoms in the unit cell. The number of atoms to be refined was unexpectedly large; in order to improve the observation/parameters ratio, additional intensity data were collected in the form of the complete shell,  $60^\circ < 2\theta < 70^\circ$ .

The structure refinement was very ill-conditioned, the thermal parameters for some like-type atoms refining from high positive to negative values; other parameters oscillated. When refinement had reached 3.1%, it was realized that the problems encountered were being caused by the near-singularity of the matrix associated with refining a centrosymmetric structure in a non-centrosymmetric space group (Ermer & Dunitz 1970). There was, in fact, a centre of symmetry midway between the Ba atoms, and all four Al atoms were positioned at centres of symmetry. Refinement in space group  $P\bar{1}$  was much more satisfactory, and converged to a value of  $R = 3.1\%$  using anisotropic thermal parameters and data to  $2\theta = 60^\circ$ . The addition-

TABLE 1. CRYSTAL DATA

|   |
|---|
| Hydrodresserite: $\text{BaAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}$  |
| Source: Francon quarry, St-Michel, Montreal Island, Quebec.   |
| Formula Weight: 433.397   |
| Crystal System: Triclinic, $Z = 2$ .  |
| Space Group: $P1$ or $P\bar{1}$ ; $P\bar{1}$ confirmed by structure determination.  |
| Cell Dimensions: $a = 9.7545(5)$ , $b = 10.4069(5)$ , $c = 5.6322(3)\text{\AA}$ ,<br>$\alpha = 95.695(5)$ , $\beta = 92.273(5)$ , $\gamma = 115.643(4)^\circ$ . |
| $[\lambda(\text{MoK}\alpha_1 = 0.709300\text{\AA})]$  |
| Linear absorption coefficient: $\mu(\text{MoK}\alpha) = 41.25 \text{ cm}^{-1}$  |
| Density: $D_{\text{calc}} = 2.817 \text{ Mg m}^{-3}$ ,<br>$D_{\text{obs}} = 2.80 \text{ Mg m}^{-3}$ (Jambor <i>et al.</i> 1977b)                                |
| Intensity Data: 2 hemispheres of data measured with $\text{MoK}\alpha$ radiation to $2\theta = 70^\circ$ , 4544 reflections, 4104 with $I > 1.65\sigma(I)$ .    |

TABLE 3. ATOMIC POSITIONAL AND THERMAL PARAMETERS

| FUNCTION              | ATOM  | x          | y          | z          | U <sub>11</sub> | U <sub>22</sub> | U <sub>33</sub> | U <sub>12</sub> | U <sub>13</sub> | U <sub>23</sub> |
|-----------------------|-------|------------|------------|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                       | Ba    | 0.14318(2) | 0.18123(2) | 0.21261(2) | 1.462(6)        | 1.536(6)        | 1.080(5)        | 0.638(4)        | 0.018(4)        | -.098(4)        |
|                       | Al(1) | 0.0        | 0.5        | 0.5        | 1.08(4)         | 1.23(4)         | 0.40(3)         | 0.68(3)         | 0.14(3)         | 0.18(3)         |
|                       | Al(2) | 0.0        | 0.5        | 0.0        | 1.05(4)         | 1.10(4)         | 0.44(3)         | 0.61(3)         | 0.11(3)         | 0.12(3)         |
|                       | Al(3) | 0.5        | 0.5        | 0.0        | 0.99(4)         | 1.09(4)         | 0.49(3)         | 0.49(3)         | 0.11(3)         | 0.24(3)         |
|                       | Al(4) | 0.5        | 0.5        | 0.5        | 1.01(4)         | 1.07(4)         | 0.41(3)         | 0.46(3)         | 0.05(3)         | 0.11(3)         |
| FIRST<br>CARBONATE    | C(1)  | 0.0471(2)  | 0.2772(2)  | 0.7143(4)  | 1.16(8)         | 1.21(8)         | 1.05(8)         | 0.70(6)         | 0.15(6)         | 0.22(6)         |
|                       | O(1)  | 0.0403(2)  | 0.3368(2)  | 0.9245(3)  | 1.72(7)         | 1.41(6)         | 0.66(6)         | 0.92(6)         | 0.18(5)         | 0.15(5)         |
|                       | O(2)  | 0.0376(2)  | 0.3351(2)  | 0.5231(3)  | 1.92(7)         | 1.53(7)         | 0.67(6)         | 1.11(6)         | 0.18(5)         | 0.19(5)         |
|                       | O(3)  | 0.0660(2)  | 0.1642(2)  | 0.6941(3)  | 2.92(9)         | 1.81(8)         | 1.36(7)         | 1.76(7)         | 0.48(6)         | 0.32(6)         |
| SECOND<br>CARBONATE   | C(2)  | 0.3953(2)  | 0.2263(2)  | 0.6884(4)  | 1.47(8)         | 1.12(8)         | 0.97(8)         | 0.56(7)         | 0.28(6)         | 0.16(6)         |
|                       | O(4)  | 0.4185(2)  | 0.2917(2)  | 0.9048(3)  | 2.05(7)         | 1.27(6)         | 0.78(6)         | 0.68(6)         | 0.10(5)         | 0.22(5)         |
|                       | O(5)  | 0.4187(2)  | 0.2969(2)  | 0.5055(3)  | 1.91(7)         | 1.36(7)         | 0.72(6)         | 0.74(6)         | 0.15(5)         | 0.32(5)         |
|                       | O(6)  | 0.3513(3)  | 0.0926(2)  | 0.6517(4)  | 5.21(14)        | 0.95(7)         | 2.04(9)         | 0.97(8)         | 1.39(9)         | 0.27(6)         |
| HYDROXYL<br>OXYGENS   | O(7)  | 0.1329(2)  | 0.5925(2)  | 0.7756(3)  | 1.07(6)         | 1.22(6)         | 0.63(6)         | 0.29(5)         | 0.15(5)         | 0.21(5)         |
|                       | O(8)  | 0.3833(2)  | 0.5120(2)  | 0.7457(3)  | 1.07(6)         | 1.94(7)         | 0.76(6)         | 1.05(6)         | 0.14(5)         | 0.25(5)         |
|                       | O(9)  | 0.1446(2)  | 0.5636(2)  | 0.2713(3)  | 1.05(6)         | 1.16(6)         | 0.77(6)         | 0.54(5)         | 0.02(5)         | 0.08(5)         |
|                       | O(10) | 0.6400(2)  | 0.5367(2)  | 0.7661(3)  | 0.86(6)         | 1.49(7)         | 0.67(6)         | 0.69(5)         | 0.06(5)         | 0.21(5)         |
| WATER<br>OXYGENS      | O(11) | 0.1643(2)  | 0.9554(2)  | 0.9492(4)  | 2.23(9)         | 2.10(9)         | 2.81(10)        | 0.88(7)         | 0.83(8)         | 1.11(7)         |
|                       | O(12) | 0.5764(4)  | 0.1591(3)  | 0.1717(6)  | 4.42(15)        | 4.00(15)        | 4.04(13)        | 2.46(16)        | 0.36(12)        | 0.77(12)        |
|                       | O(13) | 0.3152(3)  | 0.8664(3)  | 0.3114(5)  | 3.11(12)        | 2.43(12)        | 3.98(13)        | 0.89(9)         | 0.93(10)        | -.16(9)         |
| HYDROXYL<br>HYDROGENS | H(1)  | 0.174(5)   | 0.654(4)   | 0.784(6)   | (0.97)          |                 |                 |                 |                 |                 |
|                       | H(2)  | 0.327(4)   | 0.528(4)   | 0.749(6)   | (1.26)          |                 |                 |                 |                 |                 |
|                       | H(3)  | 0.179(4)   | 0.621(4)   | 0.288(6)   | (0.99)          |                 |                 |                 |                 |                 |
|                       | H(4)  | 0.678(4)   | 0.507(4)   | 0.773(6)   | (1.01)          |                 |                 |                 |                 |                 |
| WATER 1<br>HYDROGENS  | H(5)  | 0.220(5)   | 0.993(4)   | 0.869(7)   | (2.38)          |                 |                 |                 |                 |                 |
|                       | H(6)  | 0.202(5)   | 0.920(4)   | 1.029(7)   | (2.38)          |                 |                 |                 |                 |                 |
| WATER 2<br>HYDROGENS  | H(7)  | 0.521(6)   | 0.188(5)   | 0.119(9)   | (4.15)          |                 |                 |                 |                 |                 |
|                       | H(8)  | 0.581(6)   | 0.167(5)   | 0.319(9)   | (4.15)          |                 |                 |                 |                 |                 |
| WATER 3<br>HYDROGENS  | H(9)  | 0.329(5)   | 0.928(5)   | 0.419(8)   | (3.17)          |                 |                 |                 |                 |                 |
|                       | H(10) | 0.404(5)   | 0.893(5)   | 0.261(8)   | (3.17)          |                 |                 |                 |                 |                 |

