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# THE CRYSTAL STRUCTURE OF GEMINITE, $Cu^{2+}(AsO_3OH)(H_2O)$, A HETEROPOLYHEDRAL SHEET STRUCTURE

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## ABSTRACT

The crystal structure of geminite, $Cu^{2+}(AsO_3OH)(H_2O)$, triclinic, *a* 9.841(2), *b* 10.818(2), *c* 15.733(3) Å, α 95.71(2), β 90.94(2), γ 103.11(2)°, *V* 1621.9(6) Å$^3$, $C\bar{1}$, $Z = 16$, has been solved by direct methods and refined to an *R* index of 3.0% for 3263 observed reflections, measured with Mo*K*α X-radiation. There are four unique $Cu^{2+}$ sites, each coordinated by six anions in a [4 + 2]-distorted octahedral arrangement; this distortion of the coordination polyhedra is associated with the Jahn–Teller effect. There are four unique $As^{5+}$ sites, each coordinated by three oxygen atoms and an OH group in a distorted tetrahedral arrangement; the three As–O distances are shorter than the As–OH distance in each tetrahedron, in accord with the prediction of bond-valence theory. The $Cu\phi_6$ polyhedra share edges to form $[Cu\phi_4]$ chains parallel to [010]; $As\phi_4$ tetrahedra cross-link these chains into sheets parallel to (001), and there are two symmetrically distinct but topologically identical sheets in the structure. These sheets are linked into a three-dimensional structure by a network of H bonds, accounting for the perfect cleavage and platy habit of geminite.

*Keywords:* geminite, crystal structure, arsenate, copper, hydrogen bonding.

## SOMMAIRE

Nous avons affiné la structure cristalline de la géminite, $Cu^{2+}(AsO_3OH)(H_2O)$, triclinique, *a* 9.841(2), *b* 10.818(2), *c* 15.733(3) Å, α 95.71(2), β 90.94(2), γ 103.11(2)°, *V* 1621.9(6) Å$^3$, $C\bar{1}$, $Z = 16$, par méthodes directes jusqu'à un résidu *R* de 3.0% pour 3263 réflexions observées, mesurées avec rayonnement Mo*K*α. Il y a quatre sites distincts occupés par des atomes $Cu^{2+}$, chacun étant coordonné par six anions dans un agencement octaédrique difforme [4 + 2]; cette distorsion des polyèdres de coordinence résulterait de l'effet de Jahn–Teller. Il y a quatre sites distincts occupés par des atomes de $As^{5+}$, chacun coordonnés par trois atomes d'oxygène et un groupe hydroxyle dans un agencement tétraédrique difforme. Les trois liaisons As–O sont plus courtes que la liaison As–OH, selon la prédiction de la théorie des valences de liaison. Les polyèdres $Cu\phi_6$ partagent des arêtes pour former des chaînes $[Cu\phi_4]$ parallèles à [010]. Les tétraèdres $As\phi_4$ assurent la liaison entre ces chaînes pour former des feuillets parallèles à (001); la structure contient deux feuillets qui sont symétriquement distincts mais topologiquement identiques. Ces feuillets sont liés dans une trame tri-dimensionnelle par un réseau de liaisons hydrogène, ce qui rend compte du clivage parfait et de la morphologie en plaquettes de la géminite.

(Traduit par la Rédaction)

*Mots-clés:* géminite, structure cristalline, arsenate, cuivre, liaisons hydrogène.

## INTRODUCTION

Geminite is a hydroxy-hydrated divalent-copper arsenate described from Cap Garone, France by Sarp & Perroud (1990). It has the formula $Cu(AsO_3OH){\cdot}H_2O$, as stated by Sarp & Perroud (1990) in their conclusions and as confirmed by the structure determination reported here. Geminite owes its name to the fact that it is extensively twinned. However, the symmetry is triclinic, and this fact encouraged us to try to solve the structure. We have an extensive program on the investigation of hydroxy-hydrated $Cu^{2+}$ oxysalts (Eby & Hawthorne 1993, and references therein), and this work was done as part of this program.

