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Elena S. Zhitova

Crystal Chemistry of  
Natural Layered Double  
Hydroxides

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## ABSTRACT

The thesis contains results of the first comprehensive crystal chemical study of natural layered double hydroxides (LDHs) from the Kovdor alkaline massif (Kola peninsula, Russia) and the Bazhenovo ultramafic massif (middle Urals, Russia). Various samples were studied by single crystal X-ray diffraction, powder X-ray diffraction, microprobe chemical analysis, and infrared spectroscopy. It has been shown that the studied samples from both deposits belong to quintinite,  $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}][(\text{CO}_3)(\text{H}_2\text{O})_3]$ , and not manasseite or hydrotalcite as was thought previously. Studies have shown that quintinite has at least four structurally confirmed polytypic modifications: *2H-3c* [6R], *1M*, *2H* and *2H-1c*, three of which (*2H-3c*, *1M*, *2H*) are completely new and previously unknown, whereas the fourth polytype (*2H-1c*) is close to the one described previously. An improved scheme for the description of polytypes with stacking layers (in case of ordering of cations in the octahedral layers) is proposed.

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- AII Zhitova E.S., Zolotarev A.A., Krivovichev S.V., Yakovenchuk V.N. Cation ordering and threefold superstructure in Quintinite-2H from the Kovdor alkaline massif, Kola peninsula, Russia // Clays, clay minerals and layered materials — CMLM2009. Moscow. 2009. P.90.
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- AXI Zhitova E.S., Zolotarev A.A., Krivovichev S.V., Yakovenchuk V.N., Pakhomovsky Ya. A. X-ray diffraction study of three structurally different quintinites from the Kovdor alkaline massif (Kola peninsula, Russia) // Fedorov session 2012. P.115–116. (in Russian)
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# 1 INTRODUCTION

Layered Double Hydroxides (LDHs) are natural minerals and synthetic materials, which also commonly known as «hydrotalcites», «hydrotalcite-manasseite-group minerals» and «anionic clays». These compounds are characterized by structures based upon double brucite-like hydroxide layers  $[M_n^{2+}M_n^{3+}(\text{OH})_{2(m+n)}]^{m+}$ , where  $M^{2+} = \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}$ , etc.;  $M^{3+} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{Mn}^{3+}$ , etc. The positive charge of the layer is balanced by interlayer species that may consist of anions ( $\text{CO}_3^{2-}, \text{Cl}^-, \text{SO}_4^{2-}$ , etc.) or both anions and cations ( $\text{Na}^+, \text{Ca}^{2+}, \text{Sr}^{2+}$ , etc.). Due to their layered character, LDHs display polytypism and layer stacking disorder. Polytype diversity of LDHs has been described in detail by Bookin and Drits (1993), Bookin *et al.* (1993), and Drits and Bookin (2001), who developed a structural nomenclature for the polytypes observed in this group.

Due to their crystal structures and physical properties LDHs have become important to industry and found applications in catalysis, drug delivery media, absorption of heavy ions and non-ionic organic compounds, photochemistry, electrochemistry, the reduction of oxidized pollutants such as nitrates and carbon dioxide sequestration (Duan and Evans, 2006; Kameda *et al.*, 2012a,b; Kameda and Yoshika, 2011; Newman and Jones, 1998; G enin *et al.*, 2006, 2008, Mills *et al.*, 2012). Another area of interest in LDHs is the theory of the origin of life on the Earth. It had been suggested that clay mineral complexes with organic molecules could constitute the first organisms (Bernal 1951, 1967; Cairns-Smith, 1982). For the MgAl LDHs similar to those studied in this work, Mg-Al cation order is important for catalytic activity correlated with the number and arrangement of adjacent  $\text{Al}^{3+}$  sites (Kim *et al.*, 2003). Different distribution of Al in a Mg hydroxide matrix also results in different charge distribution in the layer, which is critically important for intercalation reactions. Structural features of LDHs such as cation ordering, charge distribution and polytypism have an immediate influence upon their properties and have been under extensive experimental and theoretical investigations recently.

