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Dimorphism of $\text{MnHAsO}_4(\text{H}_2\text{O})$: natural monoclinic krautite and its synthetic triclinic modification

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Abstract: The crystal structure of natural krautite, $\text{MnHAsO}_4(\text{H}_2\text{O})$, was re-evaluated from a cotype specimen, confirming the previously reported monoclinic symmetry for this mineral (space group $P2_1$, $Z = 8$, $a = 8.0093(5)$, $b = 15.9372(10)$, $c = 6.8065(4)$ Å, $\beta = 96.534(2)^\circ$ at room temperature, 5662 structure factors, 302 parameters, $R1 = 0.0295$, $wR2 = 0.0770$). Although hydrogen atoms could not be located from the single crystal X-ray diffraction study, the higher accuracy and precision of the results allowed to derive the hydrogen-bonding scheme ($\text{O}\cdots\text{O} = 2.55\text{--}2.90$ Å) in the crystal structure of krautite. Crystals of synthetic $\text{MnHAsO}_4(\text{H}_2\text{O})$ were grown by mixing aqueous solutions of $\text{NH}_4\text{H}_2\text{AsO}_4$ and MnSO_4 and keeping the formed gel at 105°C for several days. The obtained triclinic crystals were systematically and polysynthetically twinned by contact on (010). Separation of reflections from two individual domains made it possible to determine and refine the crystal structure (space group $P\bar{1}$, $Z = 8$, $a = 8.0105(16)$, $b = 15.991(4)$, $c = 6.8029(12)$ Å, $\alpha = 92.635(8)$, $\beta = 96.534(2)$, $\gamma = 90.151(8)^\circ$ at room temperature, 7226 structure factors, 255 parameters, $R1 = 0.0445$, $wR2 = 0.1381$). The triclinic polymorph of $\text{MnHAsO}_4(\text{H}_2\text{O})$ does not show a direct group-subgroup relation with monoclinic krautite. Triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$ is closely related with other triclinic $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ ($M = \text{Co}, \text{Cu}, \text{Zn}, \text{Mg}$) mineral phases. Quantitative structural comparisons between the five $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ compounds revealed a high similarity between the Mn and Co members, and between the Zn and Mg members,

respectively. Subtle distinctions between the two pairs are ascribed to a different hydrogen-bonding scheme. Although the Cu member has a similar hydrogen-bonding scheme as the Mn and Co pair, its structural similarity with triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$ is low due to the strain of the crystal structure caused by the Jahn-Teller distortions of the $[\text{CuO}_6]$ octahedra.

Keywords: arsenate; crystal structure (re)determination; manganese; mineral phases; structural relation; dimorphism.

Dedicated to Professor Christian Näther on the occasion of his 60th birthday.

1 Introduction

A multitude of anhydrous or hydrous phases exist in the system Mn/As/O/(H), both in the form of minerals or as synthetic compounds. Part of these phases have extensively been used as insecticides during the first part of the 20th century [1]. Due to the persistent toxicity of arsenic not only for beneficial insects but also for mammals, application of arsenic-containing crop-protecting agents was later banned [2]. Nevertheless, arsenic remains one of the naturally most abundant hazardous substances [3], with particular risks for poisoning drinking water sources in some areas of the world like in Bangladesh [4]. For identification of these inorganic phases in soils, detailed knowledge of their formation conditions and crystal structures is required. The great number of naturally occurring arsenic compounds can be explained by the ability of arsenic acid to form different types of anions that can be present as isolated tetrahedral species like AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- or as condensed anions with arsenic in a tetrahedral and/or an octahedral coordination by oxygen [5]. Another reason for the diversity within the system Mn/As/O/(H) pertains to the different stable oxidation states that both Mn and As can exhibit, viz. +II/+III and +III/+V, respectively. Table 1 compiles crystallographic data for all Mn/As/O/(H) phases that have been structurally characterized and deposited in the Inorganic Crystal Structure Database (ICSD [6]) up to date.

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Table 1: Crystallographic literature data (in Å, °) of phases in the Mn/As/O/(H) system. Oxidation states for manganese (+II or +III) and for arsenic (+III) are indicated; all other phases contain arsenic in oxidation state +V.

