Dioskouriite, CaCu₄Cl₆(OH)₄·4H₂O: A New Mineral Description, Crystal Chemistry and Polytypism

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Abstract: A new mineral, dioskouriite, CaCu₄Cl₆(OH)₄·4H₂O, represented by two polytypes, monoclinic (2M) and orthorhombic (2O), which occur together, was found in moderately hot zones of two active fumaroles, Glavnaya Tenoritovaya and Arsenatnaya, at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. Dioskouriite seems to be a product of the interactions involving high-temperature sublimate minerals, fumarolic gas and atmospheric water vapor at temperatures not higher than 150 °C. It is associated with avdoninite, belloite, chlorothionite, eriochalcite, sylvite, halite, carnallite, mitscherlichite, chrysothallite, sanguite, romanorlovite, flinteite, and -2M M. Dioskouriite-2O is optically biaxial (+), α = 1.695(4), β = 1.715(8), γ = 1.750(6) and β = 1.730(6) Å. The Raman spectrum is reported. The chemical composition (wt%, electron microprobe data, H₂O calculated by total difference; dioskouriite-2O/dioskouriite-2M is: K₂O 0.03/0.21; MgO 0.08/0.47; CaO 8.99/8.60; CuO 49.24/49.06; Cl 32.53/32.66; H₂O(calc.) 16.48/16.38; -O=Cl −7.35/−7.38; total 100/100. The empirical formulae based on 14 O + Cl and 0% apfu are: dioskouriite-2O: Ca₁.₀₄(Cu₁.₀₂Mg₀.₂₀)₂⁺(Cu₁.₄³Ca₁.₃₉Zn₀.₀₅)O₁₄Cl₂(OH)₃.₉₀O₁₄Cl₁₀⁻4H₂O; dioskouriite-2M: (Ca₁.₀₀K₀.₃₂)₂⁺(Cu₁.₀₁Mg₀.₇₈)₂⁺(Cu₁.₆₄Zn₀.₂₈)O₁₄Cl₂(OH)₃.₈₃O₁₈Cl₁₀⁻4H₂O. Dioskouriite-2M has the space group P2₁/c, a = 7.2792(8), b = 10.3000(7), c = 20.7589(2) Å, β = 100.238(11)°, V = 1531.6(2) Å³ and Z = 4; dioskouriite-2O: P2₁/a, a = 7.3193(7), b = 10.3710(10), c = 20.560(3) Å, V = 1560.6(3) Å³ and Z = 4. The crystal structure (solved from single-crystal XRD data, R = 0.104 and 0.081 for dioskouriite-2M and -2O, respectively) is unique. The structures of both polytypes are based upon identical BAB layers parallel to (001) and composed from Cu²⁺-centered polyhedra. The core of each layer is formed by a sheet A of edge-sharing mixed-ligand octahedra centered by Cu(1), Cu(2), Cu(3), Cu(5) and Cu(6) atoms, whereas distorted Cu(4)(OH)Cl₃ tetragonal pyramids are attached to the A sheet on both sides, along with the Ca(OH)₂(H₂O)₂Cl₂ eight-cornered polyhedra, which provide the linkage of the two adjacent layers via long Ca−Cl bonds. The Cu(4) and Ca polyhedra form the B sheet.
difference between the 2M and 2O polytypes arises as a result of different stacking of layers along the c axis. The cation array of the layer corresponds to the capped kagomé lattice that is also observed in several other natural Cu hydroxychlorides: atacamite, clinoatacamite, bobkingite and avdoninite. The mineral is named after Dioskouri, the famous inseparable twin brothers of ancient Greek mythology, Castor and Polydeuces, the same in face but different in exercises and achievements; the name is given in allusion to the existence of two polytypes that are indistinguishable in appearance but different in symmetry, unit cell configuration and XRD pattern.

**Keywords:** dioskouriite; calcium copper hydroxide chloride; new mineral; crystal structure; polytype; kagomé lattice; fumarole; Tolbachik volcano; Kamchatka

### 1. Introduction

Chlorides, oxychlorides and hydroxychlorides (hydroxide chlorides or chloride hydroxides, depending on the ratio of \( \text{Cl}^- \) and \( \text{OH}^- \) anions in a formula) of divalent copper are numerous in nature: thirty-five such minerals are known, with only atacamite, an orthorhombic \( \text{Cu}_2(\text{OH})_3\text{Cl} \), being widespread in nature, whereas others are considered as rare or extremely rare species. In this chemical family of natural compounds, thirty-one minerals contain \( \text{OH} \) or \( \text{H}_2\text{O} \). The majority of the hydrogen-bearing \( \text{Cu}^{2+} \) chlorides and hydroxychlorides are supergene minerals typically formed in the oxidation zones of copper-containing ores. At the same time, there is another geological setting in which minerals containing both species-defining \( \text{Cu}^{2+} \) and \( \text{Cl}^- \) are diverse: oxidizing-type volcanic fumaroles [1,2]. Four \( \text{H} \)-free \( \text{Cu}^{2+} \) chlorides and oxychlorides are reliably known only from active fumaroles, namely tolbachite, \( \text{CuCl}_2 \) [3], melanothallite, \( \text{Cu}_2\text{OCl}_2 \) [4], ponomarevite, \( \text{K}_4\text{Cu}_4\text{OCl}_{10} \) [5], and sanguite, \( \text{KCuCl}_3 \) [6]. Tolbachite, melanothallite and ponomarevite crystallize directly from gaseous phase as volcanic sublimes in the high-temperature zones (>200 °C of fumaroles, whereas in moderately hot zones (<200 °C, mainly at 70–150 °C) of the same fumarole system, a specific copper (hydroxy)chloride mineralization is formed as a result of complex interactions between fumarole gas, atmospheric water/vapor and earlier-crystallized high-temperature minerals [2,7]. This mineral assemblage, best studied on the material from the active fumarole fields of the Tolbachik volcano, Kamchatka, Russia, includes sanguite, belloite, \( \text{CuCl(OH)} \), eriochalcite, \( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} \), mitscherlichite, \( \text{Cu}_4\text{Cl}_6(\text{OH})_4 \cdot 4\text{H}_2\text{O} \) [2], avdoninite, \( \text{K}_2\text{Cu}_8\text{Cl}_8(\text{OH})_4 \cdot 2\text{H}_2\text{O} \) [8,9], romanorlovite, \( \text{K}_3\text{Cu}_9\text{Cl}_{25}(\text{OH})_4 \cdot 2\text{H}_2\text{O} \) [10], chrysothallite, \( \text{K}_3\text{Cu}_6\text{Ti}^{2+}\text{Cl}_{17}(\text{OH})_4 \cdot 2\text{H}_2\text{O} \) [11], feodosiyyite, \( \text{Cu}_{11}\text{Mg}_2\text{Cl}_{18}(\text{OH})_8 \cdot 16\text{H}_2\text{O} \) [12], and dioskouriite, described in this paper.

Dioskouriite, \( \text{CaCu}_4\text{Cl}_6(\text{OH})_4 \cdot 4\text{H}_2\text{O} \), is the third natural Ca-Cu hydroxychloride, after calumetite, \( \text{CaCu}_4\text{Cl}_2(\text{OH})_8 \cdot 3.5\text{H}_2\text{O} \) [13,14], and centennialite, \( \text{CaCu}_3\text{Cl}_2(\text{OH})_6 \cdot 0.7\text{H}_2\text{O} \) [13]. It is worthy to note that “vonderechnite”, described in 2018 as a new mineral species with the idealized formula \( \text{CaCu}_4\text{Cl}_2(\text{OH})_8 \cdot 4\text{H}_2\text{O} \) [15], was discredited in 2019 after the determination of its identity with calumetite [14].

Dioskouriite is crystallized as two polytypes, monoclinic and orthorhombic, which occur together. This feature determined the choice of its name: dioskouriite (Cyrillic: диоскурит), named after Dioskouri, the famous inseparable twin brothers of Greek mythology (in Greek, Διόσκουροι, which means Διός Κούροι, Dias or Zeus’ sons), Castor and Polydeuces, the same in face but different in exercises and achievements. This alludes to the existence of two polytypes that are indistinguishable in appearance but different in symmetry, unit cell parameters and X-ray diffraction pattern in the same sample.

