REVIEW

Of the *member* of the dissertation council for the dissertation of *Ilya Viktorovich Kornyakov* on the topic: "*Synthesis and Crystal Chemistry of Novel Mineral-related Divalent Copper Compounds*", submitted for the degree of *candidate* of geological and mineralogical sciences in a scientific speciality 1.6.4. Mineralogy, Crystallography. Geochemistry, Geochemical Methods of Mineral Exploration

General comments

The science in this thesis is of high quality and the coverage of the subject area is both detailed and extensive.

As expertly explained by Mr. Kornyakov, Cu^{2+} has very interesting stereochemical properties due to the Jahn-Teller effect, particularly where the coordination polyhedron is six O^{2-} ions arranged at the corners of an octahedron. Because of these properties, solid solution of Cu^{2+} with other divalent ions of similar coordination (*e.g.*, Mg^{2+}, Fe^{2+}, Co^{2+} *etc.*) is more complicated than is usually the case for divalent cations, a situation that has generated a lot of crystallographic work on Cu^{2+} oxysalt minerals and their synthetic analogues. Partly because of the presence of Cu^{2+} and Cu^{3+} in high-temperature oxide superconductors, there has been a lot of work reported in the Physics and Chemistry literature that has both drawn on previous work on minerals and extended it to non-mineral phases of great physical and technological interest. This synergy has led to much new science, *e.g.*, the search for quantum spin liquids in mineral and mineral-like structures, and the very recent discovery of its presence in herbertsmithite: $Cu_3Zn(OH)_6Cl_2$.

Detailed analysis of Cu^{2+} oxysalt minerals were presented 20-30 years ago, and since then, there have been (1) numerous discoveries of new Cu^{2+} oxysalt minerals; and (2) discovery of the presence of novel physical properties, *e.g.*, high-temperature superconductivity, quantum spin liquids, in Cu^{2+} oxysalt crystal structures.

Consequently, it is long-past time for a new detailed examination of Cu^{2+} *oxysalt minerals from a structural perspective, and Mr. Kornyakov does this extremely well in this thesis.* He is comprehensive in his coverage of copper minerals and has extended the hiearchy to some synthetic copper oxysalts. In particular, he has extended the hierarchy to include anion-centered (OCu_4) oxysalt minerals and synthetics, something that was missing in previous classifications of copper oxysalt minerals because of the previous lack of appreciation of this type of coordination prior to the work of Stanislav Filatov and Sergey Krivovichev.

Mr. Kornyakov has synthesized very many interesting copper-oxysalt compounds and in doing so, has shown the effectiveness of the chemical vapor transport (CVT) technique for synthesizing intermediate- and high-temperature minerals. This is of particular geological interest as the CVT technique simulates transport of geochemical constituents and crystallization of the resultant minerals during volcanic activity, particularly in its later stages. This also seems to have the advantage that large (>0.1 mm) crystals are generally produced, a great improvement over normal cold-sealed hydrothermal pressure vessels. This approach has the great advantage that the resulting minerals can be characterized by single-crystal X-ray diffraction and structure solution and refinement.

Stylistic Comments

It is common practice in the academic communities in which I have worked to comment in detail on the style of the language in which the thesis is written. I am not sure of the custom in Russia, but I have made some such comments here to help Mr. Kornyakov. I should emphasize that his writing is already reasonably in accord with the quality of writing in the general mineralogical literature, and my objective is not to be critical but to be helpful in his future work.

[1] The word "octahedral" derives from the Greek "okto" meaning "eight" and "hedron" meaning "seat", *i.e.*, something with eight flat faces (as an octahedron), and the same for other "-----hedral" words. Thus once cannot have an "octahedral chain" as a chain does not have 8 flat faces, it is a "chain of octahedra". Similarly, one cannot have an "octahedral cation" as an ion cannot have 8 flat faces; it can be "octahedrally coordinated" as its ligands lie at the corners of an octahedron.

[2] Water is a liquid, H_2O is a molecule. Although most papers make this error, one should not use the word "water" when one means "H_2O". Logically, it will lead one to describing "ice" as "water" when ice does not have the same physical properties or stability as water. Similarly, water does not have the same physical properties as H_2O in a crystalline hydrate.

[3] Mr. Kornyakov uses the expression "the mean valence of a bond" several times on page 228, and this is a fairly common expression in the mineralogical literature.

However, the International Union of Pure and Applied Chemistry defines valence as follows: "*The maximum number of univalent atoms (originally hydrogen or chlorine atoms) that may combine with an atom of the element under consideration, or with a fragment, or for which an atom of this element can be substituted*".

Thus valence is a positive integer, and is the property of an atom, not a chemical bond. One should use the expression "*bond valence*" which is a measure of the strength of a chemical bond.

[4] The symbols < > indicate "mean" and so the work "mean" is not necessary in the expression "mean <O-Cu-O> angle", just "<O-Cu-O> angle" is all that is needed.

An important scientific result

[5] On page 217, Mr. Kornyakov writes: "Additional Cu^{2+}-centered polyhedra are attached from both sides of the layers to form kagomé net of copper atoms (Fig. 17d)".

This is an important statement and warrants more explanation when Mr. Kornyakov publishes anything on the presence of this net in future papers. Fig. 17d resembles the sheet of tetrahedra in mica, and most readers will expect other atoms at the centres of these tetrahedra. This will need to be explained and all the linkages between the Cu atoms described in this net.

This is an extremely interesting observation as a "kagomé net of copper atoms" also occurs in the spin-1/2 kagomé lattice antiferromagnetic herbertsmithite. I and others have often speculated that many other Cu^{2+} oxysalt minerals based on sheets of edge-sharing $Cu^{2+}\varphi_6$ octahedra ($\varphi = O^{2-}$,

$(OH)^{-}$, Cl^{-}, $(H_2O)^{0}$) could also exhibit interesting physical properties such as superconductivity and quantum spin-liquid behavour because of the constituent kagomé net of Cu^{2+} ions.

This is something that is well worth investigating further, particularly in terms of the details of the Cu-Cu interactions that give rise to these interesting properties. The work of Mr. Kornyakov presented here provides the structural framework to do so.

Dissertation of *Full name* on the topic: "*Ilya Viktorovich Kornyakov* " *meets* the basic requirements established by Order No.11181/1 dd. 19.11.2021 "On the procedure for awarding academic degrees at St. Petersburg State University". The applicant *Ilya Viktorovich Kornyakov* deserves to be awarded the academic degree of *candidate* of geological and mineralogical sciences in a scientific speciality 1.6.4. Mineralogy, Crystallography. Geochemistry, Geochemical Methods of Mineral Exploration. Paragraphs 9 and 11 of the specified Order have not been violated.

Member of the Dissertation Council

Academic degree, academic title, position	signature	Full name
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Date April 28/2022