Phase; mineral name	Space group	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	Ref.
α -Mn ^{II} ₃ (AsO ₄) ₂ ; –	<i>P</i> 2 ₁ / <i>n</i>	5.4278	6.8421	9.1696	90	96.480	90	[7]
β -Mn ^{II} ₃ (AsO ₄) ₂ ; –	<i>P</i> 2 ₁ / <i>c</i>	9.1129	11.7658	6.4204	90	98.727	90	[7]
Mn ^{II} ₂ As ₂ O ₇ ; –	<i>C</i> 2/ <i>m</i>	6.7454	8.7561	4.8004	90	102.723	90	[8]
Mn ^{II} As ₂ O ₆ ; –	<i>P</i> $\bar{3}1m$	4.7956	4.7956	4.6923	90	90	120	[9]
Mn ^{III} AsO ₄ ; –	<i>P</i> 2 ₁ / <i>n</i>	6.6833	8.9303	4.7914	90	93.813	90	[10]
Mn ^{II} ₂ As ₂ O ₅ ; –	<i>I</i> 2/ <i>a</i>	10.1815	13.3254	14.579	90	90.096	90	[11]
Mn ^{III} AsO ₄ (H ₂ O) _{1.2} ; –	<i>C</i> 2/ <i>c</i>	7.0311	7.8250	7.4656	90	112.145	90	[12]
Mn ^{II} ₂ As ₂ O ₇ (H ₂ O) ₂ ; –	<i>P</i> 2 ₁ / <i>n</i>	6.6576	14.5552	7.8147	90	94.935	90	[13]
Mn ^{II} (H ₂ AsO ₄) ₂ (H ₃ AsO ₄) ₂ ; –	<i>P</i> $\bar{1}$	5.5602	7.4100	8.4276	100.11	98.578	92.744	[14]
Mn ^{II} (HAsO ₄)(H ₃ AsO ₄)(H ₂ O) _{0.5} ; –	<i>P</i> $\bar{1}$	4.9750	5.4747	13.603	98.86	93.63	99.09	[14]
Mn ^{II} ₅ As ^{III} ₃ O ₉ (OH,Cl); magnussonite	<i>Ia</i> $\bar{3}$ <i>d</i>	19.680	19.680	19.680	90	90	90	[15]
Mn ^{II} ₃ (AsO ₄) ₂ (H ₂ O) _{4.5} ; castellarroite	<i>P</i> 2 ₁ / <i>n</i>	8.7565	13.468	18.652	90	94.876	90	[16]
Mn ₂ ^{II} (AsO ₄)(OH); sarkinite	<i>P</i> 2 ₁ / <i>c</i>	10.2188	13.6127	12.779	90	108.834	90	[17]
Mn ₂ ^{II} (AsO ₄)(OH); eveite	<i>P</i> <i>n</i> <i>n</i> <i>m</i>	8.5478	8.7207	6.2961	90	90	90	[18]
Mn ^{II} ₅ (AsO ₄) ₂ (OH) ₄ ; arsenoclasite	<i>P</i> 2 ₁ 2 ₁ 2 ₁	18.290	5.75	9.31	90	90	90	[19]
Mn ^{II} ₅ (AsO ₄) ₂ (OH) ₄ (H ₂ O) ₄ ; akrochordite	<i>P</i> 2 ₁ / <i>c</i>	5.682	17.627	6.832	90	99.49	90	[20]
Mn ^{II} ₇ (AsO ₄) ₂ (OH) ₈ ; allactite	<i>P</i> 2 ₁ / <i>a</i>	11.03	12.12	5.51	90	114.07	90	[21]
Mn ^{II} ₇ (HAsO ₄) ₄ (AsO ₄) ₂ ; –	<i>P</i> $\bar{1}$	6.810	8.239	10.011	104.31	108.94	101.25	[22]
Mn ^{II} ₂ Mn ^{III} AsO ₄ (OH) ₄ ; flinkite	<i>P</i> <i>n</i> <i>m</i> <i>a</i>	9.483	13.030	5.339	90	90	90	[23]
Mn ^{II} ₉ (OH) ₉ (As ^{III} O ₃)(As ^V O ₄) ₂ (H ₂ O) ₂ ; synadelphite	<i>P</i> <i>n</i> <i>m</i> <i>a</i>	10.754	18.865	9.884	90	90	90	[24]
Mn ^{II} HAsO ₄ (H ₂ O); krautite	<i>P</i> 2 ₁	8.012	15.956	6.801	90	96.60	90	[25]
Mn ^{II} ₅ (HAsO ₄) ₂ (AsO ₄) ₂ (H ₂ O) ₄ ; miguelromeroite	<i>C</i> 2/ <i>c</i>	18.030	9.2715	9.7756	90	96.266	90	[26]
Mn ^{II} Mn ^{III} ₂ (AsO ₄) ₂ (OH) ₂ (H ₂ O) ₄ ; coralloite	<i>P</i> 1	5.5828	9.7660	5.54551	94.467	111.348	93.850	[27]
(Mn ^{II} ₅ (H ₂ O) ₈)(HAsO ₄) ₂ (AsO ₄) ₂ (H ₂ O) ₂ ; geigerite	<i>P</i> $\bar{1}$	7.944	10.691	6.770	80.97	84.20	81.85	[28]

During hydrothermal studies aimed at growing single crystals of the manganese(II) arsenite Mn^{II}₅(As^{III}O₃)₃(OH), i.e. Cl-free magnussonite [15], in some of the batches synthetic krautite, MnHAsO₄(H₂O), was obtained as a minor by-product in the polycrystalline bulk, apparently generated by oxidation of As^{III} to As^V. A closer examination of the original crystal structure refinement of synthetic krautite, published in 1979 [25], revealed some unsatisfactory results such as high standard uncertainties for atomic coordinates, an isotropic refinement of the displacement parameters for all atoms and a high reliability factor $R = 0.112$. Hence, a more accurate crystal-structure refinement of both natural and synthetic krautite from single-crystal data deemed appropriate. The results of these studies are presented herein.

2 Experimental

2.1 Synthesis

Crystals of synthetic krautite, MnHAsO₄(H₂O), were grown under mild hydrothermal conditions, following a modified procedure described by Deiß [29]. At room temperature, an aqueous solution of NH₄H₂AsO₄ was added dropwise and under constant stirring to an aqueous

solution of MnSO₄ which resulted in the formation of a colorless gel; the arsenate solution was added until a pH of ≈ 5 was reached. The precipitate then was heated in the mother liquor in a closed vessel at 105 °C under autogenous pressure for several days, which resulted in the formation of tabular crystals with a light-pink color and up to 0.5 mm in size.

Light-pink tabular crystals of natural krautite were separated from a cotype specimen (inventory number J 8927; inventoried in 1930) from Nagyág, Transsylvania (today Sacarîmb, Hunedoara Co., Romania) deposited at the Natural History Museum in Vienna, Austria. In order to ascertain the chemical composition of these crystals, representative tabular, horizontally oriented crystal and cleavage fragments were carbon-coated and studied by energy-dispersive X-ray analyses (EDX) using a JEOL JSM-6610LV scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (Bruker e-FlashHR+) and Bruker Esprit 2.0 software. Using an acceleration voltage of 15 kV, a counting time of 60 s and a dead time <5%, a total of six spot analyses of four different fragments were carried out. The spot analyses produced minor beam damage (tiny cracks in each case), probably due to loss of some water from the structure. All analyses showed that the fragments are chemically pure within standard ranges of error; only in one analysis a trace amount of Si was observed. Any M^{II} impurities are below the estimated detection limit of ~ 0.02 at% (for Mg this limit is slightly higher due to the strong overlap of the Mg K α peak with the As L α peak, despite excellent peak deconvolution by the software). The observed Mn:As ratio is $\approx 1:1$.

