

Table 8. MoSi₂ structure type (tetragonal)⁽¹⁾

	a (Å)	$\sigma(a)$ (Å)	c (Å)	$\sigma(c)$ (Å)	Vol. (Å ³)	D (Å)	E (Å)
GdAg ₂	3.728	0.001	9.296	0.006	129.2	3.099	3.057
DyAg ₂	3.6957	0.0002	9.213	0.001	125.8	3.071	3.031
GdAu ₂	3.7320	0.0006	9.014	0.003	125.5	3.004	3.036
DyAu ₂	3.6940	0.0006	8.956	0.003	122.2	2.985	3.009

⁽¹⁾ *Strukturbericht*, **1**, 741 (1931).

Table 9. CuTi₃ structure type (tetragonal)^{(1), (2)}

Dy₃In $a = 4.602 \pm 0.004$ Å, $c = 4.945 \pm 0.004$ Å, Vol. = 104.7 Å³

⁽¹⁾ Pearson, (1958), p. 618.

⁽²⁾ Due to the relative values of the scattering factors, the existence of ordering could not be detected.

in order to verify the choice of the structure. Powder diagrams of alloys intermediate to the single phase regions gave evidence that if any homogeneity ranges exist, they must be quite narrow.

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The Hydrogen Positions in Portlandite, Ca(OH)₂, as Indicated by the Electron Distribution

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X-ray diffraction and Fourier synthesis techniques have been used to determine the electron distribution in a crystal of portlandite with sufficient accuracy to establish the hydrogen positions. The atoms have been found to occupy the following positions:

$$\begin{aligned} \text{Ca} & (0, 0, 0) \\ \text{O} & \pm \left(\frac{1}{3}, \frac{2}{3}, u\right) \\ \text{H} & \pm \left(\frac{1}{3}, \frac{2}{3}, v\right) \end{aligned}$$

with $u = 0.2330 \pm 0.0004$ and $v = 0.395 \pm 0.008$. Independent anisotropic temperature factors were introduced for the calcium and oxygen ions. Also, in the final stages of refinement, systematic differences between the observed and calculated structure factors became apparent and their causes were traced to the Hartree scattering curves for Ca⁺⁺ and O⁻⁻ which were first used in the determination of the calculated structure factors. Semi-empirical scattering curves were derived and their use leads to an excellent agreement between the observed and calculated structure factors. After this work was completed new theoretical values for the scattering factors Ca⁺⁺ and O⁻ became available and these have been compared with the derived semi-empirical values.

Introduction

Portlandite, Ca(OH)₂, and brucite, Mg(OH)₂, are isomorphous and their structures have been known for many years. They possess a simple layer structure in which each cation is at the centre of an octahedron which is defined by hydroxyl ions, one at each corner.

These octahedra may be thought of as joined together in sheets perpendicular to the three-fold axis of the trigonal crystal by having hydroxyl ions in common. The sheets are stacked vertically one above the other. The brucite structure was determined by Aminoff (1919). Megaw (1933) obtained accurate values for the

lattice constants of both brucite and portlandite and located the oxygen ions in portlandite with good accuracy. It was not possible at that time to locate the hydrogen sites by direct methods, but Bernal & Megaw (1935), on the basis of symmetry and electrostatic considerations, proposed that the O-H bonds are perpendicular to the (00·1) plane or rotate about the [00·1] direction.

Renewed interest in these structures was aroused by Mara & Sutherland (1953) who observed that the infra-red absorption spectrum of brucite shows an unexpected band with a very interesting fine structure in the region between 2.3μ and 3.5μ . They concluded that the unit cell must be larger than that found from X-ray analysis and that the positions of the hydrogen atoms had been incorrectly deduced by Bernal & Megaw (1935). Closely similar features were found in the infra-red spectrum of portlandite (Petch & Megaw, 1954). It seemed that it was time for a careful re-examination of the structures of these crystals. The first phase of this re-examination has already been reported in the literature by Petch & Megaw (1954), so it will be sufficient to say that no evidence was found, in either brucite or portlandite, for a unit cell larger than that found in the earlier X-ray work, and that the accepted space group obtained from X-ray data was confirmed. They argued further, mainly on the basis of symmetry, that the hydrogen positions proposed by Bernal & Megaw (1935) are correct, although the possibility of statistically disordered displacements of the hydrogens was not ruled out. In view of the interest in this problem it seemed worthwhile to attempt a direct determination of the hydrogen positions in one of these substances. A preliminary report (Petch, 1955) has been made on an X-ray determination of the hydrogen positions in portlandite and Busing & Levy (1957) have reported a neutron diffraction study of portlandite. Both studies support the hydrogen positions predicted by Bernal & Megaw.

