

# Distorted Tetrahedra in Strontium Copper Åkermanite

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New analogs of åkermanite:  $\text{Sr}_2\text{CuSi}_2\text{O}_7$  and  $\text{Sr}_2\text{CdSi}_2\text{O}_7$  as well as many previously synthesized analogs were obtained by a simple technique consisting of heating in air of precipitated gels of the right composition. X-ray data revealed an anomaly of the  $\text{Cu}^{2+}$  and (to a lesser extent)  $\text{Fe}^{2+}$  åkermanites which is explained by a simple geometric argument in terms of a small ( $\sim 3^\circ$ ) angular distortion of the oxygen tetrahedron surrounding the smaller divalent cation. This interpretation is consistent with previous theoretical discussions and Mössbauer data on the iron analog prepared for this study. Single crystals of cobalt åkermanites can be grown from a sodium tungstate flux.

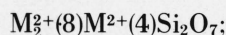
Key Words: Åkermanite; crystal chemistry; crystal growth; cupric silicate; flux growth; ion polyhedron distortion; melilite; Mössbauer spectroscopy; silicate gels; silicate synthesis; x-ray powder data.

## 1. Introduction

Nuclear magnetic resonance, Mössbauer and other spectroscopies are providing highly sensitive techniques for exploring symmetries and distortions of ionic polyhedra in crystals [1, 2].<sup>1</sup> Too few have been the crystal-chemical studies based on geometric considerations and specifically aimed at exploring symmetries of ionic environments. The purpose of this investigation was to present an example for demonstrating the power of one simple crystal-chemical method and to reveal data bearing upon their limitations especially in sensitivity. The method consists in the synthesis of a number of isostructural compounds followed by measurement and interpretation of their accurate lattice or structural parameters. The specific aim in our example is to look for distortion of tetrahedra of divalent copper ions in silicates having the melilite structure. Divalent copper ion usually causes strong distortion in both octahedral and tetrahedral sites [3, 4].

## 2. Syntheses and Cell Data

The structure of åkermanite type minerals,



$\text{M}^{2+}(8) = \text{Ca}, \text{Sr}$  and  $\text{Ba}$ ,  $\text{M}^{2+}(4) = \text{Cd}, \text{Mn}, \text{Fe}^{2+}, \text{Zn}, \text{Cu}, \text{Co}, \text{Mg}$ , and  $\text{Be}$ , was determined by Warren [5] and

Smith [6]. It consists of two equivalent ( $\text{SiO}_4$ ) tetrahedra sharing a corner on a twofold axis to form a  $\text{Si}_2\text{O}_7$  group, and one  $[\text{M}^{2+}\text{O}_4]$  tetrahedron located at the corners and the  $C$ -face centers of the tetragonal  $P4_2m$  cell. These tetrahedra are arranged in a sheet-like pattern parallel to (001). The sheets are held together along  $c$  by weaker  $\text{M}^{2+}(8)\text{—O}$  linkages (fig. 1a).

Two new analogs,  $\text{Sr}_2\text{CuSi}_2\text{O}_7$  and  $\text{Sr}_2\text{CdSi}_2\text{O}_7$  were synthesized by heating in air precipitated gels of the right composition. The following compounds with the åkermanite structure were also synthesized but these have been reported previously:  $\text{Ca}_2\text{BeSi}_2\text{O}_7$  [7, 8],  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  [9, 10],  $\text{Ca}_2\text{ZnSi}_2\text{O}_7$  [11],  $\text{Sr}_2\text{ZnSi}_2\text{O}_7$  [12],  $\text{Ca}_2\text{CoSi}_2\text{O}_7$  and  $\text{Sr}_2\text{CoSi}_2\text{O}_7$  [13], and  $\text{Sr}_2\text{FeSi}_2\text{O}_7$ ,  $\text{Sr}_2\text{MnSi}_2\text{O}_7$ ,  $\text{Ba}_2\text{FeSi}_2\text{O}_7$ ,  $\text{Ba}_2\text{MnSi}_2\text{O}_7$  [14]. The other analogs such as  $\text{Ca}_2\text{CuSi}_2\text{O}_7$ ,  $\text{Ca}_2\text{NiSi}_2\text{O}_7$  and  $\text{Sr}_2\text{NiSi}_2\text{O}_7$  could not be obtained by our method of synthesis.