The anisotropic temperature factors are expressed in the form:

$$T = \exp[-2\pi^2(U_{11}a^2h^2 + 2U_{12}a^*b^*hk + \dots)], \text{ and the values quoted are } \times 100.$$

al data to  $2\theta = 70^\circ$  were added and the two hemispheres ( $l + ve$ ,  $l - ve$ ) were averaged to give a data set of 4544 reflections, of which 440 were "unobserved" on the criterion that  $I_{obs} > 1.65\sigma(I)$ . A difference synthesis clearly revealed the four H atoms of the hydroxyl groups. These were included in the refinement with variable positional co-ordinates, and thermal parameters constrained to the isotropic equivalent of the oxygen atom to which they were bonded. Two more cycles of this procedure revealed the six H atoms of the three water molecules. The scattering curves were taken from Cromer & Mann (1968) and the anomalous scattering components from Cromer & Liberman (1970) for the following species:  $Ba^{2+}$ ,  $Al^{3+}$ , C, O for water oxygen atoms,  $O^-$  for hydroxyl oxygen atoms. For the carbonate oxygen atoms, a scattering curve for  $O^{3-}$  was prepared from a 2:1 arithmetic mean of the  $O^-$  and O curves from the same source. The hydrogen curve used was that of Stewart *et al.* (1965). With the hydrogen atoms included, their positional parameters refined and their thermal parameters constrained as before, the final residual was 2.37% for the 4544 reflections, with the "unobserved" reflec-

tions included at the locally observable threshold. Of the 440 "unobserved" reflections, only 18 calculated (fractionally) larger than this value. The positional and thermal parameters obtained from the full-matrix least-squares refinement are given in Table 3. The numerical calculations were done using the XRAY-76 system of crystallographic computer programs (Stewart *et al.* 1976). The observed and calculated structure factors are given in Table 4, available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

#### DESCRIPTION OF STRUCTURE

Figure 1 shows the structure of hydrodresserite, whereas Figure 2 illustrates the co-ordination of oxygen atoms around Al. The bond lengths and angles for the structure are set out in Table 5.