Experimental

It was decided to try to locate the hydrogen positions in portlandite rather than in brucite since some good specimens of portlandite were available, whereas it had been found that brucite crystals were rather poor, giving large composite spots and extended arcs as well as some sharp spots. Portlandite is trigonal with a hexagonal lattice and the space group $P\bar{3}m1$. A single formula-unit occupies each unit cell with the calcium atoms in the invariant positions (0, 0, 0) and the oxygen and hydrogen atoms in the special positions $\pm(\frac{1}{3}, \frac{2}{3}, z)$. The unit cell dimensions (Megaw, 1933) are:

$$c = 4.895 \pm 0.003, \quad a = 3.5853 \pm 0.0007 \text{ \AA}.$$

The specimens of portlandite used in this work came from a single large crystal prepared by the hydration of larnite by Prof. C. E. Tilley, Department

of Mineralogy and Petrology, Cambridge University. The crystal, as originally provided, had the shape of a hexagonal prism and the approximate dimensions $2.5 \times 2.5 \times 7$ mm. From this crystal there had already been cut several thin sections suitable for infra-red absorption experiments as well as one of the specimens used by Petch & Megaw (1954) for their X-ray work. From the remaining pieces two specimens were ground to cylindrical shapes with the following dimensions: No. (1) 0.16×1 mm., No. (2) 0.14×0.8 mm. Crystal No. (1), which had been less carefully ground than No. (2), was not perfectly cylindrical and its axis was at an angle of approximately 10° with respect to one of the crystallographic a -axes. Furthermore the reflexions from this specimen tended to be large and slightly composite in nature. Crystal No. (2) was an almost perfect cylinder with its axis parallel to one of the a -axes. Since they were believed to be the more accurate, the measurements from No. (2) were used for the analysis while those from No. (1) were used to check for extinction because the latter crystal was known to have a large mosaic spread.

The structure of $\text{Ca}(\text{OH})_2$ is such that the only positional coordinates that must be determined experimentally are the z parameters of the oxygen and hydrogen atoms and complete resolution of the atoms could be expected with a projection of the electron density on the $(2\bar{1}\cdot 0)$ plane. The relative integrated intensities of 52 $0k\cdot l$ reflexions were therefore measured with the Geiger-counter X-ray diffractometer described by Cochran (1950) using $\text{Mo } K\alpha$ radiation. The intensity of reflexions beyond $(\sin \theta)/\lambda = 0.76 \text{ \AA}^{-1}$ could not be measured because of the angular limitation of the counter arm. The Geiger-counter was krypton-filled with an alcohol quencher, and a standard scaling unit was used to record the intensities. Considerable care was used to ensure that the crystals were bathed in a uniform X-ray beam as it was found that an intensity gradient across the beam caused systematic differences in the reflexions produced by the same plane in the four reflecting positions. The source of X-rays was a Machlett tube operated at 40 kV. and 20 mA. The X-ray power supply unit was not stabilized, although the filament current and supply voltage could be maintained constant by separate manual controls. It was observed that after an initial warm-up period there was almost no drift over a period of several hours in the filament current and the supply voltage. This was no doubt due to the very light and constant load the electrical system in Cambridge experiences between the hours 11:30 p.m. and 6:00 a.m., an advantage which partially offset the disadvantage of being forced to work such hours by the high γ -ray background due to the cyclotron at other times. The reflexion from (03·1) was recorded at twenty-minute intervals to serve as a check on the constancy of the X-ray source and Geiger-counter efficiency. Within statistical limitations the recorded intensity of this reflexion remained constant.

Crystals No. (1) and (2) were oscillated through angular ranges of $2^\circ 20'$ and 1° respectively about the reflecting orientations, one complete oscillation being made in 1 minute. In each case the slit in the counter shield was of sufficient area to ensure that all reflected characteristic radiation was admitted to the counter. Calibrated Ni foils were used to reduce the intensities of strong reflexions to approximately 2500 counts per minute so that dead time corrections were never greater than 10%. For each reflexion the counts were first recorded with a $0.003''$ Zr foil in front of the slit and then repeated with a 'balanced' film of SrCO_3 . This procedure was used to cancel out the effect of harmonic radiation. At each of the four reflecting positions for every plane, the number of counts recorded, during an integral number of complete oscillations, was sufficient to make the standard deviation of the average count for the plane smaller than 1.2%. This average was taken as the uncorrected relative integrated intensity.

The counter readings were first corrected for dead time losses and then for background, both natural and X-ray. The balanced-filter technique (Ross, 1928) eliminated the effect of all white radiation except that within the wave-length range $0.69\text{--}0.77 \text{ \AA}$ (the wave-lengths of the Zr K and Sr K absorption edges) which was not 'balanced-out' and required a separate correction. Where applicable, corrections were made for the presence of the Ni filters used to decrease the intensity of very strong reflexions. Absorption effects were small in comparison with other possible errors and were neglected in this work. Finally the usual corrections were made for the Lorentz and polarization effects.