The archetype of LDHs is hydrotalcite  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}](\text{CO}_3)(\text{H}_2\text{O})_4$ , which was the first phase to be discovered by Hochstetter in Sweden in 1842 (Hochstetter, 1842) and it gave name firstly to the group of minerals than to the supergroup. A bit later pyroaurite  $[\text{Mg}_6\text{Fe}_2(\text{OH})_{16}](\text{CO}_3)(\text{H}_2\text{O})_4$  was discovered in L nban, V rmland, Sweden by Igelst rm

(1865). The first chemical formula of hydrotalcite was determined by E. Manasse, professor of Mineralogy at the University of Florence (Italy) in 1915 and hydrotalcite was approved as mineral specie. The first X-ray investigation was conducted by Aminoff and Broomé on pyroaurite in 1931. Frondel (1941) published an X-ray study on hydrotalcite from four localities, including the sample from the type locality. For studied samples two phases were discovered: rhombohedral one with  $a = 3.065$ ,  $c = 23.07$  Å and hexagonal phase  $a = 3.06$ ,  $c = 15.34$  Å. The name «hydrotalcite» was reserved for rhombohedral phase and hexagonal one was called manasseite what persisted. However it has been known since the study of Ingram and Taylor (1967), that the two minerals are in fact polytypic modifications (Mills *et al.*, 2012). The name «manasseite» was excluded in 2012 by Mills *et al.* (2012) and renamed to hydrotalcite-2H. Some fundamental works on crystal structures of «hydrotalcites» were published by Taylor (1969, 1973), Allmann (1968), Allmann and Donnay (1969), Allmann and Jepsen (1969). Since 1970 when the first patent for LDHs appeared the interest to those compounds has increased and they are still actively studied nowadays. Recently new nomenclature of 44 natural species of LDH phases was proposed (Mills *et al.*, 2012). This nomenclature combined all 44 minerals in hydrotalcite supergroup which includes 9 mineral groups.

Generally, LDH minerals are not frequent and they commonly found in small quantities and often intergrown, twinned or X-ray amorphous and doesn't form well-diffracting crystals, which makes working with them difficult. Due to this fact, most research on LDHs was done on synthetic materials. All the structural studies on synthetic LDHs deal with powder samples that prevent elucidation of such fine details of structure architecture as formation of superstructures due to cation ordering. In contrast to synthetic materials, natural LDHs are known to form single crystals accessible to single-crystal X-ray diffraction analysis, which allowed to identify basic features of their crystal chemistry and to demonstrate peculiarities of cation and anion ordering.

This work is based on crystal chemical study of natural minerals, which occur in well formed crystals (up to several cm) within Kovdor alkaline massif (Kola peninsula, Russia) and Bazhenovo ultramafic massif (Middle Urals, Russia), which makes them appropriate for X-ray single-crystal investigations.

New results are reported in this thesis for the crystal chemistry of natural LDHs obtained by application of area detectors of X-rays, which provide new opportunities for quantitative studies of commensurate, incommensurate and diffuse scattering features of diffraction patterns.

The main aim of this work is crystal chemical study of samples from the Kovdor alkaline (Kola peninsula, Russia) and Bazhenovo ultramafic (Middle Urals, Russia) massifs in order to study their mineralogical appurtenance, structure peculiarities (cation ordering), and polytypism.

## 2 BRIEF DESCRIPTION OF RESULTS

### 2.1 Objects and methods

Crystals studied in this work were found in the Kovdor alkaline (Kola peninsula, Russia) and Bazhenovo ultramafic (Middle Urals, Russia) massifs (**Fig. 1**). Quantitative chemical analyses were carried out using a Cameca MS-46 electron microprobe (Geological Institute of the Kola Science Centre of the Russian Academy of Sciences, Apatity, Russia) operating at 20 kV and 20-30 nA with a 20  $\mu\text{m}$  beam diameter. Infra-red absorption spectra were recorded using a Bruker Vertex IR spectrometer. The measurements were taken at room temperature, using the KBr pellets technique. Powder X-ray diffraction data were obtained on a STOE-STADI P diffractometer using  $\text{CuK}_\alpha$  radiation operating at 45 kV and 35 mA. The STOE-WINXPOW software package was used to process the diffraction data. The unit cell parameters refined from the powder data using STOE-WINXPOW.



**Fig. 1.** Samples studied in this work from the Kovdor alkaline massif (*a, b, c, e, f*) and from Bazhenovo ultramafic complex (*d*).