The compositional stability range for åkermanite-type compounds thus obtained is illustrated in terms of  $\text{M}^{2+}(8)$  and  $\text{M}^{2+}(4)$  ions in figure 2. The unit-cell dimensions measured by the x-ray method, conditions for the syntheses, and some of the physical properties are given in table 1. Indexed  $d$ -spacings, standardized internally with Si, for Sr, Cu- and Sr, Cd åkermanites are given in table 2.

All the unit-cell dimensions and the  $c/a$  ratio are plotted against the recognized value of the ionic radius [15] of the smaller cation of each Sr-analog in figure 3. All the data used in these diagrams are taken from the compounds synthesized for this study by the same method. The variation of the unit-cell dimensions for each of the analogs relative to the established ionic radii is fairly smooth except for those of the  $\text{Cu}^{2+}$ - and  $\text{Fe}^{2+}$ -analogs (fig. 3).

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

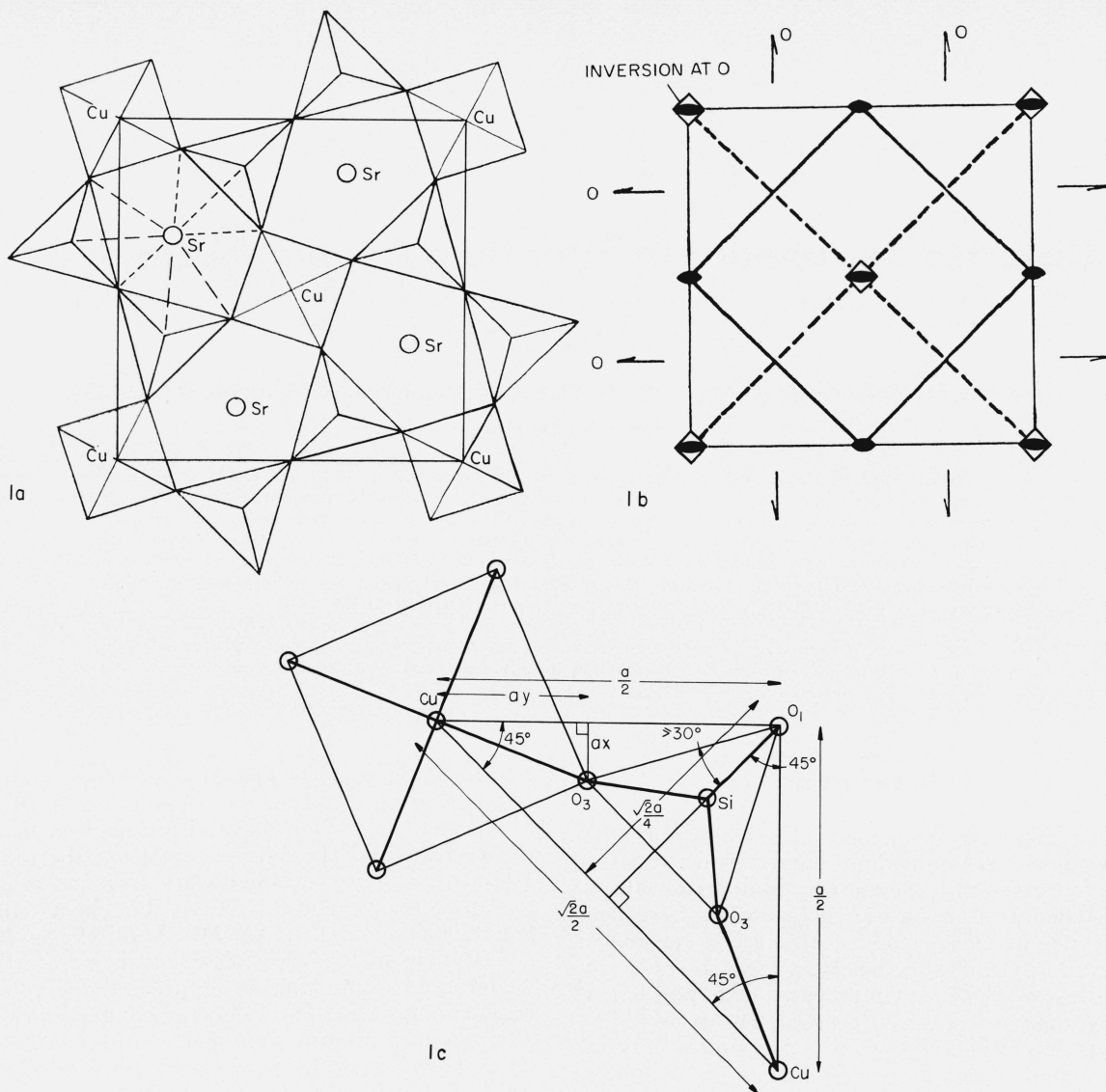


FIGURE 1. (a) The structure of Sr,Cu-åkermanite projected on (001) [after references 5 and 6]. (b) Symmetry of Sr,Cu-åkermanite structure ( $P4_2/m$ ) (Notation as in International Crystallographic Tables, Kynoch Press, 1952). (c) Schematic detail of geometry of (001) sheet (difference in size of tetrahedra exaggerated).

### 3. Geometric Considerations

The geometry of the (001) sheet (fig. 1a) of oxygen tetrahedra is overdetermined by:

