

The Crystal Structure of $\text{Mg}_2(\text{OH})_3(\text{Cl}, \text{Br}) \cdot 4\text{H}_2\text{O}$

BY P. M. DE WOLFF

Technisch Physische Dienst, T.N.O. en T.H., Delft, Holland

AND MME L. WALTER-LÉVY

Université de Paris, France

(Received 3 June 1952)

The triclinic structure of $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}$ has been studied by the method of isomorphous replacement. Atomic positions were derived from a Fourier (010) projection based on powder data, together with such information as could be gathered from the more or less diffuse (*hkl*) reflexions.

The backbone of the structure is formed by puckered layers parallel to (100), consisting of infinite double chains of MgO_6 octahedra extending in the *b* direction. Each octahedron shares two opposite edges with neighbours from its own chain, and two more with the complementary chain.

The oxygens in the corners shared by two octahedra are exactly opposite the corresponding oxygens from adjacent double chains. That explains the linkage between them; half of these corners are occupied by H_2O which is so strongly polarized that it forces the adjacent chain into a spatially uneconomical position. The anions, alternating with an equal number of water molecules so as to form rows $\parallel b$, are situated between the layers. There is a tendency towards disorder in these rows, resulting in typical diffuse-scattering phenomena which are explained in a qualitative way.

1. Introduction

The present structure determination made it necessary first to establish the correct formulae of the compounds to be studied, because their degree of hydration was still uncertain.

The composition of magnesium oxychlorides has been the object of many investigations since the discovery (Sorel, 1867) of a cement, consisting of caustic magnesia and an MgCl_2 solution, whose ability to set and harden is due to the formation of these basic chlorides.

A compound high in magnesia is always the first to precipitate. Lukens (1932) observed that only in the presence of excess solution is the initial product transformed into one of lower basicity, namely $3\text{MgO} \cdot \text{MgCl}_2 \cdot y\text{H}_2\text{O}$ or $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot n\text{H}_2\text{O}$. The water content of the latter salt has been stated as $n = 4\frac{1}{2}$ by Maeda & Yamane (1926); $n = 4$ by Robinson & Waggaman* (1909) and by Bury & Davies (1932), the method of residues being used in all these investigations; and $n = 3\frac{1}{2}$ by Feitknecht & Held (1944).

One of us (Walter-Lévy, 1937) found exactly $n = 4$ by analysis of slowly crystallized precipitates from chloride solutions supersaturated with respect to magnesia, and the same value again from a similar but more direct synthesis (cf. our 1949 (de Wolff &

Walter-Lévy, 1949) paper for a detailed description of this method).

An oxybromide of the same basicity has been discovered by Tassilly (1897), according to whom the formula $\text{Mg}_2(\text{OH})_3\text{Br} \cdot 4\frac{1}{2}\text{H}_2\text{O}$ should obtain. After having studied systematically the formation of this compound as a function of the concentration of the mother liquid, as well as its dehydration as a function of atmospheric humidity, we find that the number of water molecules is 4.

As in the case of the chlorides, a highly basic salt always precipitates first. The compound $\text{Mg}_2(\text{OH})_3\text{Br} \cdot 4\text{H}_2\text{O}$ is formed by a secondary reaction and reaches equilibrium with the mother liquid only after 10 months have elapsed.

2. Experimental details

The preparation of the chloride specimen has been described in our previous paper, cited above. The bromide has been prepared in a similar way, by slow crystallization at room temperature from a solution containing 3.5 mol./l. MgBr_2 in which 2 g./l. MgO had been dissolved previously by boiling. The precipitate was rinsed with alcohol and ether and was dried in air to constant weight under P_2O_5 . Subsequent analysis gave the following results:

$$\begin{aligned} \text{Cl}_2/\text{Mg} &= 0.252, & \text{H}_2\text{O}/\text{Mg} &= 2.73, \\ \text{Br}_2/\text{Mg} &= 0.246, & \text{H}_2/\text{Mg} &= 2.73, \end{aligned}$$

whereas the theoretical values of these ratios are $\frac{1}{4}$ and $\frac{1}{4}$, respectively.

* These authors arrived at a different result ($y = 10$ or $n = 3\frac{1}{2}$) by a trivial error in rewriting their formula $2\text{MgO} \cdot \text{HCl} \cdot 5\text{H}_2\text{O}$; the latter is in accordance with many other data in their paper.