Figure 1 shows color photomicrographs of the synthetic and natural samples.

Figure 1: Color photomicrograph of (a) pale pink tabular, subparallel crystals of natural, monoclinic krautite (cotype specimen J 8927, Natural History Museum, Vienna); (b) tabular, six-sided, very pale pink crystals of synthetic triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$, prepared at 105 °C.

2.2 Single crystal X-ray diffraction and structure analysis

Inspection of the natural and synthetic krautite crystals under a polarising microscope did not indicate twinning parallel to the planes

Figure 2: Reconstructed reciprocal space mapping of the $(0kl)$ plane of polysynthetically twinned, synthetic triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$. The inset shows an enlarged area with reflections marked with green circles for one and with white circles for the second domain generated by a 180° rotation about the b^* axis.

of the plates; due to the very flat shape of the crystals, the direction perpendicular to these planes could not be examined. For crystals of the natural specimen, X-ray diffraction data were recorded on a Bruker APEX-II system (Bruker AXS, Madison, Wisconsin, USA) equipped with a microfocus X-ray tube and a graphite monochromator, applying Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). For the synthetic crystals, the same type of radiation was used on a Bruker D8 QUEST system (Bruker AXS GmbH, Karlsruhe, Germany) equipped with an INCOATEC Microfocus Sealed Tube 3.0 and a multilayer mirror monochromator. Data sets for both types of crystals were measured at room temperature and at -173 °C to check for possible phase transitions in this temperature range, with each data collection strategy handled and optimized with APEX-3 [30]. For synthetic $\text{MnHAsO}_4(\text{H}_2\text{O})$ a close inspection of the diffraction data by using reconstructed reciprocal planes showed that all investigated crystals have triclinic symmetry and were in fact polysynthetically twinned. Use of CELL_NOW [30] revealed a 180° rotation about the b^* axis that transfers one domain into the other (Figure 2). For integration of reflection intensities using a narrow-frame algorithm with SAINT [30], the contributions of each domain and overlapping reflections were separated and written into an HKLF-5 file that eventually was used for final refinement; absorption effects were corrected with TWIN_ABS [30]. For natural krautite crystals (three crystals were investigated), monoclinic symmetry was determined, and a similar splitting of reflections like in the case of triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$ was not observed; for the natural crystals, data reduction and absorption correction with SADABS [31] followed standard procedures.

The crystal structures of both natural and synthetic $\text{MnHAsO}_4(\text{H}_2\text{O})$ were initially solved with SHELXT [32] and refined with SHELXL [33]. For better comparison with the previously reported structure model of monoclinic krautite and with the other members of the triclinic $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ series, respectively, the same non-reduced unit-cells reported for $\text{MnHAsO}_4(\text{H}_2\text{O})$ [25] and $\text{CoHAsO}_4(\text{H}_2\text{O})$ [34] were chosen¹, from which also atomic coordinates and the labelling scheme were adapted. The batch scaling factor for the two-component triclinic crystal of $\text{MnHAsO}_4(\text{H}_2\text{O})$ refined to a value of 0.35; monoclinic krautite was refined as a 1:1 inversion twin (Flack parameter

¹ The reduced cells can be transformed from the chosen non-reduced cells by the matrix (010, 001, 100).

[35] = 0.502(15)). No significant deviation from full occupancy was observed for any of the non-H atoms in both structures. The positions of the H atoms in crystals of triclinic and monoclinic $\text{MnHASO}_4(\text{H}_2\text{O})$ could not be located for the two pairs of data sets and thus were not included in the final refinements. The positions of O atoms bonded to H atoms were derived from typical As–O bond lengths and bond-valence sum (BVS) calculations [36] using the values provided by Brese & O’Keeffe [37]. O atoms that are part of an OH group are designated as OH with the consecutive atom number and O atoms of water molecules as OW in the same way.

Numerical details of the data collections and structure refinements are compiled in Table 2. Further details of the crystal structure investigations may be obtained from The Cambridge Crystallographic Data Centre (CCDC) on quoting the depository numbers listed at the end of Table 2. The data can be obtained free of charge via www.ccdc.cam.ac.uk/structures. Selected bond lengths and bond-valence sums (BVS) for monoclinic and triclinic $\text{MnHASO}_4(\text{H}_2\text{O})$ are gathered in Table 3.

3 Results and discussion

Chemical analysis and crystallographic data of $\text{MnHASO}_4(\text{H}_2\text{O})$ were first reported on a natural sample during the first description of the mineral krautite and confirmed by the synthesis of this phase. Indexation of the diffraction pattern led to a primitive monoclinic unit cell with $a = 8.00(2)$, $b = 15.93(5)$, $c = 6.79(2)$ Å, $\beta = 96.3(5)^\circ$ for the natural sample. However, the crystal structure of krautite remained undetermined at this stage [38]. Due to the lack of suitable natural material at that time, the crystal structure of $\text{MnHASO}_4(\text{H}_2\text{O})$ was subsequently solved from single-crystal X-ray data of a synthetic sample in space group $P2_1$ [25], thus confirming the monoclinic symmetry reported in the original description [38]. The authors noted a strong $P2_1/n$ pseudo-symmetry for the final $\text{MnHASO}_4(\text{H}_2\text{O})$ crystal structure model [25]. Shortly afterwards, the crystal structure determinations of analogous $\text{CoHASO}_4(\text{H}_2\text{O})$ [34] (mineral name cobaltkoritnigite [39]) and $\text{ZnHASO}_4(\text{H}_2\text{O})$ (koritnigite) [40] were reported, both with similar unit-cell parameters as $\text{MnHASO}_4(\text{H}_2\text{O})$ but with triclinic symmetry. The same is valid for the other known members of the $M^{\text{II}}\text{HASO}_4(\text{H}_2\text{O})$ series, viz. $\text{CuHASO}_4(\text{H}_2\text{O})$ (geminite) [41, 42] and $\text{MgHASO}_4(\text{H}_2\text{O})$ (magnesiokoritnigite) [43]. Apparently, the corresponding Ni member “ $\text{NiHASO}_4(\text{H}_2\text{O})$ ” has not been obtained in crystalline form [44].

