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# The Crystal Structure of Callaghanite, $Cu_8Mg_8(CO_3)_4(OH)_{24}.8\,H_2O$

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The crystal structure of callaghanite, $Cu_2Mg_2CO_3(OH)_6.2\,H_2O$, has been determined from X-ray precession and Weissenberg photographs of single crystals of the naturally occurring material. The crystal system is monoclinic, the space group is $C2/c$, and the unit-cell dimensions are $a = 10{\cdot}06$, $b = 11{\cdot}80$, $c = 8{\cdot}24$ Å; $\beta = 107°\ 18'$. There are four formula units per unit cell.

Two-dimensional Fourier syntheses and a (001) generalized projection were used to determine the final parameters of the atoms.

The carbonate group is bonded only to magnesium atoms, and one oxygen of this group is not bonded to either magnesium or copper but is hydrogen bonded to the water molecules. The Mg–(OH) bonds average 2·06 Å; the Cu–(OH) bonds, 2·01 Å; the Cu–$H_2O$ bonds, 2·23 Å; and the Mg–$H_2O$ bond, 1·89 Å. The C–O bonds are 1·41 Å, 1·41 Å, and 1·29 Å. The copper atom has four (OH) groups as nearest neighbors at a distance of 2·00 Å and a water molecule as next nearest neighbor at a distance of 2·23 Å forming a distorted pyramid around it.

## Introduction

The mineral callaghanite, $Cu_8Mg_8(CO_3)_4(OH)_{24}.8\,H_2O$ was first described by Beck & Burns (1954). These authors described the occurrence of callaghanite, gave its physical properties and determined the cell dimensions. The structural investigation of this mineral was undertaken because of the many reported variations in bond lengths between the cupric ion and its nearest neighbors. This mineral also affords the opportunity to study the coordination of copper and magnesium in a rare, complex, naturally occurring substance.

## Chemical analysis

Beck & Burns (1954) gave the structural formula as $Cu_8Mg_8Ca_2(CO_3)_4(OH)_{28}.4\,H_2O$. The minimum number of equivalent sites available in the reported space groups is four and it would be necessary to distribute the two calcium atoms statistically over four available positions. The original chemical analysis could have been in error because callaghanite occurs with calcite and dolomite. A sample of vein callaghanite in serpentine was analyzed and the results are listed in Table 1. The resultant structure confirms the correctness of $Cu_8Mg_8(CO_3)_4(OH)_{24}.8\,H_2O$. The reported density of 2·71 g.cm.$^{-3}$ is in good agreement with the calculated value of 2·65 g.cm.$^{-3}$.

Table 1. *Callaghanite: composition* and cell content*

| Constituent | Percent | Molecular proportion | Molecular ratio |
|---|---|---|---|
| CuO | 41·2 | 0·5179 | 2·035 = 2 |
| MgO | 23·4 | 0·5803 | 2·280 = 2 |
| CaO | < 0·1 | 0·0000 | 0·0000 |
| $H_2O$ | 22·39 | 1·2427 | 4·883 = 5 |
| $CO_2$ | 11·20 | 0·2545 | 1·000 = 1 |
| | 98·29 | | |

Empirical formula: $Cu_2Mg_2(CO_3)(OH)_6.2\,H_2O$.
Ideal cell content: 4.

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## Determination of structure

Single crystal X-ray diffraction precession and Weissenberg photographs taken with Mo $K\alpha$ radiation were used to obtain intensity data for the reflections ($hk0$), ($0kl$), ($hk1$) and ($h0l$). The natural crystal fragments were very irregular in shape but never exceeded the dimensions 0·1–0·2 mm.

Multiple-film techniques were used in the case of the Weissenberg photographs, and precession photographs were exposed for a series of fixed intervals of time to make certain that all intensities were on a linear scale. The relative intensities of the reciprocal-lattice spots were determined by visual comparison with calibrated intensity strips. These intensity strips were prepared from timed exposures of a diffracted beam from a crystal plane in the standard manner. The usual Lorentz and polarization corrections were applied to the measured intensities.