Table 1. *Unit-cell parameters*

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α	β	γ	ρ obs.	ρ calc. (<i>Z</i> = 2)
Mg ₂ (OH) ₃ Cl. 4 H ₂ O	8.65	6.27	7.43	101° 58'	104° 0'	73° 11'	1.859	1.858
Mg ₂ (OH) ₃ Br. 4 H ₂ O	8.99	6.32	7.47	102° 25'	103° 37'	72° 47'	2.125	2.145

The density of both halides has been determined pycnometrically in xylene (see Table 1).

Both salts were obtained in the form of a powder consisting of needle-shaped crystals up to 0.1 mm. long and a few μ thick. They were examined by the powder method, using a fourfold focusing camera of the Guinier type (de Wolff, 1948). A substantial simplification of the indexing problem resulted from the use of orientated samples. A very strong orientation effect was obtained by applying a viscous mixture of the powder and vaseline on the cellophane window of the specimen holder and smoothing this out into a uniform layer by gentle strokes with a razor blade in the desired direction of orientation.

The patterns so obtained for either halide in two orientations, corresponding to the equator and the meridian of a fibre pattern, are shown in Fig. 1. Measurements to within ± 0.1 mm. ($\pm 1\frac{1}{2}'$ in θ) proved sufficiently accurate for indexing, which was performed by a simple analytical method proposed by Ito (1949).

3. Unit cell

Both halides are triclinic. They are isomorphous and form a continuous range of mixed crystals.

Unit-cell dimensions of the chloride have been stated in our previous paper (de Wolff & Walter-Lévy, 1949). At that occasion, however, we did not pay attention to some very faint lines, which we considered to be caused by impurities. Later it appeared that they were essential and that the unit cell obtained by omitting them was not a primitive one. It corresponded to an averaged defect structure which can be avoided only by very careful preparation. This was clearly proved by the bromide specimen showing the crucial lines ($k = 1$ in Fig. 1) with exquisite contrast, whereas they were absent in other specimens prepared without special care. The new unit cell differs from the former one by having a period in the needle or *b* direction twice the old value. The other changes are not essential but are caused by the fact that the innermost reflexion with (new) $k = 1$ turned out to correspond to $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ in the old system. Hence we had to add a vector of $\pm \frac{1}{2}b$ (new) to *a* and *c*. The unit-cell parameters now take the values shown in Table 1.

4. Preliminary conclusions

A needle-like crystal habit with a period of about 6.3 Å in the needle direction is common to many hydrated basic magnesium salts; not only various halides, but also some sulphates as well as the car-

bonate artinite (Heritsch, 1948; de Wolff, 1952). In most of these cases disorder occurs of the kind we described just now, resulting in an apparent *b*-axis length of about 3.15 Å. It is fairly obvious that this value originates from a relationship with the brucite structure, in which the octahedra of oxygen surrounding the magnesium ion have an edge length of 3.11 Å. The above facts are then explained by assuming that these structures contain infinite chains of octahedra with one edge parallel to *b* and sharing the edges perpendicular to *b*. The anions are too large to comply with a period of 3.15 Å. Therefore they have to alternate with water molecules or voids, and in doing so tend to make errors, thus spoiling the odd-layer reflexions for which (to a first approximation) they alone are responsible.

The above picture, part of which was tentatively put forward by Heritsch for artinite, can be completed to a large extent for the halides when considering their unit-cell dimensions. The chains of octahedra must be sharing edges in pairs in order to comply with the formula. The difference between the *a*'s of chloride and bromide is about equal to that of the respective anion diameters, whereas the *c*'s are practically the same. Thus the double chains are evidently arranged so as to form layers parallel to (100) and the anions—alternating with H₂O molecules—are between the layers.

Trial structures based on such considerations as these yielded only a very rough agreement with intensity data. It was therefore decided to apply the method of isomorphous replacement to the (010) projection which, according to the above hypotheses, should practically solve the problem. The presence of two halogen atoms per cell made it necessary first to determine their position. Two independent methods were used: first, utilization of the rather numerous (*h*0*l*) reflexions absent both on the chloride and on the bromide pattern; secondly, a Patterson (010) projection of the bromide. Good agreement was obtained between the two results, the projected Br-Br distance found being $\frac{1}{2}a + \frac{3}{8}c$.

5. Fourier (010) projection

The intensities were measured as peak values on a photometer record. The samples for these measurements had been mixed with starch and made thicker than usual in order to eliminate preferred orientation.