Single-crystal X-ray diffraction data were collected using Stoe IPDS II Image-Plate-based X-ray diffractometer operated at 50 kV and 40 mA. More than a hemisphere of three-dimensional data were collected for each crystal using monochromatic  $\text{MoK}_\alpha$  X-radiation. The unit-cell parameters were refined by least-squares methods. The SHELXTL program package was used for all structural calculations (Sheldrick, 2008). The final models included all atomic positional parameters, anisotropic-displacement parameters for atoms of the metal hydroxide layer and refinable weighting schemes of the structure factors. The structures were solved by direct methods and the final models were checked for missing symmetry operations using the PLATON program (Speck, 2003).

## 2.2 Experimental results and discussion

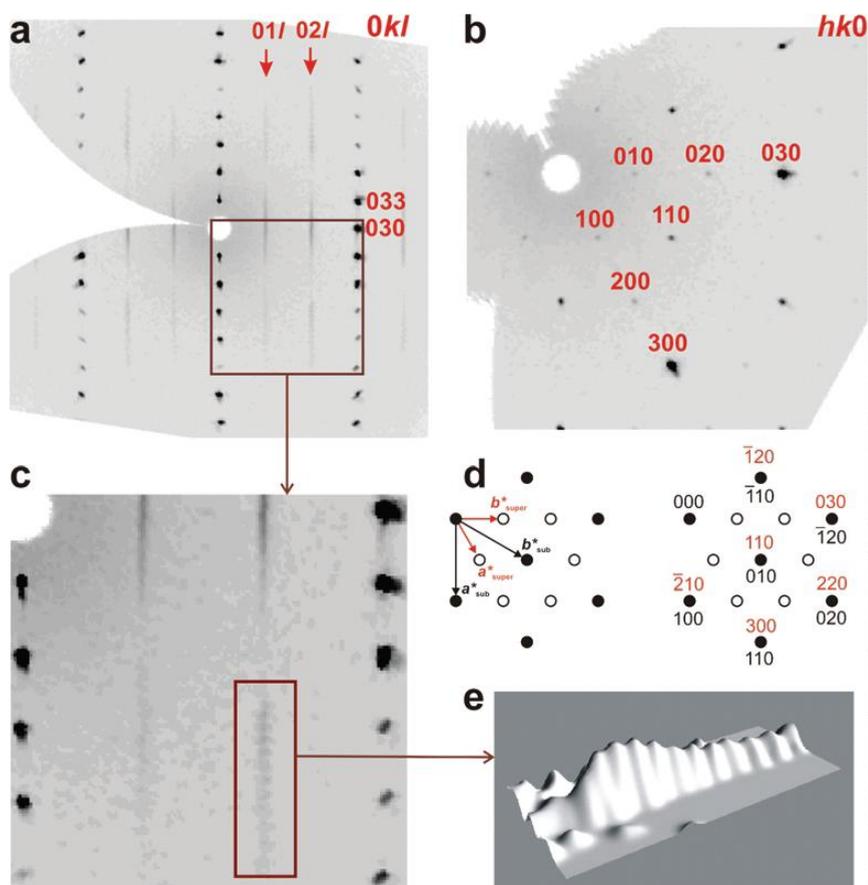
It has been found that all samples studied in this work in fact correspond to quintinite and not hydrotalcite or manasseite as was thought previously. Crystallographic data and experimental parameters of data collection and structure refinement are listed in Table 1. Below we briefly summarize some peculiarities of diffraction patterns observed and provide their interpretation from the viewpoint of superstructures and polytypism.