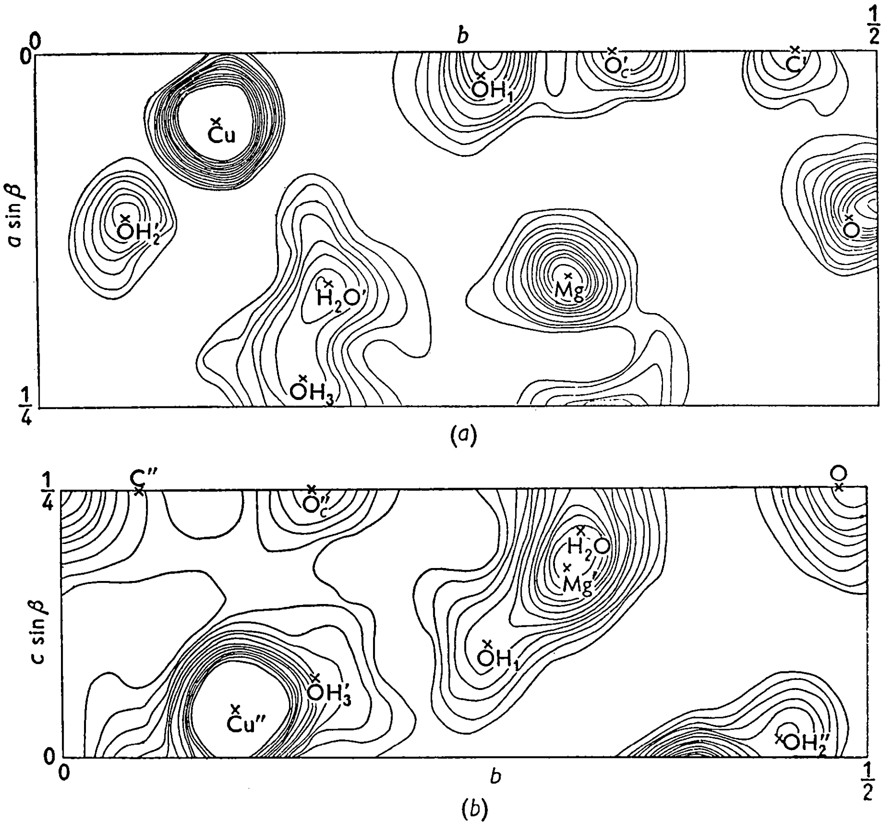

Fig. 1. (*a*) The (001) electron-density projection. (*b*) The (100) electron-density projection. The contours are in intervals of 2 e.Å$^{-2}$ from 4 e.Å$^{-2}$ to 28 e.Å$^{-2}$. Crosses mark the final locations of the atoms.

Beck & Burns (1954) gave the unit-cell dimensions of callaghanite as

$$a = 8{\cdot}24 \pm 0{\cdot}03,\quad b = 11{\cdot}80 \pm 0{\cdot}03,\quad c = 10{\cdot}06 \pm 0{\cdot}04\ \text{Å}\,,\quad \beta = 107^\circ\ 18' \pm 30'$$

and the space group as either $Aa$ or $A2/a$. The $a$ and $c$ axes have been interchanged for this investigation and the space group choices become $Cc$ or $C2/c$. Beck & Burns (1954) reported negative results in their piezoelectric experiment to determine whether callaghanite is centrosymmetrical.

The statistical tests proposed by Wilson (1949) and Howells, Phillips & Rogers (1950) were applied to the intensity data with indifferent results. The trend of the data seemed to be closer to a centric distribution and the space group was assumed to be $C2/c$ for the preliminary investigation.

Patterson projections were computed for the three zones ($hk0$), ($0kl$) and ($h0l$), and the position of the copper atoms was determined. Superposed Patterson projections with the Cu–Cu peaks as origins gave additional parameters for the magnesium and some of the oxygen atoms.

The electron-density projection (001) was computed first because it is a projection down the shortest axis and the resolution of the atoms was expected to be greatest. A series of electron-density projections and ($F_o - F_c$) syntheses resulted in the refined projection, Fig. 1(*a*). The final positions of the atoms are indicated by crosses in the figure and were determined from a back-shift correction on the final projection.

The electron-density projection (100) was investigated next. The superposition of the $(OH)_3$ and $H_2O$ groups on the copper and magnesium atoms made refinement of this projection difficult, but $z$ parameters were obtained which were used in the subsequent computation of ($hkl$) structure factors for the generalized projection. Fig. 1(*b*) is the final (100) projection.

A generalized ($hk1$) projection was computed to check the parameters obtained from the electron-density projections. The projections $C_1(x, y)$ and

Table 2. *Atomic parameters*

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cu | 0·048 | 0·108 | 0·455 |
| Mg | 0·158 | 0·317 | 0·321 |
| O | 0·117 | 0·483 | 0·250 |
| $OH_1$ | 0·017 | 0·267 | 0·105 |
| $OH_2$ | 0·118 | 0·946 | 0·482 |
| $OH_3$ | 0·230 | 0·159 | 0·425 |
| $H_2O$ | 0·336 | 0·323 | 0·289 |
| $O_c$ | 0·000 | 0·657 | 0·250 |
| C | 0·000 | 0·548 | 0·250 |

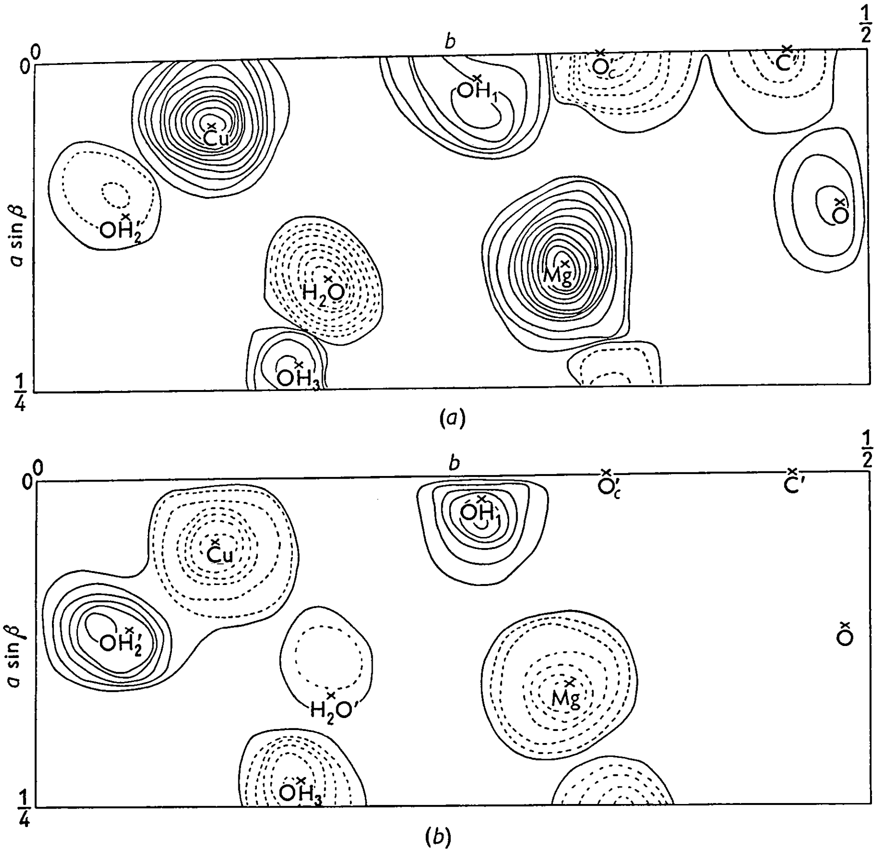

Fig. 2. (*a*) The $C_1(x, y)$ generalized projection. (*b*) The $S_1(x, y)$ generalized projection. Contours at arbitrary intervals; dashed contours are negative.

