

On the symmetry of tsumcorite group minerals based on the new species rappoldite and zincgartrellite

H. EFFENBERGER^{1*}, W. KRAUSE², H.-J. BERNHARDT³ AND M. MARTIN⁴

¹ Institut für Mineralogie und Kristallographie, Universität Wien, Althanstraße 14, A-1090 Vienna, Austria

² Henriette-Lott-Weg 8, D-50354 Hürth, Germany

³ Ruhr-Universität Bochum, Institut für Mineralogie, Universitätsstraße 150, D-44780 Bochum, Germany

⁴ Heinrich-Zille-Weg 8, D-09599 Freiberg, Germany

ABSTRACT

Rappoldite, the Co-analogue of helmutwinklerite, and zincgartrellite, the Zn-dominant analogue of gartrellite, are two new members of the tsumcorite group. Both minerals are triclinic, their structures are closely related to the parent structure, i.e. the 'tsumcorite type' ($C2/m$, $Z = 2$). The lower symmetry is caused by two different crystal-chemical requirements. Order phenomena of the hydrogen bonds cause the 'helmutwinklerite type' ($P\bar{1}$, $Z = 4$), ordering of Cu^{2+} and Fe^{3+} is responsible for the 'gartrellite type' ($P\bar{1}$, $Z = 1$).

Rappoldite was found on samples from the Rappold mine near Schneeberg, Saxony, Germany. The new species forms red to red-brown prismatic and tabular crystals up to 1 mm long. $D_{\text{calc.}} = 5.28 \text{ g/cm}^3$. $2V_z = 85(5)^\circ$, $n_x = 1.85$ (calc.), $n_y = 1.87(2)$ and $n_z = 1.90(2)$; dispersion is distinct with $r > v$; orientation is $Y \sim \parallel [\bar{1}20]$ and $X \sim \parallel c$. The empirical formula derived from electron microprobe analyses is $(\text{Pb}_{1.01}\text{Ca}_{0.01})_{\Sigma 1.02}(\text{Co}_{0.99}\text{Ni}_{0.62}\text{Zn}_{0.35}\text{Fe}_{0.02})_{\Sigma 1.98}[(\text{AsO}_4)_{1.99}(\text{SO}_4)_{0.01}]_{\Sigma 2.00}[(\text{OH})_{0.02}(\text{H}_2\text{O})_{1.98}]_{\Sigma 2.00}$ or $\text{Pb}(\text{Co,Ni})_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$. Single-crystal X-ray studies showed average $C2/m$ symmetry. Weak superstructure reflections are responsible for triclinic symmetry and enlarged cell metrics (refined from powder data): $a = 11.190(2) \text{ \AA}$, $b = 10.548(2) \text{ \AA}$, $c = 7.593(1) \text{ \AA}$, $\alpha = 100.38(1)^\circ$, $\beta = 109.59(2)^\circ$, $\gamma = 98.96(1)^\circ$, $V = 807.6 \text{ \AA}^3$, $Z = 4$. The superstructure results from the hydrogen-bond scheme, but faint streaks indicate some disorder. All investigated rappoldite crystals are twinned by reflection on $(2\bar{3}0)$ which corresponds to the mirror plane of the average $C2/m$ cell. Helmutwinklerite is isotypic with rappoldite and probably also with pure thometzekite; sulphatian thometzekite is monoclinic.

Zincgartrellite forms green-yellow rosette-like aggregates on samples from the Tsumeb mine, Namibia. The $D_{\text{calc.}} = 5.30 \text{ g/cm}^3$. $2V_x = 87(5)^\circ$, $n_x = 1.91(2)$, $n_y = 1.94$ (calc.) and $n_z = 1.97(2)$. Electron-microprobe analyses and Mössbauer data yielded the empirical formula $(\text{Pb}_{0.97}\text{Ca}_{0.04})_{\Sigma 1.01}(\text{Zn}_{0.91}\text{Cu}_{0.51}\text{Fe}_{0.59}\text{Al}_{0.03})_{\Sigma 2.04}[(\text{AsO}_4)_{1.96}(\text{SO}_4)_{0.01}]_{\Sigma 1.97}[(\text{OH})_{0.81}(\text{H}_2\text{O})_{1.31}]_{\Sigma 2.12}$ or $\text{Pb}(\text{Zn,Fe,Cu})_2(\text{AsO}_4)_2(\text{H}_2\text{O,OH})_2$. The structural formula is $\text{Pb}(\text{Zn,Fe}_{1-x})(\text{Zn}_x\text{Cu}_{1-x})(\text{AsO}_4)_2(\text{OH})_{1-x}(\text{H}_2\text{O})_{1+x}$ with $0.4 < x < 0.8$. Gartrellite is defined by $x < 0.4$. Helmutwinklerite has x near to 1 and is defined by a cell with fourfold volume. Single-crystal X-ray studies of zincgartrellite proved space group $P\bar{1}$ caused by ordering of Fe^{3+} and Cu at one atomic site. Cell parameters (refined from powder data): $a = 5.550(1) \text{ \AA}$, $b = 5.620(1) \text{ \AA}$, $c = 7.621(1) \text{ \AA}$, $\alpha = 68.59(1)^\circ$, $\beta = 69.17(1)^\circ$, $\gamma = 69.51(1)^\circ$, $V = 200.1 \text{ \AA}^3$, $Z = 1$.

KEYWORDS: tsumcorite group minerals, rappoldite, zincgartrellite, helmutwinklerite, gartrellite, thometzekite, crystal symmetry, crystal chemistry, crystal structure, infrared spectra.

Introduction

THE minerals of the tsumcorite group show a remarkable variety in their chemical composition and crystal symmetry. The general formula is $\text{Me}(1)\text{Me}(2)_2(\text{XO}_4)_2(\text{OH,H}_2\text{O})_2$: $\text{Me}(1) = \text{Pb, Ca}$,

* E-mail: herta.silvia.effenberger@univie.ac.at

Bi, Na; $Me(2) = Fe^{3+}, Co, Ni, Cu, Zn, Mn^{3+}, Al; X = P, As, V, S$ (Krause *et al.*, 1998*a,b*, 1999*a,b* and references therein). However, the particular elements and their combinations occur with different frequency and show different crystal-chemical effects. At least two different valences are possible for each of the cations $Me(1)$, $Me(2)$ and X . Charge balance is achieved by a coupled exchange at these positions and by adapting the ratio $OH:H_2O$. Most of the tsumcorite group minerals have space-group symmetry $C2/m$. Details of the structure type were discussed by Tillmanns and Gebert (1973). This parent structure of the whole mineral group is denoted 'tsumcorite type'. Two different phenomena are responsible for a symmetry reduction: (1) order between Cu and Fe requires two distinct $Me(2)$ sites ('gartrellite type'); and (2) two H_2O molecules per formula unit (pfu) require a reorganization of the hydrogen bonding scheme ('helmutwinklerite type'). Both symmetry reductions result in triclinic unit cells, which differ in their cell volume. At the time of preparing the earlier papers (Krause *et al.*, 1998*a,b*) the only triclinic members of the tsumcorite group were gartrellite, $Pb(Cu,Zn)(Fe,Zn)(AsO_4)_2(OH,H_2O)_2$, phosphogartrellite, $PbCuFe(PO_4)_2(OH,H_2O)_2$ and helmutwinklerite, $PbZn_2(AsO_4)_2 \cdot 2H_2O$. Due to insufficient data, the definition of a separate Zn-dominant mineral between helmutwinklerite and gartrellite was impossible. The evidence for triclinic symmetry of helmutwinklerite was very poor; the larger unit cell was based on only a few extremely weak superstructure reflections.

In the meantime, the new mineral rappoldite, $Pb(Co,Ni)_2(AsO_4)_2 \cdot 2H_2O$, was discovered, and it can be regarded as the Co analogue of helmutwinklerite. Additional analytical and structural data have now justified the definition of zincgartrellite, $Pb(Zn,Cu)(Zn,Fe)(AsO_4)_2(OH,H_2O)_2$, as an independent mineral. The investigations were mainly based on a new technology (CCD area detector for X-ray single-crystal diffractometer): weak X-ray spots and streaks which were not seen before could be detected. These results were essential for the discussion given in the present paper.

The name rappoldite is for the type locality, the Rappold mine near Schneeberg, Saxony, Germany. Type material is deposited in the collection of the Bergakademie Freiberg, Germany. Zincgartrellite has been found on samples from the Tsumeb mine, Namibia. The name was chosen to show the relationship to

gartrellite. Type material is preserved in the collection of the Institut für Mineralogie, University of Bochum, Germany. Detailed data on zincgartrellite were reported previously (Krause *et al.*, 1998*a*) under the name 'zincian gartrellite' (sample number #081), which is identical to the type material described in this paper. Both the minerals and mineral names have been approved by the IMA Commission on New Minerals and Mineral Names (rappoldite: #98-015; zincgartrellite: #98-014).