**Table 1.** Crystallographic data and refinement parameters for quintinite polytypes

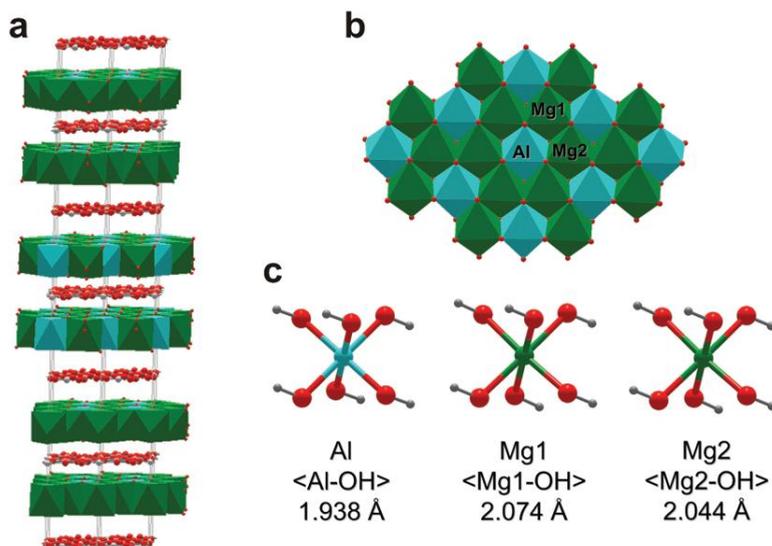
Polytype	Quintinite-2H-3c	Quintinite-1M	Quintinite-2H	Quintinite-2H-1c
Crystallographic data				
Ideal formula	$[\text{Mg}_4\text{Al}_2(\text{OH})_{12}](\text{CO}_3)(\text{H}_2\text{O})_3$			
Crystal system	Trigonal	Monoclinic	Hexagonal	Trigonal
Space group	R32	C2/m	$P6_3/mmc$	$P-3c1$
Unit-cell parameters $a, b, c$ (Å), $\beta$ (°)	5.2745(6), 5.2745(6), 45.364(10), 90	5.266(2), 9.114(2), 7.766(3), 103.17(3)	3.0446(9), 3.0446(9), 15.178(5), 90	5.2720(6), 5.2720(6), 15.113(3), 90
Unit-cell volume (Å <sup>3</sup> )	1093.0(3)	362.9(2)	121.84(6)	363.76(8)
Z	3	1	1	2
Data collection				
$\theta$ range (°)	2.69-29.10	4.47-29.16	2.69-29.26	2.29 - 29.76
$h, k, l$ ranges	-7 → 6, -7 → 6, ±61	±7, 0 → 12, -10 → 0	-4 → 3, ±3, ±20	±7, -7 → 6, ±20
Total reflections collected	3414	511	829	3304
Unique reflections	668	511	84	330
Unique reflections $F > 4\sigma(F)$	484	304	76	304
Data completeness to $\theta_{\text{max}}$ (%)	99.5	97.9	90.3	95.6
Structure refinement				
Refinement method	Full-matrix least-squares on $F^2$			
Weighting coefficients $a, b$	0.0877, 4.2621	0.0666, 0.2562	0.0185, 0.2743	0.0817, 0.6432
Extinction coefficient	0.006(2)	-	0.00(6)	0.17(3)
Data/restraints/parameters	668/0/59	511/2/65	84/1/19	330/0/38
$R_1 [F > 4\sigma(F)], wR_2 [F > 4\sigma(F)]$	0.055, 0.182	0.031, 0.102	0.046, 0.088	0.0603, 0.1778
$R_1$ all, $wR_2$ all	0.072, 0.203	0.055, 0.119	0.053, 0.088	0.0643, 0.1741
Goodness-of-fit on $F^2$	1.170	0.996	1.285	1.181
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.45, -0.80	0.32, -0.28	0.55, -0.26	0.95, -0.74

### 2.2.1 Quintinite-2H-3c[6R] (Kovdor)

Inspection of the reconstructed reciprocal lattice slices showed presence of strong, sharp reflections and rows of weak reflections (**Fig. 2**). Indexing based on the strong set of sublattice reflections resulted in a small subcell with parameters  $a = 3.045$  and  $c = 15.12$  Å, which agree approximately with unit cell parameters of the  $2H_1$  polytype of Mg-Al LDHs (Bookin and Drits, 1993). The weak superlattice reflections define a rhombohedral supercell with unit-cell parameters:  $a = 5.2745(7)$ ,  $c = 45.36(1)$  Å. The geometrical relationship between sublattice and superlattice reflections is shown in **Fig. 2**. Sublattice reflections correspond to conditions  $h-k = 3n$  and  $l = 3n$ , whereas rows of weak intensity maxima extending parallel to  $c^*$  occur at  $h-k \neq 3n$ . Sharp Bragg reflections originate from basic layer stacking of metal hydroxide layers, while weak reflections indicate the formation of 3-D cation superlattices due to the Mg-Al ordering (Krivovichev *et al.*,



**Fig. 2.** The (100) (a) and (001) (b) sections of reciprocal diffraction space (quintinite-2H-3c[6R]) containing both sharp and diffuse reflections; the latter can be separated into closely separated weak reflections as can be seen from the enlarged part of the (100) section (c). The relations between subcell and supercell in the reciprocal lattice section ( $hk0$ ) is shown in d. Three-dimensional reconstruction of diffuse streak is shown in (e).