$S_1(x, y)$ are shown in Fig. 2. The final atomic parameters are listed in Table 2.

The assignment of the $H_2O$ molecule to the peak at $x = 0{\cdot}336$, $y = 0{\cdot}323$ and $z = 0{\cdot}289$ is an assumption based upon its relationship to the copper atom and one of the oxygen atoms of the carbonate group. There is no unequivocal evidence that the $H_2O$ molecule occupies these coordinates and not those of one of the positions assigned to an (OH) group.

The observed and calculated structure factors are listed in Table 3. Anisotropic temperature factors were computed by least-square methods by minimizing the function

$$\Sigma W(hkl)\left[\ln \frac{F_o}{A_c \exp -[\alpha_0+\alpha_1h^2+\alpha_2k^2+\alpha_3l^2+\alpha_4hl]}\right]^2,$$

where $A_c$ is the geometric structure factor, $\exp[-\alpha_0]$ is a scaling factor and $W(hkl)$ is a weighting function equal to $|F_o|$ (Ladell & Post, 1954). The values of the temperature factors are:

$$\alpha_0=0{\cdot}09,\ \alpha_1=0{\cdot}001,\ \alpha_2=0{\cdot}009,\ \alpha_3=0{\cdot}010,\ \alpha_4=0{\cdot}005\,.$$

The values of the discrepancy factors are:

$$R(hk0) = 0{\cdot}126,\ R(0kl) = 0{\cdot}189,\ R(h0l) = 0{\cdot}221,$$
$$R(hkl) = 0{\cdot}201,\ R(\text{overall}) = 0{\cdot}183\,.$$

Only observed structure factors were considered in the determination of $R$. The $f$ values for copper and magnesium are those of Brindley & James (1944) and the $f$ values for carbon and oxygen are those of McWeeny (1951).

## Estimation of precision

The magnitude of random errors in atomic coordinates was investigated using Cruickshank's expressions for the standard deviation (Cruickshank, 1949) and using the differences, $\Delta F$, between the magnitudes of the observed and calculated structure factors.

The average values of $p$ and $\varrho_0$ for the respective atoms were taken from the (001) electron-density projection because in it the atoms are best resolved. The lack of resolution in the other projections makes it necessary to assume that $\sigma(x) = \sigma(y) = \sigma(z)$. The values for $p$, $\varrho_0$ and $\sigma(x)$ are listed in Table 4.

## Discussion of the structure

Fig. 3 is two perspective views of the structure of callaghanite. The interatomic distances and bond angles are listed in Table 5.

Each copper atom in the structure has four (OH) groups as nearest neighbors, e.g. $OH_2$, $OH_2'$, $OH_1'$ and