Occurrence and physical data

Rappoldite was found in 1991 on samples from the dumps of the Rappold mine (Rappold-Fundgrube), Schneeberg-Neustädte, Saxony, Germany. Access to the dumps was only possible in the course of excavation works in that area from March to October 1991. The samples were originally believed to contain tsumcorite (Martin and Schlegel, 1992). Subsequent studies showed this material to be a new mineral, namely the Co analogue of helmutwinklerite. The type specimen is ~10 mm in diameter. It consists of quartz overgrown with rappoldite crystals in small rosette-like crystal aggregates which are red in colour. Rappoldite forms idiomorphic crystals. They are prismatic or tabular, up to 1 mm in length and up to 0.3 mm in diameter. Red-brown aggregates of tabular crystals have also been found, which were shown to be intergrowths with small amounts of cobaltlotharmeyerite. Additional secondary minerals within the collected dump material are cobaltaustinite, scorodite, barium-pharmacosiderite, olivenite, conicalcite, erythrite, arseniosiderite, mimetite and beudantite. Accompanying ore minerals are native silver and bismuth, acanthite, galenite, pyrite and skutterudite.

Zincgartrellite was discovered on specimens from the Tsumeb mine, Namibia. The new mineral forms aggregates up to 0.5 mm which are composed of very small yellow-green tabular crystals (< 0.1 mm). The poor development of the crystals and their intensive intergrowth prevented the complete determination of the physical and optical data. The investigated samples can be attributed to the mining period 1975–1980 and were purchased by G. Tremmel at that time in Namibia. In the type specimen, zincgartrellite is grown on massive chalcocite covering an area of ~4 cm². It is associated with wulfenite, duftite, β -duftite (intermediate between duftite and

SYMMETRY OF TSUMCORITE GROUP MINERALS

conichalcite, Kharisun *et al.*, 1998), cuproadamite, and olivenite.

The physical and optical data of rappoldite and zincgartrellite are given in Table 1.

Chemical composition

Chemical analyses of rappoldite and zincgartrellite were carried out by means of electron microprobe measurements. The results are compiled in Table 2. No other elements with atomic numbers >8 were detected. The standards used were mimetite (As,Pb), CuS (Cu); andradite (Fe,Ca), Bi₂S₃ (Bi), AlPO₄ (Al), SrSO₄ (S), ZnO (Zn), NiO (Ni); and Co metal (Co). A direct determination of H₂O was not possible due to the small amount of pure material available. The water contents were therefore recalculated from the ideal compositions. Only small amounts of Ca substituting for Pb at the *Me*(1) position and of S substituting for As at the *X* position could be detected. Mössbauer investigations showed the Fe in zincgartrellite to be completely trivalent (cf. Krause *et al.*, 1998a, sample #081). Rappoldite and zincgartrellite are completely soluble in warm dilute hydrochloric acid.

Rappoldite contains only traces of trivalent cations at the *Me*(2) position and therefore has

two H₂O molecules pfu. The empirical formula based on 10 oxygen atoms is (Pb_{1.01}Ca_{0.01})_{Σ1.02}(Co_{0.99}Ni_{0.62}Zn_{0.35}Fe_{0.02})_{Σ1.98}[(AsO₄)_{1.99}(SO₄)_{0.01}]_{Σ2.00}[(OH)_{0.02}(H₂O)_{1.98}]_{Σ2.00} or in a simpler form, Pb(Co,Ni)₂(AsO₄)₂·2H₂O.

The electron microprobe analyses of zincgartrellite indicate a distinct solid solution involving Zn, Cu, Fe and minor Al. The empirical formula based on 10 oxygen atoms is (Pb_{0.97}Ca_{0.04})_{Σ1.01}(Zn_{0.91}Cu_{0.51}Fe_{0.59}Al_{0.03})_{Σ2.04}[(AsO₄)_{1.96}(SO₄)_{0.01}]_{Σ1.97}[(OH)_{0.81}(H₂O)_{1.31}]_{Σ2.12}. This sample was used for optical investigations, X-ray work (including single-crystal structural refinements), and Mössbauer studies (see Krause *et al.*, 1998a). Further samples, not suitable for these investigations, showed even higher Zn contents up to 13 wt.% ZnO with the corresponding chemical formula of Pb_{1.03}(Zn_{1.08}Cu_{0.50}Fe_{0.37}Al_{0.03})_{Σ1.98}(AsO₄)_{1.99}[(OH)_{0.45}(H₂O)_{1.59}]_{Σ2.04}. The simplified formula of zincgartrellite is Pb(Zn,Fe,Cu)₂(AsO₄)₂(H₂O,OH)₂, the structural formula is Pb(Zn_xFe_{1-x}³⁺)(Zn_xCu_{1-x})(AsO₄)₂(OH)_{1-x}(H₂O)_{1+x}. The definition field of zincgartrellite and gartrellite was estimated somewhat arbitrarily from the triclinic distortion of selected *hkl* pairs within the gartrellite–zincgartrellite–helmutwinklerite series. Accepting that the

TABLE 1. Physical and optical properties of rappoldite and zincgartrellite.

Property	Rappoldite*	Zincgartrellite
Habit	prismatic [1̄20]	tabular on {111}
Morphology	{210}, {001}	{111}
Lustre	vitreous	vitreous
Diaphaneity	transparent	transparent to translucent
Colour	red to red-brown	green-yellow
Streak	light yellow brown	yellow
Fluorescence	none	none
Hardness (Mohs)	4.5	4.5
Tenacity	brittle	brittle
Fracture	conchoidal	not determined
Cleavage	none observed	none observed
Density	5.28 g/cm ³ (calc.)	5.30 g/cm ³ (calc.)
Optical character	biaxial positive	biaxial negative
2V	85(5) ^o	87(5) ^o
Refractive indices	1.85 (calc.), 1.87(2), 1.90(2)	1.91(2), 1.94 (calc.), 1.97(2)
Dispersion	<i>r</i> > <i>v</i> , distinct	not determined
Orientation	<i>Y</i> ~ [1̄20], <i>X</i> ~ <i>c</i>	not determined
Pleochroism	none	weak, <i>X</i> = <i>Z</i> pale yellow, <i>Y</i> yellow

* The orientation is given with respect to the triclinic supercell

TABLE 2. Microprobe analyses of rappoldite and zincgartrellite.

Constituent	Mean [‡]	Rappoldite Range	Calculated*	Mean [§]	Zincgartrellite Range	Calculated [†]
PbO	35.27	34.64–36.11	34.82	33.49	31.89–35.83	33.66
CaO	0.12	0.00–0.38	0	0.35	0.08–0.64	0.35
Bi ₂ O ₃	0.11	0.00–0.30	0	—	—	—
Fe ₂ O ₃	0.28	0.09–0.86	0	7.23	6.59–7.68	7.28
Al ₂ O ₃	<0.05	—	—	0.26	0.08–0.53	0.24
CuO	<0.05	—	—	6.26	5.19–7.15	6.25
ZnO	4.52	3.58–4.96	4.44	11.40	10.51–12.21	11.38
CoO	11.60	10.64–2.17	11.69	< 0.05	—	—
NiO	7.31	6.59–8.34	7.58	< 0.05	—	—
As ₂ O ₅	35.82	34.55–36.45	35.85	34.72	32.78–36.58	35.92
SO ₃	0.11	0.02–0.19	0	0.13	0.00–0.25	0.13
H ₂ O (calc.)	5.62	—	5.59	4.3	—	4.8
Total	100.76	—	100	98.62	—	100.00

* calculated for $\text{Pb}_{1.00}(\text{Co}_{1.00}\text{Ni}_{0.65}\text{Zn}_{0.35})_{\Sigma 2.00}(\text{AsO}_4)_{2.00}(\text{H}_2\text{O})_{2.00}$

[†] calculated for $(\text{Pb}_{0.96}\text{Ca}_{0.04})_{\Sigma 1.00}(\text{Zn}_{0.89}\text{Cu}_{0.50}\text{Fe}_{0.58}^{3+}\text{Al}_{0.03})_{\Sigma 2.00}[(\text{AsO}_4)_{1.99}(\text{SO}_4)_{0.01}]_{\Sigma 2.00}[(\text{OH})_{0.61}(\text{H}_2\text{O})_{1.39}]_{\Sigma 2.00}$

[‡] mean of 11 analyses

[§] mean of 16 analyses

gradient of the curve near $x = 1.0$ is indefinite, equal ranges for gartrellite and zincgartrellite were assumed (Fig. 1). Samples with $0 < x < 0.4$ should be assigned to gartrellite, those with $0.4 < x < \sim 0.8$ to zincgartrellite. Samples with x close to 1.0 are helmutwinklerite which is separated from zincgartrellite by distinct structural features. It should be mentioned that the experimentally verified substitution of $2\text{Zn} \rightleftharpoons \text{Fe}+\text{Cu}$ coupled with a substitution $\text{OH} \rightleftharpoons \text{H}_2\text{O}$ for charge balance indicates a continuous transition between gartrellite and zincgartrellite. The transition between zincgartrellite towards a pure Zn end-member is not proved. An interruption of the chemical transition is possible. For samples with practically 2 Zn atoms pfu ($x \sim 1.0$) a distinct ordering scheme of the hydrogen bonds causes an important change in the crystal structure. Cell metrics and IR spectra are similar for gartrellite and zincgartrellite but they differ fundamentally for helmutwinklerite. Due to the fact that the structural building principles of helmutwinklerite and zincgartrellite are different, these two minerals should not be considered as simple structure variants. Consequently, zincgartrellite is an independent mineral, not isotypic with helmutwinklerite. On the other hand the extensive incorporation of Zn differentiates zincgartrellite from gartrellite.

