

## Crystal-structure refinement of stottite, $\text{FeGe}(\text{OH})_6$

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### ABSTRACT

The structure of stottite was refined from three-dimensional X-ray diffraction data ( $a = 7.594(4) \text{ \AA}$ ,  $c = 7.488(6) \text{ \AA}$ , space group  $P4_2/n$ ,  $Z = 4$ ). The structure proposed by Strunz et al. (1958) is largely confirmed, although a significant change in the presumed location of O(3) is reported, as well as anisotropic temperature factors. The structure of stottite consists of a network of corner-sharing  $\text{Fe}(\text{OH})_6$  and  $\text{Ge}(\text{OH})_6$  octahedra alternating in three dimensions. The lowering of symmetry from an ideal cubic symmetry is largely accomplished by rigid rotation of the cation polyhedra. The average Fe–O distance is  $2.159 \text{ \AA}$ , whereas the average Ge–O distance is  $1.910 \text{ \AA}$ , in overall agreement with interatomic distances determined by EXAFS (Bernstein and Waychunas, 1987).

### INTRODUCTION

Stottite,  $\text{FeGe}(\text{OH})_6$ , was described as a new mineral from the Pb–Cu–Zn ore deposit at Tsumeb, Namibia, by Strunz et al. (1958). It occurs in the lower oxidized zone at Tsumeb, where a fracture zone from the surface intersects the sulfide-rich ore body at about 800–900 m below the surface. The sulfide ore in this region consists mostly of tennantite, chalcocite, bornite, and significant amounts of the Ge-rich sulfides germanite and renierite. Variable amounts of galena, pyrite, sphalerite, and other sulfides are also present (Strunz et al., 1958; Söhnge, 1964). Within this lower oxidized zone, the sulfide minerals have been largely replaced by metal carbonates, oxides, sulfates, arsenates, phosphates, and hydroxides, many of which occur as euhedral crystals in cavities. Stottite occurs in this environment as anhedral masses to euhedral crystals as much as 1 cm across. Its color ranges from nearly colorless to dark brown; less commonly, it is pale green, orange, or red. Euhedral stottite crystals at Tsumeb are modified pseudo-octahedral tetragonal dipyrramids (Strunz et al., 1958). Goniometric data of Strunz et al. on such crystals indicate tetragonal symmetry with  $c/a \approx 0.987$ . These results are in accord with the powder X-ray diffraction data of Strunz et al. that indicate  $c/a \approx 0.989$ . The crystal morphology, together with powder and Laue single-crystal X-ray diffraction patterns, were interpreted by Strunz et al. to indicate space group  $P4_2/n$ . Strunz et al. also reported a slight anomalous biaxiality to the optical properties (a small  $2V$ , dispersion  $r > v$ ), with three measurable refractive indices:  $\alpha = 1.728$ ,  $\beta = 1.737$ ,  $\gamma = 1.738$  (alternatively,  $\epsilon = 1.728$ ,  $\omega = 1.7375$ ).

Zemann (1959) predicted that stottite should have a crystal structure isotypic with  $\text{NaSb}(\text{OH})_6$  (space group  $P4_2/n$ ), containing Fe and Ge in the nearly octahedral Na and Sb sites, respectively. Both cation sites are on symmetry centers, whereas the OH groups are in general positions. Zemann predicted average Fe–O and Ge–O octahedral bond lengths of 2.14 and 1.89  $\text{ \AA}$ , based on the bond lengths in other oxides and hydroxides. Strunz and Giglio (1961) performed a single-crystal X-ray diffraction structure determination on stottite that essentially confirmed the structure proposed by Zemann. They used two-dimensional Patterson maps and Fourier synthesis to determine the atomic positions. The unit-cell dimensions ( $a = 7.55$ ,  $c = 7.47 \text{ \AA}$ ) were those determined by Strunz et al. (1958) through X-ray powder diffraction. Strunz and Giglio (1961) concluded that Fe occurs in elongated octahedral coordination with Fe–O bond lengths of 2.10, 2.11, and 2.19  $\text{ \AA}$  (avg. 2.13  $\text{ \AA}$ ), and Ge occurs in flattened octahedral coordination with Ge–O bond lengths of 1.98, 1.99, and 1.92  $\text{ \AA}$  (avg. 1.96  $\text{ \AA}$ ). The  $R$  (reliability) factors for the structure determinations are large (13–21%) for a simple structure, indicating uncertainties in the determinations. The octahedral Ge–O bond lengths are, in particular, different from the lengths of 1.88–1.89  $\text{ \AA}$  observed in other Ge-bearing compounds.