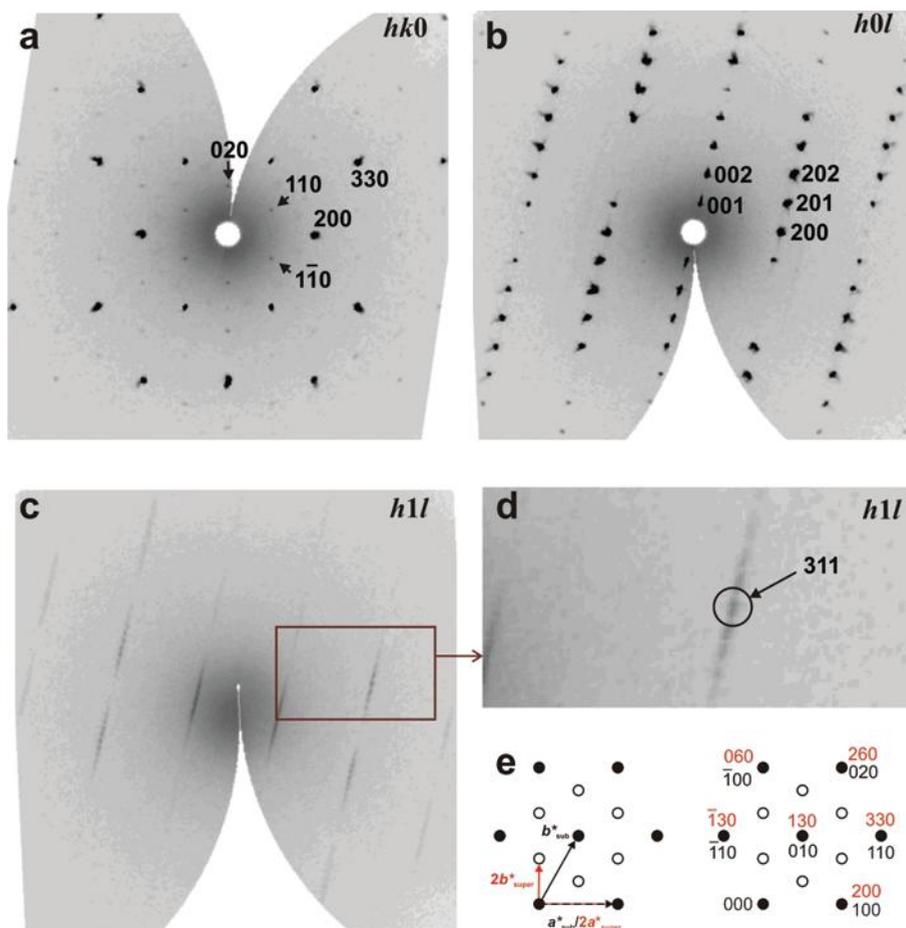


**Fig. 3.** The structure of quintinite- $2H$ - $3c[6R]$  (Q1) (a), a projection of the double hydroxide layer (b) and the geometry of the  $M(\text{OH})_6$  octahedra (c).

2010a, Krivovichev *et al.*, 2012). In the structure of quintinite- $2H$ - $3c[6R]$ , Mg and Al are completely ordered on distinct sites, allowing formation of honeycomb structure (Fig. 3b) and resulting in a tripling of the  $c$  parameter. The effect of cation ordering in natural LDHs with  $M^{2+} = \text{Mg}^{2+}$  and  $M^{3+} = \text{Al}^{3+}$  is governed by the tendency to minimize  $M^{3+}$ - $M^{3+}$  repulsive interaction, what is energetically favored and in agreement with the cation avoidance rule (Loewenstein, 1954; Trave *et al.*, 2002). There are three symmetry-independent octahedrally coordinated cation sites in the structure. As the scattering factors of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  cations are nearly identical, the only way to distinguish between Mg and Al sites is to evaluate M-O bond lengths. The structure refinement indicates that one M site has bond lengths in the range 1.936-1.940 Å and two M sites have bond lengths of 2.042-2.045 and 2.070-2.077 Å (Fig. 3c). Thus, bond lengths distinguish two distinct types of site that are consistent with ordered occupancy by Al (shorter bonds) and Mg (longer bonds) (Krivovichev *et al.*, 2012a; Krivovichev *et al.*, 2012). The  $2H$ - $3c[6R]$  structure is a superstructure of  $2H$  polytype produced by cation ordering in octahedral layers. According to the LDH polytype nomenclature (Bookin and Drits, 1993), the layer stacking in quintinite- $2H$ - $3c[6R]$  can be described as ...AC = CA = AC... (with A and C being positions of hydroxide ions and b position of cations) and corresponds to that of the two-layer  $2H_1$  polytype, as observed for manasseite and quintinite- $2H$  by Arakcheeva *et al.* (1996). However, in contrast to the Brazilian quintinite, the unit cell of our crystal contains six layers. The tripling of the  $c$  parameter is caused by the Mg-Al ordering in the  $[\text{Mg}_2\text{Al}(\text{OH})_6]^+$  layer (Fig. 3a).