Only 20 observed reflexions were used, reaching up to $\theta = 35^\circ$ for Cu radiation. Beyond this value overlapping of reflexions occurs with rapidly increasing frequency.

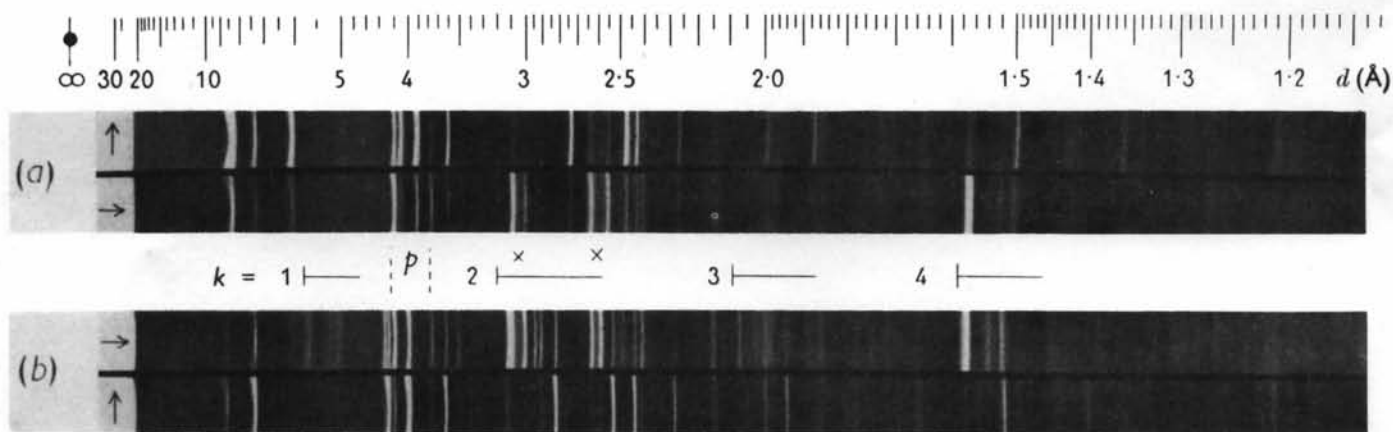


Fig. 1. Powder photographs of (a) $Mg_2(OH)_3Cl \cdot 4H_2O$, and (b) $Mg_2(OH)_3Br \cdot 4H_2O$. The needle-shaped crystallites (needle axis $\parallel b$) have been oriented in the direction of the arrow. Note the layer bands $k = 1, 2, 3, 4$ and the diffuse regions in the second layer band, marked with crosses. The lines p are paraffin reflexions from the binding agent in the sample.

In deriving $|F|$ values from the measurements the non-structural intensity factors were disregarded, except the factor $\sin^2 \theta$ from the Lorentz factor. The values $|F|_0 = (\sin \theta) / I_0$ for the chloride and bromide, both in arbitrary units, were then compared with the

Table 2

hkl	$\sigma F _0^{\text{Br}}$	$ F _0^{\text{Cl}}$	$\sigma F _0^{\text{Br}} - F _0^{\text{Cl}}$	$\cos \varphi_{\text{Cl}}$	Sign F_{Cl}
100	14	44	-30	-0.9	+
001	38	22	+16	+0.4	+
10 $\bar{1}$	6	32	-26	-0.7	+
200	71	52	+19	+0.7	+
20 $\bar{1}$	100	76	+24	+0.9	+
002	76	50	+26	-0.7	+
201	26	26	0	-0.4	\pm
30 $\bar{1}$	91	66	+25	-1.0	-
202	122	104	+18	-1.0	-
10 $\bar{3}$	83	62	+21	+1.0	+
003	35	10	+25	-0.9	-
20 $\bar{3}$	57	44	+13	-0.9	-
40 $\bar{1}$	43	29	+14	+0.9	+
302	45	53	-8	+0.9	-
40 $\bar{2}$	46	26	+20	+0.7	+
401	78	60	+18	-0.9	-
40 $\bar{2}$	44	37	+7	-0.7	-
50 $\bar{2}$	45	37	+8	-0.9	-
30 $\bar{4}$	0	30	-30	+0.9	-
40 $\bar{4}$	78	67	+11	-1.0	-

calculated halogen contribution, and a scaling factor σ was sought which would make the difference $\sigma|F|_0^{\text{Br}} - |F|_0^{\text{Cl}}$ proportional to the latter, thereby assuming the (010) projection to be centro-symmetrical. The amount of agreement which we finally obtained (see Table 2) was thought quite convincing in that respect. The halogen contribution is listed in Table 2 as the cosine of the halogen phase angle.