IR absorption spectra

The FT-IR spectra (Fig. 2) were taken on a Nicolet 5PC instrument equipped with a diamond microcell. They are practically identical for rappoldite and helmutwinklerite with distinct absorption bands at 1590 cm^{-1} (water bending motion). The OH-stretching motion is split into sharp absorption bands at $\sim 3585\text{ cm}^{-1}$ and $\sim 3535\text{ cm}^{-1}$ indicating weak hydrogen bonds. The spectrum of zincgartrellite features distinct differences: it shows only a weak absorption band at 1570 cm^{-1} due to the lower portion of H_2O molecules, whereas the absorption in the range of $\sim 3550\text{ cm}^{-1}$ is missing. Instead of this there is a broad absorption ranging from $\sim 3500\text{ cm}^{-1}$ to 2500 cm^{-1} with a maximum at 3100 cm^{-1} indicating strong to very strong hydrogen bonds. Multiple bonds beyond $\sim 1000\text{ cm}^{-1}$ are from the arsenate groups. The spectrum of zincgartrellite is similar to that of tsumcorite, ferrilotharmeyerite, and gartrellite (Krause *et al.*, 1998a). The different appearance of the IR spectra in the 3550 cm^{-1} region may serve as an easy method to distinguish between helmutwinklerite and zincgartrellite. Moreover, from the IR spectrum, samples belonging to the helmutwinklerite type can clearly be distinguished from those belonging to the tsumcorite or gartrellite type.

SYMMETRY OF TSUMCORITE GROUP MINERALS

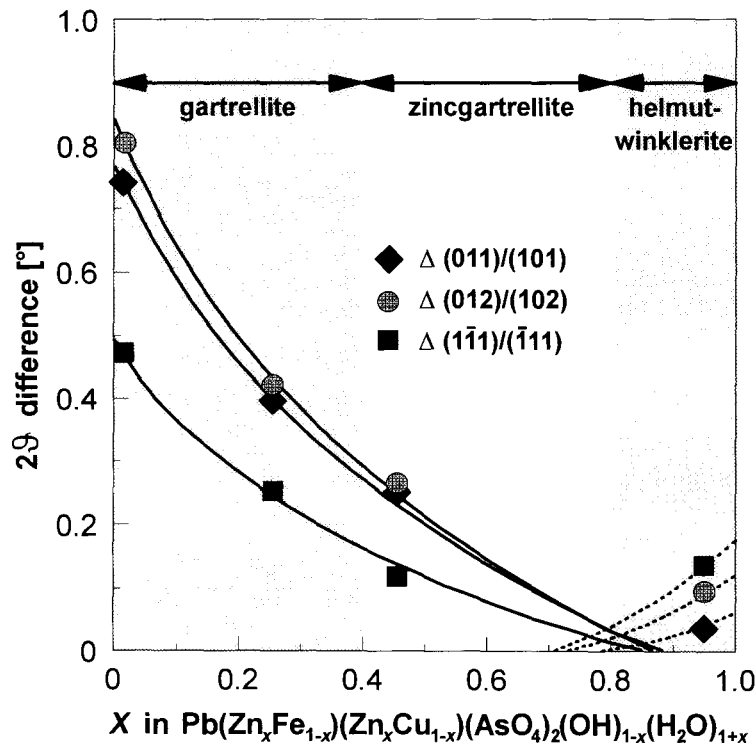


FIG. 1. Triclinic distortion within the gartrellite–zincgartrellite–helmutwinklerite series. The splitting is shown for three selected pairs $2\theta_{hkl}$ (Cu-K α radiation) for different amounts of Zn within the relevant sample according to the formula $\text{Pb}(\text{Zn}_x\text{Fe}_{1-x})(\text{Zn}_x\text{Cu}_{1-x})(\text{AsO}_4)_2(\text{OH})_{1-x}(\text{H}_2\text{O})_{1+x}$.

X-ray investigation

Powder pattern

The XRD data of the investigated minerals are similar and correspond with the other tsumcorite group minerals. The XRD data of rappoldite are given in Table 3. Indexing is based on the true triclinic supercell. The superstructure reflections were not observed in the powder pattern due to their weak intensities. For the XRD data of zincgartrellite see Krause *et al.* (1998a; Table 4b ‘zincian gartrellite’). Cell parameters derived from the powder data (abstract and Table 4) were confirmed by single-crystal investigations.

Helmutwinklerite and rappoldite

Helmutwinklerite was first described by Süsse and Schnorrer (1980). Schmetzer *et al.* (1985) determined a tsumcorite-like pseudocell with $C2/m$ symmetry and cell dimensions similar to

those of tsumcorite. From additional very weak superstructure reflections these authors deduced a triclinic supercell with a sixteenfold cell volume: $a = 4 \times 5.600 \text{ \AA} = 22.400(4) \text{ \AA}$, $b = 4 \times 5.609 \text{ \AA} = 22.436(4) \text{ \AA}$, $c = 7.616(3) \text{ \AA}$, $\alpha = 70.21(2)^\circ$, $\beta = 70.02(3)^\circ$, $\gamma = 69.24(2)^\circ$. These observations were roughly confirmed during investigations by Krause *et al.* (1998a). However, at least the strongest of the superstructure reflections showed a systematic non-space group extinction for the hkl reflections ($h = 2n+1$ or $k = 2n+1$ and $h, k = 4n+2$). At that time it was impossible to decide whether the other superstructure reflections were not observed because the intensities were too weak or whether other structure models have to be applied. The distribution of the intensities gave an approximate $C2/m$ symmetry for the pseudocell, whereas the superstructure reflections and the cell metrics showed distinct violation of the Laue-symmetry $2/m$. A structure model was given for the triclinic pseudocell; the anisotropy of the

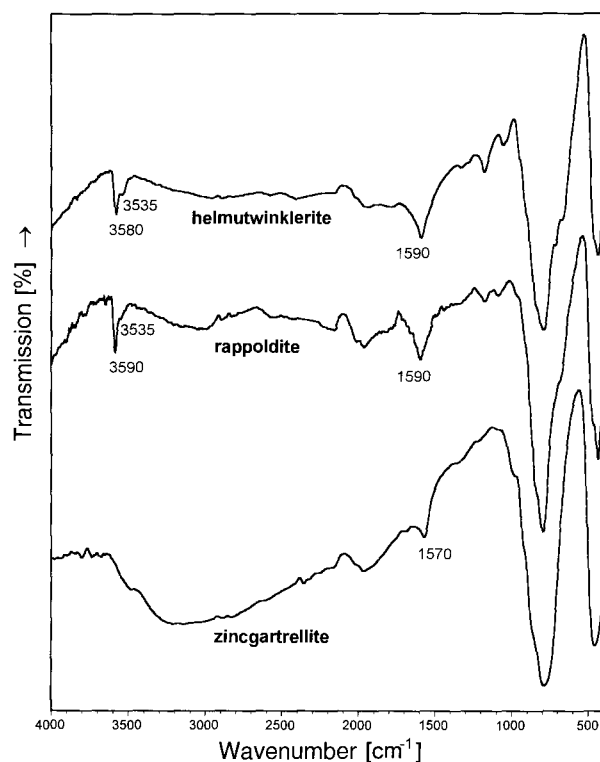


FIG. 2. IR spectra of helmutwinklerite, rappoldite and zincgartrellite.

displacement parameters was large, especially for the atoms O(1) and O(4).

For the present single-crystal X-ray studies, an automatic four-circle diffractometer equipped with a CCD-area detector was used. A few rappoldite crystals and the crystal chip of helmutwinklerite used formerly (Krause *et al.*, 1998a) were investigated by this new technique. Due to the improved signal-to-noise ratio, information within the reciprocal space was obtained which could not be seen on X-ray film investigations even when the exposure time was very long (Weissenberg and precession technique). The intensity distribution for helmutwinklerite and rappoldite is basically the same, but it differs from all the other investigated tsumcorite group minerals. The strong reflections correspond roughly with a monoclinic *C*-centred cell, characteristic of the tsumcorite type (monoclinic subcell). The additional reflections are weak, but clearly seen. They definitely do not cause fourfold triclinic subcell parameters *a* and *b* as described earlier. The distribution of the superstructure

reflections is shown schematically in Fig. 3a. Indexing is possible based on the assumption of a twinned triclinic supercell with fourfold cell volume as compared to the triclinic subcell. The twin plane $\{2\bar{3}0\}$ corresponds to the mirror plane of the space group $C2/m$ in the average cell, i.e. the twin plane $(1\bar{1}0)$ observed for the gartrellite-type minerals. All investigated samples of rappoldite and helmutwinklerite are twinned. The cell parameters and their transformations are given in Table 4; the relations in the direct space are given in Fig. 3b. For convenience throughout this paper, the three principally different cells are referred to as 'tsumcorite type cell' (space group $C2/m$, average monoclinic subcell, $Z = 2$), 'gartrellite-type cell' (space group $P\bar{1}$, average triclinic subcell, $Z = 1$) and 'helmutwinklerite-type cell' (space group $P\bar{1}$, true triclinic supercell, $Z = 4$).

The intensity of the superstructure reflections is weak. In rappoldite the average intensity of the main reflections is 4437 whereas that of the superstructure reflections is only 137. In addi-

SYMMETRY OF TSUMCORITE GROUP MINERALS

TABLE 3. Powder diffraction data of rappoldite.