The new mineral, its species name dioskouriite and the names of both its polytypes, dioskouriite-2M for monoclinic and dioskouriite-2O for orthorhombic one, were approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2015–106). The names of dioskouriite polytypes are given in accord with the nomenclature of polytypes, polytypoids and polymorphs [16]. The type specimen of dioskouriite is
deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the catalog number 95282.

2. Occurrence and Mineral Associations

Dioskouriite was found in upper, moderately hot zones of two active fumaroles, Glavnaya Tenoritovaya (Major Tenorite) (holotype) and Arsenatnaya (cotype) situated at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption 1975–1976, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41′ N 160°14′ E, 1200 m asl). Specimens with the new mineral were collected by us in July 2014.

The Second scoria cone is a monogenetic volcano about 300 m high and 0.1 km³ in volume formed in 1975. It is located 18 km SSW of the active volcano Ploskiy Tolbachik [17]. Both above-mentioned fumaroles occur at its summit. The Glavnaya Tenoritovaya fumarole is described in [11] and the Arsenatnaya fumarole in [18].

In Glavnaya Tenoritovaya, dioskouriite was found in sulfate-chloride incrustations and is associated with avdoninite, belloite, chlorothionite, eriochalcite, sylvite, halite, carnallite, mitscherlichite, chrysothallite, sanguite, romanorlovite, feodosiyite, mellizinkalite, flinteite, kainite, gypsum, sellaite and an incompletely studied K-Pb-Cu chloride; hematite, tenorite and chalcocyanite are earlier sublime minerals.

In Arsenatnaya, dioskouriite and avdoninite are the latest mineral in vugs of basalt scoria altered by fumarolic gas. They are closely associated with earlier sublimate minerals: hematite, tenorite, chlorophlogopite, diopside, clinoenstatite, sanidine, halite, apatite group sulfates, anhydrite, pseudobrookite, powellite and Cr⁶⁺-bearing baryte.

The temperatures we measured using a chromel–alumel thermocouple in areas where the new mineral was found during its collection were 100–120 °C. Dioskouriite was probably formed not as a result of direct crystallization from a gaseous phase but as a product of the interactions involving earlier-formed high-temperature sublimate Cu- and Ca-bearing minerals, HCl-containing fumarolic gas and atmospheric components (at first, water vapor) at relatively low temperatures, presumably not higher than 120–150 °C.

3. Methods

The density of dioskouriite was measured by flotation in heavy liquids (bromoform + dimethylformamide) for the sample with the predominance of the 2O polytype.

The Raman spectrum of dioskouriite (sample with a mixture of both polytypes) was obtained using an EnSpectr R532 spectrophotometer (Department of Mineralogy, Moscow State University) with a green laser (532 nm) at room temperature. The output power of the laser beam on the sample was about 4 mW. The spectrum was processed in the range from 100 to 4000 cm⁻¹ with the use of a holographic diffraction grating with 1800 mm⁻¹ and a resolution equal to 6 cm⁻¹. The diameter of the focal spot on the sample was about 15 µm with 40x objective. The spectrum was acquired on a polycrystalline sample.

Scanning electron microscopic (SEM) studies in secondary electron (SE) mode were carried out and chemical composition was determined for all studied samples using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Department of Petrology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 20 nA and a 5-µm beam diameter. H₂O was not analyzed because of the paucity of pure material.

Powder X-ray diffraction (XRD) data were collected using a Rigaku RAXIS Rapid II (X-ray Diffraction Resource Center, St. Petersburg State University, St. Petersburg, Russia) diffractometer with a curved image plate detector and a rotating anode with Varimax microfocus optics, using CoKα radiation, in Debye–Scherrer geometry, at an accelerating voltage of 40 kV, a current of 15 mA and an exposure time 15 min. The distance between the sample and the detector was 127.4 mm. The data were processed using osc2xrd software [19].
Single-crystal XRD studies were carried out using a Bruker APEX II DUO diffractometer (X-ray Diffraction Resource Center, St. Petersburg State University, St. Petersburg, Russia) (2M polytype) and an Oxford Diffraction SuperNova diffractometer (X-ray Diffraction Resource Center, St. Petersburg State University, St. Petersburg, Russia) (2O polytype), both equipped with CCD detectors (MoKα radiation).

Due to the low stability of dioskouriite in moist air and its solubility in water (see below, Section 4.4), we (1) preserved the specimens by hermetic sealing and (2) prepared polished samples for electron microprobe studies using purified kerosene, without water.

4. Results

4.1. General Appearance and Physical Properties

In both fumaroles, dioskouriite occurs as well-shaped or crude crystals up to 0.01 mm × 0.04 mm × 0.1 mm in size. The crystals are tabular to lamellar, sometimes pseudo-hexagonal, or flattened prismatic, with domatic terminations that are typically sword-like (Figure 1). The crystals are combined in groups or crusts (Figures 1 and 2) up to 1 × 2 mm² in area and up to 0.05 mm thick, overgrowing basalt scoria or incrustations of earlier sublimate minerals covering the surface of basalt scoria.

Both single-crystal and powder XRD data show that the crystals of dioskouriite in both fumaroles are, in fact, parallel, syntactic intergrowths of two polytypes, 2M and 2O, in different proportions, which display considerable variations from grain to grain. In order to study each polytype, we tried to separate samples with the maximum contents of the 2M or 2O modification using XRD techniques.

Figure 1. Morphology of dioskouriite from the Glavnaya Tenoritovaya fumarole (a–c) and from the Arsenatnaya fumarole (d): (a,b)—crystal groups; (c)—crystal crust with overgrowing crude equant crystals of carnallite; (d)—crystal crust overgrowing basalt scoria. SEM (secondary electron, SE) images.
Dioskouriite is transparent, bright green with light green streaks and has a vitreous luster. The mineral is brittle, with uneven fractures. One direction of distinct cleavage (assumed, based on the structure data (see below), as (001) and one direction of imperfect cleavage were observed under the microscope. The Mohs hardness is ca. 3. The measured density is 2.75(1) g cm\(^{-3}\). Density calculated using the empirical formulae was 2.820 g cm\(^{-3}\) for dioskouriite-2M and 2.765 g cm\(^{-3}\) for dioskouriite-2O.

![Figure 2. Crystals, crystal clusters and crusts of green dioskouriite with light blue chlorothionite and colorless carnallite and sylvite. The holotype specimen from the Glavnaya Tenoritovaya fumarole. Field of view width, 3.5 mm.](image)

### 4.2. Optical Data

In plane-polarized transmitted light, dioskouriite demonstrates distinct pleochroism: Z (grass green) > Y (yellowish-green) > X (pale yellowish-green). The mineral is optically biaxial (+), \(\alpha = 1.695(4), \beta = 1.715(8), \gamma = 1.750(6)\) (589 nm); 2\(V\)\(_{\text{meas.}}\) = 70(10)\(^\circ\), 2\(V\)\(_{\text{calc.}}\) = 75.5\(^\circ\). Dispersion of optical axes is very strong, \(r < v\). These data were obtained for the sample with the predominant 2O polytype. The crystals demonstrate straight extinction parallel to the elongation.

### 4.3. Raman Spectroscopy

The Raman spectrum of dioskouriite is shown in Figure 3. Bands in the range from 3600 to 3200 cm\(^{-1}\) correspond to O–H stretching vibrations. We assigned the strong band with a maximum at 3460 cm\(^{-1}\) to vibrations of hydroxyl groups, whereas its distinct low-frequency shoulder with a maximum at 3380 cm\(^{-1}\) was assigned to vibrations of H\(_2\)O molecules. The band at 1590 cm\(^{-1}\) corresponds to H–O–H bending vibrations of H\(_2\)O molecules. The bands with maxima at 940, 910 and 830 cm\(^{-1}\) are assigned to O–H libration (in other terms, Cu\(^{2+}\)···O–H bending) modes. The bands at 500 and 420 cm\(^{-1}\) correspond to Cu\(^{2+}\)–O stretching vibrations, whereas the bands with wavenumbers 300 cm\(^{-1}\) and lower can be assigned to Ca–O stretching vibrations and to lattice modes involving, in particular, Cu\(^{2+}\)–Cl and Ca–Cl vibrations.
The Raman spectrum of dioskouriite and its enlarged low-frequency fragment.

