indicates that the type 4H must have been formed in the initial stages of crystal growth and later transformed into the rhombohedral polytype 12R owing to layer displacements. This explanation is supported by the X-ray photographs of the second crystal, which was similarly found to be a mixture of type 12R (upper part) and 4H (lower part) in syntactic coalescence with each other. The arcing was found to be present to an even greater degree. The third crystal was identified as a mixture of 12R and 16H in syntactic coalescence with each other. It could not be ascertained in this case which of these belonged to the upper or lower part, respectively, of the crystal. However, the formation of a type 12R from 16H, or *vice versa*, can, in principle, be understood on the basis of layer-transposition mechanism.

Out of the two possible structures of 12R, the formation of structure (a) is less probable than the structure (b) theoretically also. The structure (b) is formed by slip between the molecular sheets themselves which are held together by weak van der Waals forces of attraction and can therefore easily slip with respect to one another under a small stress. The creation of

structure (a) will need the mutual displacements of layers within a molecular sheet itself, which is highly unlikely as the forces within a sheet are purely ionic in nature giving rise to a strong binding.

The type 12R, because it can be generated from the common type 4H, should be expected to occur more frequently than any other rhombohedral polytype of cadmium iodide. This conclusion is substantiated by the observation of three crystals of this type.

References

AGRAWAL, V. K. & TRIGUNAYAT, G. C. (1967). *Z. Kristallogr.* In the press.
CHADHA, G. K. & TRIGUNAYAT, G. C. (1967). *Acta Cryst.* **22**, 573.
JAGODZINSKI, H. (1954). *Neues Jb. Miner.* **3**, 49.

The Crystal Structure of Pyroaurite*

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Rhombohedral pyroaurite ($R\bar{3}m$, $a=3\cdot1094\pm2$, $c=23\cdot4117\pm9$ Å, at 21°) consists, like hexagonal sjögrenite ($P6/mmc$, $a=3\cdot113\pm3$, $c=15\cdot61\pm1$ Å), of positively charged brucite-like layers $[Mg_6Fe_2^{III}(OH)_{16}]^{2+}$ alternating with disordered negatively charged interlayers $[CO_3.4H_2O]^{2-}$ ($Z=\frac{2}{3}$ for pyroaurite). Mg and Fe are randomly distributed among the octahedral positions. The OH layer sequence in pyroaurite is $-BC-CA-AB-BC-$. The water molecules of the (liquid-like) interlayer prefer positions about 0·56 Å off the threefold axis connecting two OH groups of adjacent brucite-like layers. The following distances were found: Me–OH 2·06, OH–OH 2·72 (3×) and 3·11 (6×), OH–H$_2$O 2·93 Å; ∠ OH–H$_2$O–OH 158°. During the refinement with 283 reflections the residual dropped to $R=6\cdot1\%$. The interlayer only contributes to the 00*l* and 10*l* reflections.

Introduction

The carbonate-hydroxides $Mg_6M_2^{III}(OH)_{16}CO_3.4H_2O$ ($M^{III}=Fe$, Al, or Cr) are known to occur in two dimorphic forms: the hexagonal sjögrenite group has $a\sim3\cdot1$ and $c\sim15\cdot5$ Å; the rhombohedral pyroaurite group has the same a value but c is about 23·2 Å (Aminoff & Broomé, 1930; Frondel, 1941). The two forms are very similar in their physical properties and are therefore nearly indistinguishable without the help of X-rays. According to Frondel (1941) the species in this group of minerals are the following:

M^{III}	Space group $R\bar{3}m$	Space group $P6/mmc$
Fe	Pyroaurite	Sjögrenite
Al	Hydrotalcite	Manasseite
Cr	Stichtite	Barbertonite