Four Al atoms are located in the plane  $y = \frac{1}{2}$  at centres of symmetry:  $0, \frac{1}{2}, \frac{1}{2}$ ;  $0, \frac{1}{2}, 0$ ;  $\frac{1}{2}, \frac{1}{2}, 0$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ . Carbonate ions link adjacent Al atoms into two zig-zag ribbons along  $0, \frac{1}{2}, z$ ;

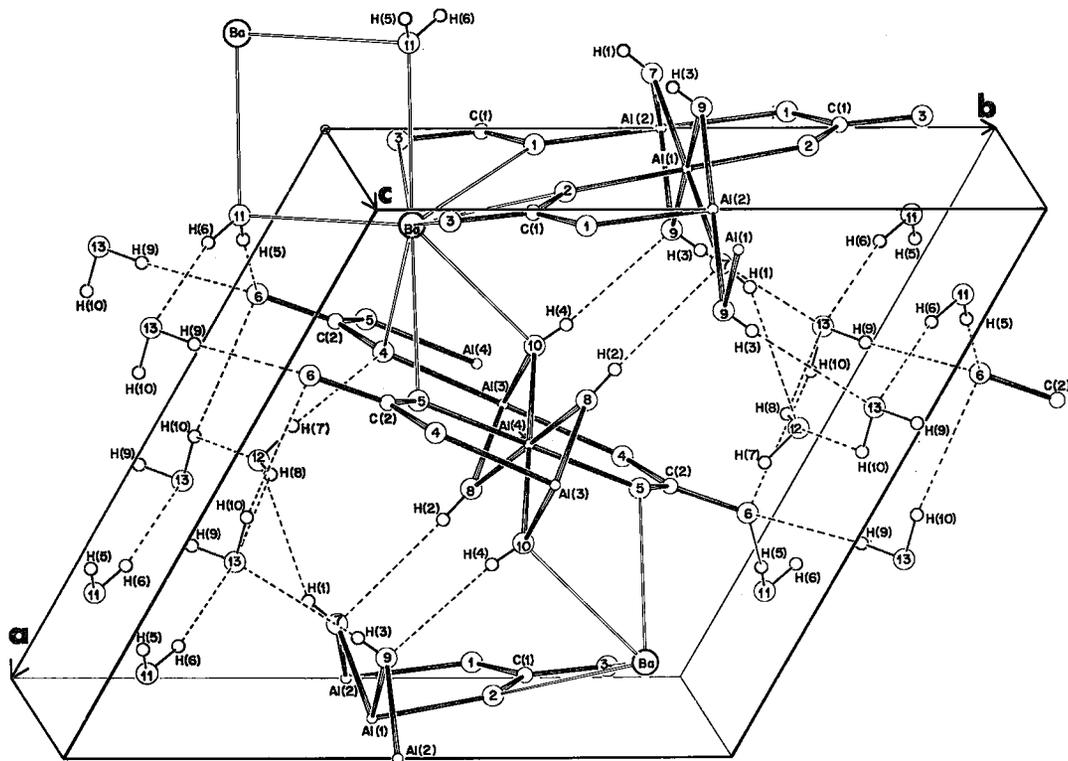


Fig. 1. The unit cell with some surrounding atoms added to illustrate the bonding in the structure. Hydrogen bonds are indicated by dashed lines. Oxygen atoms are marked by the numerical designation given in Table 3.

$\frac{1}{2}, \frac{1}{2}, z$ , each *zig* being related to a *zag* through the aluminum atoms. A square of four hydroxyl oxygen atoms surrounds each Al atom, each oxygen being bonded to two metal atoms, with the carbonate oxygen atoms at the remaining positions of a somewhat distorted octahedral *trans* configuration (Fig. 2). The hydroxyl ions that surround the row of Al atoms at  $\frac{1}{2}, \frac{1}{2}, z$  are hydrogen-bonded to the hydroxyl ions surrounding the Al atoms at  $0, \frac{1}{2}, z$  and  $1, \frac{1}{2}, z$ . The hydroxyl ions O(7)–H(1) and O(9)–H(3), bonded to Al atoms [Al(1), Al(2)] in the latter two rows, are almost normal to the plane at  $y = \frac{1}{2}$ , and are hydrogen-bonded to water molecules in the interleaving parts of the structure.

The carbon–oxygen bonds of the carbonate groups are not of equal length. Those with oxygen bonded also to Al are significantly longer than the terminal oxygen–carbon bonds: [C(1)–O(1) 1.298(3), C(1)–O(2) 1.304(3), C(1)–O(3) 1.262(3) Å; C(2)–O(4) 1.296(3), C(2)–O(5) 1.295(3), C(2)–O(6) 1.257(3) Å].

Barium is nine-co-ordinated: it is bonded to Water 1 [O(11), H(5), H(6)] at a distance of 2.741(3) Å and to its symmetry equivalent through the origin at 2.771(2) Å. A parallelogram of Ba, O(11), Ba, O(11) is thus formed around the origin. Ba is bonded to two terminal carbonate oxygen atoms O(3) in adjacent unit cells along  $z$ , at distances of 2.845(2), 2.995(2) Å. It is bonded also to four non-terminal carbonate oxygen atoms: O(1) at 2.839(2), O(2) at 2.775(2), O(4) at 3.102(2) and O(5) at 2.802(2) Å. The ninth co-ordinating oxygen is the hydroxyl oxygen O(10). A very approximate mirror plane through Ba, O(11), O(11) and O(10) relates O(3) to O(3)<sup>1</sup>, O(1) to O(2) and O(4) to O(5).

#### HYDROGEN-BONDING NETWORK

The interhydroxyl hydrogen bonding has been mentioned, but is discussed here in more detail. The oxygen O(8) of hydroxyl group O(8)–H(2) is close to  $sp^2$  hybridization, being bonded to