4.4. Chemical Data

The chemical composition of both polytypes of dioskouriite is given in Table 1. Contents of other elements with atomic numbers higher than carbon are below detection limits.

Table 1. Chemical composition of dioskouriite.

| Constituent | Dioskouriite-2O | Dioskouriite-2M | Probe Standard |
|-------------|-----------------|-----------------|---------------|
|             | Wt% * Range SD  | Wt% ** Range SD |               |
| K₂O         | 0.05 0.00-0.12  | 0.03 0.21       | 0.19          |
| MgO         | 0.08 0.02-0.21  | 0.07 0.47       | 0.20          |
| CaO         | 8.99 8.56-9.36  | 3.2 8.60       | 0.39          |
| CuO         | 49.24 48.67-50.56 | 0.81 49.06   | 2.29          |
| Cl          | 32.53 31.10-33.17 | 0.80 32.66   | 1.78          |
| H₂Ocalc *** | (16.48) - -     | (16.38) - -   | -             |
| −O=Cl       | −7.35 - -       | −7.38 - -     | -             |
| Total       | 100.00 - -      | 100.00 - -    | -             |

* Averaged for six spot analyses; ** averaged for four spot analyses; *** calculated by total difference. SD—standard deviation.

The empirical formulae calculated on the basis of 14 O + Cl atoms per formula unit (apfu; the OH/O/H₂O ratios correspond to 4 H₂O molecules pfu) are:
1. dioskouriite-2O: Ca₁.₀₄(Cu₄.₀₂Mg₀.₀₁)Σ₄.₄₃[Cl₅.₉₆(OH)₃.₉₂O₀.₁₄]Σ₁₀⁻⁴H₂O;
2. dioskouriite-2M: (Ca₁.₀₀K₀.₀₃)Σ₄.₄₃[Cl₄.₉₉(OH)₃.₈₂O₀.₁₈]Σ₁₀⁻⁴H₂O.

The idealized, end-member formula is Ca₅Cl₄(OH)₄·4H₂O, which requires CaO 8.67, CuO 49.17, Cl 32.87, H₂O 16.71, −O=Cl −7.42 and total 100 wt%.

Dioskouriite readily dissolves in H₂O at room temperature. It is unstable under room conditions and completely alters to a light blue earthy aggregate of Cu²⁺ and Ca chlorides and carbonates for several months or even days, depending on the air moisture.

4.5. X-ray Crystallography and Crystal Structure

Powder XRD data of both polytypes of dioskouriite are given in Table 2. The unit cell parameters calculated from the powder data are as follows: dioskouriite-2M: a = 7.291(4), b = 10.293(3), c = 20.79(1) Å, β = 100.66(5)° and V = 1533(2) Å³; dioskouriite-2O: a = 7.306(2), b = 10.376(3), c = 20.62(1) Å and V = 1563(2) Å³.
### Table 2. Powder X-ray diffraction data (d in Å) of the two polytypes of dioikosrite.

| $d_{\text{obs}}$ | $d_{\text{calc}}$ | $h k l$ | $d_{\text{obs}}$ | $d_{\text{calc}}$ | $h k l$ |
|------------------|-------------------|--------|------------------|-------------------|--------|
| 100              | 10.29             | 3      | 100              | 10.214            | 3      |
| 3                | 9.26              | 7      | 3                | 9.197             | 7      |
| 3                | 7.30              | 5      | 3                | 7.252             | 5      |
| 22               | 5.960             | 35     | 22               | 5.884, 5.881      | 35     |
| 7                | 5.754             | 13     | 7                | 5.680             | 13     |
| 11               | 5.492             | 6      | 11               | 5.452, 5.444      | 6      |
| 16               | 5.170             | 5      | 16               | 5.150, 5.107      | 5      |
| 5.035            | 8                 | 28     | 5.035            | 4.994             | 28     |
| 6                | 4.636             | 10     | 6                | 4.599             | 10     |
| 2                | 3.806             | 10     | 2                | 3.798             | 10     |
| 1                | 3.611             | 10     | 1                | 3.626, 3.611      | 10     |
| 1                | 3.355             | 10     | 1                | 3.585, 3.582      | 10     |
| 3                | 3.418             | 10     | 3                | 3.405             | 10     |
| 5                | 3.300             | 10     | 5                | 3.312, 3.254      | 10     |
| 3                | 3.221             | 10     | 3                | 3.312, 3.310      | 10     |
| 3                | 3.131             | 10     | 3                | 3.133, 3.114      | 10     |
| 6                | 3.080             | 10     | 6                | 3.097, 3.067, 3.066, 3.062 | 10 |
| 1.05, 0.5, 0.5   | 0.5                | 1.05, 0.5, 0.5 | 3.097, 3.067, 3.066, 3.062 | 0.5 |
| 0.5, 0.5, 0.5    | 0.5                | 1.05, 0.5, 0.5 | 3.097, 3.067, 3.066, 3.062 | 0.5 |
| 1.428, 1.426     | 1.5                | 1.428, 1.426 | 1.428, 1.426     | 1.5 |
| 1.426, 1.424     | 1.5                | 1.426, 1.424 | 1.426, 1.424     | 1.5 |
| 1.371, 1.370     | 1.5                | 1.371, 1.370 | 1.371, 1.370     | 1.5 |
| 1.272, 1.277, 1.275, 1.269 | 0.414 | 1.272, 1.277, 1.275, 1.269 | 0.414 |

For the calculated patterns, only reflections with intensities $\geq 0.5$ are given; ** for the unit cell parameters calculated from single-crystal data, the strongest reflections are marked in bold. The distinct increase, in comparison with the calculated values, in the reflections (given in italics) in the pattern of the 2M polytype could be caused by the admixture of the 2O polytype.
The structures of both polytypes of dioskouriite were studied using single crystals. The crystal structures were solved by direct methods and refined to $R_1 = 0.1039$ for 1805 independent reflections with $I > 2\sigma(I)$ (dioskouriite-$2M$) and to $R_1 = 0.0881$ for 1478 independent reflections with $I > 2\sigma(I)$ (dioskouriite-$2O$). The crystal structure refinement revealed the presence of “ghost” electron density peaks in both structure models on the $z$ levels, corresponding to the positions of Cu atoms (in $2O$ polytype) and of Cu, Cl and Ca atoms (in $2M$ polytypes). The existence of these peaks was interpreted as being induced by stacking faults, i.e., by the presence of domains of another polytype in the studied crystals, as frequently observed in layered mineral structures [20,21].

Crystal data, data collection information and structure refinement details are given in Table 3, atom coordinates and displacement parameters are in Table 4a,b and Table 5a,b, selected interatomic distances are in Table 6 and the bond valence calculations are in Tables 7 and 8.

**Table 3.** Crystal data, data collection information and structure refinement details for dioskouriite-$2M$ and dioskouriite-$2O$.