Localization of the hydrogen atoms and refinement of the structure

The observed structure factors, F_o 's, were used in an F_o -synthesis to obtain a projection of the electron density in $\text{Ca}(\text{OH})_2$ on the $(21\cdot0)$ plane. The calcium and oxygen ions were completely resolved in this projection. The calcium ions appeared elongated in the c -direction and were surrounded by strong diffraction ripples due to the termination of the Fourier series. In this case the F_o -synthesis is not of much use in determining hydrogen positions because the high electron density, due to the heavy ions, and the presence of the diffraction ripples on the electron density, tend to mask small electron density features such as would be produced by a hydrogen atom.

The $(F_o - F_c)$ -synthesis (Cochran, 1951), in which the F_c 's are calculated on the basis of a model structure not containing the hydrogen atoms, is particularly suited to this problem. Besides showing up the contribution of the hydrogen atoms more clearly, the difference synthesis eliminates, or at least greatly reduces, the effect of Fourier series-termination errors. Difference syntheses in which the F_c 's were calculated

on the basis of a model structure containing only the calcium and oxygen atoms were first used to locate the hydrogen atoms. The technique of the difference synthesis was also used, in the final stages, to refine the z coordinates for the oxygen and hydrogen atoms.

The observed structure factors were placed on an absolute basis by scaling against the calculated values. In the first difference synthesis, the model structure consisted of the calcium ion at the origin of the cell with the oxygens at the positions obtained from the F_o -synthesis. Structure factors were calculated using scattering factors for Ca^{++} and O^{--} from *Internationale Tabellen* modified by an isotropic temperature correction of the form

$$\exp \{ -B [(\sin \theta)/\lambda]^2 \}.$$

The initial value $B = 0.88 \text{ \AA}^2$ was obtained from the slope of the $\log_e (F_o/F_c)^2$ against $(\sin \theta)^2/\lambda^2$. The most prominent features of this first difference synthesis were symmetrical kidney-shaped regions of positive and negative electron density around each calcium position. These features indicated a strongly anisotropic temperature vibration of the calcium ion. Since alternating ripples of positive and negative electron densities spread out from these regions and tended to mask other effects it was necessary to make appropriate corrections.

In succeeding difference syntheses anisotropic temperature corrections

$$\exp \{ -(B_z \cos^2 \varphi_{(0k\cdot l)} + B_x \sin^2 \varphi_{(0k\cdot l)}) [(\sin \theta)/\lambda]^2 \}$$

were applied to the calcium scattering factors. The angle $\varphi_{(0k\cdot l)}$ is that subtended by the c -axis and the line joining the point $(0k\cdot l)$ in the reciprocal lattice to the origin. B_z and B_x are constants proportional to the mean square displacement of the ion in a direction parallel and perpendicular, respectively, to the c -axis.

After corrections had been made for the anisotropic thermal vibrations of the calcium ions, the most prominent feature on the $(\rho_o - \rho_c)$ map was a peak of positive electron density about 0.8 \AA in the c -direction from the oxygen position in the region proposed by Bernal & Megaw (1935) as a hydrogen atom site. However, the peak was superposed on a broad band of positive electron density. At this point a comparison of the F_o 's with the F_c 's (calculated on the basis of a model structure containing the hydrogen atoms as well as the calcium and oxygen atoms) showed that for the $00\cdot1$ and $01\cdot1$ reflexions the F_o 's were smaller than the F_c 's by amounts greater than ten times the standard deviation of the F_o 's. Furthermore, when the F_o 's from crystals No. (1) and (2) were scaled to give the same mean value these same two reflexions from crystal No. (2) were very much smaller than from crystal No. (1). It seemed certain that these two very strong reflexions with small values of $(\sin \theta)/\lambda$ were subject to errors due to extinction although no other reflexions appeared to have been affected. Therefore, in all later difference syntheses either calculated values

or properly scaled reflexions from crystal No. (1) were used for these two terms, 00·1 and 01·1. The immediate effect of this was the removal of the broad positive band of electron density leaving the positive peak well defined.

In the next ($F_o - F_c$)-synthesis the hydrogen atoms were also included in the model structure at the positions suggested by the preceding difference synthesis. The contributions of the hydrogen atoms to the F_c 's were calculated using the Hartree scattering curve for a neutral hydrogen atom which was corrected for thermal vibrations. The temperature corrections were isotropic with $B = 0.7 \text{ \AA}^2$. The result was the complete removal of the prominent peak without changing the background on which the peak had been superposed in the preceding ($\rho_o - \rho_c$) electron density map.