Table 3. *Observed and calculated structure factors*

| h | k | l | $F_o$ | $F_c$ |
|---|---|---|---|---|
| 2 | 0 | 0 | 118 | 162 |
| 4 | 0 | 0 | 17 | 15 |
| 6 | 0 | 0 | 61 | 60 |
| 8 | 0 | 0 | 25 | -14 |
| 10 | 0 | 0 | 85 | -99 |
| 12 | 0 | 0 | 36 | -41 |
| 14 | 0 | 0 | 27 | -27 |
| 0 | 2 | 0 | 24 | -21 |
| 0 | 4 | 0 | 126 | -128 |
| 0 | 6 | 0 | 23 | 28 |
| 0 | 8 | 0 | 47 | 16 |
| 0 | 10 | 0 | 60 | 65 |
| 0 | 14 | 0 | 83 | -110 |
| 0 | 16 | 0 | 23 | 6 |
| 0 | 18 | 0 | 63 | 68 |
| 1 | 1 | 0 | 91 | 107 |
| 1 | 3 | 0 | 78 | -58 |
| 1 | 5 | 0 | 191 | -216 |
| 1 | 9 | 0 | 91 | 80 |
| 1 | 11 | 0 | 32 | 36 |
| 1 | 13 | 0 | 73 | -77 |
| 1 | 15 | 0 | 42 | -39 |
| 1 | 17 | 0 | 32 | 29 |
| 1 | 19 | 0 | 50 | 64 |
| 2 | 2 | 0 | 50 | 56 |
| 2 | 4 | 0 | 55 | -55 |
| 2 | 6 | 0 | 137 | -153 |
| 2 | 8 | 0 | 101 | 116 |
| 2 | 10 | 0 | 63 | 57 |
| 2 | 12 | 0 | 36 | -43 |
| 2 | 14 | 0 | 59 | -48 |
| 2 | 18 | 0 | 42 | 42 |
| 3 | 1 | 0 | 50 | 48 |
| 3 | 3 | 0 | 9 | -14 |
| 3 | 5 | 0 | 69 | -64 |
| 3 | 7 | 0 | 13 | 17 |
| 3 | 9 | 0 | 91 | 83 |
| 3 | 11 | 0 | 78 | 79 |
| 3 | 13 | 0 | 73 | -73 |
| 4 | 2 | 0 | 63 | -64 |
| 4 | 4 | 0 | 85 | -79 |
| 4 | 6 | 0 | 78 | -69 |
| 4 | 8 | 0 | 82 | 82 |
| 4 | 10 | 0 | 19 | -9 |
| 4 | 12 | 0 | 19 | -6 |
| 5 | 7 | 0 | 55 | 47 |
| 5 | 9 | 0 | 19 | 18 |
| 5 | 11 | 0 | 36 | 36 |
| 6 | 2 | 0 | 91 | -84 |
| 6 | 4 | 0 | 36 | 30 |
| 6 | 6 | 0 | 55 | 46 |
| 6 | 8 | 0 | 59 | -56 |
| 6 | 10 | 0 | 19 | -10 |
| 7 | 1 | 0 | 86 | -85 |
| 7 | 3 | 0 | 82 | 74 |
| 7 | 5 | 0 | 23 | 15 |
| 7 | 9 | 0 | 46 | -38 |
| 7 | 11 | 0 | 27 | -19 |
| 8 | 4 | 0 | 86 | 93 |
| 8 | 6 | 0 | 55 | 45 |
| 8 | 8 | 0 | 36 | -36 |
| 8 | 10 | 0 | 69 | -80 |
| 8 | 14 | 0 | 50 | 54 |
| 9 | 1 | 0 | 73 | -70 |
| 9 | 5 | 0 | 86 | 80 |
| 9 | 7 | 0 | 23 | -17 |
| 9 | 9 | 0 | 91 | -100 |
| 9 | 13 | 0 | 27 | 34 |
| 10 | 2 | 0 | 19 | 15 |
| 10 | 4 | 0 | 82 | 96 |
| 10 | 6 | 0 | 36 | 19 |
| 10 | 10 | 0 | 78 | -80 |
| 10 | 14 | 0 | 59 | 73 |
| 11 | 1 | 0 | 78 | -78 |
| 11 | 3 | 0 | 50 | 48 |
| 11 | 5 | 0 | 82 | 74 |
| 11 | 9 | 0 | 46 | -51 |
| 11 | 13 | 0 | 32 | 30 |
| 11 | 15 | 0 | 42 | 41 |
| 12 | 2 | 0 | 55 | -52 |
| 12 | 4 | 0 | 46 | 42 |
| 12 | 6 | 0 | 55 | 58 |
| 12 | 8 | 0 | 55 | -57 |
| 12 | 10 | 0 | 42 | -43 |
| 13 | 1 | 0 | 42 | -43 |
| 13 | 3 | 0 | 32 | 30 |
| 13 | 5 | 0 | 36 | 45 |
| 13 | 7 | 0 | 23 | 22 |
| 0 | 0 | 2 | 69 | 58 |
| 0 | 0 | 4 | 115 | 114 |
| 0 | 0 | 6 | 34 | -30 |
| 0 | 0 | 8 | 31 | -37 |
| 0 | 0 | 10 | 26 | -28 |
| 0 | 2 | 2 | 52 | 51 |
| 0 | 2 | 3 | 166 | -151 |
| 0 | 2 | 4 | 93 | 95 |
| 0 | 2 | 5 | 151 | -137 |
| 0 | 2 | 7 | 42 | -32 |
| 0 | 2 | 9 | 23 | -29 |
| 0 | 4 | 1 | 100 | -99 |
| 0 | 4 | 2 | 130 | -134 |
| 0 | 4 | 4 | 44 | -42 |
| 0 | 4 | 5 | 16 | 11 |
| 0 | 4 | 7 | 36 | -46 |
| 0 | 4 | 8 | 34 | 51 |
| 0 | 4 | 9 | 25 | 8 |
| 0 | 6 | 1 | 109 | 119 |
| 0 | 6 | 2 | 171 | -168 |
| 0 | 6 | 3 | 89 | 80 |
| 0 | 6 | 4 | 9 | 3 |
| 0 | 6 | 5 | 59 | 83 |
| 0 | 6 | 7 | 44 | 57 |
| 0 | 6 | 9 | 19 | 16 |
| 0 | 8 | 1 | 32 | 28 |
| 0 | 8 | 2 | 61 | 85 |
| 0 | 8 | 3 | 9 | 17 |
| 0 | 8 | 4 | 9 | 9 |
| 0 | 8 | 5 | 44 | 55 |
| 0 | 8 | 6 | 36 | -46 |
| 0 | 8 | 7 | 50 | 55 |
| 0 | 8 | 8 | 7 | -2 |
| 0 | 10 | 1 | 40 | -31 |
| 0 | 10 | 2 | 27 | 39 |
| 0 | 10 | 4 | 9 | 22 |
| 0 | 10 | 5 | 9 | -12 |
| 0 | 10 | 6 | 9 | 9 |
| 0 | 10 | 7 | 32 | -57 |
| 0 | 12 | 1 | 26 | 30 |
| 0 | 12 | 2 | 36 | -43 |
| 0 | 12 | 3 | 52 | -101 |
| 0 | 12 | 4 | 9 | -15 |
| 0 | 12 | 5 | 38 | -56 |
| 0 | 12 | 6 | 9 | -9 |
| 0 | 14 | 2 | 27 | -39 |
| 2 | 0 | 2 | 182 | 184 |
| 2 | 0 | 4 | 66 | 99 |
| 2 | 0 | 6 | 56 | 31 |
| 2 | 0 | 8 | 31 | 43 |
| 2 | 0 | $\bar{2}$ | 23 | 7 |
| 2 | 0 | $\bar{4}$ | 66 | -11 |
| 2 | 0 | $\bar{6}$ | 108 | -110 |
| 2 | 0 | $\bar{8}$ | 52 | -48 |
| 2 | 0 | $\overline{10}$ | 25 | -26 |
| 4 | 0 | 2 | 85 | 101 |
| 4 | 0 | 4 | 75 | 69 |