## EXPERIMENTAL

The material used here was obtained from Dr. Halil Sarp; it is part of the material described by Sarp & Perroud (1990). Crystals were gently crushed and examined in cross-polarized light. A small fragment (Table 1) that showed no visible signs of twinning was mounted on a Nicolet *R*3*m* automated four-circle X-ray diffractometer, and 40 randomly selected reflections were aligned automatically. Cell dimensions (Table 1) and the orientation matrix were derived by least-squares refinement of the setting angles. The cell obtained is significantly different from that of Sarp & Perroud (1990); this is discussed in a later section.

TABLE 1. MISCELLANEOUS INFORMATION FOR GEMINITE

| | | | |
|---|---|---|---|
| $a$ (Å) | 9.841(2) | crystal size (mm) | 0.04 x 0.06 x 0.10 |
| $b$ | 10.818(2) | Radiation/Mon | Mo$K\alpha$/Graphite |
| $c$ | 15.733(3) | Total no. of $I$ | 5015 |
| $\alpha$ (°) | 95.71(2) | No. of $\lvert F \rvert$ | 4758 |
| $\beta$ | 90.94(2) | No. of $\lvert F_o \rvert > 5\sigma$ | 3263 |
| $\gamma$ | 103.11(2) | $R$(azimuthal) % | 4.2 → 1.7 |
| $V$ (Å$^3$) | 1621.9(6) | $R$(obs) % | 3.0 |
| Sp. Gr. | $C\bar{1}$ | $wR$(obs) % | 3.3 |
| $\mu$ (cm$^{-1}$) | 134 | | |

Cell content: $16[Cu(AsO_3OH)(H_2O)]$

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma|F_o^2|]^{1/2}$, $w = 1$

A total of 5015 reflections was collected according to the procedure of Hawthorne & Groat (1985) using the parameters reported in Table 1. Absorption corrections were done by the psi-scan method, reducing $R$(azimuthal) from 4.2 to 1.7%. The usual data-reduction corrections, together with some averaging, resulted in 4758 unique reflections, of which 3263 exceeded five standard deviations above background and were considered as observed.

## STRUCTURE SOLUTION AND REFINEMENT

Scattering factors were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). All calcu-