The assumption that $\text{MnHASO}_4(\text{H}_2\text{O})$ in fact does not belong to the monoclinic, but to the triclinic crystal system has previously been made [40] but was not confirmed afterwards. The results of the current redeterminations clearly revealed monoclinic symmetry for the natural material, and triclinic symmetry for the crystals grown

under hydrothermal conditions at a temperature of 105 °C. It should be noted that crystals prepared in the same way at 90 °C in fact have monoclinic symmetry, just like single crystals grown from a gel at room temperature [25, 45] or polycrystalline material obtained by evaporation of the solvent at 60 °C [46]. The following discussion is based on the data that resulted in the better reliability factor for each studied crystal, i.e. the 23 °C data for krautite and the –173 °C data for triclinic $\text{MnHASO}_4(\text{H}_2\text{O})$.

3.1 Crystal structure of krautite

The current redetermination of natural krautite confirms the previous model [25] with higher precision and accuracy, with satisfactory reliability factors and with all atoms refined with anisotropic displacement parameters. The crystal structure of krautite is layered and comprised of (010) sheets. Within a sheet, $[\text{MnO}_5(\text{H}_2\text{O})]$ (Mn1, Mn2) and *cis*- $[\text{MnO}_4(\text{H}_2\text{O})(\text{OH})]$ (Mn3, Mn4) octahedra are linked by edge-sharing into chains extending parallel to [101]. Adjacent chains are connected through $\text{AsO}_3(\text{OH})$ tetrahedra by sharing two corners with each of the four hydrogen arsenate anions. The average Mn–O bond lengths of the $[\text{MnO}_6]$ octahedra (Table 3) are in good agreement with the grand mean value of 2.199(85) Å calculated on basis of 1908 bonds and 318 polyhedra [48]. Likewise, the individual As–OH and As–O distances of the $\text{AsO}_3(\text{OH})$ tetrahedra match with literature values of 1.728(19) Å for As–OH bonds in HASO_4^{2-} groups and a grand mean value of 1.667(18) Å for As–O bonds to non-protonated O atoms [48].

The cohesion between the (010) sheets is accomplished by hydrogen-bonding interactions only, which explains the perfect cleavage parallel to {010} described for the mineral [25, 38]. Numerical details of the hydrogen-bonding scheme are compiled in Table 4, and a view of the crystal structure including the hydrogen bonds is given in Figure 3. All OH groups are involved in strong hydrogen bonds to O atoms of $[\text{MnO}_5(\text{H}_2\text{O})]$ octahedra and $\text{AsO}_3(\text{OH})$ groups with O···O distances between 2.55 and 2.60 Å. Two of these strong interactions are intralayer hydrogen bonds to O atoms that are shared between $[\text{MnO}_5(\text{H}_2\text{O})]$ octahedra and $\text{AsO}_3(\text{OH})$ groups (O7H···O9; O8H···O10), and the other two strong hydrogen bonds are established between adjacent layers to $\text{AsO}_3(\text{OH})$ groups (O15H···O2; O16H···O1). The four water molecules are involved in intra- and interlayer hydrogen-bonding interactions of medium strengths with O···O distances between 2.68 and 2.90 Å.

Table 2: Crystal data and details of data collections and refinements for monoclinic krautite and triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$.

	Monoclinic krautite		Triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$	
Temperature/ $^{\circ}\text{C}$	23	–173	27	–173
Formula	$\text{MnHAsO}_4(\text{H}_2\text{O})$	$\text{MnHAsO}_4(\text{H}_2\text{O})$	$\text{MnHAsO}_4(\text{H}_2\text{O})$	$\text{MnHAsO}_4(\text{H}_2\text{O})$
Formula weight	212.88	212.88	212.88	212.88
Diffractionmeter	Bruker APEX-II	Bruker APEX-II	Bruker D8 QUEST	Bruker D8 QUEST
Radiation; wavelength/ $\text{\AA}$	$\text{Mo K } \bar{\alpha}$; 0.71073	$\text{Mo K } \bar{\alpha}$; 0.71073	$\text{Mo K } \bar{\alpha}$; 0.71073	$\text{Mo K } \bar{\alpha}$; 0.71073
Space group (No.)	$P2_1(4)$	$P2_1(4)$	$P\bar{1}(2)$	$P\bar{1}(2)$
Crystal description	Light-pink plate	Light-pink plate	Light-pink lath	Light-pink lath
Crystal dimensions/ mm^3	$0.09 \times 0.08 \times 0.01$	$0.09 \times 0.08 \times 0.01$	$0.10 \times 0.03 \times 0.01$	$0.10 \times 0.03 \times 0.01$
Formula units Z	8	8	8	8
$a/\text{\AA}$	8.0093(5)	7.9865(4)	8.0105(16)	7.9874(6)
$b/\text{\AA}$	15.9372(10)	15.9108(7)	15.991(4)	15.9341(13)
$c/\text{\AA}$	6.8065(4)	6.7951(3)	6.8029(12)	6.7997(5)
$\alpha/^{\circ}$	90	90	92.635(8)	93.015(3)
$\beta/^{\circ}$	96.534(2)	96.4999(12)	96.589(9)	96.539(3)
$\gamma/^{\circ}$	90	90	90.151(8)	90.145(3)
Volume/ $\text{\AA}^3$	863.18(9)	857.91(7)	864.7(3)	858.56(11)
X-ray density/ g cm^{-3}	3.28	3.30	3.27	3.30
μ/mm^{-1}	10.57	10.64	10.55	10.63
Range $\theta_{\min}$ – $\theta_{\max}/^{\circ}$	2.56 $\rightarrow$ 31.37	2.56 $\rightarrow$ 33.56	2.56 $\rightarrow$ 36.42	2.56 $\rightarrow$ 36.42
Range h ; k ; l	–11 $\rightarrow$ 11; –23 $\rightarrow$ 23; –9 $\rightarrow$ 9	–12 $\rightarrow$ 12; –24 $\rightarrow$ 24; –10 $\rightarrow$ 10	–13 $\rightarrow$ 13; 0 $\rightarrow$ 26; –11 $\rightarrow$ 11	–13 $\rightarrow$ 13; 0 $\rightarrow$ 26; –11 $\rightarrow$ 11
Measured reflections	24869	26600	7226	8010
Independent reflections	5662	6432	7226	8010
Observed reflections [$I > 2\sigma(I)$]	5302	5868	5877	6947
R_{int}	0.0372	0.1132	–	–
Absorption correction	SADABS	SADABS	TWINABS	TWINABS
Coeff. of transmission $T_{\min}$; $T_{\max}$	0.49; 0.75	0.47; 0.77	0.62; 0.88	0.58; 0.92
Structure solution and refinement	SHELXS, SHELXL	SHELXS, SHELXL	SHELXS, SHELXL	SHELXS, SHELXL
Number of parameters	254	154	255	255
Extinction coefficient (SHELXL)	–	–	0.0036(7)	0.0011(3)
$R[F^2 > 2\sigma(F^2)]$; $wR(F^2 \text{ all})$	0.0295; 0.0770	0.0495; 0.1299	0.0445; 0.1381	0.0402; 0.1098
Flack parameter	0.502(15)	0.514(19)	–	–
Goof	1.055	1.034	1.066	1.052
CSD number	2129531	2129530	2129532	2129533