(i) The  $a$ -cell parameter directly and accurately measurable by x-ray powder data.

(ii) The established space-group symmetry,  $P4_2/m$ , including a twofold axis parallel to the  $z$  axis on which lies the unique oxygen of the  $Si_2O_7$  group; the 4 inversion point on which the  $M^{2+(4)}$  ion is situated; and the diagonal mirror plane parallel to the  $z$  axis ensuring for example that the  $O_1$ -Si direction projected on (001) is at  $45^\circ$  to the  $x$  and  $y$  axes. (See fig. 1b.)

(iii) The sum of the ionic radii; with an uncertainty of about 1 percent in some values for

$$R_{M-O} = \{R[M^{2+(4)}] + R[O^{2-}]\},$$

for example when  $M^{2+}$  is Cu.

(iv) The "tetrahedral angles"  $2\varphi_{Si}$  and  $2\varphi_M$  bisected by the  $z$ -axis direction. It is unlikely that  $2\varphi_{Si}$  departs greatly from  $109\frac{1}{2}^\circ$ , and even if it did it would be even less likely to be greatly dependent on the nature of the  $M^{2+(4)}$  ion. Angle  $2\varphi_M$  is thus the only "tetrahedral angle" subject to wide variations.

Algebraically the three variable cell coordinates ( $xyz$ ) for the oxygen ( $O_3$  in fig. 1a) shared by the Si and  $M^{2+}$  tetrahedra are related by five independent equations (see fig. 1c). The first two are derived from the horizontal tetrahedron edge; the third relates to an inclined tetrahedron edge; the fourth and fifth are

TABLE 1. The unit-cell dimensions, the physical properties, and the conditions for the syntheses of åkermanites