It seemed fairly conclusive that the prominent positive peak represented the electron density due to a hydrogen atom. However there were several points in the background where the electron density, some positive and some negative, was two-thirds that of the largest peak. These humps and hollows in the electron density seemed much too large to be due to experimental errors in the measurement of the integrated intensities. These anomalies led to an investigation of the scattering factors. A plot of ($F_o - F_c$) versus $(\sin \theta)/\lambda$ revealed systematic differences which seemed to be associated with the scattering factors used for the calcium ions. Therefore, a semi-empirical scattering curve was derived by taking the Hartree f curve for Ca^{++} as a first approximation and adjusting it in certain regions of $(\sin \theta)/\lambda$. These adjustments were made in such a way as to bring the F_o 's and F_c 's more nearly into agreement while maintaining a smooth scattering curve with no discontinuities. When

this semi-empirical f curve, modified to compensate for the anisotropic thermal vibrations of the calcium atoms, was used in the calculation of the F_c 's the anomalous humps and hollows in the difference synthesis were reduced to about half their previous heights or depths and the reliability factor $R \equiv \sum ||F_o| - |F_c|| / \sum |F_o|$ was reduced from 0.021 to 0.017. The 'thermal factors', B_z and B_x , were adjusted by trial and error to make $|\rho_o - \rho_c|$ as small and as symmetrical as possible in the region of the calcium ion position at the origin. The final values obtained in this way are listed in Table 1; the estimated probable errors represent the amounts by which the B 's must be changed to produce changes equal to the standard deviation in the electron density in the region of the calcium ion. The semi-empirical scattering factors for Ca^{++} , modified by the temperature corrections, are given in Table 2 for a series of values of $(\sin \theta)/\lambda$.

Although the humps and hollows on the background of the difference synthesis were considerably reduced by the use of the semi-empirical curve for Ca^{++} they

Table 1. *Position parameters and temperature factors with their probable errors*

The neutron diffraction data has been taken from Busing & Levy (1957).

Parameter	X-ray diffraction	Neutron diffraction
z_o	0.2330 ± 0.0004	0.2341 ± 0.0003
z_H	0.395 ± 0.008	0.4248 ± 0.0006
$B_x(\text{Ca})$	$0.68 \pm 0.03 \text{ \AA}^2$	$0.70 \pm 0.07 \text{ \AA}^2$
$B_z(\text{Ca})$	$1.50 \pm 0.03 \text{ \AA}^2$	$1.25 \pm 0.09 \text{ \AA}^2$
$B_x(\text{O})$	$0.89 \pm 0.05 \text{ \AA}^2$	$0.73 \pm 0.05 \text{ \AA}^2$
$B_z(\text{O})$	$0.82 \pm 0.05 \text{ \AA}^2$	$0.93 \pm 0.05 \text{ \AA}^2$
$B_x(\text{H})$	$0.7 \pm 0.7 \text{ \AA}^2$	$4.23 \pm 0.14 \text{ \AA}^2$
$B_z(\text{H})$	$0.7 \pm 0.7 \text{ \AA}^2$	$1.34 \pm 0.10 \text{ \AA}^2$

Table 2. *A comparison of the semi-empirical, Hartree and Freeman scattering factors for doubly ionized calcium*

These values have been corrected to allow for the anisotropic thermal vibrations of the calcium ions
The same temperature corrections were applied to each type of scattering factor

$10^{-8} \times (\sin \theta)/\lambda$	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	
Parallel to c-axis	Semi-empirical scattering factors	16.55	15.11	12.96	11.14	9.72	8.42	7.36	6.43	5.67	4.94	4.28	3.70	3.20
	Hartree	16.5		13.2		10.1		7.3		5.6		4.3		3.2
	Freeman	16.68		13.57		10.23		7.56		5.67		4.30		3.21
Perpendicular to c-axis	Semi-empirical	16.68	15.46	13.45	11.71	10.45	9.35	8.40	7.63	6.96	6.31	5.75	5.24	4.80
	Hartree	16.7		13.6		10.8		8.3		6.8		5.8		4.8
	Freeman	16.82		14.02		11.01		8.62		6.96		5.78		4.84

Table 3. *A comparison of the semi-empirical scattering factors for singly ionized oxygen in $\text{Ca}(\text{OH})_2$ at room temperature with Freeman's theoretical values*

The theoretical values have been modified with thermal factors $B_z = 1.16 \text{ \AA}^2$ and $B_x = 1.22 \text{ \AA}^2$

$10^{-8} \times (\sin \theta)/\lambda$	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	
Parallel to c-axis	Semi-empirical O^-	7.45	6.27	5.18	4.20	3.39	2.77	2.31	1.97	1.70	1.47	1.27	1.11	0.99
	Freeman O^-	7.74		5.50		3.66		2.47		1.73		1.27		0.97
Perpendicular to c-axis	Semi-empirical O^-	7.45	6.27	5.17	4.19	3.37	2.76	2.28	1.95	1.67	1.43	1.24	1.08	0.95
	Freeman O^-	7.74		5.48		3.64		2.44		1.70		1.25		0.94

still seemed larger than one would expect from a consideration of the accuracy with which the integrated intensities had been measured. Careful examination of the F_o 's and F_c 's revealed further systematic differences which were traced to the scattering factors used for the oxygen ions. The Hartree f curve for doubly ionized oxygen had been used in the calculations of the F_c 's. However, with each neutral hydrogen atom (assumed in the use of the Hartree f curve) at a distance of 0.8 Å from its nearest oxygen neighbour, as had been revealed by the difference syntheses, there could be no justification for using the scattering factors for doubly ionized oxygen. In this case it was more difficult to obtain a semi-empirical scattering curve because a theoretical scattering curve for singly ionized oxygen, which might have been used as first approximation, was not available at that time. First an average of the Hartree scattering factors for doubly ionized oxygen and neutral oxygen was used but this resulted in an increase in R and the appearance of new