| 4 | 0 | 6 | 10 | 30 |
| 4 | 0 | 8 | 27 | 24 |
| 4 | 0 | $\bar{2}$ | 93 | 83 |
| 4 | 0 | $\bar{4}$ | 226 | -213 |
| 4 | 0 | $\bar{6}$ | 223 | -211 |
| 4 | 0 | $\bar{8}$ | 56 | -48 |
| 4 | 0 | $\overline{10}$ | 40 | -40 |
| 6 | 0 | 2 | 60 | -44 |
| 6 | 0 | 4 | 81 | 78 |
| 6 | 0 | 6 | 48 | 74 |
| 6 | 0 | $\bar{2}$ | 182 | -201 |
| 6 | 0 | $\bar{4}$ | 157 | -161 |
| 6 | 0 | $\bar{6}$ | 70 | -91 |
| 6 | 0 | $\bar{8}$ | 35 | -29 |
| 6 | 0 | $\overline{10}$ | 17 | 17 |
| 8 | 0 | 2 | 27 | -30 |
| 8 | 0 | 4 | 17 | 13 |
| 8 | 0 | $\bar{2}$ | 91 | -99 |
| 8 | 0 | $\bar{6}$ | 66 | -125 |
| 8 | 0 | $\bar{8}$ | 31 | 2 |
| 10 | 0 | 2 | 43 | -59 |
| 10 | 0 | $\bar{2}$ | 50 | -68 |
| 10 | 0 | $\bar{4}$ | 33 | -43 |
| 10 | 0 | $\bar{6}$ | 45 | -100 |
| 10 | 0 | $\bar{8}$ | 45 | 112 |
| 12 | 0 | $\bar{2}$ | 35 | -40 |
| 12 | 0 | $\bar{6}$ | 17 | 31 |
| 1 | 1 | 1 | 32 | 43 |
| 1 | 3 | 1 | 32 | 18 |
| 1 | 5 | 1 | 96 | -115 |
| 2 | 2 | 1 | 22 | -20 |
| 2 | 4 | 1 | 32 | 13 |
| 2 | 6 | 1 | 75 | -84 |
| 2 | 8 | 1 | 59 | -63 |
| 2 | 10 | 1 | 54 | 62 |
| 2 | 14 | 1 | 37 | 33 |
| 3 | 1 | 1 | 32 | 36 |
| 3 | 3 | 1 | 65 | 87 |
| 3 | 5 | 1 | 59 | -54 |
| 3 | 7 | 1 | 37 | -36 |
| 3 | 9 | 1 | 48 | -31 |
| 3 | 11 | 1 | 75 | 80 |
| 3 | 13 | 1 | 48 | 44 |
| 4 | 2 | 1 | 32 | 26 |
| 4 | 4 | 1 | 48 | 72 |
| 4 | 6 | 1 | 59 | -100 |
| 4 | 8 | 1 | 96 | -138 |
| 4 | 10 | 1 | 59 | 68 |
| 4 | 12 | 1 | 54 | 41 |
| 4 | 14 | 1 | 37 | -12 |
| 5 | 1 | 1 | 48 | 59 |
| 5 | 3 | 1 | 139 | 173 |
| 5 | 5 | 1 | 37 | -29 |
| 5 | 7 | 1 | 65 | -77 |
| 5 | 11 | 1 | 70 | 71 |
| 6 | 2 | 1 | 187 | 197 |
| 6 | 6 | 1 | 48 | -41 |
| 6 | 8 | 1 | 65 | -64 |
| 6 | 12 | 1 | 75 | 81 |
| 7 | 1 | 1 | 48 | 59 |
| 7 | 3 | 1 | 91 | 137 |
| 7 | 5 | 1 | 32 | -27 |
| 7 | 7 | 1 | 65 | -70 |
| 7 | 11 | 1 | 54 | 54 |
| 7 | 13 | 1 | 37 | 20 |
| 8 | 2 | 1 | 54 | 53 |
| 8 | 4 | 1 | 65 | 75 |
| 8 | 6 | 1 | 54 | -48 |
| 8 | 8 | 1 | 65 | -81 |
| 8 | 10 | 1 | 59 | 72 |
| 8 | 12 | 1 | 48 | 51 |
| 9 | 1 | 1 | 43 | 46 |
| 9 | 3 | 1 | 48 | 59 |
| 9 | 11 | 1 | 48 | 36 |
| $\bar{1}$ | 1 | 1 | 129 | -167 |
| $\bar{1}$ | 3 | 1 | 27 | -13 |
| $\bar{1}$ | 5 | 1 | 65 | 7 |
| $\bar{1}$ | 7 | 1 | 65 | 48 |
| $\bar{1}$ | 9 | 1 | 48 | 19 |
| $\bar{1}$ | 11 | 1 | 65 | -64 |
| $\bar{1}$ | 13 | 1 | 54 | -68 |
| $\bar{2}$ | 2 | 1 | 133 | -161 |
| $\bar{2}$ | 6 | 1 | 139 | 120 |
| $\bar{2}$ | 8 | 1 | 75 | 55 |
| $\bar{2}$ | 12 | 1 | 70 | -95 |
| $\bar{2}$ | 16 | 1 | 43 | 49 |
| $\bar{3}$ | 1 | 1 | 37 | -26 |
| $\bar{3}$ | 3 | 1 | 81 | -73 |
| $\bar{3}$ | 5 | 1 | 32 | 19 |
| $\bar{3}$ | 7 | 1 | 192 | 206 |
| $\bar{3}$ | 9 | 1 | 37 | 27 |
| $\bar{3}$ | 11 | 1 | 81 | -96 |
| $\bar{3}$ | 13 | 1 | 54 | -37 |
| $\bar{3}$ | 15 | 1 | 37 | 41 |
| $\bar{4}$ | 2 | 1 | 262 | -263 |
| $\bar{4}$ | 6 | 1 | 65 | 58 |
| $\bar{4}$ | 8 | 1 | 59 | 37 |
| $\bar{4}$ | 12 | 1 | 91 | 122 |
| $\bar{4}$ | 16 | 1 | 54 | 64 |
| $\bar{5}$ | 1 | 1 | 65 | -85 |
| $\bar{5}$ | 3 | 1 | 113 | -136 |
| $\bar{5}$ | 5 | 1 | 37 | 29 |
| $\bar{5}$ | 7 | 1 | 129 | 144 |
| $\bar{5}$ | 11 | 1 | 70 | -59 |
| $\bar{6}$ | 2 | 1 | 75 | -114 |
| $\bar{6}$ | 4 | 1 | 81 | -137 |
| $\bar{6}$ | 6 | 1 | 70 | 83 |
| $\bar{6}$ | 8 | 1 | 54 | 52 |
| $\bar{6}$ | 10 | 1 | 70 | -69 |
| $\bar{7}$ | 1 | 1 | 59 | -61 |
| $\bar{7}$ | 3 | 1 | 65 | -75 |
| $\bar{7}$ | 7 | 1 | 43 | 44 |
| $\bar{7}$ | 9 | 1 | 48 | 40 |
| $\bar{7}$ | 11 | 1 | 70 | -72 |
| $\bar{7}$ | 13 | 1 | 48 | -31 |
| $\bar{8}$ | 2 | 1 | 43 | -51 |
| $\bar{8}$ | 8 | 1 | 43 | 35 |
| $\bar{8}$ | 10 | 1 | 37 | -10 |
| $\bar{9}$ | 5 | 1 | 37 | 19 |
| $\overline{10}$ | 4 | 1 | 65 | 73 |
| $\overline{11}$ | 1 | 1 | 65 | 71 |
| $\overline{12}$ | 2 | 1 | 70 | 70 |
| $\overline{12}$ | 12 | 1 | 75 | 43 |
| $\overline{13}$ | 1 | 1 | 48 | 31 |
| $\overline{13}$ | 3 | 1 | 54 | 55 |
| $\overline{13}$ | 7 | 1 | 54 | -63 |