$$\text{CuK}\alpha_1 = 1.54050 \times 10^{-10} \text{ m}(\text{\AA})$$

Formulas	$a$ in $\text{m} \times 10^{-10}$ (\AA)	$c$ in $\text{m} \times 10^{-10}$ (\AA)	$c/a$	$V$ in $\text{m}^3 \times 10^{-30}$ (\AA <sup>3</sup> )	Sp. Gr.	Temp. (°C)	Pressure bars	Time hr	Index of refraction $N$ (mean value)	Color
Ca <sub>2</sub> CoSi <sub>2</sub> O <sub>7</sub>	7.835	5.025	0.6413	309.9	3.26	950	1	24	1.650	Blue.
Ca <sub>2</sub> ZnSi <sub>2</sub> O <sub>7</sub>	7.829	5.017	.6408	307.5	.....	1100	1	20	.....	Colorless.
Ca <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	7.800	5.012	.6425	304.9	.....	1050	1	20	.....	Colorless.
Ca <sub>2</sub> BeSi <sub>2</sub> O <sub>7</sub>	7.416	4.995	.6735	274.7	.....	1050	1	20	.....	Colorless.
Sr <sub>2</sub> CdSi <sub>2</sub> O <sub>7</sub>	8.228	5.188	.6305	351.2	.....	900	1	20	1.67	Colorless.
Sr <sub>2</sub> MnSi <sub>2</sub> O <sub>7</sub>	8.121	5.164	.6358	339.7	.....	750	3,000	48	1.645	Greenish white.
Sr <sub>2</sub> FeSi <sub>2</sub> O <sub>7</sub>	8.108	5.122	.6317	336.7	.....	750	3,000	48	1.665	Dark brown.
Sr <sub>2</sub> CuSi <sub>2</sub> O <sub>7</sub>	8.087	5.076	.6276	331.9	.....	950	1	20	.....	Black.
Sr <sub>2</sub> CoSi <sub>2</sub> O <sub>7</sub>	8.021	5.157	.6428	331.7	3.98	950	1	48	.....	Dark blue.
Sr <sub>2</sub> ZnSi <sub>2</sub> O <sub>7</sub>	7.999	5.169	.6462	330.7	.....	1100	1	20	.....	Colorless.
Sr <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	7.999	5.156	.6445	329.9	.....	900	1	20	.....	Colorless.

TABLE 2. X-ray powder data for Sr, Cu- and Sr, Cd-åkermanites

(Cu, K radiation, Ni filtered). Space Group, P4<sub>2</sub>m tetragonal

$hkl$	Sr <sub>2</sub> CuSi <sub>2</sub> O <sub>7</sub>			Sr <sub>2</sub> CdSi <sub>2</sub> O <sub>7</sub>		
	$d$ in $\text{m} \times 10^{-10}$ (\AA) obs.	$I/I_0$	$d$ in $\text{m} \times 10^{-10}$ (\AA) calc.	$d$ in $\text{m} \times 10^{-10}$ (\AA) obs.	$I/I_0$	$d$ in $\text{m} \times 10^{-10}$ (\AA) calc.
101	4.296	3	4.299	4.38	2	4.38
111	3.798	50	3.797	3.864	60	3.869
210	3.616	8	3.616	3.689	5	3.689
201	3.162	80	3.162	3.222	80	3.228
211	2.947	100	2.945	3.005	100	3.006
220	2.857	20	2.858	2.913	50	2.910
310	2.556	60	2.556	2.609	50	2.602
221	2.490	10	2.491	2.529	10	2.536
102	2.419	10	2.422	2.475	3	2.472
301	.....	.....	.....	2.420	5	2.422
112	2.313	8	2.320	.....	.....	.....
311	2.285	5	2.288	2.325	5	2.323
212	2.077	50	2.077	2.119	20	2.121
400	2.021	2	2.021	2.059	25	2.059
410	1.961	30	1.961	2.001	10	1.997
330	.....	.....	.....	1.937	15	1.940
222	1.898	40	1.898	1.932	15	1.936
401	1.878	10	1.880	1.919	3	1.912
411	1.829	20	1.830	1.862	10	1.863
420	1.808	5	1.808	.....	.....	.....
312	1.801	50	1.802	1.837	50	1.836
331	1.784	25	1.785	1.814	30	1.816
113	1.621	3	1.623	1.656	5	1.657
203	1.561	5	1.561	1.594	8	1.594
213	1.533	30	1.533	1.567	3	1.565
511	1.515	10	1.515	1.547	5	1.541
223	1.458	5	1.457	1.485	2	1.485
303	.....	.....	.....	1.462	5	1.461

$$a = 8.087 \times 10^{-10} \text{ m}(\text{\AA}); c = 5.076 \times 10^{-10} \text{ m}(\text{\AA});$$

$$a = 8.228 \times 10^{-10} \text{ m}(\text{\AA}); c = 5.188 \times 10^{-10} \text{ m}(\text{\AA}).$$