The chloride was chosen for the Fourier projection because termination effects might be less harmful here. The signs of all $20F$'s except one, namely (201), followed unambiguously from the data in Table 2. A first projection was calculated with F_{201} positive, but a decided improvement was obtained afterwards by changing this sign.

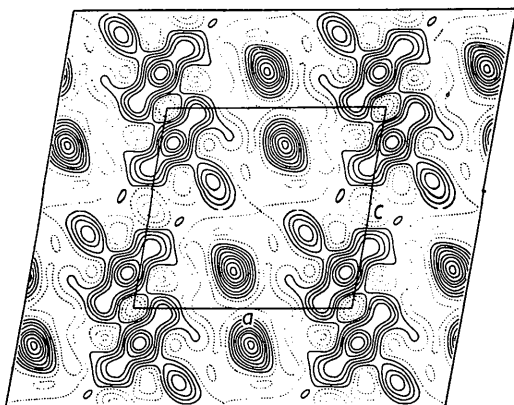


Fig. 2. Fourier (010) projection of $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}$. Contour lines are at equal intervals. Electron density is positive for the full lines and for the first broken line, and zero midway between the first and the second broken lines.

6. Discussion

Notwithstanding the presence of strong termination effects, we recognize in Fig. 2 the unmistakable projection of double chains of octahedra sharing edges, seen end-on. The corresponding maxima have about the same height (note that the zero electron-density level is midway between the first and second broken contour lines) as they should have if magnesium in the usual 6-coordination with oxygen forms the chains, each peak corresponding to two overlapping atoms O+O or Mg+Mg. Of the bruto formula, one O and one Cl is now left. By placing these in overlapping positions to form the remaining oval-shaped peak, good agreement between expected and observed height of the maxima is again obtained. The calculated F values (Fig. 3) were prepared from the coordinates of

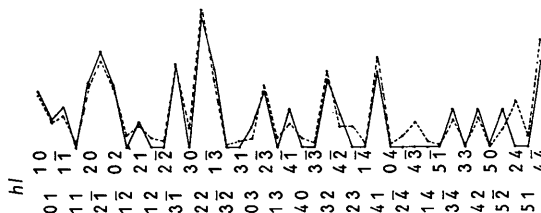


Fig. 3. Observed (full line) and calculated (broken line) values of $|F(h0l)|$ for $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}$.

the maxima (assuming exact superposition of the two atoms concerned except for the Cl-O peak), the Cl coordinates being taken from the Patterson projection and those of O chosen to give the best fit with the projection and with observed intensities.

7. The y coordinates

Since the atoms of the double chain repeat in the y direction with a pseudo-period of $\frac{1}{2}b$, they do not contribute appreciably to the odd layers. Consequently, these offer a simple means for determining the y component of the distance between the two

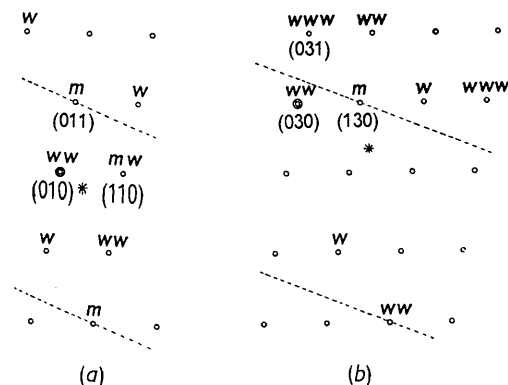


Fig. 4. The reciprocal-lattice planes (a) $k=1$ and (b) $k=3$ of $\text{Mg}_2(\text{OH})_3\text{Br} \cdot 4\text{H}_2\text{O}$, showing observed intensities (w = weak, m = medium). The lines form the locus of points for which the two bromine atoms are in phase. The projection of (000) is indicated with an asterisk.

halogen atoms. An accurate determination is, however, very difficult because many reflexions with k odd show distinct line broadening. In view of these complications we contented ourselves with a qualitative examination of the reciprocal-lattice planes $k = 1$ and $k = 3$ of the bromide (see Fig. 4). From the x and z coordinates we already knew the direction and spacing of the lines on which the bromine ions are in phase. These lines were now drawn through the strongest reflexions in the third layer, after which the corresponding lines in the first layer proved to agree fairly with observed intensities of (hkl) reflexions.