TABLE 2. FINAL POSITIONAL AND DISPLACEMENT (x $10^4$) PARAMETERS FOR GEMINITE

| Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Cu(1) | 0.49866(8) | 0.13660(7) | 0.04077(5) | 96(3) | 55(3) | 153(4) | −4(3) | 46(3) | 7(3) | 104(2) |
| Cu(2) | 0.48345(8) | 0.62955(7) | 0.45349(5) | 107(3) | 70(3) | 134(3) | 3(3) | 25(3) | −2(3) | 108(2) |
| Cu(3) | 0.01012(8) | 0.60394(7) | 0.44019(5) | 97(3) | 72(3) | 116(3) | 19(3) | 1(3) | −4(3) | 98(2) |
| Cu(4) | 0.02707(8) | 0.11589(7) | 0.06574(5) | 97(3) | 64(3) | 96(3) | 3(2) | 26(3) | −3(3) | 89(2) |
| As(1) | 0.26543(6) | 0.82512(5) | 0.39740(4) | 70(3) | 62(2) | 84(3) | 5(2) | 11(2) | 6(2) | 74(2) |
| As(2) | 0.24963(6) | 0.88816(6) | 0.08837(4) | 67(3) | 68(3) | 87(3) | 12(2) | 12(2) | 16(2) | 73(2) |
| As(3) | 0.23023(6) | 0.37903(6) | 0.40751(4) | 68(3) | 89(3) | 87(3) | 18(2) | 8(2) | 4(2) | 83(2) |
| As(4) | 0.30803(6) | 0.33700(5) | 0.10421(4) | 66(3) | 48(2) | 79(3) | 11(2) | 10(2) | 9(2) | 65(2) |
| O(1) | 0.3268(5) | 0.7021(4) | 0.3564(3) | 157(22) | 98(19) | 174(22) | 11(16) | 47(17) | 58(17) | 138(13) |
| O(2) | 0.1242(5) | 0.7808(4) | 0.4571(3) | 107(20) | 92(19) | 141(20) | 8(15) | 47(16) | −8(16) | 118(12) |
| O(3) | 0.3854(5) | 0.9373(4) | 0.4567(3) | 104(20) | 103(19) | 107(19) | 7(15) | −23(15) | −8(15) | 110(12) |
| O(4) | 0.2912(5) | 0.8134(5) | 0.1688(3) | 249(25) | 207(23) | 110(20) | 74(17) | 28(18) | 138(20) | 171(14) |
| O(5) | 0.1219(5) | 0.7994(4) | 0.0219(3) | 95(19) | 77(18) | 132(20) | 11(15) | −14(15) | −16(15) | 107(12) |
| O(6) | 0.3881(5) | 0.9569(4) | 0.0328(3) | 93(19) | 84(19) | 179(21) | 9(16) | 80(16) | −5(16) | 122(12) |
| O(7) | 0.1148(4) | 0.2967(4) | 0.4696(3) | 80(19) | 72(18) | 142(20) | 15(15) | 43(15) | −20(15) | 103(12) |
| O(8) | 0.3729(5) | 0.4591(4) | 0.4655(3) | 109(20) | 108(20) | 190(22) | 50(16) | −74(17) | −29(16) | 143(13) |
| O(9) | 0.2661(5) | 0.2839(4) | 0.3237(3) | 181(22) | 141(21) | 106(20) | 13(16) | 40(17) | 46(17) | 141(13) |
| O(10) | 0.3838(5) | 0.2163(4) | 0.1225(3) | 118(20) | 85(18) | 141(20) | 42(15) | 29(16) | 40(15) | 110(12) |
| O(11) | 0.1454(4) | 0.2858(4) | 0.0610(3) | 83(19) | 100(19) | 148(20) | 58(15) | −17(15) | 2(15) | 111(12) |
| O(12) | 0.3996(5) | 0.4445(4) | 0.0436(3) | 123(20) | 58(18) | 85(18) | 4(14) | 42(15) | −12(15) | 94(11) |
| OH(1) | 0.2046(5) | 0.8932(5) | 0.3159(3) | 210(24) | 159(21) | 110(20) | 5(16) | −4(17) | 84(19) | 154(14) |
| OH(2) | 0.1882(5) | 0.0149(4) | 0.1364(3) | 136(21) | 131(20) | 135(20) | 1(16) | 29(16) | 61(17) | 130(13) |
| OH(3) | 0.1553(5) | 0.4892(4) | 0.3635(3) | 151(22) | 138(21) | 171(21) | 59(17) | 20(17) | 70(17) | 144(13) |
| OH(4) | 0.2999(5) | 0.4234(4) | 0.1998(3) | 254(25) | 99(20) | 88(19) | −17(15) | 52(17) | 39(18) | 149(13) |
| OW(1) | 0.0910(6) | 0.5877(5) | 0.1824(4) | 235(27) | 251(27) | 294(28) | 43(22) | −22(22) | 77(22) | 256(17) |
| OW(2) | 0.0537(5) | 0.0754(5) | 0.3401(3) | 202(24) | 164(22) | 165(22) | 10(17) | 25(18) | 104(19) | 167(14) |
| OW(3) | 0.4376(5) | 0.1241(5) | 0.3267(3) | 203(25) | 190(23) | 165(22) | 54(18) | 1(18) | 86(19) | 177(15) |
| OW(4) | 0.4726(5) | 0.6672(4) | 0.1792(3) | 184(23) | 141(23) | 112(20) | 20(16) | 48(17) | 69(18) | 140(13) |
| H(1) | 0.248(9) | 0.868(9) | 0.263(3) | 32(8) | | | | | | |
| H(2) | 0.262(7) | 0.092(5) | 0.135(6) | 32(8) | | | | | | |
| H(3) | 0.231(7) | 0.562(6) | 0.355(6) | 32(8) | | | | | | |
| H(4) | 0.284(10) | 0.367(7) | 0.246(4) | 32(8) | | | | | | |
| H(5) | 0.122(11) | 0.519(7) | 0.208(7) | *50 | | | | | | |
| H(6) | 0.168(8) | 0.663(6) | 0.181(7) | *50 | | | | | | |
| H(7) | 0.092(10) | −0.001(6) | 0.339(6) | 32(8) | | | | | | |
| H(8) | 0.125(7) | 0.122(8) | 0.305(5) | 32(8) | | | | | | |
| H(9) | 0.500(8) | 0.118(9) | 0.279(4) | 32(8) | | | | | | |
| H(10) | 0.379(8) | 0.187(7) | 0.330(6) | 32(8) | | | | | | |
| H(11) | 0.430(9) | 0.610(7) | 0.221(5) | 32(8) | | | | | | |
| H(12) | 0.403(8) | 0.720(8) | 0.181(6) | 32(8) | | | | | | |