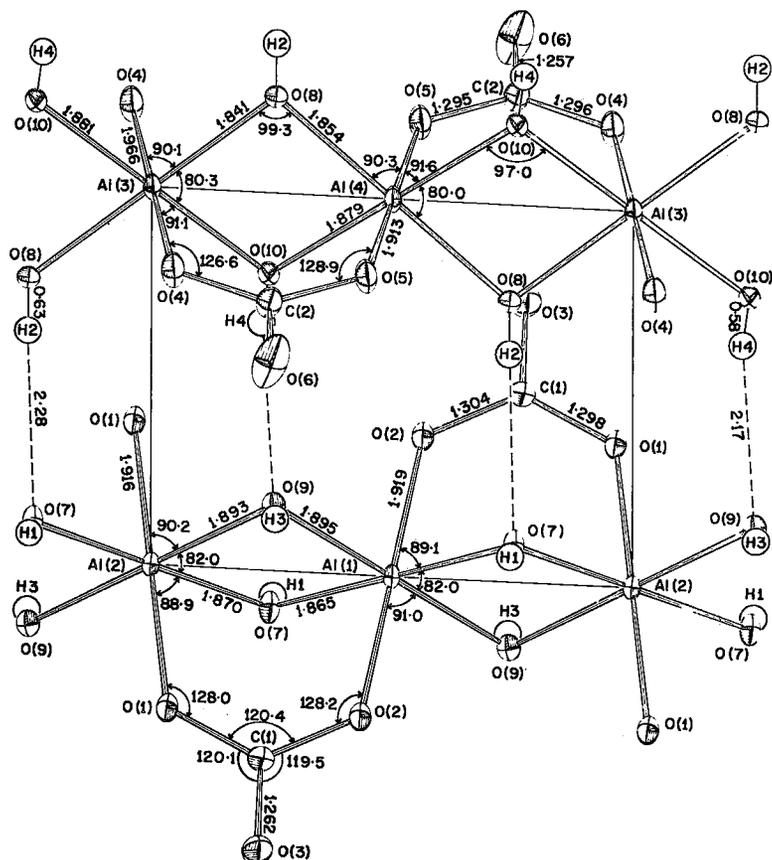


FIG. 2. A segment of the structure near  $y = \frac{1}{2}$  illustrating the Al-O octahedra, edge-sharing to form ribbons, which extend along  $O, \frac{1}{2}, z$  and  $\frac{1}{2}, \frac{1}{2}, z$ . The interribbon hydrogen-bonding between hydroxyl groups is shown by dashed lines. The outlined area between Al atoms extends from 0 to 1 in  $z$  (left to right) and from 0 to  $\frac{1}{2}$  in  $x$  (upward). The bond lengths are given in Ångströms and the angles in degrees. The thermal ellipsoids are illustrated at 50% probability (Johnson 1965).

two metal atoms and to a single hydrogen, but not being the acceptor of any hydrogen bond. The interbond angles at O(8) are somewhat distorted from the theoretical  $120^\circ$ , but their sum is about  $360^\circ$ , *i.e.* Al(3), Al(4), O(8) and H(2) are virtually coplanar. Oxygen O(10) of the immediately adjacent hydroxyl group is close to  $sp^3$  hybridization, being bonded to two Al atoms, to its own hydrogen atom H(4) and also to Ba in an approximately tetrahedral co-ordination. This hydroxyl group is a hydrogen-bond donor to O(9). The two hydroxyl oxygen atoms in the second ribbon also have close to tetrahedral co-ordination: each is co-ordinated to two aluminum atoms and a hydrogen, and each is a hydrogen-bond acceptor from the hy-

droxyl groups in the ribbon above or below. Hydroxyl O(7)-H(1) is a hydrogen-bond donor to Water 2 [O(12), H(7), O(8)], where hydroxyl O(9)-H(3) is a donor to Water 3 [O(13), H(9), H(10)]. Where hydrogen-bond distances are given in this section, they refer to the H...O longer distance of the asymmetric O-H...O bond and not to the donor...acceptor distance.

Water 1 [O(11), H(5), H(6)] is co-ordinated to two Ba atoms and is thus very firmly bonded. It cannot accept hydrogen bonds, O(11), being already tetrahedrally co-ordinated, but it is a hydrogen-bond donor through both its hydrogen atoms: by means of O(11)-H(5)...O(6) it is very strongly bonded [1.85(4) Å] to a terminal carbonate oxygen, and *via* O(11)-H(6)...