The best single crystals are available for the iron compounds sjögrenite and pyroaurite. The crystal structure of the hexagonal sjögrenite has already been reported (Allmann & Lohse, 1966: $a=3\cdot113\pm3$, $c=15\cdot61\pm1$ Å). It consists of positively charged brucite-like layers $[Mg_6Fe_2(OH)_{16}]^{2+}$ and negatively charged interlayers $[CO_3.4H_2O]^{2-}$. Since it consists of two kinds of layer this structure has been called a *hybrid layer structure* (Evans & Allmann, 1967). The brucite-like layers are stacked very regularly and form the backbone of the structure. These layers are separated by

single layers of oxygen atoms (hereafter called inter-layers) representing water molecules and carbonate groups, which are extensively disordered in their positions. Preferred loci for these oxygen atoms could be found at about 0·5 Å radially distant from the three-fold axes that connect the OH groups of two adjacent brucite layers. No preferred positions could be found for the carbon atoms of the carbonate anions.

The CO_3^{2-} anions are situated horizontally within the interlayer planes. According to the given formula, 8 unit meshes of one interlayer contain 4 water molecules and one carbonate anion. Because a non-rotating CO_3 group needs the place of only 3 unit meshes, there is room for one more water molecule. This fifth water molecule would raise D_x from 2·10 (for $4H_2O$) to 2·16 g.cm^{-3} (for $5H_2O$). The presence of some excess water is indeed indicated by many analyses as well as by the measured density of 2·11 g.cm^{-3} (Frondel, 1941, reports 2·11 for sjögrenite and 2·14 for pyroaurite).

The aim of the present structure determination is to find out whether, besides the difference in the layer stacking, there are significant structural differences between sjögrenite and pyroaurite in the layers themselves. Furthermore pyroaurite is a model structure for many synthetic hydroxides and hydroxy-salts (e.g. Feitknecht, 1953); two of these have already been found in nature: $4Ni(OH)_2.NiOOH$ (Jambor & Boyle, 1964) and $4Mg(OH)_2.(Ni,Fe)OOH$ (Lapham, 1965). Eardleyite, $(Ni,Zn)_6Al_2(OH)_{16}CO_3.4H_2O$, also may have the same structure (Anderson & Whelan, 1962).

Experimental

Platy samples of sjögrenite-pyroaurite from Långban, Sweden, were studied in this investigation. Mostly they were intergrowths (001) [100] on (001) [100] of the two phases, pyroaurite forming the outermost layers, i.e. the layers grown last. Precession photographs of the easily oriented plane $(001)_0^*$ showed whether the crystal under examination was pure pyroaurite or not. If not, medium strong 100 reflections occurred besides the strong 110 reflections. Then the crystals were adjusted with a^* parallel to the dial axis and an $(010)_0^*$ pattern was taken. This is the best plane in reciprocal space to decide whether one is dealing with sjögrenite, pyroaurite, or an intergrowth of the two (Fig. 1). By comparing the intensities of hexagonal and rhombohedral reflections one can also estimate the relative amount of each phase. The $(1\bar{1}0)_0^*$ pattern is exactly the same for both phases and therefore cannot be used to distinguish them. Furthermore, because the two structures differ only in the stacking sequence, all rows parallel to c^*
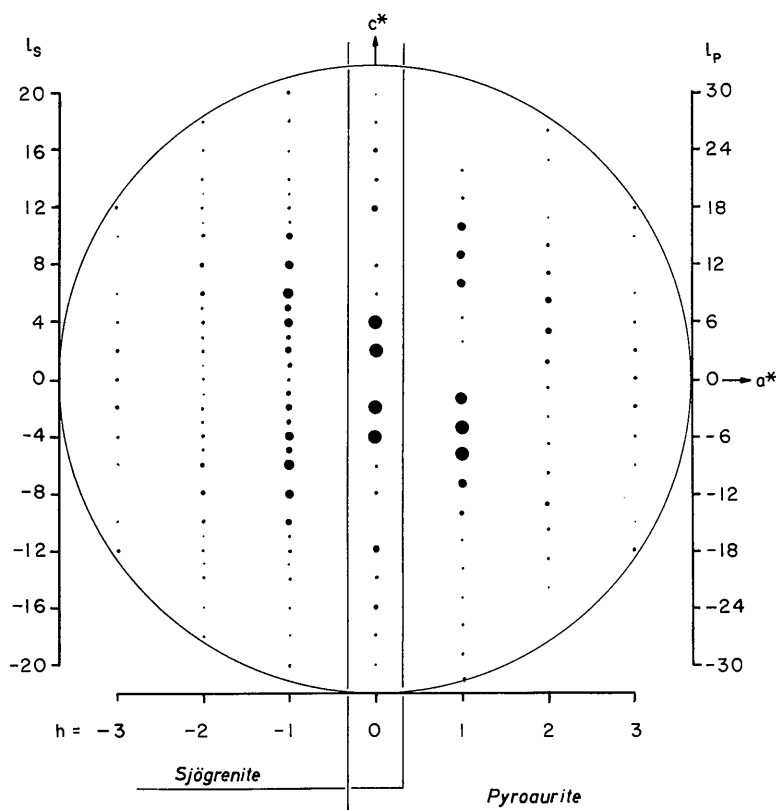