| Polytype          | Dioskouriite-$2M$                          | Dioskouriite-$2O$                          |
|-------------------|--------------------------------------------|--------------------------------------------|
| Ideal formula     | CaCu$_4$(OH)$_4$Cl$_6$·4H$_2$O              |                                            |
| Ideal formula weight | 647.04                                    |                                            |
| Temperature, K    | 293(2)                                     |                                            |
| Crystal system    | Monoclinic                                 | Orthorhombic                               |
| Space group; Z    | $P2_1/c; 4$                                | $P2_12_12_1; 4$                            |
| Crystal data, data collection information and structure refinement details for dioskouriite-$2M$ and dioskouriite-$2O$. |
| Unit cell dimensions, Å, $^a$ | $a = 7.2792(8)$, $b = 10.0300(7)$, $c = 1531.6(2)$ | $a = 7.3193(7)$, $b = 10.3710(10)$, $c = 1560.6(3)$ |
| $V$, Å$^3$        | 1531.6(2)                                  | 1560.6(3)                                  |
| $\mu$, mm$^{-1}$  | 6.881                                      | 6.752                                      |
| $F_{000}$         | 1256                                       | 1256                                       |
| Crystal size, mm  | 0.01 × 0.04 × 0.06                         | 0.01 × 0.05 × 0.07                        |
| Absorption correction | Bruker APEX II DUO                        | Oxford Diffraction SuperNova               |
| $\theta$ range, $^\circ$ | 1.98–28.28                                | 3.41–28.28                                |
| Index ranges      | $-9 \leq h \leq 9$, $-13 \leq k \leq 13$, $-27 \leq l \leq 27$ | $-5 \leq h \leq 9$, $-13 \leq k \leq 9$, $-27 \leq l \leq 27$ |
| Reflections collected | 12590                                      | 9477                                       |
| Independent reflections | 3846 ($R_{int} = 0.1692$)                | 3866 ($R_{int} = 0.1477$)                |
| Independent reflections with $I > 2\sigma(I)$ | 1805                                       | 1478                                       |
| Data reduction    | CrysAlisPro, version 1.171.36.32 [22]      |                                            |
| Absorption correction | Multi-scan (empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm) | Direct methods                           |
| Structure solution | Full-matrix least-squares on $F^2$       |                                            |
| Refinement method | Direct methods                             |                                            |
| Refined parameters $^*$ | 187                                       | 201                                        |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.1039$, $wR_2 = 0.2574$            | $R_1 = 0.0881$, $wR_2 = 0.2023$            |
| Goodness of Fit (GoF) | 1.009                                      | 0.952                                      |
| Largest difference peak and hole, e/Å$^3$ | 4.61 and −2.72                           | 1.53 and −1.25                            |

$^*$ The number of refined parameters is given taking into account positions of the “ghost” peaks present due to stacking faults.
Table 4. (a) Coordinates, equivalent displacement parameters ($U_{eq}$, in Å$^2$) of atoms and site multiplicities ($Q$) for dioskouriite-2M; (b) Residual peaks related to dioskouriite-2O in the difference Fourier map of dioskouriite-2M.

| Atom | $x$      | $y$      | $z$      | $U_{eq}$ | $Q$ |
|------|----------|----------|----------|----------|-----|
| Cu(1)| 0        | 0        | 0        | 0.0220(6)| 2   |
| Cu(2)| 0        | 0.5      | 0        | 0.0251(7)| 2   |
| Cu(3)| 0.7468(3)| 0.25540(14)| $-$0.00584(9)| 0.0235(5)| 4   |
| Cu(4)| 0.8073(3)| 0.12383(17)| 0.12094(9)| 0.0318(6)| 4   |
| Cu(5)| 1        | 0        | 0        | 0.0215(6)| 2   |
| Cu(6)| 0.5      | 0.5      | 0        | 0.0240(7)| 2   |
| Ca   | 0.6720(6)| 0.4029(3)| $-$0.15357(17)| 0.0369(9)| 4   |
| Cl(1)| 0.2829(7)| 0.3672(4)| 0.0669(2)| 0.0398(11)| 4   |
| Cl(2)| 0.7835(7)| $-$0.1288(3)| 0.0794(2)| 0.0385(11)| 4   |
| Cl(3)| 0.6082(7)| 0.1382(4)| 0.1902(2)| 0.0414(11)| 4   |
| Cl(4)| 0.90988(17)| 0.3549(9)| $-$0.0054(5)| 0.030(3)| 4   |
| O(1)| 0.9088(17)| 0.3549(9)| $-$0.0054(5)| 0.030(3)| 4   |
| Cu(3')| 0.246(4)| 0.254(2)| $-$0.0036(12)| 1.89   |
| Cu(4')| 0.311(5)| 0.126(3)| 0.1189(13)| 1.62   |

Table 5. (a) Coordinates, equivalent displacement parameters ($U_{eq}$, in Å$^2$) of atoms and site multiplicities ($Q$) for dioskouriite-2O; (b) Residual peaks related to dioskouriite-2M in the difference Fourier map of dioskouriite-2O.

| Site | $x$      | $y$      | $z$      | $U_{eq}$ | $Q$ |
|------|----------|----------|----------|----------|-----|
| Cu(1)| 0.1262(18)| 0.2504(13)| 0.4997(7)| 0.0205(18)| 4   |
| Cu(2)| 0.6288(6)| 0.7491(3)| 0.5003(2)| 0.0199(8)| 4   |
| Cu(3)| 0.3741(4)| 0.50486(19)| 0.57083(13)| 0.0226(6)| 4   |
| Ca   | 0.3805(11)| 0.6525(4)| 0.3472(2)| 0.0322(11)| 4   |
| Cl(1)| 0.3727(9)| 0.2827(4)| 0.4284(3)| 0.0240(11)| 4   |
| Cl(2)| 0.8826(10)| 0.6166(5)| 0.5678(3)| 0.0314(12)| 4   |
| Cl(3)| 0.3772(9)| 0.1219(5)| 0.5792(3)| 0.0290(11)| 4   |
| Cl(4)| 0.3754(11)| 0.7083(5)| 0.5775(3)| 0.0329(13)| 4   |
| Cl(5)| 0.1371(10)| 0.3867(6)| 0.6906(3)| 0.0352(13)| 4   |
| Cl(6)| 0.5985(11)| 0.3791(7)| 0.6953(3)| 0.0455(18)| 4   |
| O(1)| 0.1959(18)| 0.4036(13)| 0.5480(8)| 0.022(4)| 4   |
| O(2)| 0.6915(18)| 0.8965(14)| 0.5564(8)| 0.022(4)| 4   |
| O(3)| 0.0543(18)| 0.0998(12)| 0.4522(8)| 0.022(4)| 4   |
| O(4)| 0.5619(16)| 0.6053(13)| 0.4452(7)| 0.017(3)* 4   |
| O(5)| 0.1514(4)| 0.4940(17)| 0.3123(9)| 0.055(6)| 4   |
| O(6)| 0.594(3)| 0.4842(18)| 0.3109(10)| 0.053(6)| 4   |
| O(7)| 0.165(2)| 0.7942(15)| 0.2990(10)| 0.041(5)| 4   |
| O(8)| 0.611(3)| 0.7887(17)| 0.2917(9)| 0.055(6)| 4   |
| Cu(1')| 0.609(18)| 0.250(12)| 0.507(7)| 3.48   |
| Cu(2')| 0.073(6)| 0.749(4)| 0.497(2)| 3.28   |
| Cu(3')| 0.854(2)| 0.505(14)| 0.4852(8)| 4.47   |
| Cl(1')| 0.374(1)| 0.374(1)| 0.62103(13)| 0.0276(6)| 4   |
| Cl(2')| 0.3727(9)| 0.1219(5)| 0.5792(3)| 0.0280(11)| 4   |
| Cl(3')| 0.3754(11)| 0.7083(5)| 0.5775(3)| 0.0329(13)| 4   |
| Cl(4')| 0.1371(10)| 0.3867(6)| 0.6906(3)| 0.0352(13)| 4   |
| Cl(5')| 0.5985(11)| 0.3791(7)| 0.6953(3)| 0.0455(18)| 4   |
| Cl(6')| 0.1959(18)| 0.4036(13)| 0.5480(8)| 0.022(4)| 4   |
| O(1')| 0.611(3)| 0.7887(17)| 0.2917(9)| 0.055(6)| 4   |

* $U_{iso}$
Table 6. Selected interatomic distances (Å) in the structures of dioskouriite-2M and dioskouriite-2O.