Table 4. *Standard deviation of atomic parameters*

| | Cu | Mg | OH | O | C |
|---|---|---|---|---|---|
| $p$ | 10·52 | 6·84 | 8·76 | 11·53 | 11·17 |
| $\varrho_0$ (e.Å$^{-2}$) | 88·00 | 32·10 | 17·80 | 14·70 | 12·50 |
| $\sigma(x)$ (Å) | 0·007 | 0·030 | 0·042 | 0·038 | 0·046 |

$OH_3$ in Fig. 3, at a distance of 2·00 Å. The four (OH) groups do not lie exactly in the same plane and are at the corners of a slightly puckered trapezium with edges 2·75, 3·00, 2·73, and 2·67 Å in length. The atom, Cu, Fig. 3, lies just above the center of the trapezium. The $H_2O$ molecule is the next nearest neighbor to the copper atom at a distance of 2·23 Å. It is at the apex of an askew pyramid which has the trapezium as its base and which encloses the copper atom. $H_2O'$ in Fig. 3 is skewed toward the trapezium edge, $OH_1'$–$OH_3$. The bond angles $OH_3$–Cu–$H_2O'$ and $OH_1'$–Cu–$H_2O'$ are 76° 49′ and 82° 07′, respectively.

The cupric ion usually has four nearest neighbors

Table 5. *Interatomic distances and bond angles*

| | | | |
|---|---|---|---|
| Cu–$OH_2$ | 2·03 Å | Cu–OH–Cu′ | 92° 57′ |
| Cu–$OH_2'$ | 2·00 | Cu–$OH_3$–Mg | 95 18 |
| Cu–$OH_3$ | 2·01 | Cu–$OH_1'$–Mg | 94 15 |
| Cu–$OH_1'$ | 2·01 | Cu–$OH_3$–Mg″ | 100 22 |
| Cu–$H_2O'$ | 2·23 | Cu–$H_2O$–Mg″ | 98 01 |
| Cu–$OH_2''$ | 3·97 | Cu–$OH_1'$–Mg′ | 108 14 |
| Cu–Cu′ | 2·90 | Mg–OH–Mg′ | 95 57 |
| Cu–Cu″ | 3·21 | Mg–OH–Mg″ | 107 15 |
| Cu–Mg | 3·04 | $OH_1'$–Mg–$H_2O$ | 130 03 |
| Cu–Mg′ | 3·26 | $OH_1$–Mg–$OH_3'$ | 166 55 |
| Cu–Mg″ | 3·14 | $OH_3$–Mg–O | 163 30 |
| $O_c$–$H_2O''$ | 2·64 | $OH_1$–Mg–$OH_1'$ | 75 21 |
| O–$H_2O$ | 2·84 | $OH_3$–Mg–$OH_3'$ | 72 09 |
| O–$OH_3'$ | 3·14 | $OH_3$–Mg–$H_2O$ | 83 29 |
| O–$OH_1$ | 2·71 | $OH_3'$–Mg–O | 99 02 |
| O–$OH_1'$ | 3·14 | O–C–O | 114 39 |
| $OH_1$–$OH_1'$ | 2·52 | $OH_1'$–Cu–$OH_2$ | 166 58 |
| $OH_1$–$H_2O$ | 3·17 | $OH_2'$–Cu–$OH_3$ | 171 05 |
| $OH_1$–$OH_3$ | 3·12 | $OH_2$–Cu–$OH_2'$ | 86 04 |
| Mg–O | 2·03 | $OH_1'$–Cu–$OH_2'$ | 96 09 |
| Mg–$OH_3$ | 2·09 | $OH_2$–Cu–$OH_3$ | 82 44 |
| Mg–$OH_3'$ | 2·07 | $OH_1'$–Cu–$OH_3$ | 85 49 |
| Mg–$OH_1$ | 2·00 | $OH_3$–Cu–$H_2O'$ | 76 49 |
| Mg–$OH_1'$ | 2·12 | $OH_1'$–Cu–$H_2O'$ | 82 07 |
| Mg–$H_2O$ | 1·89 | O–Mg–$OH_1$ | 84 31 |
| Mg–Mg′ | 3·04 | O–Mg–$OH_1'$ | 98 43 |
| Mg–Mg″ | 3·36 | O–Mg–$H_2O$ | 92 13 |
| C–O | 1·41 | $OH_1'$–Mg–$H_2O$ | 109 52 |
| C–$O_c$ | 1·29 | $OH_3$–Mg–$OH_1$ | 99 56 |
| $OH_1'$–$OH_3$ | 2·73 | $OH_3$–Mg–$OH_1'$ | 80 51 |
| $OH_1'$–$OH_2'$ | 3·00 | $O_c$–C–O | 122 20 |
| $OH_1'$–$H_2O'$ | 2·79 | | |
| $OH_2$–$OH_2'$ | 2·75 | | |
| $OH_2$–$OH_3$ | 2·67 | | |
| $OH_3$–$OH_3'$ | 2·45 | | |
| $OH_3$–$H_2O'$ | 2·64 | | |