Fig. 1. Reciprocal lattice planes $(010)_0^*$ of pyroaurite (right half of the Figure with $h=0, 1, 2, 3$) and sjögrenite (left half with $h = -3, -2, -1, 0$), as obtained by precession films with Mo $K\alpha$ radiation and $\mu=30°$.

with $-h+k=3n$ are identical for the two phases. So, for instance, the rows $[001]_{00}^*$ and $[001]_{30}^*$ of the $(010)_0^*$ net are also indistinguishable.

With the use of precession photographs as a guide, an intergrowth of pyroaurite and sjögrenite was cut with a razor blade parallel to (001) until a piece of pure pyroaurite remained. It had the following dimensions: 0.06 (c) $\times 0.2$ (b^*) $\times 0.3$ (a) mm^3. This single crystal was used for the intensity measurements and for getting the following data:

$a = 3.1094 \pm 2$, $c = 23.4117 \pm 9 = 3 \times 7.8039 \pm 3$ Å

Formula $[Mg_6Fe_2^{III}(OH)_{16}]^{2+}[CO_3 . 4H_2O]^{2-}$

$V = 196.02$ Å^3, $Z = 3/8$

$D_m = 2.13 \pm 1$, $D_x = 2.102$ g.cm^{-3}

Space group $R\bar{3}m$.

The lattice constants were obtained at 21 °C from a $(010)_0^*$ back-reflection Weissenberg film with Cu $K\alpha$-radiation ($\lambda\alpha_1 = 1.54051$, $\lambda\alpha_2 = 1.54433$ Å) and were refined with the help of the least-squares program LCLS of C. W. Burnham.

Because of the non-integral value of Z, Frondel (1941) had doubled the values for both a and c, thus getting $Z = 3$. But there are no reflections even on overexposed films to justify this doubling. If there is an ordering of Mg and Fe, which differ considerably in scattering power, at least some additional weak reflections should occur indicating this ordering. But even in the small cell found by X-rays one gets an integral Z value for the brucite layers, if one writes it $(Mg, Fe)(OH)_2$. Then Z equals 3. The interlayer, however, is completely disordered and behaves more like a liquid. This will be discussed later. Because of the statistical distribution of Mg and Fe in the brucite

layer, the formula need not be stoichiometric and the ratio Mg:Fe may well differ from 3:1.

The X-ray intensities were measured on an automatic Supper–Pace diffractometer with [100] as rotation axis: equi-inclination Weissenberg principle, Mo $K\alpha$ radiation, Zr filter, step scanning. 744 reflections in the four layers $(100)_i^*$, $i = 0, 1, 2, 3$ were measured and corrected for absorption ($\mu = 17.3$ cm^{-1}) by the GNABS program of C. W. Burnham. Equivalent structure factors were then averaged, yielding a set of 283 independent F_o values (Table 1). 87 reflections were measured once, 109 twice, 6 three times, 58 four times, and 23 five or more times. 22 reflections out of these 283 were too weak to be measurable.