TABLE 5. BOND LENGTHS (Å) AND INTERBOND ANGLES (°) WITH STANDARD DEVIATIONS

| 1. Coordination of Ba:     |           |  |           |   |                   |                                    |                    |   |                    |
|----------------------------|-----------|--|-----------|---|-------------------|------------------------------------|--------------------|---|--------------------|
| Atom                       | d(Å)      | O(2)   | O(3)      | O(3) <sup>1</sup>                         | O(4) <sup>1</sup> | O(5)                               | O(10) <sup>2</sup> | O(11) <sup>3</sup>                            | O(11) <sup>4</sup> |
| O(1)                       | 2.839(2)  | 73.91(5)                                       | 118.76(6) | 44.97(6)                                  | 82.39(5)          | 125.50(5)                          | 68.91(5)           | 112.29(6)                                     | 64.74(6)           |
| O(2)                       | 2.775(2)  | —  | 46.42(6)  | 117.17(6)                                 | 129.60(5)         | 89.06(5)                           | 75.62(5)           | 160.95(5)                                     | 80.83(6)           |
| O(3)                       | 2.845(2)  | —  | —         | 152.32(6)                                 | 142.75(5)         | 73.23(5)                           | 102.33(5)          | 120.62(7)                                     | 89.94(6)           |
| O(3) <sup>1</sup>          | 2.955(2)  | —  | —         | —   | 64.28(5)          | 133.68(5)                          | 91.70(5)           | 67.38(7)                                      | 63.33(6)           |
| O(4) <sup>1</sup>          | 3.103(2)  | —  | —         | —   | —                 | 69.59(5)                           | 54.32(5)           | 69.43(5)                                      | 127.30(6)          |
| O(5)                       | 2.802(2)  | —  | —         | —   | —                 | —                                  | 56.59(5)           | 100.43(6)                                     | 162.98(6)          |
| O(10) <sup>2</sup>         | 2.764(2)  | —  | —         | —   | —                 | —                                  | —                  | 123.38(6)                                     | 132.15(7)          |
| O(11) <sup>3</sup>         | 2.741(3)  | —  | —         | —   | —                 | —                                  | —                  | —   | 85.75(7)           |
| O(11) <sup>4</sup>         | 2.771(2)  | —  | —         | —   | —                 | —                                  | —                  | —   | —                  |
| 2. Aluminum coordination:  |           |  |           |   |                   |                                    |                    |   |                    |
| Al(1) - O(2)               | 1.919(2); | O(2) - Al(1) - O(7)                            | 89.07(8)  |   |                   | Al(2) - O(1) <sup>1</sup>          | 1.916(2);          | O(1) <sup>1</sup> - Al(2) - O(7) <sup>1</sup> | 88.87(8)           |
| Al(1) - O(7)               | 1.865(1); | O(2) - Al(1) - O(9)                            | 90.97(8)  |   |                   | Al(2) - O(7) <sup>1</sup>          | 1.870(2);          | O(1) <sup>1</sup> - Al(2) - O(9)              | 90.16(8)           |
| Al(1) - O(9)               | 1.895(2); | O(7) - Al(1) - O(9)                            | 98.00(7)  |   |                   | Al(2) - O(9)                       | 1.893(2);          | O(7) <sup>1</sup> - Al(2) - O(9)              | 98.05(7)           |
| Al(3) - O(4) <sup>1</sup>  | 1.966(2); | O(4) <sup>1</sup> - Al(3) - O(8) <sup>1</sup>  | 89.88(8)  |   |                   | Al(4) - O(5)                       | 1.913(2);          | O(5) - Al(4) - O(8)                           | 89.70(8)           |
| Al(3) - O(8) <sup>1</sup>  | 1.841(2); | O(4) <sup>1</sup> - Al(3) - O(10) <sup>1</sup> | 91.08(7)  |   |                   | Al(4) - O(8)                       | 1.854(2);          | O(5) - Al(4) - O(10)                          | 91.65(7)           |
| Al(3) - O(10) <sup>1</sup> | 1.881(2); | O(8) <sup>1</sup> - Al(3) - O(10) <sup>1</sup> | 80.31(8)  |   |                   | Al(4) - O(10)                      | 1.879(2);          | O(8) - Al(4) - O(10)                          | 80.04(8)           |
| 3. Carbonate groups:       |           |  |           |   |                   |                                    |                    |   |                    |
| C(1) - O(1)                | 1.298(3); | O(1) - C(1) - O(2)                             | 120.4(2)  |   |                   | C(2) - O(4)                        | 1.296(3);          | O(4) - C(2) - O(5)                            | 121.0(2)           |
| C(1) - O(2)                | 1.304(3); | O(1) - C(1) - O(3)                             | 120.1(2)  |   |                   | C(2) - O(5)                        | 1.295(3);          | O(4) - C(2) - O(6)                            | 120.5(2)           |
| C(1) - O(3)                | 1.262(4); | O(2) - C(1) - O(3)                             | 119.5(2)  |   |                   | C(2) - O(6)                        | 1.257(3);          | O(5) - C(2) - O(6)                            | 118.5(2)           |
|                            |           | Al(2) <sup>5</sup> - O(1) - C(1)               | 128.0(2)  |   |                   |                                    |                    | Al(3) <sup>5</sup> - O(4) - C(2)              | 126.6(2)           |
|                            |           | Al(1) - O(2) - C(1)                            | 128.2(2)  |   |                   |                                    |                    | Al(4) - O(5) - C(2)                           | 128.9(1)           |
| 4. Hydroxyl groups:        |           |  |           |   |                   |                                    |                    |   |                    |
| H(1) - O(7)                | 0.59(3);  | H(1) - O(7) - Al(1)                            | 120(4);   | H(3) - O(9) - Al(1)                       | 111(4);           | Al(1) - O(7) - Al(2) <sup>5</sup>  | 97.88(6)           |   |                    |
| H(2) - O(8)                | 0.63(5);  | H(1) - O(7) - Al(2) <sup>5</sup>               | 126(4);   | H(3) - O(9) - Al(2)                       | 115(4);           | Al(1) - O(9) - Al(2)               | 96.03(7)           |   |                    |
| H(3) - O(9)                | 0.54(3);  | H(2) - O(8) - Al(3) <sup>5</sup>               | 128(4);   | H(4) - O(10) - Al(3) <sup>5</sup>         | 113(4);           | Al(4) - O(8) - Al(3) <sup>5</sup>  | 99.28(10)          |   |                    |
| H(4) - O(10)               | 0.58(5);  | H(2) - O(8) - Al(4)                            | 132(4);   | H(4) - O(10) - Al(4)                      | 122(3);           | Al(4) - O(10) - Al(4) <sup>5</sup> | 97.00(8)           |   |                    |
| 5. Water molecules:        |           |  |           |   |                   |                                    |                    |   |                    |
| O(11) - H(5)               | 0.72(4);  | H(5) - O(11) - H(6)                            | 106(5);   | Ba <sup>6</sup> - O(11) - Ba <sup>4</sup> | 94.26(8)          |                                    |                    |   |                    |
| O(11) - H(6)               | 0.78(5);  |  |           | Ba <sup>6</sup> - O(11) - H(5)            | 101(4)            |                                    |                    |   |                    |
| O(12) - H(7)               | 0.78(6);  | H(7) - O(12) - H(8)                            | 111(6);   | Ba <sup>6</sup> - O(11) - H(6)            | 110(3)            |                                    |                    |   |                    |
| O(12) - H(8)               | 0.82(5);  |  |           | Ba <sup>4</sup> - O(11) - H(5)            | 120(3)            |                                    |                    |   |                    |
| O(13) - H(9)               | 0.85(5);  | H(9) - O(13) - H(10)                           | 103(4);   | Ba <sup>4</sup> - O(11) - H(6)            | 122(3)            |                                    |                    |   |                    |
| O(13) - H(10)              | 0.80(5);  |  |           | H(5) - O(11) - H(6)                       | 106(5)            |                                    |                    |   |                    |

Superscripts used above and in Table 6 refer to the following equivalent positions;

|                    |                    |                  |                   |
|--------------------|--------------------|------------------|-------------------|
| 1. $x, y, -1+z$    | 3. $x, -1+y, -1+z$ | 5. $x, y, 1+z$   | 7. $1-x, 1-y, -z$ |
| 2. $1-x, 1-y, 1-z$ | 4. $-x, 1-y, 1-z$  | 6. $x, 1+y, 1+z$ | 8. $x, 1+y, z$    |

O(13) it is quite strongly bonded [2.15(5) Å] to Water 3 [O(13), H(9), H(10)].