|                  | Dioskouriite-2M                                  | Dioskouriite-2O                                  |
|------------------|--------------------------------------------------|--------------------------------------------------|
| Cu(1) − O(2)     | 1.910(10) × 2                                    |                                                 |
| − Cl(3)          | 2.341(4) × 2                                     |                                                 |
| − Cl(2)          | 2.808(5) × 2                                     |                                                 |
| Cu(2) − O(1)     | 1.917(9) × 2                                     |                                                 |
| − Cl(4)          | 2.480(5) × 2                                     |                                                 |
| − Cl(1)          | 2.651(5) × 2                                     |                                                 |
| Cu(3) − O(3)     | 1.956(11)                                        |                                                 |
| − O(1)           | 1.966(11)                                        |                                                 |
| − O(4)           | 1.983(11)                                        |                                                 |
| − O(2)           | 1.996(12)                                        |                                                 |
| − Cl(4)          | 2.627(4)                                         |                                                 |
| − Cl(3)          | 2.664(4)                                         |                                                 |
| Cu(4) − O(4)     | 2.022(12)                                        |                                                 |
| − O(2)           | 2.049(12)                                        |                                                 |
| − Cl(6)          | 2.220(5)                                         |                                                 |
| − Cl(5)          | 2.239(5)                                         |                                                 |
| − Cl(2)          | 2.737(4)                                         |                                                 |
| Cu(5) − O(4)     | 1.904(9)                                         |                                                 |
| − Cl(3)          | 2.382(4)                                         |                                                 |
| − Cl(2)          | 2.744(5)                                         |                                                 |
| Cu(6) − O(3)     | 1.926(10)                                        |                                                 |
| − Cl(4)          | 2.453(5)                                         |                                                 |
| − Cl(1)          | 2.660(5)                                         |                                                 |
| Ca − O(8)        | 2.377(13)                                        |                                                 |
| − O(7)           | 2.403(17)                                        |                                                 |
| − O(6)           | 2.458(18)                                        |                                                 |
| − O(5)           | 2.46(2)                                          |                                                 |
| − O(4)           | 2.461(15)                                        |                                                 |
| − O(3)           | 2.469(16)                                        |                                                 |
| − O(2)           | 2.48(2)                                          |                                                 |
| − O(1)           | 2.492(12)                                        |                                                 |
| − Cl(1)          | 2.957(5)                                         |                                                 |
| − Cl(6)          | 3.222(5)                                         |                                                 |

Table 7. Bond-valence calculations for dioskouriite-2M.

| Site | Cu(1) | Cu(2) | Cu(3) | Cu(4) | Cu(5) | Cu(6) | Ca | Σ |
|------|-------|-------|-------|-------|-------|-------|----|----|
| Cl(1)| -     | 0.17  | -     | -     | -     | 0.17  | 0.20| 0.54|
| Cl(2)| 0.11  | 0.17  | -     | -     | -     | -     | -  | 0.38|
| Cl(3)| 0.40  | 0.27  | 0.17  | -     | -     | -     | 0.29| 0.93|
| Cl(4)| -     | -     | -     | 0.52  | -     | -     | -  | 0.52|
| Cl(5)| -     | -     | -     | 0.55  | -     | -     | 0.10| 0.65|
| Cl(6)| -     | -     | -     | -     | -     | -     | 0.10| 0.65|
| O(1) | OH    | 0.53  | 0.46  | -     | -     | -     | 0.24| 1.23|
| O(2) | OH    | 0.54  | 0.42  | 0.37  | -     | -     | -  | 1.33|
| O(3) | OH    | -     | -     | 0.47  | -     | -     | 0.51| 1.24|
| O(4) | OH    | -     | -     | 0.44  | 0.40  | 0.54  | -  | 1.38|
| O(5) | H₂O   | -     | -     | -     | -     | -     | 0.30| 0.30|
| O(6) | H₂O   | -     | -     | -     | -     | -     | 0.29| 0.29|
| O(7) | H₂O   | -     | -     | -     | -     | -     | 0.32| 0.32|
| O(8) | H₂O   | -     | -     | -     | -     | -     | 0.33| 0.33|
| Σ    | 2.10  | 1.94  | 2.14  | 1.98  | 2.06  | 1.94  | 2.04| -  |

Bond-valence parameters were taken from [23]. Bond-valence sums for Cl⁻ anions, OH⁻ groups and H₂O molecules do not include contributions from hydrogen bonds.
| Site | Cl(1) | Cl(2) | Cl(3) | Cl(4) | Ca | Σ |
|------|-------|-------|-------|-------|----|---|
| Cl(1) | 0.39  | -     | 0.16  | -     | -  | 0.89 |
| Cl(2) | 0.34  | 0.16  | -     | -     | 0.20 | 0.51 |
| Cl(3) | 0.120.12 | -     | 0.13  | -     | -  | 0.37 |
| Cl(4) | 0.15  | 0.280.26 | 0.17 | -     | 0.71 |
| Cl(5) | 0.50  | -     | 0.50  | 0.09  | 0.59 |
| Cl(6) | 0.52  | -     | 0.52  | -     | -  |
| O(1) = OH | 0.49 | -     | 0.41  | 0.40  | 1.30 |
| O(2) = OH | 0.46 | -     | 0.44  | -     | 1.16 |
| O(3) = OH | 0.53 | -     | 0.39  | 0.40  | - |
| O(4) = OH | 0.50 | -     | 0.42  | -     | 1.18 |
| O(5) = H2O | 0.44 | -     | -     | 0.26  | 0.26 |
| O(6) = H2O | -    | -     | -     | 0.27  | 0.27 |
| O(7) = H2O | -    | -     | -     | 0.31  | 0.31 |
| O(8) = H2O | -    | -     | -     | 0.25  | 0.25 |
| Σ    | 1.99  | 1.81  | 1.99  | 1.95  | 1.90 |

Bond-valence parameters were taken from [23]. Bond-valence sums for Cl\(^{-}\) anions, OH\(^{-}\) groups and H\(_2\)O molecules do not include contributions from hydrogen bonds.

5. Discussion

5.1. Structure Description and Identification

Dioskouriite crystallizes as two polytypes, monoclinic and orthorhombic, with their unit cells differing from one another in the value of the β angle, which is about 100° for the monoclinic polytype (Table 3). Their crystal structures are shown in Figures 4 and 5 in polyhedral and ball-and-stick presentations, respectively. The difference between these polytypes arises as a result of different layer stacking along the c axis (Figure 5). The layers (see below) have identical structures and compositions in both polytypes and the mode of their interrelations is the same, which points out that in the case of dioskouriite, we observe a “classical” case of polytypism, similar to the numerous examples of layered minerals: micas, chlorites, hydrotalcite-group members, hilgardite, lamprophyllite, etc. Since both monoclinic and orthorhombic polytypes of the mineral contain two layers per unit cell, they are labeled as dioskouriite-2M and dioskouriite-2O, respectively.

There are four types of cation coordination observed in both polytypes, three for Cu\(^{2+}\) and one for Ca (see Figure 6, where each type is identified with particular crystallographic sites in both structures). The Cu atoms have a mixed-ligand coordination consisting of O and Cl atoms, previously reviewed in [24].

The first type of Cu coordination is octahedral (Oct1) and is composed from four Cl and two O atoms. Two Cl and two O atoms are arranged to form a (CuO\(_2\)Cl\(_2\)) square with trans-configuration of O and Cl, which is complemented by two additional Cl atoms as apices of a [(CuO\(_2\)Cl\(_2\))Cl\(_2\)] octahedron. The octahedra are distorted due to the Jahn–Teller effect [25–27]. The distortion can be measured in terms of the difference between the <Cu–Cl\(_{eq}\)> and <Cu–Cl\(_{ap}\)> average bond lengths, Δ\(_{ap-eq}\), where Cl\(_{eq}\) and Cl\(_{ap}\) are the equatorial and apical Cl atoms, respectively. The value of Δ\(_{ap-eq}\) varies from 0.171 to 0.467 Å and is at a minimum for the Cu2 atom in the 2M polytype. This type of Cu coordination, [6] = [(2O + 2Cl)-trans + 2Cl], is typical for mixed-ligand Cu\(_6\)Cl\(_8\) coordination polyhedra and has been observed in the crystal structures of avdoninite, K\(_2\)Cu\(_2\)Cl\(_8\)(OH)\(_4\)·2H\(_2\)O [9,28], melanothallite, Cu\(_2\)OC\(_2\) [29], and eriochalcite, CuCl\(_2\)·2H\(_2\)O [30].