The symmetry in reciprocal space is somewhat higher than required by the Laue group $\bar{3}m$, because $F(hkl)$ equals $F(hk\bar{l})$ not only for the hhl reflections, but for all reflections with $-h+k=3n$. These reflections were also considered to be equivalent and were averaged before being included in the final set of 283 independent reflections. This special symmetry is possible only if all atoms are placed on threefold axes or if their z coordinates are equal to $n/6$, n integral.

Structure refinement

It was already known (Allmann & Lohse, 1966) that the sequence of the OH layers in pyroaurite is $-BC-CA-AB-BC-$ and not the only other possibility $-CB-AC-BA-CB-$ (A, B, C standing for the three threefold axes in $x, y = 0, 0; \frac{2}{3}, \frac{1}{3}; \frac{1}{3}, \frac{2}{3}$). Therefore the refinement could be started with already good approximations. The same scattering factors were used as for sjögrenite: O^- and $\frac{1}{4}(3Mg^{2+} + Fe^{3+})$ from *International*

Table 1. *Observed (F_o) and calculated (F_c with interlayer, F_c' without interlayer) structure factors of pyroaurite*

The sequence of the columns is l, $k \times F_o$, $k \times F_c'$, $k \times F_c$, if four columns (*i.e.* for 00l, 10l, 11l, and 20l); and l, $k \times F_o$, $k \times F_c$, if three columns ($k = 60.47$ if referred to the hexagonal cell setting). The unobserved reflections are given as $F_{min}/\sqrt{3}$ and are marked by *.

Tables for X-ray Crystallography (1962). The interlayer, $\frac{1}{8}CO_3 + \frac{1}{2}H_2O$, was approximated by an O^- ion at $0,0,\frac{1}{2}$ with a high thermal vibration perpendicular to [001]. The unobserved reflections were included with their most probable value: $F_{min}/\sqrt{3}$. With anisotropic temperature factors the residual dropped in four cycles of least-squares refinement to $R = 6 \cdot 1\%$ ($R = 5 \cdot 8\%$ for the observed reflections alone) (program of Busing, Martin & Levy, 1962). The final coordinates and temperature factors ($Å^2$) are compared with the starting parameters taken from the sjögrenite structure in Table 2. Next an attempt was made to approximate the interlayer by distributing the pseudo-ion O^- over six sites of position $18(g)$ in $0 \cdot 185, 0, \frac{1}{2}$. These points are on twofold axes about $0 \cdot 56$ Å off the threefold axis through $0, 0, \frac{1}{2}$. The parameters of (Mg, Fe) and OH did not significantly change in this refinement; for the $\frac{1}{6}O^-$ in $18(g)$, B_{11} became $10 \cdot 6 \pm 16$ and B_{33} $2 \cdot 42 \pm 26$. The residuals were the same as for the first approximation ($6 \cdot 1\%$ and $5 \cdot 8\%$).

The calculated standard deviation of z_{OH} is only $\pm 0 \cdot 002$ Å. This value really may be somewhat higher, but z_{OH} is the only positional parameter to be refined using the set of the 283 measured reflections. Even if
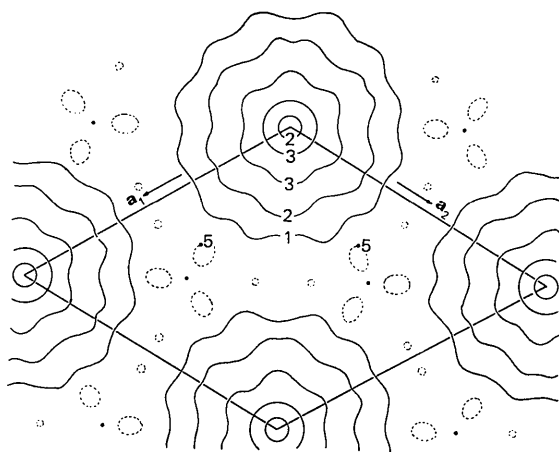
Fig. 2. Electron density section ϱ $(x, y, \frac{1}{2})$ of pyroaurite through the interlayer in e.$Å^{-3}$. The electron density is everywhere positive; the 0·5 line is broken.