$h k l$	d_{calc}	I_{calc}	d_{obs}	I_{obs}	$h k l$	d_{calc}	I_{calc}	d_{obs}	I_{obs}
001	6.926	19	6.920	22	42 $\bar{3}$	2.017	9	2.017	10
2 $\bar{1}$ 0	5.072	3	5.056	3	2 $\bar{1}$ 3	1.931	14	1.925	13
020	5.045	4			023	1.925	14		
2 $\bar{1}$ 1	4.673	75			21 $\bar{4}$	1.898	11		
		81	4.670	97				1.898	10
0 $\bar{2}$ 1	4.670				2 $\bar{3}$ 3	1.870	11	1.870	8
21 $\bar{1}$	4.493	43	4.490	26	2 $\bar{3}$ 3	1.863	11	1.863	8
210	4.192	25	4.192	14	6 $\bar{1}$ 1	1.857	4		
2 $\bar{1}$ 1	3.685	5	3.672	3	2 $\bar{5}$ 2	1.849	13	1.846	12
021	3.665	5			25 $\bar{1}$	1.848	5		
002	3.462	13	3.462	26	442	1.846	12		
21 $\bar{2}$	3.453	6			4 $\bar{2}$ 2	1.843	7		
022	3.260	74	3.256	100	042	1.833	8	1.833	6
2 $\bar{1}$ 2	3.255	74			421	1.811	3		
2 $\bar{3}$ 0	3.172	39	3.170	29	402	1.768	3	1.763	3
211	3.072	100	3.072	56	232	1.762	3		
2 $\bar{3}$ 1	2.888	45	2.890	40	631	1.744	14	1.744	8
231	2.879	44			213	1.743	3		
401	2.763	45	2.760	37	6 $\bar{1}$ $\bar{1}$	1.741	9		
231	2.754	45			061	1.737	14		
421	2.595	3	2.581	25	44 $\bar{1}$	1.736	9	1.731	38
041	2.587	3			004	1.732	23		
2 $\bar{1}$ 2	2.581	30			424	1.727	19		
022	2.571	32			613	1.703	28		
402	2.570	26	2.568	46	25 $\bar{3}$	1.700	29	1.700	21
23 $\bar{2}$	2.566	25			442	1.696	7		
400	2.563	10			632	1.691	6		
230	2.552	11			630	1.691	4		
4 $\bar{2}$ 0	2.536	22	2.537	14	252	1.687	7	1.687	8
040	2.522	21	2.521	16	062	1.687	6		
21 $\bar{3}$	2.501	21	2.502	25	060	1.682	5	1.626	11
422	2.337	17	2.335	27	444	1.630	14		
042	2.335	18			424	1.627	15		
42 $\bar{2}$	2.247	11	2.245	5	610	1.623	6		
4 $\bar{2}$ 1	2.213	16	2.212	6	440	1.619	6	1.585	7
041	2.200	15	2.199	7	253	1.618	3		
420	2.096	15	2.096	7	460	1.586	27	1.577	5
441	2.022	9	2.022	9	6 $\bar{1}$ 1	1.577	17	1.569	5
251	2.021	10			251	1.569	18		

Philips powder diffractometer PW1710, Cu-K α radiation, external standard: Si; texture effects not considered. Calculations were performed using the program LAZY PULVERIX (Yvon *et al.*, 1977) according to the results of structure refinements; reflections with $I_{\text{calc}} \geq 3$ are listed; indexing accords with the triclinic supercell.

tion, faint streaks are observed. Their intensity is ~2–3 times greater than the background intensity. The superstructure reflections are located along these streaks. It is assumed that the streaks are caused by disorder phenomena connected with the hydrogen bonds even in the triclinic supercell. Structural changes were considered possible at low temperatures.

Therefore an additional data set was collected for rappoldite at $T = 100$ K. The ratio of intensities between the substructure reflections, superstructure reflections and streaks is maintained qualitatively in the temperature interval between 100 K and 293 K. Therefore, the refined structural parameters are nearly the same for both measurements.

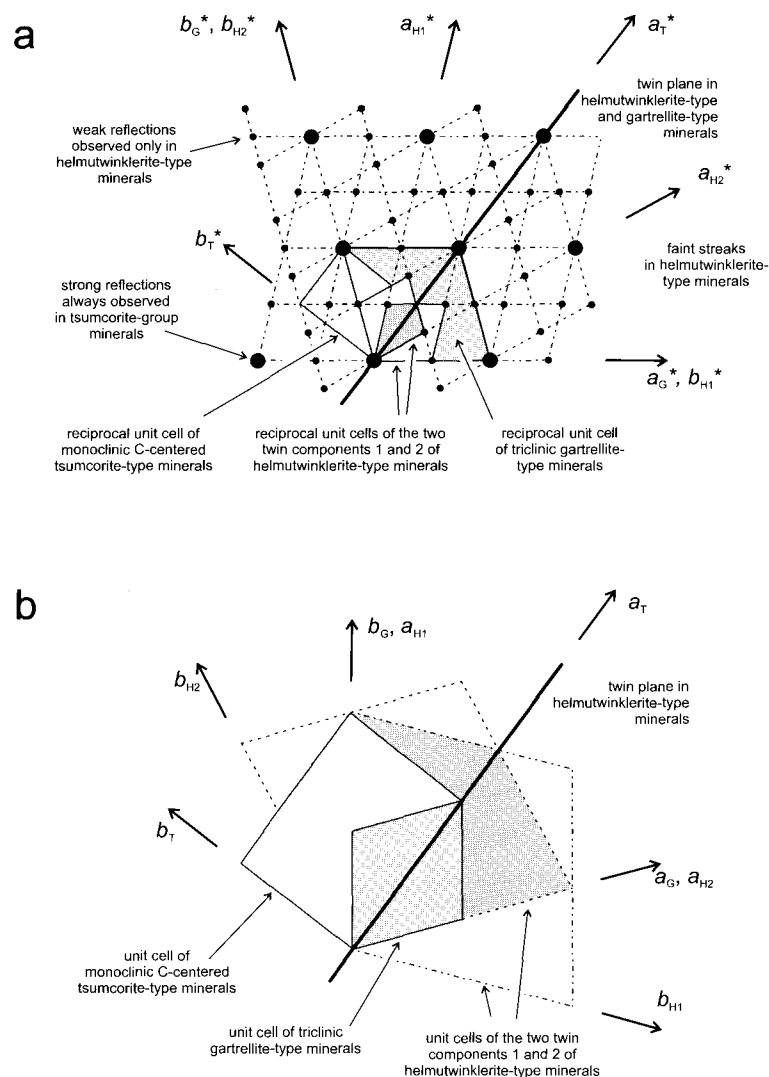


FIG. 3. (a) Relations between the reciprocal unit cells of tsumcorite group minerals: (i) the monoclinic *C*-centred tsumcorite type (a_T^* , b_T^*); (ii) the triclinic gartrellite type (a_G^* , b_G^*); and (iii) the two twin components observed for the helmutwinklerite type (a_{H1}^* , b_{H1}^* and a_{H2}^* , b_{H2}^*). (b) Relations between the unit cells of tsumcorite group minerals: (i) the monoclinic *C*-centred tsumcorite type (a_T , b_T); (ii) the triclinic gartrellite type (a_G , b_G); and (iii) the two twin components observed for the helmutwinklerite type (a_{H1} , b_{H1} and a_{H2} , b_{H2}).

Structure models of helmutwinklerite and rappoldite were refined in the true triclinic supercell, the average triclinic and average monoclinic subcells starting from the atomic parameters of tsumcorite (Tillmanns and Gebert, 1973) after appropriate transformations. The differences of the results of refinements (atomic

coordinates, anisotropic displacement parameters and residuals) in the triclinic and the monoclinic average subcells are similar. In both models, large anisotropies of the displacement parameters of the atoms O(1) and O(4) were found. The displacements of the Pb, Me(2) and As atoms are inconspicuous, and of the other atoms, moderate.

TABLE 4. Cell parameters for rappoldite, helmutwinklerite, and zingartrellite. Data are refined from the powder diffraction patterns. The cell parameters of helmutwinklerite are from Krause *et al.* (1998a). The transformation matrices for rappoldite and helmutwinklerite are from the triclinic supercell to the triclinic average subcell ($\frac{1}{2} 0 0 / \frac{1}{4} \frac{1}{2} 0 / 0 0 \bar{1}$) and from the triclinic supercell to the monoclinic average subcell ($\frac{3}{4} \frac{1}{2} 0 / -\frac{1}{4} \frac{1}{2} 0 / 0 0 1$).