The second type of Cu coordination in dioskouriite polytypes is also octahedral (Oct2), [6] = [(4O) + 2Cl], and consists of a planar (CuO\(_4\)) square complemented by two Cu–Cl bonds to the apical Cl atoms. This type of coordination is even more common and has been observed in the crystal structures of atacamite and clinoatacamite.
(two Cu$_2$(OH)$_3$Cl polymorphs [31,32]), leningradite, PbCu$_3$(VO$_4$)$_2$Cl$_2$ [33], chloroxiphite, Pb$_3$CuO$_2$(OH)$_2$Cl$_2$ [34], and ilinskite, NaCu$_5$O$_2$(SeO$_3$)$_2$Cl$_3$ [24].

Figure 4. The crystal structures of dioskouriite-2M (left drawing) and dioskouriite-2O (right drawing) projected along the $b$ axis. Only cation-centered polyhedra are shown. The unit cells are outlined.

Figure 5. The layer built by Cu$^{2+}$-centered polyhedra with different labeling of Cu sites for dioskouriite-2M (a) and dioskouriite-2O (b). Legend: Cu, Cl, O and Ca atoms are shown as small green, large green, red and blue spheres, respectively; the Cu–Cl bonds shorter and longer than 2.5 Å are shown as dual-band cylinders and black lines, respectively.
Figure 6. Four types of cation coordination in the crystal structures of dioskouriite-2M and dioskouriite-2O (see text for details). Legend as in Figure 5. Oct, BTP and SP mean octahedral, bicapped trigonal prismatic and (distorted) square pyramidal coordination of cation, respectively.

The third type of the Cu coordination is fivefold and can be described as distorted square pyramidal (SP). The base of the square pyramid is formed by two O and two Cl atoms in a cis-configuration with an additional Cl atom at the apex, \([5] = [(\text{2O+2Cl})-\text{cis}] + \text{Cl}\). The only other known example of such a \(\text{CuO}_n\text{Cl}_m\) configuration is avdoninite, \(\text{K}_2\text{Cu}_5\text{Cl}_8(\text{OH})_4\cdot\text{2H}_2\text{O}\) [9,28].

There is one symmetrically independent Ca site in both structures that has an eightfold coordination that can be described as follows. The oxygen atoms of OH groups and \(\text{H}_2\text{O}\) molecules form a trigonal prism around Ca atoms with the Ca–O distances in the range from 2.377(13) to 2.492(12) Å (dioskouriite-2M) and from 2.403(17) to 2.48(2) Å (dioskouriite-2O); two Cl anions with elongated Ca–Cl distances (2.957(5) and 3.222(5) Å (dioskouriite-2M); 2.964(7) and 3.248(8) Å (dioskouriite-2O)) complete the coordination polyhedron of Ca cation. The geometry of this coordination can therefore be described as bicapped trigonal prismatic (BTP), which is one of the three most common eightfold coordinations known in inorganic chemistry, along with dodecahedral and square antiprismatic coordinations [35].

The crystal structures of both polytypes are based upon complex layers of ca. 1-nm thickness. The layers are stacked along the \(c\) axis and can be considered as built up from the sheets of the two types, \(A\) and \(B\), with the \(A\) sheet sandwiched between two \(B\) sheets, so the layers have the formula \(\text{BAB}\).

The projections of the \(A\) and \(B\) sheets are shown in Figure 7.

Figure 7. The projections of the \(A\) (a) and \(B\) (b) sheets in the crystal structure of dioskouriite-2O along the \(c\) axis. Legend as in Figures 5 and 6.
The A sheet, which is at the core of the BAB layer, is constructed as follows. The Oct₁ octahedra share their trans $\text{Cu}_{\text{eq}}-\text{Cu}_{\text{ap}}$ edges to form chains running parallel to the $a$ axis (Figure 7a). The chains are linked via Oct₂ octahedra that share four of their $\text{O}_{\text{eq}}-\text{Cl}_{\text{ap}}$ edges with adjacent Oct₁ octahedra so that sheets are formed. The B sheets contain isolated BTP and SP polyhedra (Figure 7b) that are attached to the A sheet via $\text{Cu}-\text{OH}, \text{Ca}-\text{OH}, \text{Cu}-\text{Cl}$ and $\text{Ca}-\text{Cl}$ bonds.

The linkage of the BAB layers is provided by the long $\text{Ca}-\text{Cl}$ bonds oriented approximately perpendicular to the plane of the layers (Figure 5). The 2M and 2O polytypes of dioskouriite can be easily distinguished from one another using powder XRD data. The most reliable diagnostic sign is the presence of relatively strong reflections with $d \approx 5.4-5.5$ Å in the powder XRD pattern of dioskouriite-2M (the $-112$ and $111$ reflections with close $d$ values that can appear as a singlet in the measured XRD diagram), which are absent in the XRD pattern of dioskouriite-2O (Table 2).

The high values of a crystallographic agreement factor $R$ (10.39% for dioskouriite-2M and 8.81% for dioskouriite-2O) are due to the stacking faults, which reflect the occurrence of both polytypes in the same crystal. Analysis of residual electron density peaks in different Fourier syntheses indicated that the two strongest peaks for dioskouriite-2M (Table 4b) and the nine strongest peaks for dioskouriite-2O (Table 5b) correspond to the positions of the Ca and Cu atoms when the layers are shifted relative to each other by $a/2$. The residual electron density peaks observed for the 2O polytype approximately correspond to the cation positions of the 2M polytype and vice versa. Both 2M and 2O polytypes are maximum degree of order (MDO) polytypes, which are the simplest of the possible ordered sequences and usually correspond to the most frequently occurring polytypes in the family [36].

5.2. Relations to Other Species

The crystal structures of dioskouriite polytypes are related to the structures of minerals and synthetic inorganic compounds consisting of layers based upon Cu$^{2+}$ cation arrays with a capped kagomé geometry. The latter is one of the most common cationic patterns in Cu oxysalts that possess interesting magnetic properties such as a spin-liquid state [37-43]. From a geometrical point of view, a kagomé net is a tiling of a plane consisting of regular triangles and hexagons (Figure 8). In the capped kagomé pattern, each triangle is capped either from above or below by an additional node, so each triangle in the plane forms the basis of a regular tetrahedron oriented up or down relative to the plane of the net. In most of the structures, the kagomé pattern is distorted, i.e., the ideal hexagonal geometry of the net is violated. Among Cu hydroxychlorides, a distorted kagomé geometry has been observed in atacamite and clinoatacamite, $\text{Cu}_2(\text{OH})_3\text{Cl}$ [32,44], bobkingite, $\text{Cu}_5(\text{OH})_8\text{Cl}_2\cdot2\text{H}_2\text{O}$ [45], and avdoninite, $\text{K}_2\text{Cu}_5\text{Cl}_6(\text{OH})_4\cdot2\text{H}_2\text{O}$ [9,28]. The capped kagomé geometry can be derived from the cristobalite- or pyrochlore-type arrangement of Cu atoms observed in atacamite and clinoatacamite [44], as shown in Figure 8. The Cu array in these two $\text{Cu}_2(\text{OH})_3\text{Cl}$ polymorphs can be described as a framework of corner-sharing “empty” Cu₄ tetrahedra (Figure 8a). Cutting it into layers along the (011) plane in atacamite results in the formation of a 2D layer with a capped kagomé geometry (Figure 8b,c), i.e., a planar arrangement of Cu atoms with all triangles capped by additional Cu atoms located on both sides of the sheet. In all the minerals mentioned above, except for the dioskouriite polytypes, the arrays are homometallic, i.e., they are composed of Cu atoms only. In contrast, the cationic array of the BAB layer in dioskouriite consists of Cu and Ca atoms, where half of the triangles are capped by Ca.
In the real structures of the Cu hydroxychloride minerals, the capped kagomé arrays are decorated by Cl atoms and (OH) groups and the modes of the decoration differ from structure to structure. Figure 9 shows the ball-and-stick representations of the A-type layers in atacamite, clinoatacamite, bobkingite and avdoninite. In all cases, the topology of the interatomic linkage is the same and the layers have the overall formula $[\text{Cu}_3\phi_8]$, where $\phi = \text{Cl}, \text{OH}$. In the crystal structures of atacamite, clinoatacamite and bobkingite, the stoichiometry of the layers is $[\text{Cu}_3(\text{OH})_6\text{Cl}_2]$, whereas the crystal structures of avdoninite and dioskouriite polytypes are based upon the $[\text{Cu}_3(\text{OH})_4\text{Cl}_4]$ layers. Ideally, the layers with different Cl–OH arrangements can be described using idealized diagrams, shown in Figure 10. Figure 10a shows an ideal geometry, whereas Figure 10a–e provide the schemes of distribution of Cl and OH over anionic sublattices in different minerals. The deviations from the ideal geometry due to the different sizes of Cl$^-$ and (OH)$^-$ anions may be essential, as can be seen in Figure 9.