$\sigma(z_{OH})$ is greater than $\pm 0 \cdot 002$ Å, the standard deviations of the distances given in Table 4 will still be less than $0 \cdot 01$ Å.

If the interlayer is omitted in structure-factor calculations, the residual becomes $R = 10 \cdot 6\%$. By comparing the rows separately, one can see that the interlayer contributes only to the $00l$ and $10l$ reflections, as was found in sjögrenite too (Table 3).

In Table 1 the observed and calculated structure factors are given with inclusion of the approximated interlayer (parameters in Table 2). For the reflections $00l$, $10l$, $11l$, and $20l$, F_c values also are given, which have been calculated without the interlayer.

If the interlayer were completely disordered, only the $00l$ reflections would be affected by it. Its influence on the $10l$ reflections, however, shows that there is a concentration of scattering matter around $(0, 0, \frac{1}{2})$. This can best be seen on the electron density section $\varrho(x, y, \frac{1}{2})$ (Fig. 2; for comparison: $\varrho(0, 0, 0) = 116$ e.$Å^{-3}$) and on the electron density projection $\varrho(x, z)$ (Fig. 3).

Description and discussion of the structure

Pyroaurite is built up of brucite-like layers $[(Mg, Fe^{III}) (OH)_2]^{0 \cdot 25+}$ with an OH sequence $-BC-CA-AB-BC-$. The distance between two adjacent metal layers equals $c/3 = 7 \cdot 80$ Å. Because the brucite layers are only about $4 \cdot 9$ Å thick, an empty space of about $2 \cdot 9$ Å is left between them. This space is occupied by a disordered interlayer $[\frac{1}{8}CO_3 + \frac{1}{2}H_2O]^{0 \cdot 25-}$. The water molecules prefer a place about $0 \cdot 56$ Å from the line connecting two adjacent OH groups. $0 \cdot 56$ Å is the mean square thermal displacement resulting from $B_{11} = 31$ $Å^2$. About the same value follows from the interpretation of Fig. 2.

The interatomic distances that result from the given coordinates, with interlayer H_2O in position $18(g)$: $0 \cdot 185, 0, \frac{1}{2}$, are given in Table 4. The distances parallel to the z axis between layers are the same in pyroaurite and sjögrenite: Mg, Fe layer to OH layer $1 \cdot 02$ Å; between OH layers in brucite layer, $2 \cdot 04$ Å; OH layer to interlayer, $2 \cdot 88$ Å.

The thermal vibrations are also very similar (Table 3). The metal ions and OH vibrate both more in the direc-

Table 2. *Atomic coordinates and anisotropic temperature factors* ($Å^2$)*for pyroaurite*

The starting parameters were taken from the sjögrenite structure.

		Final parameters					Starting parameters		
		x	y	z	B_{11}	B_{33}	z	B_{11}	B_{33}
(Mg, Fe)	in $3(a)$	0	0	0	$0 \cdot 58 \pm 3$	$1 \cdot 35 \pm 3$	0	$0 \cdot 49 \pm 2$	$1 \cdot 22 \pm 3$
OH	in $6(c)$	0	0	$0 \cdot 37693 \pm 7$	$0 \cdot 87 \pm 4$	$1 \cdot 34 \pm 4$	$0 \cdot 37680 \pm 7$	$0 \cdot 51 \pm 3$	$1 \cdot 06 \pm 5$
O^-	in $3(b)$	0	0	$\frac{1}{2}$	$30 \cdot 8 \pm 20$	$2 \cdot 29 \pm 24$	$\frac{1}{2}$	$31 \cdot 8 \pm 22$	$1 \cdot 56 \pm 27$