humps and hollows in the background of the $(\rho_o - \rho_c)$ electron density map. Therefore a semi-empirical scattering curve for singly ionized oxygen was obtained by altering the Hartree scattering curve for doubly ionized oxygen in such a way as to minimize the systematic differences between the F_o 's and F_c 's while maintaining a smooth curve. The F_c 's were then calculated using this semi-empirical f curve modified by anisotropic temperature corrections. This change resulted in a further reduction in R from 0.017 to 0.012 and a smoothing of the $(\rho_o - \rho_c)$ background. The final background, in which the maximum deviation of $|\rho_o - \rho_c|$ from zero is only 2.1 times the standard deviation of the electron density, is shown in Fig. 1(b). Table 3 shows the scattering factors, modified by temperature corrections, used for the oxygen ions in the final difference syntheses. The 'thermal factors', which were adjusted to make $|\rho_o - \rho_c|$ as small as possible in the region of the oxygen positions, had the final values listed in Table 1.

Further difference syntheses were used to refine the z coordinates of the oxygen and hydrogen atoms by adjusting z_o and z_H until $\partial(\rho_o - \rho_c)/\partial z$ vanished at z_o and z_H . In the final stages of refinement it was observed that for the 02.0 reflexion F_o exceeded F_c by more than five times the standard deviation $\sigma(F_o - F_c)$. Therefore, in the belief that it suffered from an unknown experimental error, this reflexion

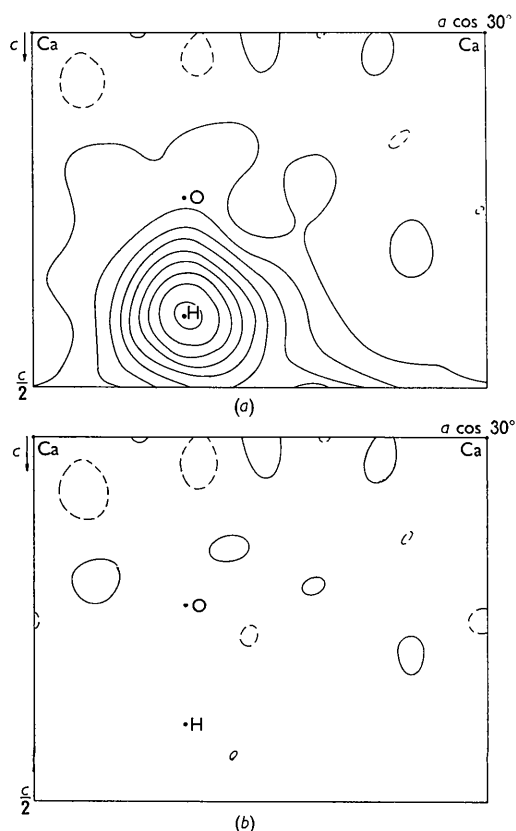


Fig. 1. (a) A projection on the $(2\bar{1}0)$ plane of the electron density in the asymmetric unit of $\text{Ca}(\text{OH})_2$ from which the calcium and oxygen ions have been subtracted. In this $(F_o - F_c)$ -synthesis the values for the F_o 's obtained with crystal No. (2) were used except for the terms (00.1), (01.1) and (02.0). Calculated values of the F_o 's were used for these three terms in place of the observed values. The contours are drawn at every $0.1 \text{ e.}\text{\AA}^{-2}$ with the zero contour omitted and the negative contours dotted. (b) As in (a) except that the hydrogen atom has also been subtracted.