## 2.2.2 Quintinite-1M (Kovdor and Bazhenovo)

The three-dimensional diffraction pattern of quintinite-1M contains weak diffuse discrete streaks which clearly indicated the formation of a 2-D superstructure due to Mg-Al ordering (Fig. 4) as it was observed for quintinite-2H-3c[6R]. The integration of weak superlattice reflections into indexing of the diffraction pattern, which was possible using Stoe Integration software (X-Area = 1.42; Stoe, 1997), gave a C-centred monoclinic cell (Table 1). Metal hydroxide layers in monoclinic quintinite have almost perfect Mg-Al ordering which can be inferred from average Mg-O (2.044 Å) and Al-O (1.944 Å) bond lengths. We infer that this cation ordering is responsible for the appearance of



**Fig. 4.** Reconstructed sections of reciprocal space obtained for quintinite-1M:  $hk0$  section (a: note weak reflections with odd  $h$  and  $k$  indices),  $h0l$  section (b: note the presence of sharp Bragg reflections),  $h1l$  section (c: note the presence of only weakly discrete diffraction streaks elongated along the  $c^*$  axis), and enlarged part of the  $h1l$  section showing the position of the 311 reflection (d). The scheme in (e) shows the choice of reciprocal space vectors and indexing of reflections in the  $hk0$  section (the black and red colours indicate subcell and supercell vectors and indices, respectively).

weak superstructure reflections, which correspond to the  $h-k \neq 3n$  reflections of Mg-Al ordered quintinite-2H-3c[6R] (Krivovichev *et al.*, 2010a). The ordering of  $M^{2+}$  and  $M^{3+}$  cations in brucite-like layer for quintinite-1M results in symmetry reduction: from rhombohedral (3R<sub>1</sub> polytype) to monoclinic (1M) and the formation of superstructure. It is noteworthy that, before our work, monoclinic symmetry has never been observed previously in natural or synthetic LDHs having di- and trivalent cations. This symmetry reduction is induced by the Mg-Al ordering in metal hydroxide layers and the ordered stacking of these layers. Taking into account the small difference in Mg and Al scattering factors, it is perhaps surprising that Mg-Al ordering is registered by the appearance of weak superstructure reflections.

### 2.2.3 Mg-Al-disordered quintinite-2H (Kovdor)

Initial indexing of diffraction patterns provided unit cells with parameters  $a \approx 3.05$ ,  $c \approx 15.1$  Å, characteristic of manasseite, Mg<sub>3</sub>Al-CO<sub>3</sub> LDH (Table 1). Inspection of  $hk1$  and  $h0l$  sections of reciprocal space (Fig. 5) showed the almost complete absence of superstructure reflections which would indicate Mg-Al ordering in metal hydroxide layers, as has been observed for ordered quintinite polytypes (Krivovichev *et al.*, 2010a,b). The structures were solved in space group  $P6_3/mmc$ . The stacking sequence of layers can be expressed as ...=AC=CA=..., i.e. with hydroxide anions in A and C, and cations in the b positions. As the structure shows no signs of cation ordering, the studied crystals can be characterized as an Mg-Al-disordered 2H polytype of quintinite, in contrast to Mg,Al-ordered quintinite-2H-1c and quintinite-2H-3c reported by Arakcheeva *et al.* (1996) and Krivovichev *et al.* (2010a), respectively. The observed disorder is probably the result of a higher temperature of formation of the samples compared with the ordered polytypes. This suggestion is in general agreement with the previous observations that demonstrated, for the Mg-Al system, a higher temperature of formation of the

