Evaluation of the thesis by Elena S. Zhitova
"Crystal chemistry of natural layered double hydroxides"

A hydrotalcite mineral group unites 44 species with two-dimensional (2D) layered structures. These minerals present a natural family in a class of ionic lamellar compounds with crystal structures formed of positively charged brucite-like layers and anions (with salvation molecules) in an interlayer space – so called layered double hydroxides (LDHs). They display unique physical and chemical properties similar to those of clay minerals: high specific surface area, memory effect, high anion exchange and dispersive capacities, etc. Significant progress has been achieved in the last years in the use of LDHs' for the removal of organic, inorganic and nuclear wastes from contaminated waters, the separation of carbon dioxide from flue gas, biomedical applications, and in their applied study as novel hybrid materials with non-trivial optical and magnetic properties. A key structural characteristic of LDH materials is a distribution of metal atoms usually in 2+ and 3+ oxidation states between edge sharing octahedra, which is controlled by electrostatic forces. Therefore they can be used as precursors or templates for the formation of nanocatalysts with specific morphology surface structure of high dispersion. Besides, LDH crystals can be slashed into positively-charged 2D nanosheets, which can be used as building blocks for further assembling with various catalytically active anions.

Most experimental studies of LDH properties have been done using polycrystalline or powder material that is rather easily obtained in laboratory. However, deep understanding of physical properties and material design can be achieved only if fine details of crystal structures are known. The objective difficulties in growing LDHs' mono crystals, described in the present dissertation, have not permitted thus far receiving structural information that would be precise enough for farther progress in the understanding of the peculiarities of their crystal chemistry. But our contemporary possibilities of modern X-ray technology allowed to Elena Zhitova to obtain new and very important information regarding LDHs crystal chemistry. These results are based on X-ray investigation of very small mono crystals of LDH minerals found in Kola Peninsula and Middle Urals (Russia), where they are formed at the late stages of hydrothermal activity as a result of secondary hydrothermal alteration of spinel.

The thesis of Elena Zhitova presents results of crystal structure analysis of four polytypic modification of mineral quintinite, $[Mg_4Al_2(OH)_{12}][(CO_3)(H_2O)_3]$. It is worth mentioning that all the studied samples have the Mg:Al ratio equal to 2:1 and thus belong to quintinite, and not to manasseite or hydrotalcite as they were considered before. The author has shown that the Mg_2Al stoichiometry demonstrates a strong tendency toward cation ordering and the formation of superstructures; yet the present research also confirmed the existence of the Mg,Al-disordered quintinite. The author's conclusion that variations in cations' ordering in different quintinite polytypes seem to represent the result of changing temperature, is in line with the modern ideas that disordered structures are formed under higher temperatures than more ordered ones. The dissertation is well written; it contains good pictures confirming the authors' hypothesis and conclusions; all the presented results are sound and improve our knowledge concerning the LDH crystal chemistry.

In the same time I would like to turn the author's attention to certain points that require additional explication or corrections. I actually missed some explanation or at least discussion concerning the additional *h0l* reflections in Fig.6, which do not fit to the unit cell suggested for the quintinite-2*H*-1*c* crystal. There is no plausible reasoning or proof in the thesis about the character of the anions' distribution in an interlayer region, despite the fact that some hypotheses on this subject are presented in articles published by the author.

Some minor points are as follows: 1. PIV and PV indication in the list of included articles do not coincide with those actually presented. 2. In my opinion equal *a* and *b* unit cell parameters of trigonal (hexagonal) crystal should not be repeated (Table 1). 3. "Imaging plate", not "Image

plate" (page 12). 4. There is no enough information concerning the 2H-1C crystal structure. The given abstract (PV) does not permit a qualified review of presented results.

In spite of the remarks offered above, the overall quality of research presented for evaluation is very high and certainly satisfies the requirements of the Ph.D. degree.

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