The topological relations between the crystal structures of dioskouriite and other natural Cu hydroxychlorides indicate the energetical stability of the kagomé geometry. The kagomé arrays in dioskouriite polytypes are distorted and therefore less interesting from the viewpoint of their magnetic properties. Nevertheless, it is worthy of investigation, which needs a pure synthetic material. Since no artificial analogs of dioskouriite have been reported so far, its synthesis may be a reasonable task.
5.3. Structural Complexity and Relative Stability

The structural complexity of the two polytypes has been estimated using the information-based parameters elaborated in [46,47] and taking into account the H-correction [48]. Both crystal structures belong to the category of complex structures (500–1000 bit/cell), with dioskouriite-2M being slightly more complex (5.019 bit/atom and 622.230 bit/cell) than dioskouriite-2O (4.954 bit/atom and 614.320 bit/cell). The information densities for the 2M and 2O polytypes are equal to 0.406 and 0.394 bit/Å³, respectively. The difference in information density correlates well with the difference in physical densities—2.820 and 2.765 g/cm³, respectively. This allows to consider the 2O polytype as being slightly less stable (or metastable) compared to the 2M polytype. One may also consider the 2O polytype as a high-temperature phase and the 2M polytype as a low-temperature phase. The same kind of relation has been observed in a number of minerals and inorganic compounds: the metastable high-temperature polymorph possessing lower density and lower complexity compared to the stable low-temperature polymorph (see [46] and [49] for a recent discussion of the topic). However, there are very small doubts that both polytypes are energetically close to each other and that this causes their common formation and the presence of domains of both polytypes in the same crystals. The existence of stacking faults and intimate intergrowths of the two polytypes may indicate the oscillating temperature and/or kinetic regime of crystallization of the mineral inside volcanic fumaroles.

Figure 9. The [Cu₃φ₈] layers (φ = Cl, OH) in the crystal structures of atacamite (parallel to (011) (a); clinoatacamite (parallel to (011) (b); bobkingite (parallel to (001) (c) and avdoninite (parallel to (100) (d). Legend as in Figure 5.
and the presence of domains of both polytypes in the same crystals. The existence of stacking faults and intimate intergrowths of the two polytypes may indicate the oscillating temperature and/or kinetic regime of crystallization of the mineral inside volcanic fumaroles.

Figure 10. The idealized model of the [Cu$_3$φ$_8$] layer (φ = Cl, OH) (a) and the schemes of the OH/Cl population in the crystal structures of atacamite (b), clinoatacamite (c), bobkingite (d), avdoninite (e) and dioskouriite polytypes (f).

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References

1. Vergasova, L.P.; Filatov, S.K. A study of volcanogenic exhalation mineralization. *J. Volcanol. Seismol.* 2016, 10, 71–85. [CrossRef]

2. Pekov, I.V.; Zubkova, N.V.; Pushcharovsky, D.Y. Copper minerals from volcanic exhalations—a unique family of natural compounds: Crystal chemical review. *Acta Crystallogr.* 2018, 74, 502–518. [CrossRef]

3. Vergasova, L.P.; Filatov, S.K. A new mineral, tolbachite, CuC$_2$. *Dokl. Akad. Nauk SSSR* 1983, 270, 415–417. (In Russian) [CrossRef]

4. Vergasova, L.P.; Filatov, S.K. Chemical formula and crystal chemical characterization of melanothallite, Cu$_3$OCl$_2$. *Zapiski RMO* 1982, 124, 562–565. (In Russian)

5. Vergasova, L.P.; Filatov, S.K.; Serafimova, E.K.; Semenova, T.F. Ponomarevite, K$_4$Cu$_3$Cl$_6$(OH)$_4$H$_2$O. *Russ. Geol. Geophys.* 2020, 61, 675–688.

6. Chukanov, N.V.; Murashko, M.N.; Zadov, A.E.; Bushmakin, A.F. Avdoninite, K$_2$Cu$_3$Cl$_6$(OH)$_4$H$_2$O, a new mineral from volcanic exhalations and from the zone of technogenesis at massive sulfide ore deposits. *Zapiski RMO* 2006, 148, 38–42. (In Russian)

7. Pekov, I.V.; Krivovichev, S.V.; Chukanov, N.V.; Pushcharovsky, V.O.; Sidorov, E.G. Avdoninite: New data, crystal structure and refined formula K$_2$Cu$_3$Cl$_6$(OH)$_4$2H$_2$O. *Geol. Ore Dep.* 2016, 58, 568–578. [CrossRef]

8. Pekov, I.V.; Pushcharovsky, D.Y.; Britvin, S.N.; Sidorov, E.G. Oxidizing-type fumaroles of the Tolbachik Volcano, a mineralogical and geochemical unique. *Russ. Geol. Geophys.* 2017, 59, 601–608. [CrossRef]

9. Pekov, I.V.; Zubkova, N.V.; Belakovskiy, D.I.; Lykova, I.S.; Yapskurt, V.O.; Stapor, E.G. Avdoninite, K$_4$Cu$_3$Cl$_6$(OH)$_4$H$_2$O, a new mineral from volcanic exhalations and from the zone of technogenesis at massive sulfide ore deposits. *Zapiski RMO* 2006, 148, 38–42. (In Russian)

10. Pekov, I.V.;Britvin, S.N.; Chukanov, N.V.; Pushcharovsky, V.O.; Sidorov, E.G. Avdoninite: New data, crystal structure and refined formula K$_2$Cu$_3$Cl$_6$(OH)$_4$2H$_2$O. *Geol. Ore Dep.* 2016, 58, 568–578. [CrossRef]

11. Pekov, I.V.; Yapskurt, V.O.; Britvin, S.N.; Chukanov, N.V.; Pushcharovsky, V.O.; Sidorov, E.G. Romanorolvite, a new copper and potassium hydroxychloride from the Tolbachik volcano, Kamchatka, Russia. *Geol. Ore Dep.* 2017, 59, 601–608. [CrossRef]

12. Pekov, I.V.; Zubkova, N.V.; Belakovskiy, D.I.; Lykova, I.S.; Yapskurt, V.O.; Sidorov, E.G.; Pushcharovsky, D.Y. Chrysothallite K$_4$Cu$_4$Ti$_3^+$Cl$_7$(OH)$_4$H$_2$O, a new mineral species from the Tolbachik volcano, Kamchatka, Russia. *Miner. Mag.* 2015, 79, 365–376. [CrossRef]

13. Crichton, W.; Müller, H. Centennialite, CaCu$_2$(OH)$_2$Cl$_2$, new minerals from volcanic and from the zone of technogenesis at massive sulfide ore deposits. *Miner. Mag.* 2016, 81, 1105–1124. [CrossRef]

14. Miyawaki, R.; Hatert, F.; Pasero, M.; Mills, S.I. New minerals and nomenclature modifications approved in 2019. *IMA Commission on New Minerals, Nomenclature and Classification (CNMNC), Newsletter 49*. *Mineral. Mag.* 2019, 83, 479–483. [CrossRef]

15. Schlüter, J.; Malcherek, T.; Pohl, D.; Schäfer, C. Vondechenite, a new hydrous calcium copper chloride hydroxide, from the Bellerberg, East-Eifel volcanic area, Germany. *N. Jb. Miner. Abh.* 2018, 195, 79–86. [CrossRef][PubMed]

16. Nickel, E.H.; Grice, J.D. The IMA Commission on New Minerals and Mineral Names: Procedures and guidelines on mineral nomenclature. *Can. Miner.* 1998, 36, 913–926.

17. Fedotov, S.A.; Markhinin, Y.K. (Eds.) *The Great Tolbachik Fissure Eruption*; Cambridge University Press: New York, NY, USA, 1983.