More recently, Bernstein and Waychunas (1987) studied the crystal chemistry of Ge and Fe in several oxides and hydroxides, including stottite, with K-edge absorption EXAFS and XANES spectroscopy using synchrotron radiation. Analyses of the stottite EXAFS spectra indicated average octahedral bond lengths of 1.879(10)  $\text{ \AA}$  for Ge–O and 2.204(10)  $\text{ \AA}$  for Fe–O. These values were obtained on stottite from Tsumeb (Smithsonian no. 141,174), although not the type sample of Strunz et al. (1958). In April 1987, the methods described by Bernstein and Waychunas (1987) were used on the type material of

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TABLE 1. Chemical analyses of stottite

	FeGe(OH) <sub>6</sub>	Strunz et al. (1958)*	This study**
GeO <sub>2</sub>	45.39	41.75	43.30
MnO <sub>2</sub>		1.08†	0.39
FeO	31.18	34.81	32.45
MgO		0.46	0.00
CaO		0.34	0.00
H <sub>2</sub> O	23.43	21.84	n.d.
Total	100.00	100.28	76.14
Number of atoms based on 6(OH)			
Ge	1.00	0.90	0.96
Mn		0.03	0.01
Fe	1.00	1.10	1.05
Mg		0.03	0.00
Ca		0.01	0.00
OH	6.00	6.00	6.00
Total	8.00	8.07	8.02

Note: n.d. = not determined.

\* Wet-chemical analysis.

\*\* Average of five microprobe analyses; see text for experimental methods.

† Recalculated from MnO = 0.88.

Strunz et al. (sample described below). An average Ge–O octahedral bond length of 1.896(10) Å was obtained; Fe data were not collected. Owing to the discrepancies of these bond lengths with those given by Strunz and Giglio (1961), a new X-ray diffraction crystal-structure refinement was undertaken.

#### SAMPLE DESCRIPTION AND COMPOSITION

A single-crystal cleavage fragment of pale-brown stottite, approximately 4 × 3 × 3 mm, was used for this study. The fragment is from the type material described by Strunz et al. (1958) (Harvard no. 111,460). The fragment displays perfect cleavage on (100) and (010), with good cleavage on (001). In polished section under the microscope the specimen is observed to be largely homogenous, although it contains local concentrations of rounded siderite inclusions 20–200 μm across. The stottite appears to be uniaxial (–), although a slight biaxiality is commonly observed, with a 2*V* of less than 2°. The density of the sample was measured as 3.61(1) g·cm<sup>–3</sup> using a Berman density balance with toluene.

The polished section was observed in a scanning electron microscope (SEM) equipped with energy-dispersive X-ray analytical equipment (EDX) at the Center for Materials Research at Stanford University (CMR). The stottite was found to contain Ge, Fe, and a trace of Mn; no other elements with *Z* > 8 were observed (<0.1 wt%). The siderite inclusions were similarly found to contain only Fe with traces of Mg, Mn, and Ca. Electron-microprobe analyses of the stottite were performed on a JEOL-733 superprobe at CMR. The instrument was operated at 15 kV and 30 nA as measured on a Faraday cup inserted into the electron beam. Standards used were natural ilmenite for Fe and Mn, synthetic Ti-bearing fassaite glass for Ca and Mg, and elemental Ge. Five points on the stottite were analyzed, with nearly identical results. In addition, two points on the siderite inclusions were ana-