Table 3: Selected bond lengths (in Å), their averaged values (av.) and bond-valence sums (BVS; in valence units) of the monoclinic and triclinic polymorphs of MnHAsO₄(H₂O).

Monoclinic krautite at 23 °C ^a			Triclinic MnHAsO ₄ (H ₂ O) at –173 °C ^a		
Mn1	O3 ⁱ	2.156(4)	Mn1	O1	2.102(3)
Mn1	O12	2.176(4)	Mn1	O3W	2.127(4)
Mn1	O5	2.181(4)	Mn1	O2	2.156(3)
Mn1	O4	2.193(4)	Mn1	O10 ^v	2.185(3)
Mn1	O17W	2.196(5)	Mn1	O1 ^{vi}	2.219(3)
Mn1	O9	2.252(4)	Mn1	O18H ^{vii}	2.273(3)
Av.; BVS		2.192; 2.03	Av.; BVS		2.177; 2.13
Mn2	O4	2.158(4)	Mn2	O5	2.155(3)
Mn2	O11 ⁱⁱ	2.169(4)	Mn2	O4	2.172(4)
Mn2	O3 ⁱ	2.182(5)	Mn2	O5 ^{vii}	2.186(3)
Mn2	O6 ⁱ	2.194(4)	Mn2	O8	2.193(3)
Mn2	O10 ⁱⁱ	2.222(4)	Mn2	O6	2.210(3)
Mn2	O18W	2.228(5)	Mn2	O7W	2.232(4)
Av.; BVS		2.192; 2.03	Av.; BVS		2.191; 2.03
Mn3	O13	2.116(4)	Mn3	O9W	2.098(4)
Mn3	O19W	2.120(6)	Mn3	O16 ⁱⁱⁱ	2.116(3)
Mn3	O11 ⁱⁱⁱ	2.163(4)	Mn3	O4	2.168(4)
Mn3	O6 ^{iv}	2.181(4)	Mn3	O8	2.178(3)
Mn3	O14	2.233(4)	Mn3	O16 ^{viii}	2.218(3)
Mn3	O7H	2.281(4)	Mn3	O15H ^{viii}	2.271(3)
Av.; BVS		2.182; 2.10	Av.; BVS		2.175; 2.15
Mn4	O20W	2.106(5)	Mn4	O19 ⁱⁱⁱ	2.148(4)
Mn4	O14	2.108(4)	Mn4	O2 ^{ix}	2.161(3)
Mn4	O12	2.167(4)	Mn4	O10	2.184(3)
Mn4	O5	2.181(4)	Mn4	O19 ^x	2.185(3)
Mn4	O13	2.225(4)	Mn4	O11W	2.186(4)
Mn4	O8H ^{iv}	2.279(4)	Mn4	O12	2.244(3)
Av.; BVS		2.178; 2.13	Av.; BVS		2.185; 2.07
As1	O1	1.673(4)	As1	O1	1.678(3)
As1	O3	1.676(4)	As1	O2 ⁱ	1.682(3)
As1	O5	1.682(4)	As1	O12 ^{vii}	1.684(3)
As1	O7H	1.750(4)	As1	O13H	1.714(3)
Av.; BVS		1.695; 4.88	Av.; BVS		1.690; 4.93
As2	O2	1.664(5)	As2	O14	1.668(3)
As2	O4	1.668(4)	As2	O5	1.671(3)
As2	O6	1.671(4)	As2	O8 ⁱ	1.671(3)
As2	O8H	1.749(4)	As2	O15H	1.751(3)
Av.; BVS		1.688; 4.98	Av.; BVS		1.690; 4.93
As3	O13	1.667(4)	As3	O16	1.670(3)
As3	O11	1.679(4)	As3	O4	1.674(3)
As3	O9	1.681(4)	As3	O6	1.678(3)
As3	O15H	1.716(5)	As3	O17H	1.720(3)
Av.; BVS		1.686; 4.99	Av.; BVS		1.686; 4.99
As4	O14 ⁱ	1.670(4)	As4	O20	1.672(3)
As4	O12	1.677(4)	As4	O10	1.677(3)
As4	O10	1.683(4)	As4	O19	1.681(3)
As4	O16H	1.713(5)	As4	O18H	1.749(3)
Av.; BVS		1.686; 4.99	Av.; BVS		1.695; 4.88