Table 6. Cu–O *bond distances*

| Compound | Cu–O (4 nearest neighbors) (Å) | Cu-anion (2 next nearest neighbors) (Å) | Reference |
|---|---|---|---|
| $CuCl_2.2\,H_2O$ | 2·01 | None | Harker, 1936 |
| $K_2CuCl_4.2\,H_2O$ | 1·97 | None | Chrobak, 1934 |
| CuO | 1·95 | None | Tunnel *et al.*, 1935 |
| $CuBr_2.3\,Cu(OH)_2$ | 1·92–2·00 | None | Aebi, 1948 |
| $CuCrO_4$ | 2·05 | 2·15 | Brandt, 1948 |
| $CuCl_2.3\,Cu(OH)_2$ | 1·94–2·07 | 2·36 | Wells, 1949 |
| $(C_{21}H_{22}O_6N)_2Cu.6\,H_2O$ | 2·30–2·60 | 2·90 | Morrison, 1951 |
| Malachite | 1·98–2·01 | 2·41–2·71 | Wells, 1951 |
| $CuCl_2.CuB_2O_4$ | 1·98 | 2·80 | Collin, 1951 |
| Cu proline dihydrate | 2·03 | 2·52 | Mathieson & Welsh, 1952 |
| $Cu(HCO_2)_2.4\,H_2O$ | 2·00 | 2·36 | Kiriyama *et al.*, 1954 |
| $Cu(NH_3)_4SO_4.H_2O$ | Nitrogen | 2·59–3·37 | Mazzi, 1955 |
| $Cu_2(CH_3COO)_4.2\,H_2O$ | 1·97 | 2·20–2·64 | van Niekerk & Schoening, 1953 |
| $Cu_8Mg_8(CO_3)_4(OH)_{24}.8\,H_2O$ | 2·00 | 2·23–3·21 | This investigation |

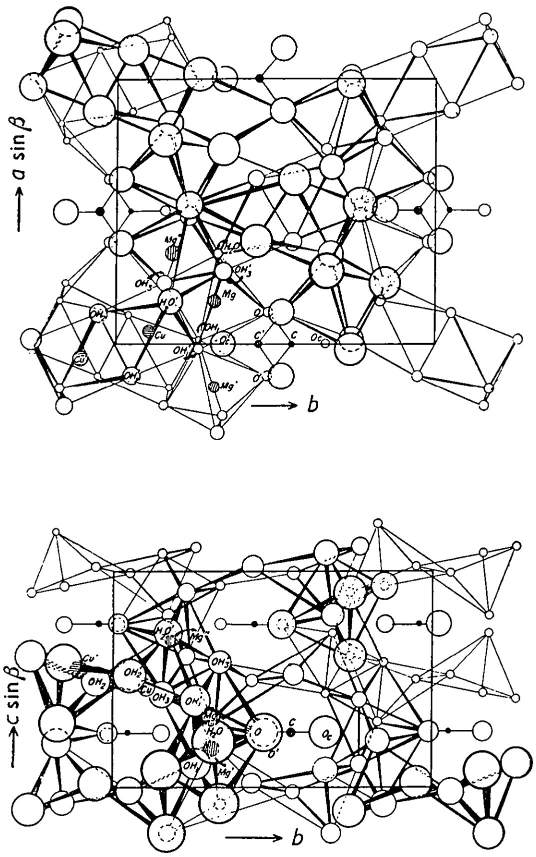

Fig. 3. Two perspective views of the structure of callaghanite. The top view is a (001) projection and the bottom view is a (100) projection.

which form a square around the copper atom. This has been reported for the structures of $CuCl_2.2\,H_2O$ (Harker, 1936), $K_2CuCl_4.2\,H_2O$ (Chrobak, 1934) and CuO (Tunnel, Posnak & Ksanda, 1935). Occasionally the cupric ion may have two additional anions at a greater distance, which, with the square, form a tetragonal dipyramid around the copper atom. This has been reported in the structures of $CuCrO_4$ (Brandt, 1948), $CuCl_2.3\,Cu(OH)_2$ (Wells, 1949), malachite (Wells, 1951), and others. A new coordination for copper was described by van Niekerk & Schoening (1953) for copper acetate. The copper atom in the structure of copper acetate has four oxygen atoms as nearest neighbors which form a square around it at a distance of 1·97 Å. The other two nearest neighbors at the apexes of a distorted tetragonal dipyramid are a water molecule and another copper atom at distances of 2·20 and 2·64 Å respectively. This is similar to the configuration in callaghanite but the Cu–Cu distance between two copper atoms in adjacent but unconnected pyramids is 3·21 Å. The Cu–Cu distance in copper acetate is partly determined by the O–C–O bond angle of the carboxyl groups which link the copper pyramids together. The only pyramid to pyramid linkage in callaghanite would be O–H–O bonds. Cu–O bond distances from the literature are listed in Table 6.