18. Pekov, I.V.; Koshlyakova, N.N.; Zubkova, N.V.; Lykova, I.S.; Britvin, S.N.; Yapskurt, V.O.; Agakhanov, A.A.; Chukanov, N.V.; Pushcharovsky, D.Y.; Turchkova, A.G.; Sidorov, E.G. Oxidizing-type fumaroles of the Tolbachik Volcano, a mineralogical and geochemical unique. *Russ. Geol. Geophys.* 2017, 59, 601–608. [CrossRef]

19. Britvin, S.N.; Dolivo-Dobrovolsky, D.V.; Krzhizhanovskaya, M.G. Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer. *Zap. Ross. Mineral. Obsb.* 2017, 146, 104–107. (In Russian)

20. Krivovichev, S.V.; Armbruster, T.; Yakovenchuk, V.N.; Pakhomonovsky, Y.A.; Men’shikov, Y.P. Crystal structures of lamprophyllite-2M and lamprophyllite-2O from the Lovozero alkaline massif, Kola peninsula, Russia. *Eur. J. Mineral.* 2003, 15, 711–718. [CrossRef]

21. Yakovenchuk, V.N.; Krivovichev, S.V.; Ivanyuk, G.Y.; Pakhomonovsky, Y.A.; Selivanova, E.A.; Zhiltova, E.A.; Kalashnikova, G.O.; Zolotarev, A.A.; Mikhailova, J.A.; Kadyrova, G.I. Khibinamite-(Ce), Ce$_2$TiO$_2$[(SiO$_4$)$_4$][HCO$_3$]$_3$(H$_2$O), a new rare-earth mineral from the pegmatites of the Khibiny alkaline massif, Kola Peninsula, Russia. *Mineral. Mag.* 2014, 78, 483–496. [CrossRef]

22. Agilent. *CrysAlis PRO*; Agilent Technologies UK Ltd.: Yarnton, UK, 2013.
23. Brese, N.E.; O’Keeffe, M. Bond-valence parameters for solids. Acta Crystallogr. 1991, 47, 192–197. [CrossRef]

24. Krivovichev, S.V.; Filatov, S.K.; Vergasova, L.P. The crystal structure of illinite, NaCu$_2$(SeO$_3$)$_2$Cl$_2$, and review of mixed-ligand CuO$_{m}$Cl$_n$ coordination geometries in minerals and inorganic compounds. Miner. Petrol. 2013, 107, 235–242. [CrossRef]

25. Jahn, H.A.; Teller, E. Stability of polyatomic molecules in degenerate electronic states. I. Orbital degeneracy. Proc. R. Soc. 1937, A161, 220–235.

26. Hathaway, B.J. Copper. In Comprehensive Coordination Chemistry; Pergamon, G.W., Ed.; Oxford: Oxford, UK, 1987; Volume 5, pp. 533–774.

27. Burns, P.C.; Hawthorne, F.C. Mixed-ligand Cu$_2^+\Phi_6$ octahedra in minerals: Observed stereochemistries and Hartree-Fock calculations. Can. Mineral. 1995, 33, 1177–1188.

28. Kahlenberg, V. On the crystal structure of K$_2$Cu$_5$Cl$_6$(OH)$_4$-2H$_2$O. Z. Anorg. Allg. Chem. 2004, 630, 900–903. [CrossRef]

29. Krivovichev, S.V.; Filatov, S.K.; Burns, P.C. The cuprite-like framework of OCu$_4$ tetrahedra in the crystal structure of synthetic melanothallite, Cu$_2$OCl$_2$, and its negative thermal expansion. Can. Mineral. 2002, 40, 1185–1190. [CrossRef]

30. Brownstein, S.; Han, N.F.; Gabe, E.J.; le Page, Y. A redetermination of the crystal structure of cupric chloride dihydrate. Z. Kristallogr. 1989, 189, 13–15. [CrossRef]

31. Brownstein, S.; Han, N.F.; Gabe, E.J.; le Page, Y. A redetermination of the crystal structure of cupric chloride dihydrate. Z. Kristallogr. 1989, 189, 13–15. [CrossRef]

32. Malcherek, T.; Schlueter, J. Structures of the pseudo-trigonal polymorphs of Cu$_2$Cl$_2$(OH)$_5$. Inorg. Chem. 2017, 56, 307–321. [CrossRef]

33. T. Malcherek, T.; Schlueter, J. Structures of the pseudo-trigonal polymorphs of Cu$_2$Cl$_2$(OH)$_5$. Inorg. Chem. 2017, 56, 307–321. [CrossRef]

34. Siidra, O.L.; Fiore, V.; Ambruster, T.; Filatov, S.K.; Pekov, I.V. The crystal structure of leningradite, PbCu$_3$(VO$_4$)$_2$Cl$_2$. Can. Mineral. 2007, 45, 445–449. [CrossRef]

35. Siidra, O.L.; Krivovichev, S.V.; Turner, R.W.; Rumsey, M.S. Chloroxiphite Pb$_3$Cu$_2$O$_2$(OH)$_2$Cl$_2$: Structure refinement and description of oxocentred OPO$_4$ tetrahedra. Mineral. 2008, 72, 793–798. [CrossRef]

36. Burdett, J.K.; Hofmann, R.; Fay, R.C. Eight-Coordination. Inorg. Chem. 1978, 17, 2553–2568. [CrossRef]

37. Merlino, S.; Perchiazzi, N.; Franco, D. Brochantite, Cu$_5$O$_{2+}$, a new mineral from New Cliffe Hill Quarry, Stanton-under-Bardon, Leicestershire, UK. Can. Mineral. 2013, 51, 267–275. [CrossRef]

38. Han, T.H.; Singleton, J.; Schlueter, J.A. Barlowite: A spin-1212 antiferromagnet with a geometrically perfect kagome motif. Phys. Rev. Lett. 2014, 113, 227203. [CrossRef] [PubMed]

39. Norman, M.R. Herbertsmithite and the search for the quantum spin liquid. Rev. Mod. Phys. 2016, 88, 041002. [CrossRef]

40. Malcherek, T.; Mihailova, B.; Welch, M.D. Structural phase transitions of clinoatacamite and the dynamic Jahn-Teller effect. Phys. Chem. Miner. 2017, 44, 307–321. [CrossRef]

41. Malcherek, T.; Mihailova, B.; Welch, M.D. Structural phase transitions of clinoatacamite and the dynamic Jahn-Teller effect. Phys. Chem. Miner. 2017, 44, 307–321. [CrossRef]

42. Smaha, R.W.; He, W.; Jiang, J.M. Materializing rival ground states in the barlowite family of kagome magnets: Quantum spin liquid, spin ordered, and valence bond crystal states. Eur. J. Mineral. 2003, 15, 267–275. [CrossRef]

43. Han, T.H.; Singleton, J.; Schlueter, J.A. Barlowite: A spin-1212 antiferromagnet with a geometrically perfect kagome motif. Phys. Rev. Lett. 2014, 113, 227203. [CrossRef] [PubMed]

44. Norman, M.R. Herbertsmithite and the search for the quantum spin liquid. Rev. Mod. Phys. 2016, 88, 041002. [CrossRef]

45. Malcherek, T.; Mihailova, B.; Welch, M.D. Structural phase transitions of clinoatacamite and the dynamic Jahn-Teller effect. Phys. Chem. Miner. 2017, 44, 307–321. [CrossRef]

46. Malcherek, T.; Mihailova, B.; Welch, M.D. Structural phase transitions of clinoatacamite and the dynamic Jahn-Teller effect. Phys. Chem. Miner. 2017, 44, 307–321. [CrossRef]

47. Krivovichev, S.V.; Filatov, S.K.; Vergasova, L.P. The crystal structure of illinite, NaCu$_2$(SeO$_3$)$_2$Cl$_2$, and review of mixed-ligand CuO$_{m}$Cl$_n$ coordination geometries in minerals and inorganic compounds. Miner. Petrol. 2013, 107, 235–242. [CrossRef]

48. Jahn, H.A.; Teller, E. Stability of polyatomic molecules in degenerate electronic states. I. Orbital degeneracy. Proc. R. Soc. 1937, A161, 220–235.