Table 4. Observed and calculated structure factors

The values of F_c include contributions from all atoms, including the hydrogens

$hk\cdot l$	F_o	F_c	$hk\cdot l$	F_o	F_c
00.1	16.53*	16.81	02.5	2.15	2.10
00.2	2.92	3.00	02.6	3.46	3.34
00.3	7.56	7.65			
00.4	11.18	11.17	0 $\bar{2}$.1	14.44	14.47
00.5	7.43	7.35	0 $\bar{2}$.2	11.50	11.51
00.6	2.22	2.09	0 $\bar{2}$.3	4.60	4.61
			0 $\bar{2}$.4	3.26	3.28
01.0	8.15	8.33	0 $\bar{2}$.5	5.80	5.78
02.0	6.78*	6.68	0 $\bar{2}$.6	5.47	5.49
03.0	10.81	10.87			
04.0	4.20	4.16	03.1	7.19	7.23
			03.2	3.30	3.38
01.1	22.59*	23.17	03.3	4.66	4.79
01.2	15.96	16.02	03.4	6.64	6.74
01.3	5.30	5.25	03.5	4.78	4.89
01.4	3.39	3.47			
01.5	6.63	6.71	0 $\bar{3}$.1	7.22	7.23
01.6	6.14	6.14	0 $\bar{3}$.2	3.42	3.38
			0 $\bar{3}$.3	4.79	4.79
0 $\bar{1}$.1	3.62	3.69	0 $\bar{3}$.4	6.74	6.74
0 $\bar{1}$.2	13.93	14.02	0 $\bar{3}$.5	4.92	4.89
0 $\bar{1}$.3	13.88	13.86			
0 $\bar{1}$.4	6.75	6.57	04.1	7.08	6.94
0 $\bar{1}$.5	2.19	2.17	04.2	6.26	6.15
0 $\bar{1}$.6	3.75	3.66	04.3	3.14	3.14
			04.4	2.44	2.40
02.1	4.22	4.25			
02.2	10.27	10.15	0 $\bar{4}$.1	3.25	3.17
02.3	10.79	10.92	0 $\bar{4}$.2	5.68	5.47
02.4	5.54	5.65	0 $\bar{4}$.3	6.29	6.16
			0 $\bar{4}$.4	3.56	3.65

* From crystal No. (1). All others from crystal No. (2).

was also given zero weight in the final synthesis from which the atomic coordinates, listed in Table 1, were obtained. The excellent agreement between the observed and calculated structure factors is shown in Table 4.

The $(\rho_o - \rho_c)$ electron density map, shown in Fig. 1(a), was obtained when the contributions from the hydrogen atoms were not included in the F_c 's and the observed structure factors for the (00·1), and (01·1) and (02·0) planes were replaced by calculated values. The large peak which has a maximum electron density of $0.93 \text{ e.}\text{\AA}^{-2}$ is believed to represent an electron associated with a hydrogen atom. This peak completely disappears, as shown in Fig. 1(b), when the hydrogen atoms are included, at the positions suggested by the peak in Fig. 1(a), in the model structure on which the F_c 's are based. It will be noticed that the background on which the peak was situated has not been changed. To check whether or not the substitution of the calculated values for the three poor reflexions could alone account for this peak, two more syntheses were carried out in which the 00·1, 01·1 and 02·0 reflexions, properly scaled, from crystal No. (1) were substituted for the three poor reflexions. The $(\rho_o - \rho_c)$ maps resulting from these two syntheses are

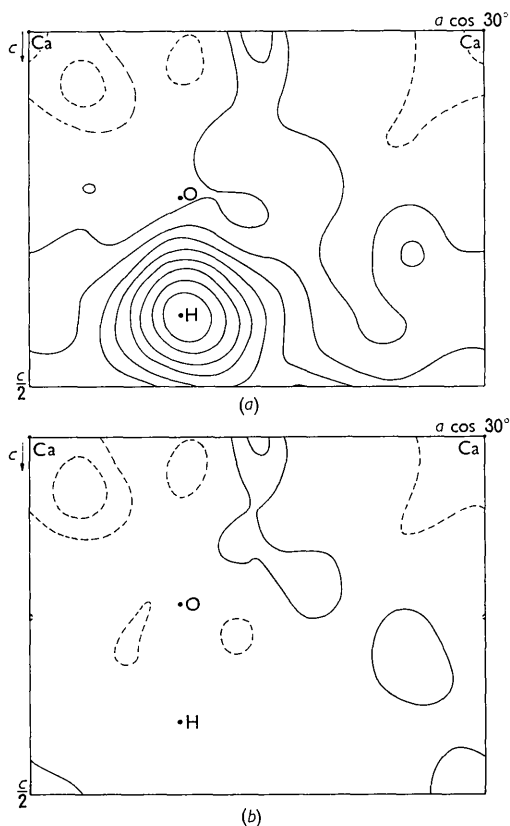


Fig. 2. (a) As in Fig. 1(a) except that the F_o values obtained with crystal No. (1) for the (00·1), (01·1) and (02·0) terms were used in place of calculated values. All the other F_o values were obtained with crystal No. (2). (b) As in (a) except that the hydrogen atom has also been subtracted.

shown in Figs. 2(a) and (b) where the hydrogen contribution has been excluded and included, respectively, in the calculation of the F_c 's. It will be observed that the general features of the $(\rho_o - \rho_c)$ maps remain unchanged although the peak electron density, $0.88 \text{ e.}\text{\AA}^{-2}$, at the hydrogen position is slightly decreased and the background is slightly more undulating.

This is to be expected as the 00·1 and 01·1 reflexions from crystal No. (1) definitely show the effects of extinction, although not nearly as strongly as these reflexions from crystal No. (2). A summation of the electron density over the area covered by the hydrogen atom in Fig. 2(a) shows that 0.79 electrons are associated with each hydrogen atom in $\text{Ca}(\text{OH})_2$.