	Rappoldite			Helmutwinklerite			Zingartrellite	
	Space group $P\bar{1}$ supercell	Space group $C2/m$ subcell	Space group $C2/m$ subcell	Space group $P\bar{1}$ supercell	Space group $C2/m$ subcell	Space group $C2/m$ subcell	Space group $P\bar{1}$ true cell	Space group $C2/m$ average cell
a [Å]	11.190(2)	5.595(1)	9.190(2)	11.220(4)	5.606(2)	9.233(4)	5.550(1)	9.177(2)
b [Å]	10.548(2)	5.572(1)	6.343(1)	10.605(4)	5.610(2)	6.367(3)	5.620(1)	6.368(2)
c [Å]	7.593(1)	7.593(1)	7.593(1)	7.617(1)	7.617(1)	7.617(1)	7.621(1)	7.621(1)
α [°]	100.38(1)	70.19(1)	90.11(1) → 90	100.60(2)	70.19(2)	90.22(2) → 90	68.59(1)	89.30(1) → 90
β [°]	109.59(2)	70.41(1)	114.18(1)	109.81(2)	69.91(2)	114.49(2)	69.17(1)	116.01(1)
γ [°]	98.96(1)	69.23(1)	90.25(1) → 90	98.81(2)	69.18(2)	90.04(2) → 90	69.51(1)	90.77(1) → 90
V [Å ³]	807.6	201.9	403.8	814.8	203.7	407.4	200.1	400.2
Z	4	1	2	4	1	2	1	2

The superstructure reflections and the diffuse streaks therefore result predominantly from order and disorder phenomena of the displacements of the atoms O(1) and O(4) and from the arrangement of the H atoms. Multiple refinement models in the triclinic supercell were tried (with and without constraints for atoms which are symmetrically equivalent in the average cells and which show low anisotropic displacement parameters) without success. The large correlation terms observed during the refinements in the true cell of rappoldite and helmutwinklerite did not allow a successful refinement. In addition, the distinct streaks observed for all investigated samples indicate strong disorder phenomena. This part of X-ray scattering was not introduced to the refinement model; it is considered that the streaks contribute to the unsuccessful refinement in the true cell. Due to the significant triclinic cell metrics, the structural parameters are given for the average triclinic subcell.

Thomtezkite

The ideal formula of thomtezkite is $\text{Pb}(\text{Cu,Zn})_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Schmetzer *et al.*, 1985). Consequently, its crystal structure is expected to be close to that of helmutwinklerite and rappoldite. Several crystals, taken from part of the type material (by courtesy of L. Krahn), were investigated using the automatic four-circle diffractometer equipped with a CCD area detector. Even frames examined using long exposure times showed neither superstructure reflections nor streaks. The cell metrics gave no hint of a triclinic distortion. This is obviously related to the significant sulphate contents of the crystals available for investigation; according to electron microprobe analyses 9 to 34 mol.% of AsO_4 are substituted by SO_4 . In contrast, Schmetzer *et al.* (1985) mentioned no sulphate in the original description of thomtezkite. Due to the fact that *Me*(1) and *Me*(2) are solely occupied by divalent cations, the incorporation of SO_4 results in an increased OH content; the average OH/ H_2O ratio in the investigated samples is 0.75:1.25. The distinct OH content of 'sulphatian thomtezkite' obviously prevents an ordering of the hydrogen bonds for the H_2O molecules and leads to the normal H_3O_2 dominant H-bonding system (Krause *et al.*, 1998a). Therefore 'sulphatian thomtezkite' is monoclinic and belongs to the tsumcorite type with space group $C2/m$.

According to various electron microprobe and X-ray powder analyses, the investigated thomtezkite samples seem to contain at least two, possibly three phases: (1) sulphatian thomtezkite, monoclinic, as proved by structure investigations (Krause *et al.*, 1998a); (2) almost sulphate-free thomtezkite with significant Fe^{3+} and Al^{3+} , probably designated to the gartrellite type; and (3) presumably in very small amounts thomtezkite in the strict sense, $\text{Pb}(\text{Cu,Zn})_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$. Only the sulphatian thomtezkite could be isolated as a pure sample for single-crystal X-ray studies. Most powder patterns of thomtezkite including the powder data given by Schmetzer *et al.* (1985) can be interpreted as a mixture of sulphatian thomtezkite [cell parameters: $a = 9.088(2)$, $b = 6.311(1)$, $c = 7.656(2)$ Å, $\beta = 116.76(2)^\circ$] and gartrellite-type thomtezkite [cell parameters: $a = 5.464(2)$, $b = 5.677(2)$, $c = 7.623(4)$ Å, $\alpha = 67.85(3)$, $\beta = 69.61(3)$, $\gamma = 69.72(3)^\circ$].

It seems likely that 'sulphate-free thomtezkite' is structurally related to helmutwinklerite and rappoldite and shows triclinic symmetry with the large unit cell containing four formula units. These considerations are supported by the fact that the displacement parameters observed for the O atoms in thomtezkite are larger than those observed for the O atoms in the other tsumcorite-type minerals. Due to lack of suitable material, no investigations on pure thomtezkite to prove these hypothetical symmetry relations, have been performed.

Zincgartrellite

Zincgartrellite is isostructural with gartrellite, but closely related to helmutwinklerite chemically. The deviation from monoclinic symmetry is small, though triclinic symmetry is evident from powder pattern, cell metrics, intensity distribution of single-crystal X-ray data, and structure investigation. Superstructure reflections or diffuse streaks (by analogy with helmutwinklerite and rappoldite) were not seen. The crystal structure was refined starting from the atomic parameters of gartrellite (Krause *et al.*, 1998a). During the final least-squares refinements, anisotropic displacement parameters were allowed to vary for the *Me* and *X* atoms but isotropic ones for the oxygen atoms. The scattering functions of the position $Me(2a) = (\text{Zn,Fe})$ were successfully refined. Due to the similar scattering power of Zn and Cu, the ratios Zn:Cu at the *Me*(2b)

SYMMETRY OF TSUMCORITE GROUP MINERALS

position was kept equal to Zn:Fe at the *Me*(2a) position according to the structural formula $Pb(Zn_xFe_{1-x})(Zn_xCu_{1-x})(AsO_4)(OH)_{1-x}(H_2O)_{1+x}$. The coordination polyhedra *Me*(2a)^[6]O₆ and *Me*(2b)^[4+2]O₆ are clearly different. The refined value Fe:Zn = Cu:Zn is 0.4(2):0.6(2) which is in reasonable agreement with the results of the electron-microprobe investigation. The cell parameters are included in Table 4.

Structure refinement

The data collection was performed using a Nonius four-circle diffractometer (Mo tube, graphite monochromator) equipped with a CCD detector with a frame size of 621 × 576 pixels (binned mode). The detector-to-sample distance was 28 mm. Data were collected in the ϕ -scan mode (total rotation 360°, scan speed: 0.1°/min; $\Delta\phi = 2^\circ/\text{frame}$). Corrections for Lorentz and polarization effects were applied in the usual way. Further details of data collection and structure refinements of rappoldite and zincgartrellite are given in Table 5. For the structure refinements neutral-atomic complex scattering functions (Wilson, 1992) and the programs SHELX-76 and SHELXL-97 (Sheldrick, 1976, 1997) were used. Structural parameters are given in Table 6 and interatomic bond distances and bond angles in Table 7.

Discussion

The *Me*(1) position

The *Me*(1) position shows a pronounced [6+2]-coordination to O atoms. The average $\langle Me(1)^{[6]}-O \rangle$ distance of rappoldite (2.597 Å) and zincgartrellite (2.59 Å) is within the range of the other tsumcorite group minerals containing Pb (2.584–2.620 Å). The two additional ligands are at ~3.0 Å. Only in thometzekite [8]-coordination with an average $\langle Me(1)^{[8]}-O \rangle$ distance of 2.688 Å was observed.

The *Me*(2) position

In the tsumcorite group minerals described earlier, the *Me*(2) position is predominantly occupied by Fe³⁺, Zn and Cu atoms; the only exception was Mn³⁺ in lotharmeyerite. Recently it became evident that other elements like Co and Ni can be incorporated (Krause *et al.*, 1999b). The position *Me*(2) in space group *C2/m* is split in the triclinic structure models. In the average triclinic subcell of rappoldite the two *Me*(2) positions are approximately half occupied by Co atoms; Ni and Zn are additional main constituents; Fe³⁺ is subordinate. During refinement, the site occupation of *Me*(2a) and *Me*(2b) in rappoldite was fixed to the analytically determined value for Ni and Fe. The Co:Zn ratio was

TABLE 5. Details of X-ray data collection and structure refinement of rappoldite (structure model for the triclinic subcell, space group *P* $\bar{1}$) and of zincgartrellite.

	Rappoldite	Zincgartrellite
Crystal dimensions [μm]	42 × 67 × 340	15 × 55 × 60
$\mu(\text{Mo-K}\alpha)$ [mm^{-1}]	32	34
Range of data collection	3° < 2 θ < 50°	3° < 2 θ < 45°
Total measured reflections	754	801
$R_{\text{int}} = \sum F_o^2 - F_o^2(\text{mean}) / \sum F_o^2$	0.082	0.54
Unique reflections (n)	664	552
Observed reflections with $F_o > 4\sigma(F_o)$	658	238
Variable parameters (p)	76	49
Max Δ/σ	≤ 0.001	≤ 0.001
$\text{Goof} = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{0.5}$	1.17	1.13
$wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$	0.135	0.203
$R = [\sum F_o - F_c] / \sum F_o $ (observed data)	0.047	0.081
$w = 1 / [\sigma^2(F_o^2) + (a * P)^2 + b * P]$, $P = ([\max(0, F_o^2)] + 2 * F_c^2) / 3$	$a = 0.0916$, $b = 1.81$	$a = 0.1367$, $b = 12.88$
Extinction coefficient	0.025(52)	not refined
Final difference Fourier map (near Pb atoms) [$\text{e}\text{\AA}^{-3}$]	-2.60 to +2.80	-1.95 to +1.63