Water 3 is less strongly held within the structure, because its donor-bonding to a terminal carbonate oxygen [O(13)-H(9) ... O(6)<sup>5</sup>, 1.97(5) Å] is not as strong as that of Water 1. However, through O(13)-H(10) it is a weak hydrogen-bond donor to two oxygens *via* a bifurcated bond: O(13)-H(10) ... O(6)<sup>2</sup>, 2.36(5) Å; O(13)-H(10) ... O(12)<sup>7</sup>, 2.48(5) Å. Oxygen O(13) is also an acceptor of three hydrogen bonds: O(9)-H(3) ... O(13), 2.30(3) Å; O(11)<sup>1</sup>-H(6)<sup>1</sup> ... O(13), 2.15(5) Å; O(12)-O(8) ... O(13), 2.40(5) Å. Water 3 is thus a hydrogen-bond donor to three oxygen atoms and a hydrogen-bond acceptor of three bonds.

Water 2 [O(12), H(7), H(8)] has the weakest hydrogen-bonding. It is a donor to a carbonate oxygen [O(12)-H(7) ... O(4), 2.18(6) Å] and to Water 3 (see above), [O(12)-H(8) ... O(13),

2.40(5) Å]. It is an acceptor of the hydrogen from the hydroxyl O(7)-H(1) ... O(12), 2.35(3) Å and of the very weak bifurcated hydrogen-bond from O(13)-H(10) ... O(12), 2.48(5) Å. Water 2 is thus the least strongly held of the three water molecules. Full details of hydrogen-bond lengths, of donor-acceptor distances and angles at oxygen and co-ordinating hydrogen atoms are set out in Table 6.

#### CALCULATED POWDER PATTERN

Jambor *et al.* (1977b) included X-ray powder data for hydrodresserite, indexed on the basis of their unit cell. The lines measured extend to  $d = 1.550$  Å, although the last eight are not indexed, and four are marked "several poss." Table 7 (deposited with the structure factors, Table 4; see Experimental section) gives the calculated powder pattern for hydrodresserite.

TABLE 6. HYDROGEN BOND DISTANCES AND ANGLES

| Donor — H ... Acceptor                            | d(H...O) <sup>Å</sup> | d(Donor...Acc.) <sup>Å</sup> | Angle at H (°) |
|---|-----------------------|------------------------------|----------------|
| Hydroxyls: 0(7) — H(1)... 0(12) <sup>2</sup>      | 2.35(3)               | 2.872(3)                     | 149(6)         |
| 0(8) — H(2)... 0(7)                               | 2.28(5)               | 2.911(4)                     | 177(4)         |
| 0(9) — H(3)... 0(13)                              | 2.30(3)               | 2.835(3)                     | 173(5)         |
| 0(10) — H(4)... 0(9) <sup>2</sup>                 | 2.17(4)               | 2.727(3)                     | 164(4)         |
| Water 1. 0(11) — H(5)... 0(6) <sup>8</sup>        | 1.85(4)               | 2.576(3)                     | 175(6)         |
| 0(11) — H(6)... 0(13) <sup>5</sup>                | 2.15(5)               | 2.916(4)                     | 166(4)         |
| Water 2. 0(12) — H(7)... 0(4) <sup>1</sup>        | 2.18(6)               | 2.934(5)                     | 176(5)         |
| 0(12) — H(8)... 0(13) <sup>2</sup>                | 2.40(5)               | 3.133(5)                     | 148(6)         |
| 0(7) <sup>2</sup> — H(1) <sup>2</sup> ... 0(12)   | 2.35(3)               | 2.872(3)                     | 149(6)         |
| 0(13) <sup>7</sup> — H(10) <sup>7</sup> ... 0(12) | 2.48(5)               | 2.987(5)                     | 119(3)         |
| Water 3. 0(13) — H(9)... 0(6) <sup>8</sup>        | 1.97(5)               | 2.770(4)                     | 172(6)         |
| 0(13) — H(10)... 0(6) <sup>2</sup>                | 2.36(5)               | 3.086(4)                     | 144(4)         |
| 0(13) — H(10)... 0(12) <sup>7</sup>               | 2.48(5)               | 2.987(5)                     | 199(3)         |
| 0(9) — H(3)... 0(13)                              | 2.30(3)               | 2.835(3)                     | 173(5)         |
| 0(11) — H(6) <sup>1</sup> ... 0(13)               | 2.15(5)               | 2.916(4)                     | 166(4)         |
| 0(12) — H(8)... 0(13)                             | 2.40(5)               | 3.133(5)                     | 148(6)         |

Angles at 0(11) given in Table 4.