Table 3. *Values of residual R (%) calculated, with and without the interlayer, for different numbers (N) of reflections*

	All reflections	All but $00l$	All but $00l$ & $10l$	$00l$ only	$10l$ only	$11l$ only	$20l$ only
N	283	267	235	16	32	16	31
R without interlayer	10·6	7·6	5·6	37·5	15·0	5·0	4·2
R with interlayer	6·1	5·9	5·6	7·9	7·4	4·5	4·4

tion [001] than perpendicular to it. The vibration of the interlayer atoms in direction [001] is fairly well represented by B_{33} of the pseudo-atom and is only somewhat higher than the corresponding vibrations in the brucite-like layer. About the vibrations of the interlayer in the (001) plane, nothing can be said because of the approximate character of the calculations. The interlayer can best be visualized as being in permanent motion, the H_2O and CO_3 changing their places by forming new hydrogen bonds and disconnecting old ones, just as the water molecules do in the liquid state. Hydrogen bonds do not exist only within the interlayer, but weak ones also go from the hydroxyl groups of the brucite layer to the interlayer.

Because there exists approximately 2·9 Å of free space between two consecutive brucite layers, the carbonate groups can only lie horizontally within the interlayer planes. This conclusion is further confirmed by the optical properties of pyroaurite: $n_O = 1·564$, $n_E = 1·543$ (Frondel, 1941). Manasse (1915) reports $n_O = 1·562$, $n_E = 1·529$. Some calculations to estimate n_O and n_E for the two cases of horizontal and of vertical carbonate groups showed that for a structure with vertical CO_3^{2-} groups the birefringence should be nearly zero or even slightly positive. For a structure with horizontal carbonate groups, however, the estimation gave a negative birefringence of about the observed values.

Comparison of pyroaurite and sjögrenite

The great similarities in the structures of the single layers and in the thermal behavior of the atoms between the two phases have already been mentioned. The configuration of the first neighbors is the same for all atoms; the configurations of the second and third nearest neighbors are the same for the metal ions; and those of the second nearest are the same for the OH ions in pyroaurite and sjögrenite. The lattice energies of the two structures should therefore be very similar and the question arises, why is the stacking so regular that it uses only one or the other of the two stacking modes? In the specimens from Långban, that I examined, no mixed-layer structures could be found. If there was an intergrowth of the two phases, the inner part of the edifice was hexagonal sjögrenite, the outer part, rhombohedral pyroaurite. This means that the crystal growth started with the hexagonal sequence $-BC-CB-BC-$. After some time it switched over to the rhombohedral sequence $-BC-CA-AB-BC-$, but at no time was there any switch back to the hexagonal mode.

This can best be explained by assuming a decreasing temperature during the formation of the sjögrenite-

pyroaurite crystals. Sjögrenite is formed at higher temperatures, pyroaurite at lower ones. But once it is formed, sjögrenite will not transform to pyroaurite at lower temperatures because of a presumably large energy barrier between the two configurations and because of the very small possible gain in lattice energy.

All hydroxides and hydroxy-salts obtained by Feitknecht (1953) by precipitation in aqueous solutions belong to the rhombohedral type, thus also indicating that this type is the low temperature form.