Symmetry codes: (i) $x, y, z + 1$; (ii) $x - 1, y, z$; (iii) $x, y, z - 1$; (iv) $x + 1, y, z$; (v) $x, y - 1, z$; (vi) $-x, -y, -z + 1$; (vii) $-x, -y + 1, -z + 1$; (viii) $-x + 1, -y + 1, -z + 1$; (ix) $x, y + 1, z$; (x) $-x + 1, -y + 2, -z + 1$

Table 3: (continued)

Monoclinic krautite at 23 °C ^a	Triclinic MnHAsO ₄ (H ₂ O) at –173 °C ^a
BVS of oxygen atoms and their coordination numbers (in parentheses).	
Monoclinic krautite. O1 (1) 1.30; O2 (1) 1.32; O3 (3) 1.99; O4 (3) 2.01; O5 (3) 1.95; O6 (3) 1.98; O7H (2) 1.32; O8H (2) 1.32; O9 (2) 1.55; O10 (2) 1.57; O11 (3) 2.00; O12 (3) 1.99; O13 (3) 2.03; O14 (3) 2.03; O15H (1) 1.15; O16H (1) 1.16; O17W (1) 0.33; O18W (1) 0.31; O19W (1) 0.41; O20W (1) 0.43	
Triclinic MnHAsO₄(H₂O). O1 (3) 2.00; O2 (3) 1.99; O3W 1.040; O4 (3) 2.01; O5 (3) 2.02; O6 (2) 1.61; O7W (1) 0.30; O8 (3) 1.94; O9W (1) 0.42; O10 (3) 1.95; O11W (1) 0.34; O12 (2) 1.54; O13H (1) 1.14; O14 (1) 1.30; O15H (2) 1.31; O16 (3) 2.06; O17H (1) 1.15; O18H (2) 1.31; O19 (3) 1.99; O20 (1) 1.32	

^aBond lengths at the different temperatures (–173 °C for monoclinic krautite and 27 °C for triclinic MnHAsO₄(H₂O)) differ by less than 0.015 Å from the given values.

Table 4: Donor...acceptor ($D \cdots A$) distances (in Å) within the hydrogen-bonding networks in the MnHAsO₄(H₂O) crystal structures.

Monoclinic krautite at 23 °C ^a			Triclinic MnHAsO ₄ (H ₂ O) at –173 °C ^a		
<i>D</i>	<i>A</i>	O...O distances	<i>D</i>	<i>A</i>	O...O distances
O7H	O9 ⁱⁱⁱ	2.596(7)	O3W	O20 ^{vii}	2.713(5)
O8H	O10 ^{iv}	2.589(6)	O3W	O7	2.869(5)
O15H	O2 ⁱⁱ	2.545(6)	O7W	O17H ^{viii}	2.780(5)
O16H	O1 ⁱ	2.588(7)	O7W	O14 ⁱⁱⁱ	2.668(5)
O17W	O15H ^{iv}	2.736(6)	O9W	O14 ^{viii}	2.680(5)
O17W	O1	2.675(7)	O9W	O11W	2.795(5)
O18W	O16H	2.788(7)	O11W	O20	2.659(5)
O18W	O2 ^v	2.680(7)	O11W	O13H ^{vii}	2.715(5)
O19W	O1 ^{vi}	2.716(8)	O13H	O14	2.556(5)
O19W	O18W ⁱⁱ	2.896(9)	O15H	O6	2.581(5)
O20W	O2	2.680(7)	O17H	O20	2.585(5)
O20W	O17W ⁱ	2.832(8)	O18H	O12 ^v	2.583(5)

Symmetry codes: (i) $-x + 1, y - 1/2, -z + 1$; (ii) $-x + 1, y + 1/2, -z + 1$; (iii) $x, y, z - 1$; (iv) $x - 1, y, z$; (v) $x, y, z + 1$; (vi) $x + 1, y, z$; (vii) $-x + 1, -y + 1, -z + 1$; (viii) $-x, -y + 1, -z + 1$

^aO...O distances at the different temperatures (–173 °C for monoclinic krautite and 27 °C for triclinic MnHAsO₄(H₂O)) differ by less than 0.02 Å from the given values.

3.2 Crystal structure of triclinic MnHAsO₄(H₂O)

The crystal structure of triclinic MnHAsO₄(H₂O) has an apparent resemblance with that of monoclinic krautite, as recognized by the very similar unit-cell parameters

Figure 3: Crystal structure of krautite (23 °C data) in polyhedral representation viewed along $[100]$, with displacement ellipsoids drawn at the 75% probability level. $[\text{MnO}_5(\text{H}_2\text{O})]$ octahedra are light-blue, $[\text{MnO}_4(\text{H}_2\text{O})(\text{OH})]$ octahedra are dark-blue and $\text{AsO}_3(\text{OH})$ tetrahedra are red. O atoms belonging to an OH group are yellow, O atoms of water molecules are green. Hydrogen bonds with the corresponding donor atoms are shown as lines with the same color.

(Table 2) and the same principal structure units, i.e. $[\text{MnO}_5(\text{H}_2\text{O})]$ and $[\text{MnO}_4(\text{H}_2\text{O})(\text{OH})]$ octahedra, $\text{AsO}_3(\text{OH})$ tetrahedra with the corresponding bond lengths and general set-up of the crystal structure. Nevertheless, there is no direct group-subgroup relation [49] between the two crystal structures. However, a close relationship of triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$ exists with the other representatives of the triclinic $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ ($M^{\text{II}} = \text{Co}, \text{Cu}, \text{Zn}, \text{Mg}$) series for which unit-cell parameters are listed in Table 5.