TABLE 6. Structural parameters for rappoldite and zinggartrellite, with average triclinic subcell, space group $P\bar{1}$. The anisotropic displacement parameters are defined as: $\exp [-2 \pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} \mathbf{a}_i^* \mathbf{a}_j^* h_i h_j]$, U_{equiv} according to Fischer and Tillmanns (1988).

atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{equiv}}/U_{\text{iso}}$					
Rappoldite									
<i>Me</i> (1) = Pb	0	0	0	0.0340(5)					
<i>Me</i> (2a) = (Co,Ni,Zn)	0	0.5	0.5	0.0210(9)					
<i>Me</i> (2b) = (Co,Ni,Zn)	0.5	0	0.5	0.0201(9)					
<i>X</i> = As	0.4241(3)	0.4220(2)	0.7751(2)	0.0203(7)					
O(1)	0.1575(19)	0.1556(18)	0.4045(17)	0.033(2)					
O(2)	0.3119(17)	0.3126(15)	0.6446(13)	0.023(2)					
O(3a)	0.2472(19)	0.6843(17)	0.2611(14)	0.030(2)					
O(3b)	0.6820(18)	0.2456(16)	0.2608(13)	0.027(2)					
O(4)	0.2838(27)	0.2803(27)	0.0056(14)	0.054(3)					
Zinggartrellite									
<i>Me</i> (1) = Pb	0	0	0	0.0479(17)					
<i>Me</i> (2a) = (Zn,Fe)	0	0.5	0.5	0.040(5)					
<i>Me</i> (2b) = (Zn,Cu)	0.5	0	0.5	0.034(3)					
<i>X</i> = As	0.4125(9)	0.4266(12)	0.7853(7)	0.032(2)					
O(1)	0.163(6)	0.166(8)	0.420(5)	0.034(9)					
O(2)	0.306(7)	0.321(9)	0.648(6)	0.052(12)					
O(3a)	0.255(7)	0.679(9)	0.258(5)	0.044(10)					
O(3b)	0.691(8)	0.238(9)	0.251(6)	0.049(10)					
O(4)	0.273(6)	0.289(8)	0.020(5)	0.037(9)					
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	Principal mean square displacements of <i>U</i>		
Rappoldite									
<i>Me</i> (1) = Pb	0.0426(7)	0.0300(6)	0.0257(6)	-0.0099(4)	-0.0084(4)	-0.0031(4)	0.049	0.029	0.023
<i>Me</i> (2a) = (Co,Ni,Zn)	0.0243(14)	0.0169(12)	0.0245(13)	-0.0112(9)	-0.0089(9)	0.0000(9)	0.031	0.021	0.012
<i>Me</i> (2b) = (Co,Ni,Zn)	0.0210(15)	0.0163(12)	0.0250(13)	-0.0103(9)	-0.0086(9)	0.0004(8)	0.029	0.019	0.012
<i>X</i> = As	0.0252(11)	0.0184(9)	0.0230(10)	-0.0100(6)	-0.0087(6)	-0.0050(6)	0.028	0.022	0.011
O(1)	0.022(6)	0.024(4)	0.065(7)	-0.018(4)	-0.027(5)	0.004(4)	0.068	0.021	0.011
O(2)	0.024(5)	0.018(4)	0.035(5)	-0.012(4)	-0.014(4)	-0.004(3)	0.038	0.020	0.010
O(3a)	0.027(6)	0.031(5)	0.040(5)	0.000(4)	-0.019(4)	-0.015(4)	0.051	0.027	0.013
O(3b)	0.031(6)	0.016(4)	0.039(5)	-0.021(4)	0.003(4)	-0.009(4)	0.052	0.027	0.004
O(4)	0.071(9)	0.079(9)	0.021(5)	-0.010(5)	-0.002(5)	-0.040(7)	0.091	0.052	0.021
zinggartrellite									
<i>Me</i> (1) = Pb	0.061(2)	0.045(3)	0.033(2)	0.003(2)	-0.020(1)	-0.014(2)	0.063	0.056	0.025
<i>Me</i> (2a) = (Zn,Fe)	0.033(6)	0.044(8)	0.029(6)	0.006(5)	-0.009(4)	-0.009(5)	0.066	0.033	0.022
<i>Me</i> (2b) = (Zn,Cu)	0.047(5)	0.026(6)	0.026(4)	0.008(4)	-0.016(4)	-0.016(4)	0.051	0.036	0.014
<i>X</i> = As	0.037(3)	0.034(5)	0.023(3)	0.005(3)	-0.015(2)	-0.010(3)	0.047	0.035	0.015

TABLE 7. Interatomic bond distances and bond angles for rappoldite (average triclinic subcell) and zincgartrellite.

Bond distances (in Å)	Rappoldite	Zincgartrellite	Bond angles (°)	Rappoldite	Zincgartrellite
<i>Me</i> (1)–O(2), 2 ×	3.022(9)	2.96(2)			
<i>Me</i> (1)–O(3a), 2 ×	2.588(9)	2.59(3)	O– <i>Me</i> (1) ^[6] –O	77.9(3) to 102.2(3)	75(1) to 105(1)
<i>Me</i> (1)–O(3b), 2 ×	2.602(8)	2.52(4)	(neighbouring ligands)		
<i>Me</i> (1)–O(4), 2 ×	2.621(12)	2.65(5)			
<i>Me</i> (2a)–O(1), 2 ×	2.090(9)	2.00(4)	O– <i>Me</i> (2a)–O		
<i>Me</i> (2a)–O(2), 2 ×	2.139(9)	2.13(4)	(neighbouring ligands)	81.4(3) to 98.6(3)	80(2) to 100(2)
<i>Me</i> (2a)–O(3a), 2 ×	2.074(9)	2.05(4)			
<i>Me</i> (2b)–O(1), 2 ×	2.072(9)	1.98(3)	O– <i>Me</i> (2b)–O	81.4(3) to 98.6(3)	78(2) to 102(2)
<i>Me</i> (2b)–O(2), 2 ×	2.154(8)	2.23(5)	(neighbouring ligands)		
<i>Me</i> (2b)–O(3b), 2 ×	2.063(9)	2.06(4)			
As–O(2)	1.697(8)	1.71(5)			
As–O(3a)	1.677(10)	1.68(3)	O–As–O	102.5(5) to 112.4(4)	106(2) to 113(2)
As–O(3b)	1.696(8)	1.71(5)			
As–O(4)	1.695(10)	1.68(3)			
O(1)···O(1)	2.64(2)	2.71(8)	O(1)···O(1)···(4)	117.9(6)	108(2)
O(1)···O(4)	2.765(15)	2.75(5)	O(1)···O(1)···(3a)	62.3(4)	57(2)
O(1)···O(3a)	3.020(13)	3.21(7)	O(1)···O(1)···(3b)	61.5(4)	58(2)
O(1)···O(3b)	3.033(13)	3.15(7)	O(4)···O(1)···(3a)	68.8(4)	66(1)
			O(4)···O(1)···(3b)	69.4(4)	64(1)

allowed to vary separately for the two positions assuming full occupation. The refined ratio is practically the same for the two sites and is in good agreement with the analytically determined value. According to the differences of the ionic radii (Shannon, 1976), the average $\langle Me(2a)/Me(2b)-O \rangle$ bond distances in rappoldite (2.101 and 2.096 Å) are slightly larger than in the Fe^{3+} -containing compounds (e.g. zinggartrellite: 2.06 and 2.09 Å), but smaller than in helmutwinklerite (2.116 and 2.107 Å). Due to the similarity of geometry, refined occupancy and displacement parameters of the $Me(2a)O_6$ and $Me(2b)O_6$ polyhedron, there is no evidence for ordering on these positions.

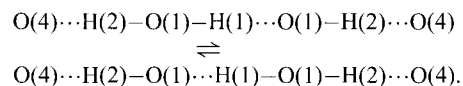
As in gartrellite, the triclinic symmetry of zinggartrellite is caused by the different stereochemical requirements of Fe and Cu. Splitting of $Me(2)$ into two sites, $Me(2a)$ and $Me(2b)$, gives the option of adopting different crystal-chemical environments: for $Me(2a)O_6$, the octahedral coordination is maintained; this coordination is favoured by the Fe^{3+} atoms. The coordination polyhedron $Me(2b)O_6$ is distorted: the elongated tetragonal bipyramidal [4+2] coordination is favoured by the Cu^{2+} atoms due to their electron configuration (Jahn-Teller effect). Zinc atoms can substitute for Fe^{3+} and Cu and therefore it occupies both of the positions $Me(2a)$ and $Me(2b)$. The bonds within the basal square, $Me(2b)-O(1)/O(3)$, are 2.03/1.91 Å in gartrellite and 1.98/2.06 Å in zinggartrellite. The axial bond lengths $Me(2b)-O(2)$ are extended to 2.30 Å in gartrellite and to 2.23 Å in zinggartrellite. The elongation correlates with the different Cu contents in the two minerals.

Hydrogen bonds

Most likely from crystal chemical considerations and cogent from structure refinements is the fact that the H-bonding scheme is responsible for the different unit cells and symmetries obtained for rappoldite and helmutwinklerite as compared to the other tsumcorite-group minerals. The chemical formulae for both rappoldite and helmutwinklerite are very close to $Me(1)Me(2)_2(XO_4)_2 \cdot 2H_2O$, whereas for the other minerals of this group, a substantial amount of H_2O is substituted by OH groups due to charge balance for the different valences of the cations $Me(1)^{1+,2+,3+}$, $Me(2)^{2+,3+}$ and $X^{4+,6+}$.