| Angles at 0(12)                       |         | Angles at 0(13)                      |         |
|---------------------------------------|---------|--------------------------------------|---------|
| H(7) — 0(12) — H(8)                   | 111(6)° | H(9) — 0(13) — H(10)                 | 103(4)° |
| H(7) — 0(12) — H(1) <sup>2</sup>      | 108(3)  | H(9) — 0(13) — H(3)                  | 130(3)  |
| H(7) — 0(12) — H(10) <sup>7</sup>     | 81(4)   | H(9) — 0(13) — H(6) <sup>1</sup>     | 102(4)  |
| H(8) — 0(12) — H(1) <sup>2</sup>      | 87(3)   | H(10) — 0(13) — H(3)                 | 114(4)  |
| H(8) — 0(12) — H(10) <sup>7</sup>     | 168(5)  | H(10) — 0(13) — H(6) <sup>1</sup>    | 100(4)  |
| H(1) ... 0(12) ... H(10) <sup>7</sup> | 91(1)   | H(3) ... 0(13) ... H(6) <sup>1</sup> | 103(1)  |
|                                       |         | H(8) ... 0(13) ... H(9)              | 67(4)   |
|                                       |         | H(8) ... 0(13) ... H(10)             | 88(4)   |
|                                       |         | H(8) ... 0(13) ... H(3)              | 81(1)   |
|                                       |         | H(8) ... 0(13) ... H(6) <sup>1</sup> | 168(2)  |

Bifurcated hydrogen bond from 0(13) — H(10) —

Angle at H(10): — 0(6)<sup>2</sup> ... H(10) ... 0(12)<sup>7</sup> 90(2)°

serite, obtained using the program POWGEN (Hall & Szymański 1975). This program calculates the Debye-Scherrer powder pattern from measured single-crystal diffractometer intensities. There is excellent agreement with the data given by Jambor *et al.* (1977b), except that all lines of the  $hk0$  zone have significantly lower calculated intensities. This is particularly evident for the strong lines of this zone [ $h\bar{k}0$ ,  $I_{\text{obs}}$ ,  $I_{\text{calc}}$ : 010, 30, 13; 220, 50, 32; 130, 70, 48; 030, 60, 26]. The reason for this can be found in the morphology of the crystals, which are elongate [001]. Preferred orientation of the laths along the length of a powder-specimen capillary will enhance the whole  $hk0$  zone of reflections. The lines with uncertain indices have now been assigned. The only error in indexing, a minor one, is for the  $d = 3.18 \text{ \AA}$  line ( $hkl = 12\bar{1}$ ,  $I < 5$ ). The  $12\bar{1}$  reflection would have an intensity of  $< 0.25$  on a scale of  $I_{\text{max}} = 100$ ; the correct index should be 320, which is also shown to be present at  $d = 3.19 \text{ \AA}$  in the original pattern.

## DISCUSSION

In the original description, dresserite (Jambor *et al.* 1969) was considered to be a barium analogue of dundasite,  $\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$ . Such an analogy may be true chemically, but it

cannot be true structurally. Although the cell dimensions of the two minerals are very similar [dundasite:  $a$  9.08,  $b$  16.37,  $c$  5.63  $\text{\AA}$ , space group  $Pbnm$  (Cocco *et al.* 1972); dresserite:  $a$  9.27,  $b$  16.8,  $c$  5.63  $\text{\AA}$ , space group  $Pbmm$ ,  $Pb2_1m$ ,  $Pbm2$  (Jambor *et al.* 1969)], later precession work (Jambor *et al.* 1977a) confirmed the difference in space groups by the finding of weak  $h0l$  reflections with  $l \neq 2n$  in dresserite. It is, therefore, not possible to make comparisons of the structure of hydrodresserite with that of dresserite by inference until the latter is known. The brief comparison will be restricted to dundasite.

The Al co-ordination is virtually identical in the two structures: dundasite has the same square of bridging hydroxyl oxygen atoms, with carbonate oxygen atoms *trans* in a distorted octahedral configuration. Even the distortions of the bond lengths and angles are very similar in both structures. The principal differences are in the atoms that make up the divalent metal co-ordination sphere. In hydrodresserite, the nine-fold co-ordination is achieved by four Al-bonded oxygen atoms of carbonate groups, two carbonate terminal oxygen atoms, one hydroxyl oxygen atom and two water oxygen atoms. In dundasite, the Al-bonded carbonate oxygen atoms account for another four bonds and a hydroxyl oxygen atom provides the ninth co-ordinating atom around Pb. The lone water molecule in dundasite is thus not bonded to a metal atom. Otherwise, the co-ordination around Ba in hydrodresserite and around Pb in dundasite is very similar: the Pb atom in dundasite and three co-ordinating oxygen atoms are on a mirror plane. The other six oxygen atoms consist of three pairs related by the mirror plane. In hydrodresserite, only a pseudo-mirror plane exists, as described earlier, and a similar combination of three atoms and three pairs of atoms is observed. The hydrogen bonding in dundasite is simpler than in hydrodresserite. The same interhydroxyl bonds occur, as well as hydroxyl-water hydrogen bonding, but the presence of only one water molecule in dundasite restricts the range of possible hydrogen-bonding, and the one water molecule merely serves to bridge the carbonate and hydroxyl segments of the structure.

The present structure shows several noteworthy effects of co-ordination on bond length. The four carbonate Al-O bonds "draw off" electrons from the adjacent C-O bonds, which are consequently longer than the terminal C-O bonds by 0.03 to 0.04  $\text{\AA}$ . There is an observed

difference in the oxygen-hydrogen bond lengths between water molecules and hydroxyl ions: the mean O-H distance in the three water molecules is  $0.79_4 \pm 0.07$  Å, whereas the mean distance in hydroxyl ions is  $0.58_4 \pm 0.04_5$  Å. The difference between these,  $0.21$  Å, is very significant.

A qualitative estimate of the "strength of bonding" of water molecules can be made from the number of bonds in which each is involved, the atoms to which they bond and the bonding distances. Based on these considerations, the most firmly bonded is Water 1 [O(11), H(5), H(6)], which is bonded to two Ba atoms. This water would not be expected to be removed without serious thermal degradation of the structure. Probably Waters 2 and 3 are lost in the dehydration from hydrodresserite to dresserite. If the intermediate phase of this dehydration reported by Jambor *et al.* (1977b) is a dihydrate, there is a strong probability that it is achieved by loss of Water 2 from hydrodresserite.