* fixed in refinement

lations were done with the SHELXTL PC (Plus) system of programs. *R* indices are of the form given in Table 1, and are expressed as percentages. The E-statistics indicate a center of symmetry. The structure was solved in the space group $P\bar{1}$, but the refined structure was not judged to be satisfactory, and a second set of intensity data was collected on the same crystal, but with a lower minimum scan-speed (2.09°/min). The first data-set showed the structural unit to be a sheet parallel to (001); however, the principal component of the sheet extended parallel to $[1\bar{1}0]$. We reoriented the cell to bring this major feature parallel to a principal axis, and thus the structure reported here has the space group $C\bar{1}$. Full-matrix refinement, including H positions, converged to an *R* index of 3.0% and a *wR* index of 3.3%. We examined the distribution of $\Delta F$ values for those reflections with the largest $|\Delta F|$ values, but there was no indication of twinning, in agreement with our optical examination and the low *R* indices. Final atomic parameters and displacement factors are given in Table 2, selected interatomic distances and angles are given in Tables 3 and 4, and a bond-valence table is displayed as Table 5. Tables of structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

## DESCRIPTION OF THE STRUCTURE

### *Cation coordination*

There are four unique $Cu^{2+}$ sites, each surrounded by an octahedral arrangement of anions. Cu(1) and Cu(2) are each coordinated to five $O^{2-}$ anions and one ($H_2O$) group; Cu(3) and Cu(4) are each coordinated to four $O^{2-}$ anions, one $(OH)^-$ group and one ($H_2O$) group. The variation in both individual and <Cu–$\phi$> ($\phi$: unspecified ligand) distances is within the range of distances compiled by Eby & Hawthorne (1993). However, the individual octahedra in geminite show quite a wide range of <Cu–$\phi$> distances: 2.096–2.151 Å (Table 3). As discussed by Brown & Shannon (1973), mean bond-lengths in crystals are affected by the dispersion of the individual bond-lengths, a result of the form of bond-valence – bond-length curves (Brown 1981). We expect this effect to be quite prominent in $^{[6]}Cu^{2+}$-oxysalt minerals because of the significant distortion associated with the Jahn–Teller instability (Jahn & Teller 1937). Accordingly, Eby & Hawthorne (1993) showed that <$Cu^{2+}$–O, OH, $H_2O$> distances have a strong linear dependence on the bond-length dispersion, $\Delta$ (= root-mean-square deviation from the mean distance), and the <Cu–$\phi$> distances in geminite follow their curve almost exactly.

There are four unique tetrahedrally coordinated As sites, with <As–$\phi$> distances between 1.686 and 1.692 Å, well within the range typically exhibited by $AsO_4$ tetrahedra. All four tetrahedral groups are acid