$\text{MnHAsO}_4(\text{H}_2\text{O})$ has the same point symmetry and very similar unit-cell parameters and atomic coordinates for Mn, As and O as the analogous Co, Zn, Mg compounds, and to a certain extent also for the Cu analogue. Since the crystal structures of the latter phases have been described in detail, here only the principal building units are

Table 5: Unit-cell parameters of triclinic $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ compounds ($Z = 8$, space group $P\bar{1}$) at room temperature.

<i>M</i>	Mn	Co	Cu ^a	Zn	Mg
<i>a</i> /Å	8.0105(16)	7.865(3)	8.093(2)	7.948(2)	7.8702(7)
<i>b</i> /Å	15.991(4)	15.699(6)	15.764(3)	15.829(5)	15.8081(6)
<i>c</i> /Å	6.8029(12)	6.719(2)	6.433(1)	6.668(2)	6.6389(14)
α /°	92.635(8)	94.25(3)	84.35(3)	90.86(2)	90.814(6)
β /°	96.589(9)	96.89(3)	95.53(3)	96.56(2)	96.193(6)
γ /°	90.151(8)	90.28(3)	93.35(3)	90.05(2)	90.094(7)
<i>V</i> /Å ³	864.7(3)	821.28	811.93	833.3	821.06
Ref.	This work	[34]	[42]	[40]	[43]

^aOriginal cell transformed with the matrix (001, 100, 010).

discussed. Common to all $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ crystal structures is the formation of sheets stacked along the longest unit-cell axis which is the *b* axis according to the typically used unit-cell setting (Table 5). Like in the monoclinic krautite crystal structure, the two-dimensional framework is constructed from edge-sharing *cis*- $[\text{M}(\text{H}_2\text{O})\text{O}_5]$ (Mn2, Mn4 for $\text{MnHAsO}_4(\text{H}_2\text{O})$) and $[\text{M}(\text{H}_2\text{O})(\text{OH})\text{O}_4]$ (Mn1 and Mn3) octahedra linked into zig-zag chains extending parallel $[101]$ and intermediate $\text{AsO}_3(\text{OH})$ tetrahedra that link the chains into (010) sheets (Figure 4). Again, adjacent sheets are solely linked through hydrogen-bonding interactions. The commonly observed contact twinning on (010) in the triclinic $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ structures (note that the Cu-dominant mineral geminite has its name from Latin *geminus* meaning twins) can also be attributed to the layered arrangement of the crystal structure.

Notwithstanding that in none of the published $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ structures H atom positions could be determined, the analysis of As–O bond lengths and BVS parameters (Tables 3 and 4) made it possible to identify all O atoms that are part of a water molecule or an OH group. In all crystal structures of the triclinic $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ series, the O atoms of the four water molecules (for the Mn member O3, O7, O9, O11) are the same, whereas the O atoms belonging to OH groups are different for the $M^{\text{II}} = \text{Mn}, \text{Co}, \text{Cu}$ set (for the Mn member O13, O15, O17, O18) compared to the $M^{\text{II}} = \text{Zn}, \text{Mg}$ set (O6, O12, O14, O20). As previously noted, all related non-H atoms in the five $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ structures have the same point symmetry and similar coordinates, and all phases crystallize in the same space group type with similar unit-cells. However, the different hydrogen bonding schemes in the $M^{\text{II}} = \text{Mn}, \text{Co}, \text{Cu}$ set and the $M^{\text{II}} = \text{Zn}, \text{Mg}$ set have a clear impact on the structural

Figure 4: Crystal structure of triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$ (–173 °C data) in polyhedral representation viewed along $[100]$. Displacement ellipsoids and color codes are as in Figure 3.

Table 6: Absolute atomic displacements (in Å) of triclinic $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ compounds relative to $\text{MnHAsO}_4(\text{H}_2\text{O})$, as well as lattice distortion (S), maximum distance d_{max} (in Å), arithmetic mean distance d_{av} (in Å) and measure of similarity (Δ). For all structures, the original atom labelling was used; O atoms that are part of an OH group are underlined, O atoms that are part of a water molecule are marked with asterisks.

Mn	Co		Cu		Zn		Mg	
Mn1	Co1	0.0642	Cu4	0.2549	Zn1	0.1311	Mg1	0.1320
Mn2	Co2	0.0387	Cu2	0.1279	Zn2	0.1242	Mg2	0.0828
Mn3	Co3	0.0920	Cu3	0.1305	Zn3	0.0665	Mg3	0.0810
Mn4	Co4	0.0399	Cu1	0.1374	Zn4	0.1505	Mg4	0.1038
As1	As1	0.0295	As4	0.3889	As1	0.2590	As1	0.2093
As2	As2	0.0489	As3	0.2215	As2	0.2343	As2	0.2221
As3	As3	0.0663	As1	0.2154	As3	0.2380	As3	0.1838
As4	As4	0.0655	As2	0.1703	As4	0.2476	As4	0.2281
O1	O1	0.0182	O12	0.2112	O1	0.0694	O1	0.0885
O2	O2	0.0311	O11	0.2716	O2	0.1261	O2	0.1170
O3W*	O3*	0.1550	H2O(4)*	0.3795	O3*	0.2605	OW3*	0.2898
O4	O4	0.0159	O2	0.1746	O4	0.1171	O4	0.1026
O5	O5	0.0703	O8	0.1262	O5	0.2448	O5	0.2172
O6	O6	0.1123	O1	0.4135	<u>O6</u>	0.1788	<u>OH6</u>	0.0724
O7W*	O7*	0.0693	H2O(2)*	0.5154	<u>O7*</u>	0.4666	<u>OW7*</u>	0.4573
O8	O8	0.0796	O7	0.2188	O8	0.0802	O8	0.0821
O9W*	O9*	0.1232	H2O(3)*	0.5792	O9*	0.4531	OW9*	0.4643
O10	O10	0.0702	O5	0.1728	O10	0.0525	O10	0.0668
O11W*	O11	0.1491	H2O(1)*	0.3620	O11*	0.3425	OW11*	0.3097
O12	O12	0.0224	O10	0.4768	<u>O12</u>	0.2027	<u>OH12</u>	0.1356
<u>O13H</u>	<u>O13</u>	0.1233	<u>OH4</u>	0.8540	<u>O13</u>	0.3303	<u>O13</u>	0.3040
O14	O14	0.0605	O9	0.3558	<u>O14</u>	0.1708	<u>OH14</u>	0.1336
<u>O15H</u>	<u>O15</u>	0.0552	<u>OH3</u>	0.3791	O15	0.1493	O15	0.1599
O16	O16	0.0846	O3	0.0536	O16	0.0726	O16	0.0777
<u>O17H</u>	<u>O17</u>	0.1231	<u>OH1</u>	0.5148	O17	0.2275	O17	0.1445
<u>O18H</u>	<u>O18</u>	0.0428	<u>OH2</u>	0.3456	O18	0.1801	O18	0.1785
O19	O19	0.0413	O6	0.1189	O19	0.2480	O19	0.2172
O20	O20	0.0690	O4	0.3302	<u>O20</u>	0.2901	<u>OH20</u>	0.2522
S	0.0125		0.0455		0.0110		0.0134	
d_{max}	0.1550		0.8540		0.4666		0.4643	
d_{av}	0.0701		0.3036		0.2041		0.1826	
Δ	0.018		0.158		0.052		0.034	