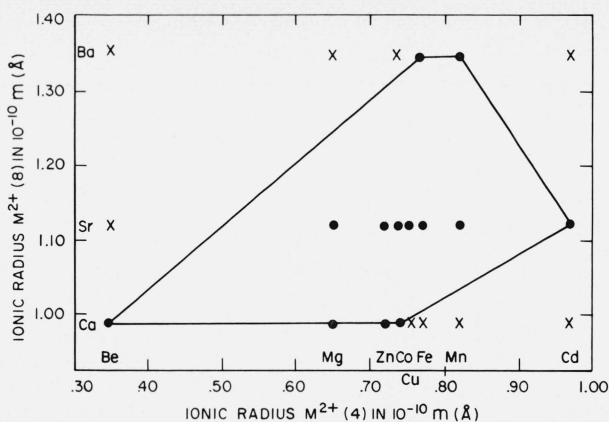


FIGURE 2. Compositional stability range for the compounds with åkermanite structure, in terms of the divalent tetrahedral cations and the divalent octahedral cations.

Ionic radii given by Ahrens.

X, Melilite not found.

●, Melilite found.

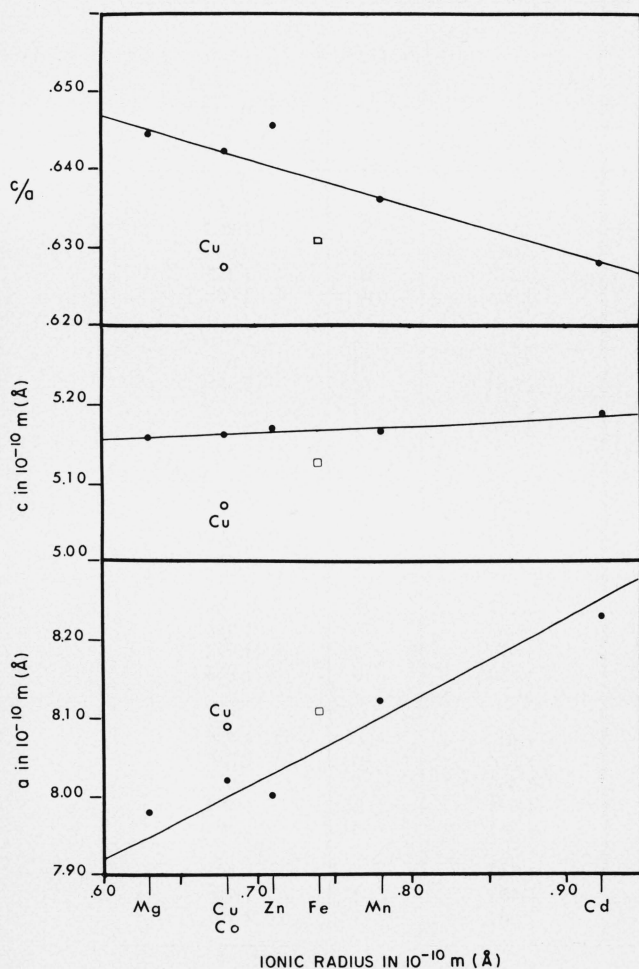


FIGURE 3. Unit-cell dimensions of the Sr-analogs of åkermanite versus the ionic radii (4-fold coordination).

Ahrens's [15] values (6-fold coordination) were used multiplied by a factor of 0.95.

projections of horizontal tetrahedron edges on cell diagonals in (001):

$$a^2(x^2 + y^2) - R_{M-O}^2 \sin^2 \varphi_M = 0 \quad (1)$$

$$a^2(\frac{1}{2} - x - y)^2 - 2R_{Si-O}^2 \sin^2 \varphi_{Si} = 0 \quad (2)$$

$$a^2(x^2 + y^2) + \frac{a^2}{4} - a^2y + c^2z^2 - 4R_{Si-O}^2 \sin^2 \varphi_{Si} = 0 \quad (3)$$

$$R_{M-O} \sin \varphi_M \cos \left[ \tan^{-1} \left( \frac{x}{y} \right) - \frac{\pi}{4} \right] + R_{Si-O} \sin \varphi_{Si} - \frac{\sqrt{2}a}{4} = 0 \quad (4)$$

$$-R_{M-O} \sin \varphi_M \sin \left[ \tan^{-1} \left( \frac{x}{y} \right) - \frac{\pi}{4} \right] + \left\{ a^2(x^2 + y^2) + \frac{a^2}{4} - a^2y \right\}^{1/2} \left\{ \cos \left[ \tan^{-1} \left( \frac{x}{y} \right) - \frac{\pi}{4} \right] \right\} - \frac{\sqrt{2}a}{4} = 0 \quad (5)$$