The space group symmetry $C2/m$ ('tsumcorite-type cell') and $P\bar{1}$ ('gartrellite type cell') is

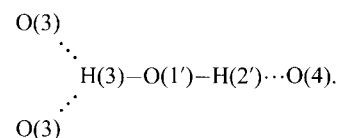
responsible for symmetrically restricted hydrogen bonds formed between two OH groups according to



The $O(1) \cdots O(1)$ distances are very short, the distances $O(1) \cdots O(4)$ are in the usual range for common hydrogen bonds. The angle $O(4)-O(1)-O(1)$ is close to that expected for a water molecule. The ideal formula for this structure type is $Me(1)Me(2)_2(XO_4)_2(OH)(H_2O)$ or even $Me(1)Me(2)_2(XO_4)_2(H_3O_2)$ (cf. Beran *et al.*, 1997). The hydrogen-bonding scheme is maintained if the symmetry is reduced to $P\bar{1}$ (gartrellite type).

An excess of (H_2O) as compared to (OH) causes additional hydrogen bonds. In helmutwinklerite and rappoldite both O(1) atoms form water molecules. The only probable acceptors not involved in an edge of the coordination polyhedra around the Me atoms are two O(3) atoms. The $O(1) \cdots O(3)$ distances of ~ 3 Å might enable a bifurcated hydrogen bond. At any rate, the $\bar{1}$ symmetry has to be violated to form two H_2O molecules (see Fig. 4):

$O(4) \cdots H(2) - O(1) - H(1) \cdots O(1')$ and



The absence of a symmetrically restricted hydrogen bond in rappoldite and helmutwinklerite is indicated by an increase of $O(1) \cdots O(1)$ to ~ 2.64 Å. Even $O(1) \cdots O(4)$ is enlarged compared to the other tsumcorite group minerals. Bent hydrogen bonds are assumed from the small angles $O(3)-O(1)-O(4)$ of $\sim 70^\circ$ and from the repulsion of the atoms H(1) and H(3). The shift of oxygen atoms responsible for these changed features is small. The anisotropic displacement parameters indicate that preferentially the atoms O(1) and O(4) are involved in the rearrangement.

Details of the hydrogen bonding scheme were not derived during the present investigations, but there seems no doubt on the principal ordering mechanism. Within the 'tsumcorite cell' the $Me(1)$ atoms have site symmetry $2/m$ and the $Me(2)$ atoms are located at inversion centres. In addition, site symmetry $2/m$ is between each two

SYMMETRY OF TSUMCORITE GROUP MINERALS

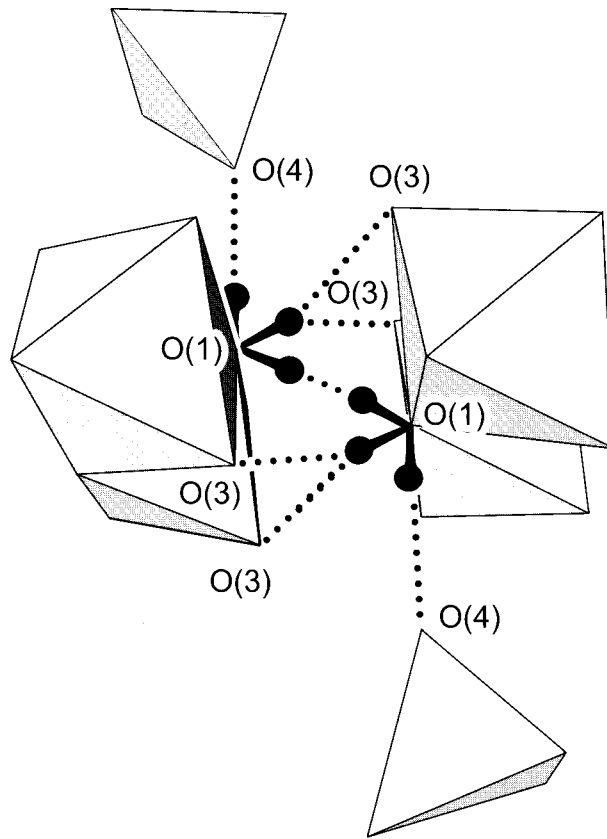


FIG. 4. Hydrogen bonds in the tsumcorite group minerals. The H atoms characteristic of the H_3O_2 group with formal $2/m$ symmetry (with the split position of the symmetrically restricted hydrogen bond) of the tsumcorite and gartrellite type compounds are shown. The contacts to further O(3) atoms are indicated. In the helmutwinklerite type, one H_2O molecule is maintained between $O(4)\cdots O(1)\cdots O(1)$; the other one is between $O(4)\cdots O(1)\cdots O(3)$.

AsO_4 tetrahedra and between two O(1) atoms (average position of the H(1) atom belonging to the symmetry-restricted hydrogen bond). Within the 'gartrellite cell' all these special positions have site symmetry $\bar{1}$. In helmutwinklerite and rappoldite the absence of the symmetrically restricted hydrogen bond causes a violation of the site symmetry at the average H(1) position. Mechanisms to adapt to these conditions are either a symmetry reduction to Pm or $P1$ or an increase of the cell volume which enables a selective removal of inversion centres. The latter is verified in helmutwinklerite and rappoldite. As shown in Fig. 5, in both twin components of the helmutwinklerite type cells, the symmetry $\bar{1}$ is maintained for parts of the $Me(2)$ atoms and

between parts of the AsO_4 tetrahedra. For all $Me(1)$ atoms and for the average H(1) positions, the space group causes site symmetry 1.

Symmetry relations

In most of the tsumcorite group species the $Me(1)$ position is occupied by divalent cations (Ca,Pb) and X by pentavalent cations (P,As,V). The cations occupying the $Me(2)$ site can be divided into three different groups depending on their charge and crystal chemical requirements: (1) divalent cations with a more or less distorted octahedral environment (Zn,Co,Ni); (2) trivalent cations with an octahedral environment (Fe,Al); and (3) divalent Cu atoms strictly in a tetragonal

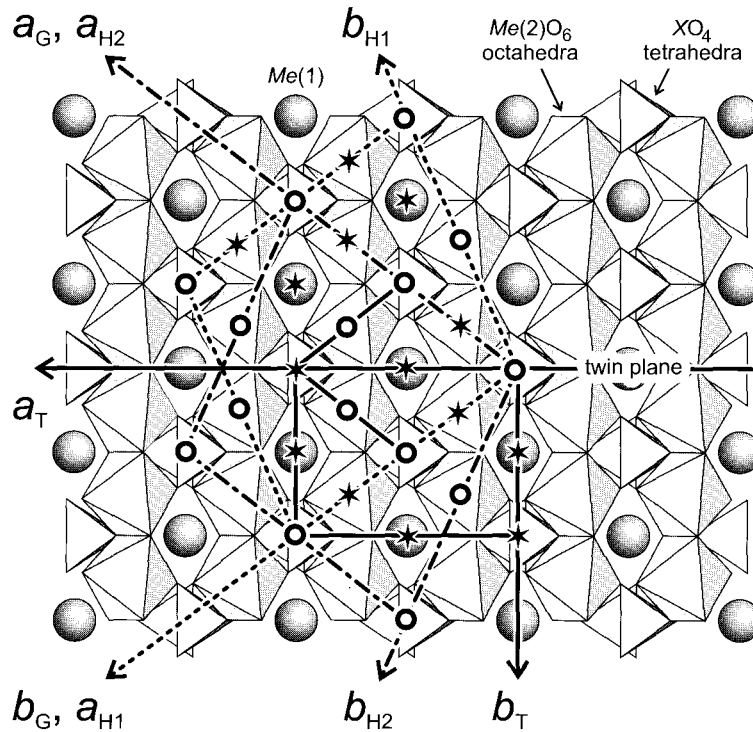


FIG. 5. Structural relations between tsumcorite group minerals: (i) monoclinic *C*-centred tsumcorite type (a_T , b_T); (ii) triclinic gartrellite type (a_G , b_G); and (iii) the two twin components observed for the helmutwinklerite type (a_{H1} , b_{H1} and a_{H2} , b_{H2}). The inversion centre in the two twin components of the helmutwinklerite type are indicated by a circle, those verified only in the tsumcorite- and gartrellite type structures are indicated by a star.

dipyramidal environment (distorted octahedron due to the Jahn-Teller effect). For discussion of the crystal symmetries, the tsumcorite group minerals are arranged in a triangle diagram with respect to the cations at the $Me(2)$ position (Fig. 6); the corners are represented by Me^{2+} (excluding Cu), Me^{3+} and Cu.

The tsumcorite group minerals can be divided into three different subgroups characterized by different structure types and related to three different areas in the triangle diagram shown in Fig. 6. This should be regarded only as a model for classifying the different structure types. In particular, the position of the border lines between the areas are assumptions based on the present stage of knowledge and need further verification by additional analyses of natural and/or synthetic samples. This might therefore be subject to changes depending on the results of new investigations.