Each magnesium atom in the structure of callaghanite has six nearest neighbors at a distance of about 2·00 Å (Table 5). These are an oxygen atom, a $H_2O$ molecule and four (OH) groups at the apexes of a distorted octahedron. The degree of distortion is best exemplified by the diagonals through the magnesium atom to the apexes. Ideally these diagonals are straight lines, but the bond angles, $OH_1'$–Mg–$H_2O$, $OH_1$–Mg–$OH_3'$, and $OH_3$–Mg–O, are 130° 03′, 166° 55′ and 163° 50′ respectively (Fig. 3 and Table 5).

Three oxygen atoms surround the carbon atoms to form the carbonate group. These four atoms lie in a plane which is parallel to the (001) plane of the crystal. Two of the oxygen atoms are 1·41 Å from the carbon atom and are shared with two magnesium atoms, e.g. Mg and Mg′ (Fig. 3). The other oxygen atom is 1·29 Å from the carbon atom and is shared by hydrogen bonds 2·64 Å in length with two $H_2O$ molecules. The difference in the C–O bond lengths can probably be explained by the manner in which the oxygen atoms are shared with surrounding cations. The two oxygen atoms bonded to the magnesium atoms have a greater C–O distance than the oxygen atom bonded only to $H_2O$ by hydrogen bonds because of the greater electrostatic attraction of the magnesium atom for oxygen.

Each copper trapezium is joined along one edge to one other copper trapezium and this other copper trapezium is always related to the first by a center of symmetry. The two trapeziums slope in the same direction, e.g. the trapeziums around Cu and Cu′ join along the edge $OH_2$–$OH_2'$ and slope away from the observer and to the right (Fig. 3). The next set of trapeziums, related to the first pair by the *c* glide, slope in the opposite direction. Each trapezium around a copper atom also joins one edge of the octahedron around the magnesium atom which is the nearest neighbor to the copper atom. In Fig. 3 this edge is $OH_1'$–$OH_3$ for Cu and Mg.

One edge of the distorted pyramid formed by the $H_2O$ molecule is also joined to the edge of another magnesium octahedron, e.g. $H_2O'$–$OH_3$ for Cu and Mg″ in Fig. 3. The magnesium in this second octahedron is always at position $(\frac{1}{2}-x, \frac{1}{2}-y, -z)$ if the first magnesium atom is at $(x, y, z)$. This is the symmetry operation of the *C* centering plus the center of symmetry.

The octahedra around Mg and Mg″ share the edge $OH_3$–$OH_3'$. The Mg octahedron also shares an edge, $OH_1$–$OH_1'$ with the Mg′ octahedron (Fig. 3). Both of these octahedra are connected to the carbonate group by sharing one each of the oxygen atoms which are at a distance of 1·41 Å from the carbon atom.

The structure of callaghanite is one in which every copper pyramid adjoins one other copper pyramid and two magnesium octahedra. Every magnesium octahedron adjoins two copper pyramids, one octahedron edge along a trapezium edge and another along the

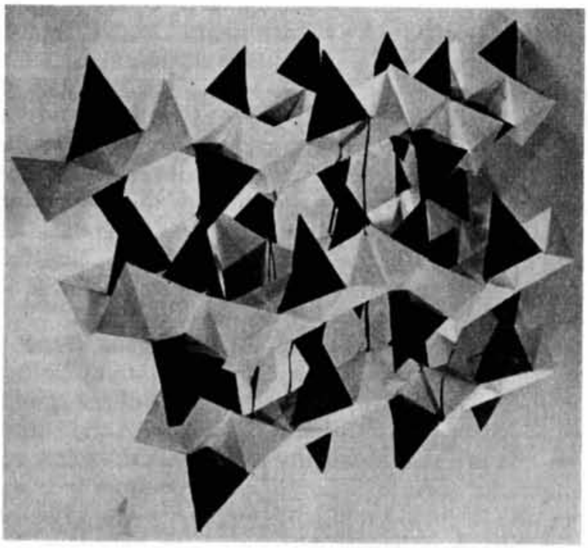

Fig. 4. Arrangement of coordination polyhedra in callaghanite. The white magnesium octahedra are linked by the black copper pyramids and carbonate groups. This view is not along a crystallographic direction.

OH–$H_2O$ pyramid edge. Every magnesium octahedron also adjoins two other magnesium octahedra along two octahedral edges, and every magnesium octahedron shares one oxygen atom with the carbonate group. The other oxygen atom of the carbonate group forms hydrogen bonds with two $H_2O$ molecules. This type of bonding for the carbonate group has been reported by Brown, Peiser & Turner-Jones (1949) and Candlin (1956) for the structure of sodium sesquicarbonate.

The net effect of the joining of the octahedra, distorted pyramids, and carbonate groups is illustrated by Fig. 4. A zigzag chain of magnesium octahedra would extend diagonally from lower left to upper right in a view of the (010) plane of the crystal. This chain is perpendicular to the *b* axis and is connected along this axis to the next chain of octahedra by alternating combinations of carbonate groups and paired copper pyramids. The copper pyramid pairs, which always adjoin along a trapezium edge, have their apexes in opposite directions.

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