Discussion of some related structures

A survey of other hybrid layer structures has been given in the sjögrenite paper (Allmann & Lohse, 1966). Here some newly found minerals with pyroaurite struc-
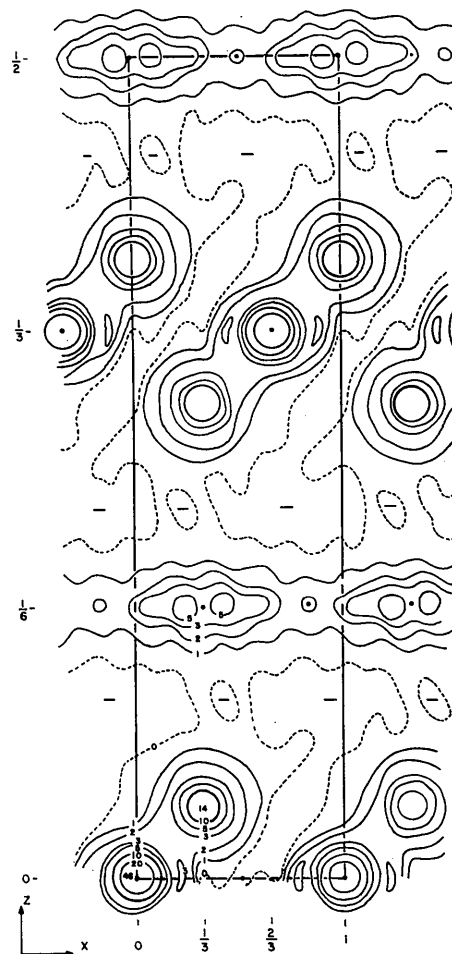

Fig. 3. Electron density projection $\varrho(x, z)$ of pyroaurite in e.Å^{-2}. The zero line is broken. (Mg, Fe) reaches $\varrho_{max} = 46$ e.Å^{-2}, OH 14, and the interlayer only 5 e.Å^{-2}.

Table 4. *Interatomic distances and angle* OH–H$_2$O–OH

Distance	Me–OH	OH–OH 3×	OH–OH 6×	OH–H$_2$O	∠OH–H$_2$O–OH
Pyroaurite	2·065	2·72	3·11	2·93 Å	158°
Sjögrenite	2·06	2·72	3·11	~2·92	~160

ture will be discussed. A large number of hydroxides and hydroxy-salts crystallizing in this structure have been described by Feitknecht (1953). The length of the a axis is always about 3·1 Å, varying somewhat with the nature of the cations in the brucite-like layer; the length of the c axis ($3 \times 7\cdot6$ Å or larger) depends mostly on the nature of the anions in the interlayer. Some of these compounds have recently been found in nature.

Jambor & Boyle (1964) describe a pulverulent yellow nickel hydroxide, $4Ni(OH)_2.NiOOH$, with $a=3\cdot07$, $c=22\cdot74$ Å. The assumed formula stems from Glemser & Einerhand (1950), who synthesized blue-black $Ni^{II}Ni^{III}$ hydroxides by anodic precipitation and found: $a=3\cdot07$, $c=23\cdot2$ Å, $D_m=2\cdot95$, $D_x=2\cdot96$ (I find $D_x=3\cdot04$). Referred to one Ni, the proposed formula becomes $NiO_{1\cdot1}.0\cdot9H_2O$. But Glemser & Einerhand themselves give the following analyses for varying grades of oxidation: $NiO_{1\cdot22}.1\cdot53H_2O$, $NiO_{1\cdot12}.1\cdot48$ H_2O, and $NiO_{1\cdot07}.2\cdot03H_2O$. Because of this excess of water found by analysis no O^{2-} ions should occur in these compounds and the formula should be written at least as $4Ni(OH)_2.Ni(OH)_3$ or $NiO_{1\cdot1}.1\cdot1H_2O$, with $D_x=3\cdot16$. As assumed by Glemser & Einerhand, $Ni(OH)_3$ forms the interlayer with one such formula spreading over four unit meshes. This would allow one more water molecule to enter the interlayer, thus resulting in the formula $4Ni(OH)_2.Ni(OH)_3.H_2O$ or $NiO_{1\cdot1}.1\cdot3H_2O$, with $D_x=3\cdot28$. The water content found by analysis, however, is even higher, and the measured density is lower, than these values. Therefore at least some of the Ni^{III} cations must be placed in the brucite-like layer and not in the interlayer. The very extreme would be: $[Ni_4^{II}Ni^{III}(OH)_{10}][OH.4H_2O]$ or $NiO_{1\cdot1}.1\cdot9H_2O$, with $D_x=2\cdot91$.