Area 1 is along the $Me^{2+}-Me^{3+}$ edge and represents the tsumcorite type. It is limited by contents of at least 0.2 Me^{3+} atoms pfu and probably no more than 0.2 Cu atoms pfu. Nearly complete solid solution between $Me_{1.8}^{2+}Me_{0.2}^{3+}$ and Me_2^{3+} is taken for granted, based on the crystal-chemical properties of the involved cations and on electron microprobe results. A great number of analyses of different species of the tsumcorite group scatter around $Me^{2+}:Me^{3+} \sim 1:1$ requiring OH:H₂O $\sim 1:1$ for charge balance. All samples plotted within this area have space-group symmetry $C2/m$.

However, the end-members with pure $Me(2)^{3+}$, i.e. two OH groups pfu, are still debatable. For mounanaite the probable substitution of OH groups by F atoms, but maintaining the space-group symmetry $C2/m$ was discussed by Krause *et al.* (1998a). Structural investigations on mawbyite were performed on crystals from the type

SYMMETRY OF TSUMCORITE GROUP MINERALS

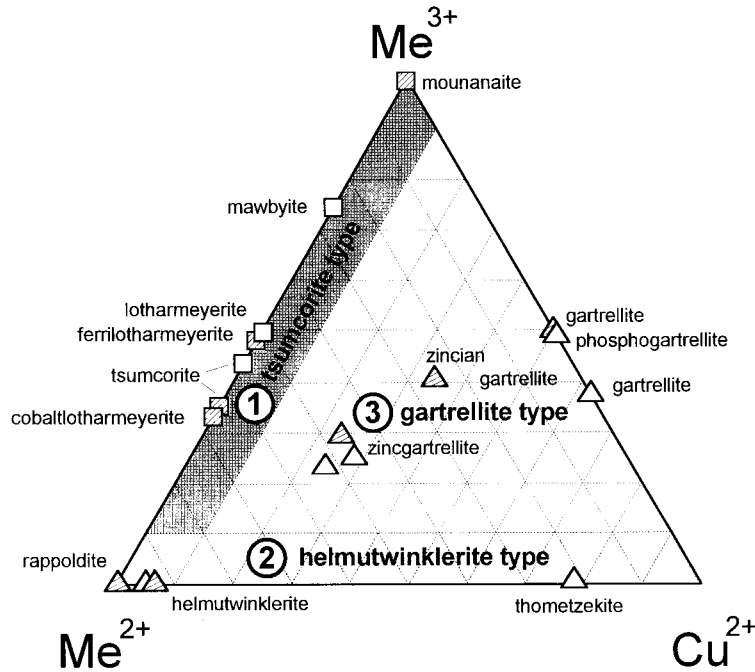


FIG. 6. The chemical composition of the tsumcorite group minerals with $Me(1)^{2+}$ and X^{5+} atoms plotted in the triangle-diagram $Cu^{2+} - Me(2)^{2+}$ (other than Cu) - $Me(2)^{3+}$. Type material samples are unfilled, those of structure investigations are hatched. Samples in areas 1, 2 and 3 belong to the tsumcorite type ($C2/m_1$, $Z = 2$), helmutwinklerite type ($P\bar{1}$, $Z = 4$), and gartrellite type ($P\bar{1}$, $Z = 1$), respectively.

specimen (Kharisun *et al.*, 1997). According to earlier analyses (Pring *et al.*, 1989), the average OH:H₂O ratio is 1.47:0.53. The tsumcorite type is also verified in a great number of synthetic compounds (references are compiled by Krause *et al.*, 1998a).

Area 2 is along the Me^{2+} -Cu edge and represents the helmutwinklerite type. Fewer than $\sim 0.2 Me^{3+}$ atoms pfu might be adopted to define the limiting composition. The ideal formula of minerals within this area is $Me(1)^{2+}Me(2)^{2+}_2(X^{5+}O_4)_2 \cdot 2H_2O$. The stability field of the helmutwinklerite type is much less certain than the tsumcorite type of area 1. The only minerals within this area are helmutwinklerite and rappoldite; synthetic compounds are unknown. Pure thometzekite, i.e. $PbCu_2(AsO_4)_2 \cdot 2H_2O$, and thometzekite with different amounts of Zn substituting for Cu, should also belong to this group. Nearly complete solid solution can be expected between Me^{2+} and Cu^{2+} . These minerals have triclinic symmetry due to the requirements of four hydrogen bonds pfu.

The unit cell is enlarged and contains four formula units caused by a partial ordering of the hydrogen bonds which avoids symmetry-restricted hydrogen-bonds.

Area 3 represents the gartrellite type and is attributed to minerals with an ordered occupancy of the $Me(2)$ site with cations of distinctly different crystal-chemical behaviour. This refers to Fe^{3+} and Cu^{2+} in the examples known so far (gartrellite, zincgartrellite and phosphogartrellite), but an order between other elements might also be possible. The symmetry of the gartrellite type minerals belonging to area 3 is triclinic with $Z = 1$. Substantially different Zn contents were found in the gartrellite-zincgartrellite series. According to chemical and structural data, Zn substitutes for both Fe and Cu in nearly equal amounts. The magnitude of the triclinic distortion is controlled by the ratio (Fe,Cu):Zn. In the pure Zn end-member the $Me(2)O_6$ polyhedra are octahedra. In this case the type structure changes to the helmutwinklerite type (area 2).

Acknowledgements

The authors thank B. Baumgartner and B. Blume for the powder diffraction measurements and E. Jägers for recording FT-IR spectra using a diamond microcell. Samples for investigation were kindly provided by G. Tremmel and L. Krahn.

References

- Beran, A., Giester, G. and Libowitzky, E. (1997) The hydrogen bond system in natrochalcite-type compounds – an FTIR spectroscopic study of the H_3O_2^- unit. *Mineral. Petrolog.*, **61**, 223–35.
- Fischer, R.X. and Tillmanns, E. (1988) The equivalent isotropic displacement factor. *Acta Crystallogr.*, **C44**, 775–6.
- Kharisun, Taylor, M.R., Bevan, D.J.M., Rae, A.D. and Pring, A. (1997) The crystal structure of mawbyite, $\text{PbFe}_2(\text{AsO}_4)_2(\text{OH})_2$. *Mineral. Mag.*, **61**, 685–91.
- Kharisun, Taylor, M.R., Bevan, D.J.M. and Pring, A. (1998) The crystal chemistry of duftite, $\text{PbCuAsO}_4(\text{OH})$ and the β -duftite problem. *Mineral. Mag.*, **62**, 121–30.
- Krause, W., Belendorff, K., Bernhardt, H.-J., McCammon, C., Effenberger, H. and Mikenda, W. (1998a) Crystal chemistry of the tsumcorite-group minerals. New data on ferrilotharmeyerite, tsumcorite, thometzekite, mounanaite, helmutwinklerite, and a redefinition of gartrellite. *Eur. J. Mineral.*, **10**, 179–206.
- Krause, W., Belendorff, K., Bernhardt, H.-J. and Petitjean, K. (1998b) Phosphogartrellite, $\text{PbCuFe}(\text{PO}_4)_2(\text{OH})\cdot\text{H}_2\text{O}$, a new member of the tsumcorite group. *Neues Jahrb. Mineral. Mh.*, 111–8.
- Krause, W., Bernhardt, H.-J. and Effenberger, H. (1999a) Symmetry of tsumcorite-group minerals. *Berichte der Deutschen Mineral. Ges., Beih. z. Eur. J. Mineral.*, **11(1)**, 136.
- Krause, W., Effenberger, H., Bernhardt, H.-J. and Martin, M. (1999b) Cobaltlotharmeyerite, $\text{Ca}(\text{Co,Fe,Ni})_2(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$, a new mineral from Schneeberg, Germany. *Neues Jahrb. Mineral. Mh.*, 505–17.
- Martin, M. and Schlegel, F. (1992) Kobaltaustinit und Tsumcorit von der Rappold-Fundgrube in Schneeberg/Sachsen. *Lapis*, **17**, 28–9.
- Pring, A., McBriar, E.M. and Birch, W.D. (1989) Mawbyite, a new arsenate of lead and iron related to tsumcorite and carminite, from Broken Hill, New South Wales. *Amer. Mineral.*, **74**, 1377–81.
- Schmetzer, K., Nuber, B. and Medenbach, O. (1985) Thometzekite, a new mineral from Tsumeb, Namibia, and symmetry relations in the tsumcorite-helmutwinklerite family. *Neues Jahrb. Mineral. Mh.*, 446–52.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, **A32**, 751–67.
- Sheldrick, G.M. (1976) *SHELX-76 Programs for Crystal Structure Determination*. Univ. Cambridge, UK.
- Sheldrick, G.M. (1997) *SHELXL-97 Program for Crystal Structure Refinement*. Univ. Göttingen, Germany.
- Süsse, P. and Schnorrer, G. (1980) Helmutwinklerite, a new arsenate mineral from Tsumeb, S.W. Africa. *Neues Jahrb. Mineral. Mh.*, 118–24.
- Tillmanns, E. and Gebert, W. (1973) The crystal structure of tsumcorite, a new mineral from the Tsumeb Mine, S.W. Africa. *Acta Crystallogr.*, **B29**, 2789–94.
- Wilson, A.J.C. (editor) (1992) *International Tables for Crystallography*, Vol. C. Kluwer, Dordrecht, The Netherlands.
- Yvon, K., Jeitschko, W., and Parthé, E. (1977) LAZY PULVERIX, a computer program for calculating X-ray and neutron powder patterns. *J. Appl. Crystallogr.*, **10**, 73–4.

[Manuscript received 7 January 2000;
revised 1 September 2000]