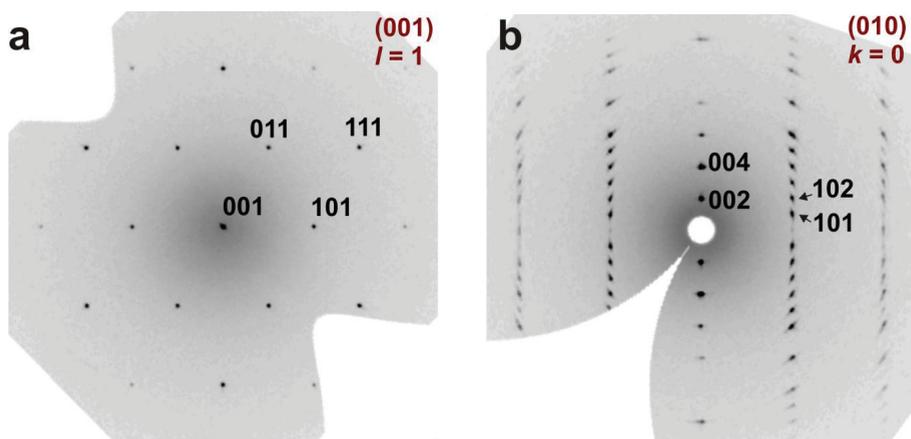


Fig. 5. The  $hk1$  (a) and  $h0l$  (b) sections of reciprocal diffraction space obtained from quintinite-2H crystals.

hexagonal (or pseudo-hexagonal in the case of quintinite-2H-3c) 2H polytype compared with the rhombohedral (or pseudo-rhombohedral polytype in the case of quintinite-1M) 3R polytype (Bellotto *et al.*, 1996). Indeed, most syntheses of LDHs are carried out at near-ambient temperatures (coprecipitation is the usual synthesis technique) and the samples obtained display either rhombohedral or random layer stacking. As far as we know, no samples with pure hexagonal (manasseite-type) layer stacking have been reported yet. As was pointed out by Pausch *et al.* (1986), in nature, hydrotalcite and manasseite ( $\text{Mg}_3\text{Al-CO}_3$  LDHs) are commonly intergrown, with manasseite forming the core and hydrotalcite the outer part of a mineral grain. Similar observations were reported by Allmann (1968) for the pyroaurite-sjögrenite ( $\text{Mg}_3\text{Fe}^{3+}\text{-CO}_3$  LDHs) crystals from Långban: rhombohedral low-temperature polymorph (pyroaurite) is always found in the outermost shell of natural crystals.

#### 2.2.4 Quintinite-2H-1c (Kovdor)

The diffraction pattern comprises both strong basic and weak superstructure Bragg reflections (Fig. 6), which indicated Mg-Al ordering in the metal hydroxide layers. Crystal structure of quintinite-2H was firstly described by Arakcheeva *et al.* (1996) on a Brazilian sample. The structure was solved in the space group  $P-62m$ , the unit cell parameters are  $a = 5.283(3)$ ,  $c = 15.150(9)$  Å. In addition to different space groups, the distinction between the structure described by Arakcheeva *et al.* (1996) and the structure of Kovdor quintinite-2H-1c lies in the architecture of the interlayer region. Arakcheeva *et al.* (1996) consider the crystal structure of Brazilian quintinite consisting of 3 types of layers. The first type is the  $[\text{Mg}_2\text{Al}(\text{OH})_6]$  octahedral layers. The second one is presented by the  $[\text{CO}_3]^{2-}$  groups. The third layer contains water molecules only. The layers of the three types alternate along the hexagonal axis and form the sequence -1-2-1-3-1-. In contrast, layers in between octahedral layers in the Kovdor quintinite-2H-1c are identical to each other and consist of both carbonate groups and water molecules.