The distance between the two halogen ions being determined in this way, we still had to establish their position with respect to the system of double chains. Even if the space group is $P\bar{1}$ there are two possibilities, for the symmetry centres of the chains (pseudo centres included) repeat at distances of only $\frac{1}{4}b$ and those of the anions with a period of $\frac{1}{2}b$.

Structure factors for the 16 reflexions with $h = 2, 1, 0, \bar{1}$; $k = 2$; $l = 1, 0, \bar{1}, \bar{2}$ were therefore calculated on the assumption that the atoms of the double chains lie in four planes perpendicular to the y axis at $\frac{1}{4}b$ separation, and that the alternating O and Cl atoms have a Cartesian y difference of $\frac{1}{2}b$. Two sets of F 's corresponding to the two above possibilities were computed and compared with actual intensities. The experimental data were qualitative, as before. We found large discrepancies with one of the said possibilities in $P\bar{1}$, but reasonable agreement with the other. Since the space group $P\bar{1}$ is acceptable in other respects too, we finally adopted the latter possibility and were now able to state the positions of all atoms except hydrogen to within an estimated r.m.s. error of ± 0.1 Å (cf. Table 3).

Table 3. Atomic positions in fractional coordinates

	x	y	y_c^*	z
2 Mg	0.055	0.400 0.900	0.375 0.875	0.188
2 OH _{II}	0.144	0.100 0.600	0.125 0.625	0.039
OH _I	-0.042	0.220	0.125	0.316
H ₂ O _I	-0.042	0.720	0.625	0.316
H ₂ O _{II}	0.278	0.861	0.875	0.394
H ₂ O _{III}	0.278	0.861	0.375	0.394
Cl	-0.438	0.812	0.592	0.188
H ₂ O _{IV}	-0.416	0.319	0.092	0.250

* See legend of Fig. 5.

8. Description of the structure; the hydrogen atoms

The structure may be visualized from Fig. 2, together with the schematic plan and elevation of Fig. 5.

From Pauling's rules it follows that the positions alternating with Cl as well as the protruding octahedron corners, must be filled by H₂O_{IV}, and H₂O_{II} and H₂O_{III} respectively. The corners shared by three octahedra can only be occupied by OH_{II}. For those shared by only two, there remain 1 OH_I+1 H₂O_I. The best electrostatic balance is obtained by letting these alternate in the same way as Cl and H₂O_{IV}. This can be effected in four ways, two of which can at once be discarded because they lead to water molecules disposed with the hydrogen atoms towards each other. Of the remaining possibilities, the configuration with Cl joining H₂O_I and H₂O_{IV}, OH_I seems much more probable than the other in which alternate H₂O-H₂O and OH-Cl bonds would be formed; hence the former was definitely adopted.

The characteristic feature of the structure appears to be that these rows of hydroxyl and water exactly face the ones from the neighbouring chains and are at the same level instead of fitting in the holes of the opposite row. The oriented binding forces which must be responsible for this situation are readily explained by the well known tetrahedral environment of H₂O_I: the two magnesium ions to which it is bound are separated by a vector $\frac{1}{2}\mathbf{b}$ so that the bond to the opposite OH_I must lie in a plane perpendicular to \mathbf{b} . The same should then be true for the fourth bond, the one with chlorine, and that is indeed what we find. The bond angle OH_I-H₂O_I-Cl of 111° is fairly near its theoretical value.

The elongation of the octahedron edges parallel to b (3.15 Å) compared with the brucite value (3.11 Å) may well be ascribed to the H₂O_I-Mg bonds tending to make an angle more near the theoretical 110° than the 90° between the corresponding bonds in brucite. Actually a value of 99° is found for this angle. The OH_I ions are of interest because they, too, have a tetrahedral environment, which seems to indicate the formation of hydroxyl bonds towards the adjoining H₂O_{IV}; the observed bond length of 2.9 Å is, however, rather large. The distance between opposite rows H₂O_I+OH_I is 2.65 Å. Starting from these rows the directions of all O-H vectors but one can be determined unambiguously so that they point either to a chlorine ion or to one of the negative poles of another water molecule or hydroxyl group.

The one exception is formed by one half of the unshared octahedron corners, H₂O_{II} in Fig. 5. These water molecules must have one proton (H¹ in Fig. 5) directed towards a Cl ion. The direction of the second proton (H²) is then determined by the double Mg-OH₂ bond and the tetrahedral angle, and is found to point to a region midway between the negative poles of the adjoining H₂O_{IV} molecules. These poles are linked themselves in a normal way through protons to other oxygens and form the usual roughly regular tetrahedron with the latter H₂O_{IV}'s protons pointing to neighbouring chlorine ions.