The standard deviation of the electron density, $\sigma(\rho_o)$, was estimated by using the formula $\sigma(\rho_o) = [(\overline{\rho_o - \rho_c})^2]^{1/2}$ (Lipson & Cochran, 1953) and averaging over the entire areas of the final $(\rho_o - \rho_c)$ maps. The values found from the maps of Figs. 1(b) and 2(b) were 0.05 and $0.08 \text{ e.}\text{\AA}^{-2}$ respectively. These are taken to be lower and upper limits because the three poor reflexions from crystal No. (2) were given zero weight in the calculation of Fig. 1(b) whereas the three reflexions from crystal No. (1), included in the calculation of Fig. 2(b), still show some extinction effects.

The standard deviations of the z coordinates of the oxygen and hydrogen atoms were found by the formula given by Lipson & Cochran (1953), p. 288.

Discussion

It is open to question whether or not the 'thermal factors', B_z and B_x , which were used to modify the semi-empirical f curves, actually represent the true thermal factors applicable to the ions in the crystal at room temperature. There is little doubt that the temperature-modified semi-empirical f curves represent conditions at the atomic sites fairly accurately. However, it may not be fair to try to resolve each scattering curve used in the $(F_o - F_c)$ -syntheses into an f curve which is applicable at absolute zero and a modifying temperature-dependent term even though the scattering curve was originally derived by a two-step process of this kind.

It should also be pointed out that no attempt was made to differentiate between thermal and electron-bonding effects on the electron distribution in the neighbourhood of the ions. The thermal factors may in fact include actual deviations from circular symmetry of the ions in projection due to bond effects but, in the discussion to follow, the thermal factors are assumed to include only effects due to thermal motions of the ions.

In the case of the calcium ions it is believed that the B 's do represent the true thermal factors applicable to the calcium ions because the semi-empirical f curve was derived from the Hartree curve with only minor changes in the region $(\sin \theta)/\lambda = 0.2 - 0.6 \text{ \AA}^{-1}$. Also the best possible fit between a temperature-modified

Hartree curve for Ca^{++} and the experimental curve is obtained when the Hartree curve is modified by temperature factors in which the values for B_z and B_x are identical with the values obtained from the experimental curve. A difference of ± 0.02 in the B 's gives a noticeably poorer fit. A scattering curve for Ca^{++} , taking into account exchange, was made available by Freeman (1957) near the end of this work. Again the best possible fit with the semi-empirical curve is obtained when the experimental values of B_z and B_x are used as temperature factors to modify the theoretical curve. A comparison of the experimental (semi-empirical) f curves for Ca^{++} as used in the $F_o - F_c$ syntheses and the temperature-modified ($B_z = 1.50$, $B_x = 0.68 \text{ \AA}^2$) Hartree & Freeman curves for the directions parallel and perpendicular to the c axis is shown in Table 2.

In the case of the oxygen ions it is much less likely that a B value can be equated to the product of a known constant and the mean square amplitude of vibration of the ion. The reason for this is that the semi-empirical f curve for singly ionized oxygen has a much poorer foundation than was the case for the doubly ionized calcium. Therefore it is more likely that the temperature-dependent term is partly needed to compensate for inadequacies in the semi-empirical f curve for O^- . A comparison of the semi-empirical f curve for singly ionized oxygen as used to represent conditions in $\text{Ca}(\text{OH})_2$ at room temperature and the temperature modified Freeman curve for singly ionized oxygen are shown in Table 3. The temperature factors $B_z = 1.16 \text{ \AA}^2$ and $B_x = 1.22 \text{ \AA}^2$, used with the Freeman curve, were used simply to bring the Freeman values into coincidence with the semi-empirical values at high values of $(\sin \theta)/\lambda$.

The Hartree f curve for atomic hydrogen modified by an isotropic temperature factor with $B = 0.7 \text{ \AA}^2$ was used in the calculation of the structure factors. It is difficult to give a logical justification for the use of the Hartree curve in this case since the whole hydrogen atom lies within the sphere where the electron-density associated with the oxygen atom is still appreciable, and therefore one would expect that each electron cloud would be seriously modified by the other. However, it was convenient to use the Hartree curve as a starting point and, as soon became evident, the experimental accuracy was not great enough to permit an investigation of departures from the Hartree curve. This is because of two reasons: firstly, the f curve drops off so rapidly with $(\sin \theta)/\lambda$ that the contribution from the hydrogens is measurable for only about half the reflexions; secondly, the hydrogen contribution to each reflexion is obtained by subtracting two large and nearly equal terms so the errors involved are large. It was found, for example, that a curve of the form $0.8 \exp \{-12 \text{ \AA}^2 (\sin^2 \theta)/\lambda^2\}$ when used to represent the f curve for hydrogen resulted in a $(\rho_o - \rho_c)$ map almost identical with the map

obtained when the temperature-modified Hartree f curve was used.