Since from simple crystal chemical considerations  $0 \ll \frac{x}{y} < 1$ ,  $\cos \left[ \tan^{-1} \left( \frac{x}{y} \right) - \frac{\pi}{4} \right]$  is an insensitive function of the other variables and,  $0.71 \ll \cos \left[ \tan^{-1} \left( \frac{x}{y} \right) - \frac{\pi}{4} \right] < 1$ . Differentiating (4) and allowing only for departures  $\Delta R_{M-O}$  and  $\Delta \varphi_M$  from established values of  $R_{M-O}$  and  $\varphi_M$  leads to a value of  $a$ , differing by  $\Delta a$  from the anticipated value:

$$0.9 (\sin \varphi_M \Delta R_{M-O} + R_{M-O} \cos \varphi_M \Delta \varphi_M) \approx \frac{\sqrt{2}}{4} \Delta a \quad (6)$$

If then an unusual value for  $a$  were alone due to an unusual value for  $R_{M-O}$  the magnitude would be  $\Delta R_{M-O} = 0.48 \Delta a$ . For Cu, Sr-åkermanite  $\Delta a$  observed is 0.087 Å (see fig. 3) whence the change in Cu-ion radius would be about 0.04 Å. Such a change is improbable so that the observed unusual value for  $a$  is more likely to be explained, at least in greater part, by a distortion of the tetrahedron.

There is stronger evidence still for this view: the signs of  $\Delta a$ ,  $\Delta c$  and  $R_{M-O}$  must be alike, unless  $|\Delta \varphi_M| > 0$ . The observed  $\Delta a$  and  $\Delta c$  are of opposite sign. The discrepancy in  $a$  thus is mostly due to a distortion of the  $M^{2+}(4)$  tetrahedron. If  $\Delta R_{M-O} = 0$ ;

$$\Delta \varphi_M \frac{\sqrt{2} \Delta a}{4 \times 0.9 R_{M-O} \cos \varphi_M} \approx +1.7^\circ$$

corresponding to a "tetrahedral angle" of about 113°. The magnitude of this distortion is not at all unlikely.

There exists another method for estimating  $\varphi_M$  on the additional assumption that the closeness of stacking of the successive layers of  $SiO_4$  and  $M^{2+}O_4$  tetrahedra is unaffected by small changes in  $\varphi_M$ . Under those conditions the discrepancy,  $\Delta c$ , between the



observed and expected values of  $c$  is due to an expansion (or, if  $\Delta c$  is negative, a contraction) of the  $M^{2+}O_4$  tetrahedra parallel to the  $z$  axis. By simple geometry it follows that  $\Delta c \approx -2R_{M-O} \sin \varphi_M \Delta \varphi_M$ . For Cu, Sr-åkermanite we observe  $\Delta c = -0.09 \text{ \AA}$  (fig. 3) corresponding to  $\Delta \varphi_M \approx +1.6^\circ$  in excellent agreement with the value deduced from  $\Delta a$ .

The  $\bar{4}$  symmetry requires that all the  $M^{2+}(4)-O_4$  "tetrahedral angles" not bisected by the  $z$ -axis direction are equal to one another, and from simple geometry that half "tetrahedral angle"  $\varphi'$  is related to  $\varphi$  by  $\cos^2 \varphi + 2 \cos^2 \varphi' = 1$ . Differentiating we obtain  $\Delta \varphi' \approx \frac{1}{2} \Delta \varphi$ , we would thus deduce for Cu, Sr-åkermanite that  $\Delta \varphi' = -0.8^\circ$ .