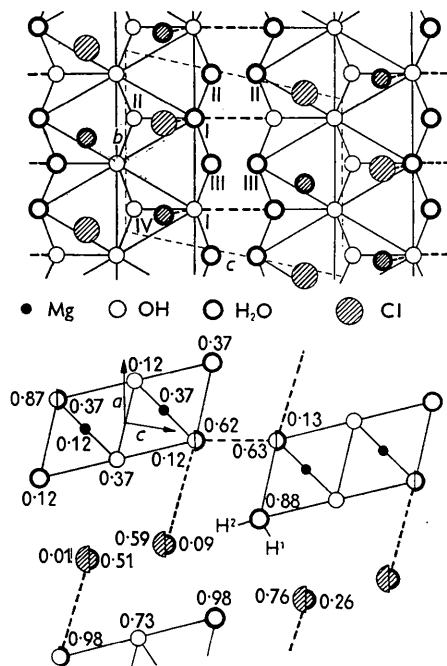


Fig. 5. The structure viewed in a direction in the plane (001) perpendicular to b (above), and parallel to b (below). Only two double chains have been drawn. The atoms between the double chains are shaded for clarity; for the same reason those behind and within the chains are not shown in the upper part. The coordinates in the lower part refer to a Cartesian system with the same origin and y axis as the crystallographic one (y_c in Table 3).

9. Diffuse scattering

Though the zone $k = 0$ is very clear, the horizontally oriented patterns of Fig. 1 show strong diffuse scattering in the 'layer bands', especially for $k = 2$.

In this band, two diffusely blackened regions appear in a position which can be explained by assuming diffuse rods in the reciprocal lattice, each rod having a constant l value. The first region is caused by $h20$ and $h2\bar{1}$, the second by $h21$ and $h2\bar{2}$. This leads us to the conclusion that the structure contains layers parallel to (100) stacked without complete periodicity. The displacements have to be parallel to b (otherwise

the equator would also show some effect), and the sharpness of the $k = 2$ lines suggests that they are at random. The layers are obviously those formed by the double chains of octahedra.

The odd-layer bands are remarkable because of the line broadening they show. This would point to defective periodicity in the halogen-water rows, in accordance with the fact already stated that these odd-layer bands appear only with carefully prepared specimens.

On that assumption the diffuse regions for $k = 2$ may be explained as follows: The primary cause is disorder in the system of halogen-water rows, which introduces a certain amount of strain in the structure. Now each layer of double chains is in itself a comparatively rigid unit so that it will have to yield to this strain as a whole. Displacements in the a - or c -direction would involve changes in bond lengths; but a shift parallel to b merely requires bond-angle variations of the weakly polarized water molecules bound to less than two magnesium ions. Hence the resulting deformation will consist chiefly of such mutual shifts, of which the diffuse regions mentioned above are the direct consequence.

References

- BURY, C. R. & DAVIES, R. H. (1932). *J. Chem. Soc.* **135**, 2009.
 FEITKNECHT, W. & HELD, F. (1944). *Helv. chim. Acta*, **27**, 1480.
 HERITSCH, H. (1948). *Miner. petrogr. Mitt.* (3), **1**, 150.
 ITO, T. (1949). *Nature, Lond.* **164**, 755.
 LUKENS, S. (1932). *J. Amer. Chem. Soc.* **54**, 2372.
 MAEDA, T. & YAMANE, S. (1926). *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **4**, 99.
 ROBINSON, W. O. & WAGGAMAN, W. H. (1909). *J. Phys. Chem.* **13**, 673.
 SOREL, PH. J. (1867). *C. R. Acad. Sci., Paris*, **65**, 102.
 TASSILLY, E. (1897). *C. R. Acad. Sci., Paris*, **125**, 605.
 WALTER-LÉVY, L. (1937). *C. R. Acad. Sci., Paris*, **204**, 1943.
 WOLFF, P. M. DE & WALTER-LÉVY, L. (1949). *C. R. Acad. Sci., Paris*, **229**, 1232.
 WOLFF, P. M. DE (1948). *Acta Cryst.* **1**, 207.
 WOLFF, P. M. DE (1952). *Acta Cryst.* **5**, 286.