relationships among the $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ compounds. The crystal structures among the members of each set are isotypic, whereas the crystal structures between the two sets are isopointal [50].

The differences caused by replacement of the cation within the triclinic $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ ($M = \text{Co}, \text{Cu}, \text{Zn}, \text{Mg}$) crystal structures were quantified with the program *compstru* [51], available at the Bilbao Crystallographic Server [52]. Atomic displacements for all atom pairs in the five structures as well as numerical values for the degree of lattice distortion (S), the maximum distance (d_{max}) between the atomic positions of paired atoms, the arithmetic mean of all distances (d_{av}) and the measure of similarity (Δ) are compiled in Table 6, with triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$ as the reference structure. The low values for Δ , d_{av} and d_{max} between isotypic $\text{MnHAsO}_4(\text{H}_2\text{O})$ and

$\text{CoHAsO}_4(\text{H}_2\text{O})$ reveal a high similarity of the two structures. In comparison, all these values between triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$ and the two isopointal crystal structures of $\text{ZnHAsO}_4(\text{H}_2\text{O})$ and $\text{MgHAsO}_4(\text{H}_2\text{O})$ are much higher. In these cases, the highest displacements of related atom pairs are developed between the O atoms of water or OH groups participating as donor atoms in the hydrogen-bonding network. Although $\text{MnHAsO}_4(\text{H}_2\text{O})$ and $\text{CuHAsO}_4(\text{H}_2\text{O})$ are considered as being isotypic due to the same type of hydrogen-bonding network, the values for S , Δ , d_{av} and d_{max} are by far the highest in the $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ series. The comparatively high strain in the crystal structure of $\text{CuHAsO}_4(\text{H}_2\text{O})$ relative to $\text{MnHAsO}_4(\text{H}_2\text{O})$ can be attributed to the Jahn-Teller distortions of the $[\text{CuO}_6]$ octahedra. The distortion with its usual splitting into four short equatorial and two long axial Cu–O distances affects also the

positions of the O atoms of water molecules or OH groups that are bonded to the Cu^{II} cations (some are part of the shorter, some of the longer Cu–O bonds), and consequently also their roles in the hydrogen-bonding scheme. All in all, the crystal structure of the Cu member exhibits a low similarity to the Mn member and to all other members of the $M^{\text{II}}\text{HAsO}_4(\text{H}_2\text{O})$ series.

4 Conclusions

The present study revealed dimorphism for the phase $\text{MnHAsO}_4(\text{H}_2\text{O})$. The crystal structure of natural, chemically pure monoclinic krautite was re-evaluated on the basis of single-crystal X-ray diffraction data from a cotype specimen. The results confirm the previously published structure model in space group $P2_1$, but with considerably higher precision and accuracy. In contrast to other previous studies that reported monoclinic symmetry for synthetic $\text{MnHAsO}_4(\text{H}_2\text{O})$ crystals, we found that the symmetry of crystals prepared under mild hydrothermal conditions (105 °C, autogenous pressure) is triclinic. Since, as noted above, crystals prepared in the same way at 90 °C and apparently at any temperature between room temperature and 90 °C, crystallize in space group $P2_1$, the temperature of formation influences the crystal symmetry, probably due to a preference for a different hydrogen-bonding scheme at higher temperature. This contradicts the general experience that high-temperature polymorphs usually have higher symmetries than their low-temperature analogues. The crystal structure of the triclinic $\text{MnHAsO}_4(\text{H}_2\text{O})$ polymorph is isotypic with $\text{CoHAsO}_4(\text{H}_2\text{O})$ and $\text{CuHAsO}_4(\text{H}_2\text{O})$ and isopointal with $\text{ZnHAsO}_4(\text{H}_2\text{O})$ and $\text{MgHAsO}_4(\text{H}_2\text{O})$. Although similarities between the monoclinic and triclinic forms of $\text{MnHAsO}_4(\text{H}_2\text{O})$ are apparent, there exists no direct group-subgroup relation between the two crystal structures. According to the available single-crystal X-ray diffraction data of the two modifications, possible temperature-dependent phase transitions do not occur between room temperature and –173 °C. Future studies with respect to formation conditions as well as thermal analyses of the monoclinic and triclinic polymorphs are required to obtain a deeper understanding of their stability fields and thermodynamic properties.

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