The positive peak at (0.333, 0.395) on the $(\rho_o - \rho_c)$ maps in Figs. 1(a) and 2(a) almost certainly represents an electron associated with a hydrogen atom. For a number of reasons it is believed that this peak cannot be due to an accumulation of errors. Firstly, the electron density at this peak is approximately eleven times as large as the standard deviation of the electron density. Secondly, the peak disappears completely when the contributions of the hydrogen atoms are included in the F_c 's. The probability of an accumulation of errors producing not only such a large peak, but also a peak with a shape identical to that of a hydrogen atom in projection, seems impossibly small. Thirdly, the value of the reliability factor R decreases from 0.023 to 0.012 when the model structure, on which the F_c 's are based, also includes the hydrogen atoms at the positions suggested by this peak. The O-H bond is thus perpendicular to the (00.1) plane, as suggested by Bernal & Megaw (1935), with an 'apparent' length of $0.79 \pm 0.04 \text{ \AA}$. It should be noted that the estimated errors in the positions of the oxygen and hydrogen atoms and the O-H bond length were calculated only on the basis of the experimental errors involved in the measurement of the reflected intensities. It is possible that the assumption of a symmetric oxygen ion is not valid and if so a slight shift in the apparent position of the hydrogen atom would result.

Busing & Levy (1957) have located the protons in $\text{Ca}(\text{OH})_2$ by means of neutron diffraction. For ease of comparison, their results have been reproduced in Table 1. The thermal factors obtained by the two techniques do not differ greatly in the cases of the calcium and oxygen atoms. The differences could be attributed to electron-bonding effects although it seems possible that the vibration amplitude of an electron cloud might differ from that of its associated nucleus. Also, the slight difference between the values given by the two techniques for the z coordinate of the oxygen atom is probably not significant. In the case of the hydrogen atom, both the positional and thermal factors differ significantly. Busing & Levy report an 'apparent' O-H internuclear distance of $0.936 \pm 0.003 \text{ \AA}$ as compared to our value of $0.79 \pm 0.04 \text{ \AA}$ for the 'apparent' distance between the maxima in the electron density associated with the two atoms. This is not unexpected since a comparison of C-H, O-H, and N-H distances as revealed by X-ray and neutron diffraction reveals a systematic shortening of the distances suggested by the peaks in the electron density relative to the internuclear distances. Such a shortening has been shown to be theoretically possible (Tomiiie, 1958) and may be accounted for by a movement of part of the electron cloud to the bond. Although the X-ray data is not very sensitive to the thermal vibrations of the hydrogen atom it would be expected that a large anisotropic motion such as that

indicated by the neutron results would be readily apparent. The fact that the electron density associated with the hydrogen atom is almost symmetric in projection suggests that either the electron cloud is strongly affected by the oxygen ion and tends to assume roughly the same vibration state as the oxygen ion or that the asymmetry due to electron bonding effects superimposed on the asymmetry produced by the thermal motion results in a symmetrical electron cloud. The X-ray diffraction results thus complement the picture provided by neutron diffraction.

The apparent O-H bond length in $\text{Ca}(\text{OH})_2$, as determined by X-ray techniques, is also shorter than O-H bonds found in other substances by X-ray methods. For example, Candlin (1956) reported O-H bond lengths of 0.88 Å and 0.91 Å in sodium sesquicarbonate and Cochran (1953) reported a value of 0.91 Å for one of the O-H bonds in salicylic acid. Although it is not unexpected that the O-H bond in $\text{Ca}(\text{OH})_2$ should be shorter than in the above mentioned substances since no hydrogen bonding is involved and, in any case, one expects a hydrogen atom to be more strongly bonded to its own oxygen atom in a hydroxide, it is likely that the effects of the thermal motions account for the major part of this apparent shortening. The apparent O-H distance probably represents the projection along the *c* axis of a longer O-H bond which makes an appreciable average angle of inclination with the *c*-axis. In view of the uncertainties regarding the thermal motion of the electron cloud as discussed in the previous paragraph, it is difficult to estimate the correction that must be applied to our apparent O-H distance. That it is very important is demonstrated by Busing & Levy who have calculated that the true internuclear O-H distance in $\text{Ca}(\text{OH})_2$ is 0.048 Å greater than the apparent distance.

The proton nuclear magnetic resonance spectrum in brucite has been studied by Elleman & Williams (1956) who, by analysing their data in terms of the structure as determined by previous X-ray work, have determined that the protons in brucite are also in the positions proposed by Bernal & Megaw. They obtained a value of 0.98 ± 0.002 Å for the distance between the oxygen nucleus and the proton. It should be added that Mara & Sutherland (1956) have examined the infra-red spectrum of brucite at the temperature of liquid nitrogen and have found that the fine structure

at the low frequency end of the absorption band disappeared. They concluded that this result shows that the bands are combination difference frequencies arising from energy levels due to an exceptionally low O-H deformation mode and that it is possible to explain the spectrum (in principle at least) without invoking a larger unit cell or changing the equilibrium positions of the hydrogen atoms from those proposed originally by Bernal & Megaw.

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