The real structure probably lies somewhere between these possibilities. The question, whether the Ni^{III} cations are in the interlayer or in the brucite-like layer or even between the two kinds of layers, can easily be answered by a $\varrho(z)$ electron density projection calculated with the 00l reflections only (see Allmann & Lohse, 1966, Fig. 2). The needed intensities can even be taken from a texture powder pattern. The presence of Ni in the interlayer should raise the corresponding peak in $\varrho(z)$ above the OH peak. Likewise Ni between the two types of layer can be recognized. The 00l reflections, however, can tell us nothing about the extent of disorder in the interlayer. Statements about the order of the interlayer must be based on a full three-dimensional set of data.

An other compound found in nature is $4Mg(OH)_2.(Ni,Fe)OOH$ with $a=3\cdot12$, $c=23\cdot19$ (or less commonly $c=23\cdot79$ Å; Lapham, 1965). It should have the same structure as that discussed above, also with a somewhat higher water content. Just before finishing this paper, I found an abstract about this structure (Lea & Mackey, 1967), describing the (OH,H_2O) sequence as $AAABBBCCC$. This sequence leads to an ordered interlayer as the (OH,H_2O) is placed just between the OH groups of two adjacent brucite-like

layers, in the same place as the pseudo-atom approximating the disordered interlayer of pyroaurite was placed. But the results of this paper make it doubtful that the interlayers in $4Mg(OH)_2.(Ni,Fe)OOH$ are completely ordered. Because of the lack of carbonate groups the degree of ordering may be higher than in pyroaurite. The given analyses do not exclude the possibility that anions other than OH^- may be in the interlayers of the discussed minerals. Probably the two hydroxides also contain some CO_3^{2-}.

Hardman & Taylor (1967) in a recent abstract of the structures of sjögrenite and pyroaurite confirm our results of 1966. Their cell constants (3·13 and 15·66 Å for sjögrenite; 3·13 and 23·49 Å for pyroaurite), however, seem to be too high. The density of pyroaurite, calculated with these values, is only 2·073 g.cm^{-3} (for $4H_2O$, but 2·13 for $5H_2O$), as compared with $D_x=2\cdot102$ and $D_m=2\cdot13$ in this paper. The space group given by Hardman & Taylor (personal communication) is $R3m$ or $R\bar{3}m$.

References

ALLMANN, R. & LOHSE, H.-H. (1966). *Neues Jb. Min. Mh.* 161.
AMINOFF, G. & BROOMÉ, B. (1930). *Kungl. Sven. Vetensk. Akad., Handl.* 9, 3, No. 5, 23.
ANDERSON, B. J. & WHELAN, J. A. (1962). *Amer. Min.* 47, 807.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A FORTRAN Crystallographic Least-Squares Program.* Oak Ridge National Laboratory, Tennessee.
EVANS, H. T., JR & ALLMANN, R. (1967). *Program of the winter meeting 1967 of the ACA in Atlanta, Georgia,* p. 39 (to appear in *Z. Kristallogr.* 1968).
FEITKNECHT, W. (1953). *Fortschr. Chem. Forsch.* 2, 670.
FRONDEL, C. (1941). *Amer. Min.* 26, 295.
GLEMSER, O. & EINERHAND, J. (1950). *Z. anorg. allg. Chem.* 261, 26, 43.
HARDMAN, L. & TAYLOR, H. F. W. (1967). Notice No. 148 of the Mineralog. Soc. London, abstract (*a*). (For a detailed paper see *Miner. Mag.* 36, 465).
International Tables for X-ray Crystallography (1962). Vol. III, p. 202–205. Birmingham: Kynoch Press.
JAMBOR, J. L. & BOYLE, R. W. (1964). *Canad. Min.* 8, 116.
LAPHAM, D. M. (1965). *Amer. Min.* 50, 1708.
LEA, S. G. & MACKAY, A. L. (1967). Notice No. 148 of the Mineralog. Soc. London, abstract (*g*).
MANASSE, E. (1915). *Atti Soc. Toscana Sci. Nat., Proc. Verb.* 24, 92.