#### 4. Discussion

Anomalous shrinkage of the  $M^{2+}$  tetrahedra along the  $c$  axis in Sr, Cu-åkermanite, and their elongation along the  $a$  axis can best explain the observations (fig. 3). This view is consistent with the prediction by Dunitz and Orgel [3] of distorted  $Cu^{2+}$  tetrahedra in the structure. For the divalent copper ion with nine  $d$ -electrons, the nonbonding  $e$  orbitals are fully occupied, and the antibonding  $t_2$  orbitals are partially occupied. A distortion which flattens the tetrahedron along the  $c$  axis will remove the orbital degeneracy. Wide departure from the normal  $c/a$  ratio in the case of the tetrahedral  $Cu^{2+}$  ion would then be directly related to the appreciable flattening of the coordination tetrahedron.

The divalent nickel ion does not form the åkermanite structure. This can also be explained by the molecular orbital theory, because the tetrahedra of  $Ni^{2+}$  ion with 8  $d$ -electrons should elongate differently from the tetrahedra of the  $Cu^{2+}$  ion [3]. Elongation parallel to one twofold axis of the tetrahedron, caused by  $Ni^{2+}$  ions, leads to a rodlike distortion of the tetrahedron. It is not difficult to see that the åkermanite structure is much less able to accommodate such a distortion which would lead to gaps between adjacent (in the  $c$ -direction)  $M^{2+}(8)$  ions. The compression of the tetrahedron parallel to one twofold axis, as occurs for the  $Cu^{2+}$  ion, causes a disklike distortion which probably facilitates good packing in the åkermanite structure. Furthermore,  $Ni^{2+}$  ion is known to have greater stabilization energy (Wells, 1962) in octahedral coordination than in tetrahedral coordination. Therefore,  $Ni^{2+}$  ion tends to form more stable octahedral compounds such as  $Ni_2SiO_4$  (olivine). Superior stability of copper 4-fold planar coordination was demonstrated by Papst for instance in Egyptian blue (square quadrivalent cupric copper) ( $CaCuSi_4O_{10}$ ) [16].

Instability of Ca, Cu-åkermanite can also be explained. The longer  $M^{2+}(8)-O$  distances, required by the flattening of  $Cu^{2+}$  tetrahedra, can be filled by  $Sr^{2+}$  but plausibly not by the smaller  $Ca^{2+}$  ion. However, similar though less prominent unit-cell flattening is observed for Sr,  $Fe^{2+}$ -åkermanite. In gillespite also,  $Fe^{2+}$  forms simple square coordination but it was found to be rather unstable compared to the  $Cu^{2+}$  compound.

Mössbauer spectroscopic examination on our Sr,  $Fe^{2+}$ -åkermanite was carried out by J. J. Spijkerman (private communication) at the National Bureau of Standards. The results showed that this compound contains  $Fe^{2+}$  and that the divalent  $Fe^{2+}$  ion is unusually distorted. These findings appear to be entirely consistent with our crystal-chemical conclusions. The same Mössbauer study also showed that this compound contains 10 to 20 percent of its iron as ferric iron (J. J. Spijkerman, private communication). The anomaly observed for its unit-cell dimension could be due to isomorphous replacement of  $Fe^{2+}$  and  $Si^{4+}$  by two  $Fe^{3+}$  ions, and, therefore, cannot be discussed with confidence comparable with that applicable to the  $Cu^{2+}$  analog.

#### 5. Appended Note on Preliminary Experiments on the Growth of Large Crystals of Åkermanites

Co analogs of Ca and Sr åkermanite were grown in a sodium tungstate flux at temperatures from 1,200 to 1,000 °C for the Sr-analogs, and from 1050 to 850 °C for the Ca-analogs. The flux/charge ratio used was approximately 10/1. Deep blue platy {001} crystals up to 5 mm in size, often twinned on {110}, were obtained. This platy crystal habit of growth indicates strongest bonding forces within sheets parallel to {100} (fig. 1). Relative stability of these Co-analogs can be attributed to the symmetrical and fully occupied ( $e^4$ ) level and the half filled ( $t_2$ )<sup>3</sup> orbitals in the  $Co^{2+}$  ion with 7  $d$ -electrons which shows undistorted tetrahedra. Single crystal growth of the copper analogs was not achieved. Sr, Cu-åkermanite when synthesized often is accompanied by  $SrSiO_3$  or the Sr analog of Egyptian blue,  $SrCuSiO_4$  (also with  $Cu^{2+}$  tetrahedra) [16].

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