TABLE 2. Cell parameters and atom locations

	x	y	z
Fe	0	0	0
Ge	½	0	0
O(1)	0.267(1)	0.443(1)	0.583(1)
O(2)	0.573(1)	0.268(1)	0.565(1)
O(3)	0.437(1)	0.421(1)	0.267(1)

lyzed. The stottite analyses are presented in Table 1, together with the wet-chemical analysis given by Strunz et al. (1958). The microprobe results give the stottite composition as approximately Fe<sub>1.05</sub>Ge<sub>0.96</sub>Mn<sub>0.01</sub>(OH)<sub>6</sub>; no Mg or Ca was detected. The analyzed siderite inclusions have a composition of approximately Fe<sub>0.8</sub>Mg<sub>0.1</sub>Mn<sub>0.07</sub>Ca<sub>0.03</sub>CO<sub>3</sub>. It is probable that much of the Mg, Ca, and Mn (and some of the Fe) found in the stottite by Strunz et al. was actually in the siderite (or other carbonate) inclusions. A significant atomic excess of Fe over Ge was found by Strunz et al. (largely because of the siderite inclusions), whereas a smaller excess was found in this study. The errors inherent in the electron-microprobe data (including the possibility of very small, disseminated siderite inclusions) do not permit a final determination of whether the Fe:Ge ratio actually differs from the stoichiometric value of one in this specimen of stottite.

#### X-RAY DIFFRACTION DATA COLLECTION

A fragment approximately 0.13 × 0.20 × 0.65 mm was cleaved from the stottite specimen described above and was mounted in an automated Huber four-circle diffractometer. Graphite-monochromatized MoK<sub>α</sub> radiation was used for determination of unit-cell dimensions and for the collection of intensities. Unit-cell parameters [*a* = 7.594 (5) Å and *c* = 7.488 (6) Å] were obtained by least-squares refinement of the diffraction angles of 15 interplanar spacings, with 2θ between 10.84 and 20.31°. The intensities of 890 reflections, corresponding to one-quarter of reciprocal space and ranging from 5.39 to 49.85° 2θ, were measured using θ–2θ scans. Three reflections (202, 020, 220) were used as standards and were collected once every 97 reflections. The intensities of the standards varied an average of 3% over the period of the data collection. After determination of the space group, the intensities were corrected for absorption (μ = 109 cm<sup>–1</sup>) and symmetrically equivalent reflections were averaged to yield a total of 251 independent observations.

Space group *P4<sub>2</sub>/n* was determined by systematic extinctions of (*hk*0), *h* + *k* odd and (00*l*), *l* odd. A Patterson map revealed the location of Fe and Ge on the special positions 4*c* and 4*d*, respectively. A difference-Fourier map of the resultant structure yielded the positions of the three oxygens. All atoms were refined, first with isotropic temperature factors and finally with anisotropic temperature factors, until no shift of atomic coordinates or temperature factors was observed. As the electron-microprobe analysis of the original sample (Table 1) indicated that the crystal had nearly ideal stoichiometry, site oc-

TABLE 3. Anisotropic temperature factors in stottite

	Fe	Ge	O(1)	O(2)	O(3)
$\beta_{11}$	0.0029(6)	0.0017(5)	0.0050(15)	0.0049(16)	0.0043(17)
$\beta_{22}$	0.0019(6)	0.0022(5)	0.0064(14)	0.0033(14)	0.0063(17)
$\beta_{33}$	0.0038(6)	0.0036(5)	0.0049(14)	0.0051(15)	0.0053(13)
$\beta_{12}$	0.0003(5)	0.0000(4)	0.0006(10)	-0.0006(10)	-0.0012(14)
$\beta_{13}$	0.0001(3)	-0.0001(2)	0.0003(11)	-0.0012(12)	-0.0007(10)
$\beta_{23}$	0.0002(2)	0.0000(2)	-0.0013(11)	-0.0001(11)	0.0000(10)

cupancies were not refined. A final difference-Fourier map was constructed in an attempt to locate the H atoms, but no candidate sites were located. The final unweighted and weighted *R* factors are 0.073 and 0.096. Atom locations are presented in Table 2, anisotropic temperature factors in Table 3, and observed and calculated structure factors in Table 4.<sup>1</sup> Systematic overestimation of low- $2\theta$  reflection intensities, particularly those for (002) and (022), indicates that secondary extinction is present; no correction, however, was attempted.