In conclusion, the interpretation of the infra-

red absorption spectra by Farrell (1977) must be reconsidered. Hydrodresserite cannot be an oxy-bicarbonate salt: the hydrogen atoms are clearly located and refined. The very strong interhydroxyl and water-carbonate hydrogen bonding observed is evidently sufficient to shift the absorption frequencies from those expected for a hydroxyl group and a carbonate ion to close to those for an oxy-bicarbonate salt.

For a long time, the author was not able to find an adequate explanation for the space-group anomaly encountered in the early stages of structure determination. The data to  $2\theta = 70^\circ$  give a non-centrosymmetric distribution of intensities when they are normalized, and the percentage distribution is virtually identical to the values given in Table 2 for the data to  $2\theta = 60^\circ$ . Marsh (1981) has discussed the errors that occur when the intensity data are normalized incorrectly by ignoring weak reflections. The data for hydrodresserite to  $2\theta = 70^\circ$  were subsequently renormalized, treating the

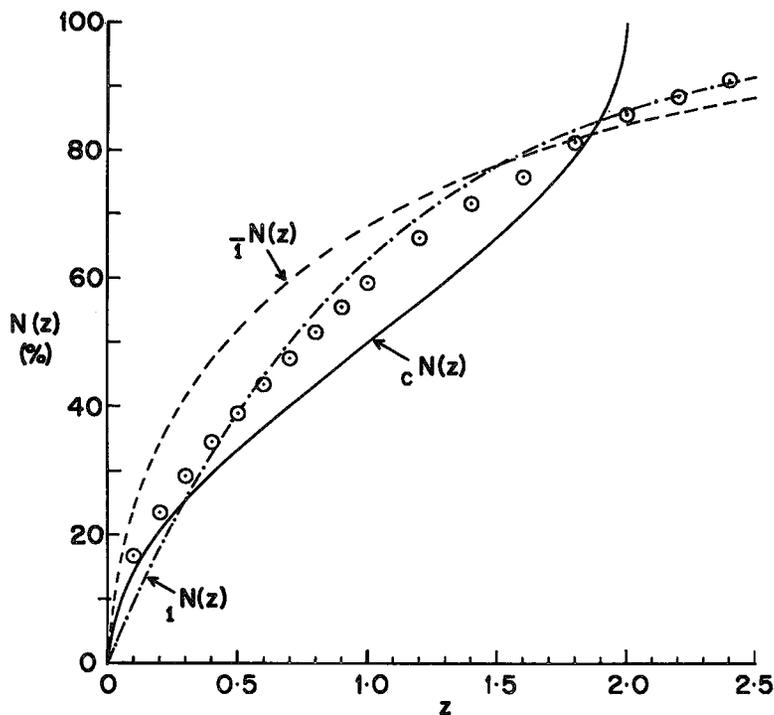


Fig. 3. Theoretical intensity-distribution curves: (a) dashed line:  $iN(z)$ , centrosymmetric distribution; (b) dashed-and-dotted line:  $jN(z)$ , non-centrosymmetric distribution (Howells *et al.* 1950); (c) solid line:  $cN(z)$  distribution arising from a centrosymmetric structure with a small number of very heavy atoms that dominate the phases (Hargreaves 1955). The intensity data for hydrodresserite (circles) fall partway between the  $cN(z)$  and the  $iN(z)$  curves, and thus appear to follow the  $jN(z)$  curve.

440 "unobserved" reflections not at their observable threshold values, but at their actual observed intensity (but  $> 0$ ), in the hope that the intensity distribution would be closer to centrosymmetric. The result was, as before, an unqualified non-centrosymmetric distribution. From the structure analysis, it is known that this is incorrect; in fact the four Al atoms are at centres of symmetry. The reason for this anomaly was finally pointed out to the author by Prof. R.E. Marsh: the statistics for centrosymmetric vs. non-centrosymmetric intensity distribution (Howells *et al.* 1950) are based on the assumption that an assembly of equal-weight atoms is randomly distributed within the structure. Although even significant deviations from the equal-weight concept do not seriously affect the intensity distribution, the presence of a small number of very heavy atoms (which totally dominate the phases) gives rise to an intensity distribution that is neither centrosymmetric nor non-centrosymmetric (Hargreaves 1955), as is shown in Figure 3. It can be seen that the observed intensity-distribution points fall part-way between the centrosymmetric curve (Howells *et al.* 1950) and the special very-heavy-atom curve [ $N(z)$ ] described by Hargreaves (1955). Evidently, the extreme case of the  $N(z)$  distribution is not achieved, though the Ba contribution to the phases is strong enough to move the distribution toward the  $N(z)$  curve from the  $iN(z)$  curve. The result is a distribution that, within experimental error, appears to follow the non-centrosymmetric  $iN(z)$  curve (Howells *et al.* 1950), even though this distribution arises from an averaging of the two centrosymmetric distributions.

The author does not have a ready answer on how to avoid this anomaly, which resulted in an incorrect initial choice of space group. The effect of refining a centrosymmetric structure in a non-centrosymmetric space group is the near-singularity of the least-squares matrix (Ermer & Dunitz 1970); this is indeed what was apparent in this work, even though the block-diagonal approximation was being used owing to the very large number of parameters (322) in the  $P1$  refinement. [Because of the nearly doubled number of parameters in the non-centrosymmetric space group, refinement is usually restricted to the block-diagonal approximation, and such singularity may not be immediately apparent (Marsh & Schomaker 1979)]. The fact that many centrosymmetric structures are being described in non-centrosymmetric space groups (Marsh 1981, Marsh & Schomaker 1979) is a source of great concern in this day of automated structure-determinations.

There appears to be no criterion for an *a priori* rejection of a non-centrosymmetric indication before a structure is solved and is being refined.

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