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN GEMINITE

| | | | |
|---|---|---|---|
| Cu(1)–O(5)d | 1.952(4) | Cu(2)–O(1) | 2.457(5) |
| Cu(1)–O(6)f | 1.992(4) | Cu(2)–O(2)a | 2.070(5) |
| Cu(1)–O(6)g | 1.981(5) | Cu(2)–O(7)h | 1.960(4) |
| Cu(1)–O(10) | 1.986(5) | Cu(2)–O(8) | 1.946(4) |
| Cu(1)–O(11)k | 2.452(5) | Cu(2)–O(8)j | 2.311(5) |
| Cu(1)–OW(1)d | 2.541(6) | Cu(2)–OW(2)h | 2.006(5) |
| <Cu(1)–O> | 2.151 | <Cu(2)–O> | 2.125 |
| Cu(3)–O(2) | 1.976(4) | Cu(4)–O(5)e | 2.384(5) |
| Cu(3)–O(3)a | 2.045(5) | Cu(4)–O(11) | 1.949(4) |
| Cu(3)–O(3)b | 1.981(4) | Cu(4)–O(12)b | 1.984(4) |
| Cu(3)–O(7)i | 2.244(5) | Cu(4)–O(12)k | 1.984(4) |
| Cu(3)–OH(3) | 2.367(5) | Cu(4)–OH(2) | 2.432(5) |
| Cu(3)–OW(3)l | 1.963(5) | Cu(4)–OW(4)b | 1.937(5) |
| <Cu(3)–O> | 2.096 | <Cu(4)–O> | 2.112 |
| As(1)–O(1) | 1.661(5) | As(2)–O(4) | 1.661(5) |
| As(1)–O(2) | 1.695(4) | As(2)–O(5) | 1.675(4) |
| As(1)–O(3) | 1.681(4) | As(2)–O(6) | 1.698(4) |
| As(1)–OH(1) | 1.706(5) | As(2)–OH(2)c | 1.732(5) |
| <As(1)–O> | 1.686 | <As(2)–O> | 1.692 |
| As(3)–O(7) | 1.671(4) | As(4)–O(10) | 1.689(5) |
| As(3)–O(8) | 1.674(4) | As(4)–O(11) | 1.679(4) |
| As(3)–O(9) | 1.683(5) | As(4)–O(12) | 1.687(4) |
| As(3)–OH(3) | 1.729(5) | As(4)–OH(4) | 1.703(4) |
| <As(3)–O> | 1.689 | <As(4)–O> | 1.690 |
| Cu(1) octahedron | | | |
| O(11)k–O(6)f | 3.354(7) | O(11)k–Cu(1)–O(6)f | 97.5(2) |
| O(11)k–O(6)g | 3.505(7) | O(11)k–Cu(1)–O(6)g | 104.0(2) |
| O(11)k–O(5)d | 2.831(6) | O(11)k–Cu(1)–O(5)d | 79.1(2) |
| O(11)k–O(10) | 2.894(6) | O(11)k–Cu(1)–O(10) | 80.7(2) |
| OW(1)d–O(6)f | 3.071(7) | OW(1)d–Cu(1)–O(6)f | 84.4(2) |
| OW(1)d–O(6)g | 3.388(7) | OW(1)d–Cu(1)–O(6)g | 96.3(2) |
| OW(1)d–O(5)d | 3.547(7) | OW(1)d–Cu(1)–O(5)d | 103.5(2) |
| OW(1)d–O(10) | 2.909(8) | OW(1)d–Cu(1)–O(10) | 78.9(2) |
| O(6)f–O(6)g | 2.474(9) | O(6)f–Cu(1)–O(6)g | 77.0(2) |
| O(6)g–O(5)d | 2.799(6) | O(6)g–Cu(1)–O(5)d | 90.7(2) |
| O(5)d–O(10) | 2.874(6) | O(5)d–Cu(1)–O(10) | 93.7(2) |
| O(10)–O(6)f | 3.023(6) | O(10)–Cu(1)–O(6)f | 98.9(2) |
| <O–O> | 3.056 | <O–Cu(1)–O> | 90.4 |
| Cu(2) octahedron | | | |
| O(2)a–O(8) | 2.947(6) | O(2)a–Cu(2)–O(8) | 94.4(2) |
| O(2)a–O(8)j | 3.461(7) | O(2)a–Cu(2)–O(8)j | 104.2(2) |
| O(2)a–O(7)h | 2.636(6) | O(2)a–Cu(2)–O(7)h | 81.7(2) |
| O(2)a–O(1) | 2.945(6) | O(2)a–Cu(2)–O(1) | 80.7(2) |
| OW(2)h–O(8) | 2.870(7) | OW(2)h–Cu(2)–O(8) | 93.1(2) |
| OW(2)h–O(8)j | 3.208(7) | OW(2)h–Cu(2)–O(8)j | 95.8(2) |
| OW(2)h–O(7)h | 2.930(6) | OW(2)h–Cu(2)–O(7)h | 95.3(2) |
| OW(2)h–O(1) | 2.876(8) | OW(2)h–Cu(2)–O(1) | 79.6(2) |
| O(8)–O(8)j | 2.634(9) | O(8)–Cu(2)–O(8)j | 75.9(2) |
| O(8)j–O(7)h | 3.069(7) | O(8)j–Cu(2)–O(7)h | 91.5(2) |
| O(7)h–O(1) | 3.226(6) | O(7)h–Cu(2)–O(1) | 93.2(2) |
| O(1)–O(8) | 3.388(7) | O(1)–Cu(2)–O(8) | 100.0(2) |
| <O–O> | 3.016 | <O–Cu(2)–O> | 90.5 |
| Cu(3) octahedron | | | |
| O(7)i–O(3)a | 3.009(7) | O(7)i–Cu(3)–O(3)a | 89.0(2) |
| O(7)i–O(3)b | 2.995(6) | O(7)i–Cu(3)–O(3)b | 90.1(2) |
| O(7)i–OW(3)l | 3.313(7) | O(7)i–Cu(3)–OW(3)l | 103.7(2) |
| O(7)i–O(2) | 2.636(6) | O(7)i–Cu(3)–O(2) | 77.0(2) |
| OH(3)–O(3)a | 2.920(6) | OH(3)–Cu(3)–O(3)a | 82.5(2) |
| OH(3)–O(3)b | 3.023(6) | OH(3)–Cu(3)–O(3)b | 87.6(2) |
| OH(3)–OW(3)l | 2.933(8) | OH(3)–Cu(3)–OW(3)l | 84.7(2) |
| OH(3)–O(2) | 3.427(7) | OH(3)–Cu(3)–O(2) | 103.8(2) |
| O(3)a–O(3)b | 2.632(8) | O(3)a–Cu(3)–O(3)b | 81.6(2) |
| O(3)b–OW(3)l | 2.987(7) | O(3)b–Cu(3)–OW(3)l | 98.5(2) |
| OW(3)l–O(2) | 2.869(6) | OW(3)l–Cu(3)–O(2) | 93.5(2) |
| O(2)–O(3)a | 2.819(7) | O(2)–Cu(3)–O(3)a | 89.0(2) |
| <O–O> | 2.964 | <O–Cu(3)–O> | 90.1 |