#### DESCRIPTION OF THE STRUCTURE

The structure as described by Strunz and Giglio (1961) is largely confirmed, although there are some significant changes. The structure proposed by Strunz and Giglio is very nearly in space group  $P4_2/nm$  (a supergroup of  $P4_2/n$ ), which was not noted by them, and will be discussed below. The present determination differs from the previous one primarily in the location of O(1), and a consequent lowering of the apparent higher symmetry to  $P4_2/n$ . Figure 1a illustrates the polyhedral linkage based upon the atom positions of Strunz and Giglio, whereas Figure 1b shows the results of the present refinement. Fe and Ge atoms form an NaCl-like structure, with the OH groups octahedrally coordinating the cations, forming an infinite, corner-sharing, three-dimensional framework of coordination octahedra. Compared to an ideal cubic arrangement (NaSbF<sub>6</sub> structure), the actual structure differs by rotation of these polyhedra; the refinement of Strunz and Giglio indicates that the polyhedra connected along the *c* axis show the same sense of rotation, whereas the present refinement indicates alternating senses of rotation.

Table 5 presents a summary of the pertinent interatomic distances and angles. Both the Fe and Ge coordination polyhedra are nearly regular octahedra, whereas the Fe-O-Ge angles average about 138°, indicating that most of the distortion from isometric symmetry in the structure is taken up by rigid rotation of the polyhedra. Although the H atoms were not located, it is probable that they lie in the larger angle formed by the Fe-O-Ge linkage (Fig. 1b); in that position the repulsion between nearest cation neighbors would be minimized.

<sup>1</sup> A copy of Table 4 may be ordered as Document AM-88-375 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

#### DETERMINATION AND DISCUSSION OF SPACE GROUP

The structure reported by Strunz and Giglio (1961) and discussed by Wyckoff (1965, p. 329-331) conforms to the space group  $P4_2/nm$ , which can be distinguished from space group  $P4_2/n$  by the systematic extinction of reflections of the type  $0kl$ ,  $k + l$  odd. These reflections are not, in fact, extinct in either the present refinement data or those of Strunz and Giglio. This point is moot, however, as it is determined that the previously reported structure is incorrect.

More problematic is the status of the space group of the other compounds reported to have this structure (Schrewelius, 1938; Wyckoff, 1965, p. 329-331), in particular AgSb(OH)<sub>6</sub> and NaSb(OH)<sub>6</sub>. If indeed these compounds have the heavy-atom positions reported by Wyckoff, but are truly in  $P4_2/n$ , then the reduction of symmetry from the apparent  $P4_2/nm$  must be solely the consequence of the various H atom positions. It is not clear that this effect would be detectable by X-ray diffraction, as H represents such a small fraction of the total electron density of these compounds. The structures of these compounds should be re-investigated in light of the present work.

A further problem was discovered when assigning symmetry to stottite on the basis of observed interplanar spacings. The unit-cell dimensions of the crystal chosen for analysis were determined on the basis of 15 interplanar spacings (Table 6), and those of a second crystal were determined on the basis of 20 interplanar spacings. In both cases, the unit-cell symmetry appeared lower than