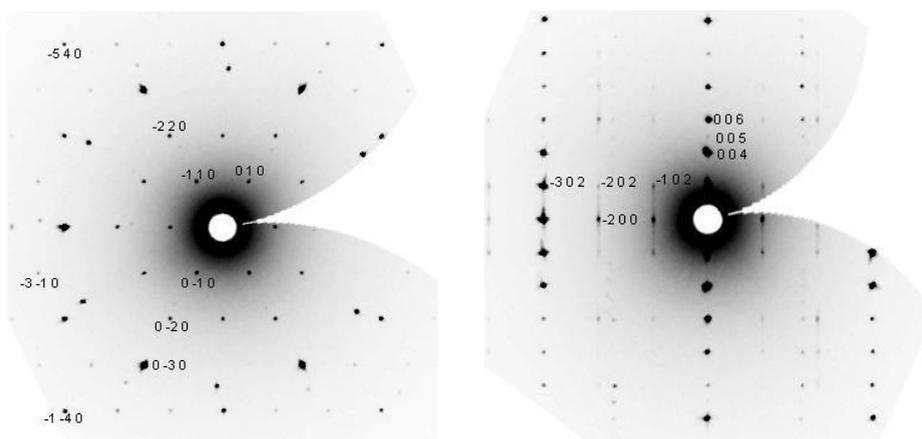


Fig. 6. (001) section of reciprocal diffraction space (left) and (010) section of reciprocal diffraction space (right) obtained from the quintinite-2H-1c crystal.

Mg<sup>2+</sup> and Al<sup>3+</sup> atoms occupy the same octahedral sites in every first and third metal-hydroxide layer, what in comparison to quintinite-2H-3c[6R] reduce the amount of layers within the unit cell from six to two. According to Bookin and Drits (1993) nomenclature, this polytype should be described as ...= AC = CA = ... what corresponds to the 2H<sub>1</sub> polytype (Bookin and Drits, 1993; Arakcheeva *et al.*, 1996) and doesn't reflect the difference between polytypes with ordered and disordered distribution of cations in brucite-like layers. It is obvious that for Mg-Al disordered polytypes cation sites are unknown and layer stacking can be described only as ...= AC = CA =..., while in Mg-Al-ordered polytype Al occupy b<sub>1</sub> and Mg may occupy b<sub>2</sub> and b<sub>3</sub> sites. Taking into account Mg-Al ordering, the full description of the layer sequence can be written as ...= Ab<sub>2</sub>C = Cb<sub>3</sub>A =... This sequence corresponds to the two-layer polytype and completely characterizes the observed structure, taking into account layer stacking and cation ordering.

In order to distinguish the «classical» manasseite ( $a \approx 3.06$ ,  $c \approx 15.34$  Å, Q3 and Q4 in this work) and «classical» quintinite ( $a \approx 5.28$ ,  $c \approx 15.15$  Å, Q6-2 and Brazilian sample (Arakcheeva *et al.*, 1996)) unit cells, additional suffix indicating a value of the  $c$  parameter compared to the 'standard' polytype may be useful. Thus, by analogy with quintinite-2H-3c the structures of the studied sample and Brazilian quintinite (Arakcheeva *et al.*, 1996) can be described as quintinite-2H-1c, indicating presence of the Mg-Al ordering and  $c \approx 15$  Å. Quintinite-2H-1c is the first cation-ordered polytype with quintinite unit cell for Kovdor samples.

## SUMMARY

In this thesis, detailed study of natural LDH polytypes allowed to identify and structurally characterize four different polytypes of quintinite, from which two have been unknown before our work. Cation ordering and superstructures observed by us in quintinite polytypes are probably common to many natural and synthetic LDHs. In particular, it is noteworthy that many minerals previously identified as manasseite or hydrotalcite appeared to be different polytypes of quintinite. For example, the first structure determination of 'hydrotalcite' was done on the mineral with the formula  $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)(\text{H}_2\text{O})_3$ , which is obviously quintinite (Allmann and Jepsen, 1969). In 1987, Drits *et al.* reported results of powder XRD studies of 'manasseite', again with the formula  $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)(\text{H}_2\text{O})_3$ , which can now be identified as quintinite-2H. Distinction of quintinite from hydrotalcite and manasseite is by means of the Mg:Al ratio (2:1 vs. 3:1) (Chao and Gault, 1997). The  $\text{Mg}_2\text{Al}$  stoichiometry shows a strong tendency to cation ordering and the formation of superstructures, as we demonstrated in our papers given at the end of this thesis. However, the present work also demonstrated that Mg,Al-disordered quintinite also exists and it is not clear whether or not the Mg,Al disorder is specifically three-dimensional, i.e. concerns only stacking disorder of fully ordered layers, or is also present within the metal hydroxide layers.

In general, we point out that polytype formation and cation ordering are definitely the result of different temperature regime of growth of quintinite crystals with samples with high symmetry and disorder being formed under elevated temperatures compared to more ordered structures.

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