TABLE 5. Interatomic distances and angles in stottite

Fe coordination	Ge coordination
Fe-O(1) 2.167(8) Å	Ge-O(1) 1.920(8) Å
-O(2) 2.167(7) Å	-O(2) 1.906(7) Å
-O(3) 2.144(7) Å	-O(3) 1.903(7) Å
O(1)-Fe-O(2) 89.3(3)°	O(1)-Ge-O(2) 88.7(3)°
O(1)-Fe-O(3) 87.7(3)°	O(1)-Ge-O(3) 89.7(3)°
O(2)-Fe-O(3) 85.9(3)°	O(2)-Ge-O(3) 89.2(3)°
O(1)-O(2) 3.04(1) Å	O(1)-O(2) 2.67(1) Å
3.08(1) Å	2.74(1) Å
O(1)-O(3) 2.99(1) Å	O(1)-O(3) 2.70(1) Å
3.11(1) Å	2.71(1) Å
O(2)-O(3) 2.94(1) Å	O(2)-O(3) 2.67(1) Å
3.15(1) Å	2.71(1) Å
	Fe-O(1)-Ge 136.5(4)°
	Fe-O(2)-Ge 137.5(4)°
	Fe-O(3)-Ge 135.3(4)°

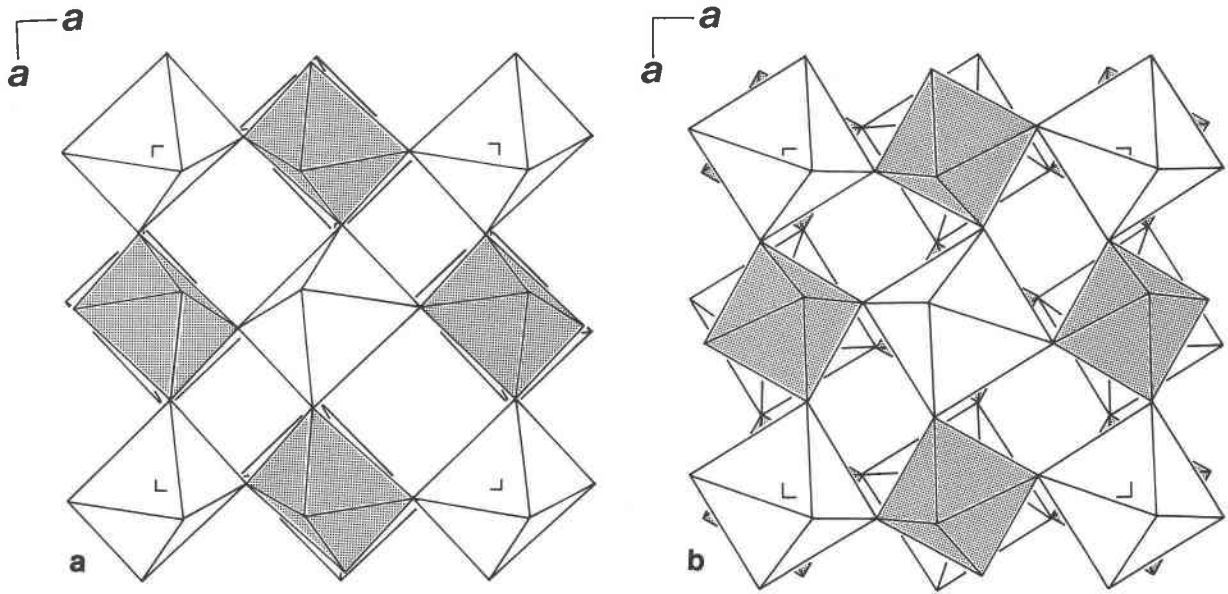


Fig. 1. Arrangement of cation polyhedra in stottite (a) from Strunz and Giglio (1961) and (b) the present study; c-axis projection; Ge polyhedra are shaded. Note in (a) that the Ge octahedra at  $(0, 0, \frac{1}{2})$  are completely eclipsed by the Fe octahedra at  $(0, 0, 0)$  and that the Fe octahedra at  $(0, \frac{1}{2}, \frac{1}{2})$  are nearly eclipsed by the Ge octahedra at  $(0, \frac{1}{2}, 0)$ .

tetragonal—either orthorhombic or, more likely, monoclinic (based on subgroup relations) with  $\beta$  ca.  $90^\circ$ . For neither crystal was the evidence so convincing as to force refinement in a lower symmetry than  $P4_2/n$ , but the discrepancies were a trifle disturbing, particularly considering the anomalous optical properties previously mentioned. Considering the structure, it is possible that twinning, which would relate any of the three principal axes, may occur and might even be produced when a crystal is cleaved, thus raising the apparent symmetry. It must be emphasized, however, that scrutiny of the peak scans revealed no case of unequivocal peak splitting, which might be expected in such a case.

Finally, the discrepancies in unit-cell parameters between the two samples must be addressed. Density measurement of the original sample yielded a value of  $3.61(1)$   $\text{g/cm}^3$ , whereas the calculated densities of the two crystals,

assuming ideal composition, are  $3.545$  and  $3.590$   $\text{g/cm}^3$ . Considering the possibility of siderite inclusions (density  $3.96$   $\text{g/cm}^3$ ) in the sample, the calculated density of the second crystal is reasonable; however, if the calculated density of the first crystal were correct, it would suggest some 17 vol% of siderite in the measured sample. Accepting the measured value and the second calculated value of the density as correct, the anomalously large unit cell of the first sample requires explanation. The fact that no elements with  $Z > 8$  were detected (except those listed in Table 1) restricts consideration to either very light elements or previously detected elements in a nonstructural position. One possibility is that  $\text{H}_2\text{O}$  molecules reside locally in the cavities centered at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ , thus inflating the unit cell. Other species, such as  $\text{CH}_4$ , could also reside on the site; however, the existence of such species in the fluid from which the stottite crystallized would have to

TABLE 6. Comparison of alternative cell choices

	a (Å)	b (Å)	c (Å)	$\alpha$ ( $^\circ$ )	$\beta$ ( $^\circ$ )	$\gamma$ ( $^\circ$ )
Sample 1, 15 reflections						
Unconstrained A	7.579(1)	7.542(2)	7.457(1)	88.99(2)	89.96(2)	90.01(3)
Tetragonal refinement	7.594(5)	—	7.488(6)	—	—	—
Unconstrained B	7.582(2)	7.536(3)	7.456(2)	89.95(4)	89.95(4)	90.02(5)
Orthorhombic refinement	7.600(5)	7.555(5)	7.473(5)	—	—	—
Sample 2, 20 reflections						
Unconstrained	7.579(3)	7.559(2)	7.546(3)	89.89(5)	89.73(6)	90.04(5)
Tetragonal refinement	7.535(6)	—	7.509(6)	—	—	—
Orthorhombic refinement	7.549(6)	7.530(6)	7.514(6)	—	—	—
Monoclinic refinement	7.547(6)	7.529(6)	7.513(6)	—	90.13(2)	—

Note: Sample 1 was examined twice (A and B), resulting in slightly different unconstrained cells. The "unconstrained" values assume zero diffractometer error, but the refinement included such errors, thus accounting for some of the difference between "unconstrained" and "refined" values.

be shown. Certainly, a detailed analysis of any such constituents would be of value.

### CONCLUSION

The crystal structure of stottite as reported by Strunz et al. (1958) is largely confirmed, although a significant change in the presumed location of O(3) and an apparent lowering of symmetry from  $P4_2/ncm$  to  $P4_2/n$  were found. The structure consists of alternating Fe(OH)<sub>6</sub> and Ge(OH)<sub>6</sub> octahedra in a three-dimensional, corner-sharing array. The lowering of symmetry from an ideal cubic symmetry is accomplished by essentially rigid rotation of these polyhedra. The present refinement differs from that of Strunz et al. in that in the previous refinement, polyhedra along the *c* axis showed similar senses of rotation, whereas the present refinement shows alternating rotation. The average Fe–O bond length is 2.159 Å, and the average Ge–O bond length is 1.910 Å, in good overall agreement with the bond lengths determined by Bernstein and Waychunas (1987) by EXAFS. As it was the discrepancy between the EXAFS-determined bond lengths and those of Strunz and Giglio (1961) that prompted this study, the usefulness of EXAFS analysis to structure determinations is demonstrated.

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