Table 3. continued

| | | | |
|---|---|---|---|
| Cu(4) octahedron | | | |
| O(5)e–O(12)b | 3.099(6) | O(5)e–Cu(4)–O(12)b | 89.9(2) |
| O(5)e–O(12)k | 2.974(7) | O(5)e–Cu(4)–O(12)k | 85.3(2) |
| O(5)e–O(11) | 2.831(6) | O(5)e–Cu(4)–O(11) | 80.9(2) |
| O(5)e–OW(4)b | 3.359(6) | O(5)e–Cu(4)–OW(4)b | 101.6(2) |
| OH(2)–O(12)b | 3.072(6) | OH(2)–Cu(4)–O(12)b | 87.6(2) |
| OH(2)–O(12)k | 3.049(6) | OH(2)–Cu(4)–O(12)k | 86.7(2) |
| OH(2)–O(11) | 3.378(7) | OH(2)–Cu(4)–O(11) | 100.3(2) |
| OH(2)–OW(4)b | 3.014(7) | OH(2)–Cu(4)–OW(4)b | 86.5(2) |
| O(12)b–O(12)k | 2.563(8) | O(12)b–Cu(4)–O(12)k | 80.5(2) |
| O(12)k–O(11) | 2.787(6) | O(12)k–Cu(4)–O(11) | 90.2(2) |
| O(11)–OW(4)b | 2.754(6) | O(11)–Cu(4)–OW(4)b | 90.3(2) |
| OW(4)b–O(12)b | 3.002(6) | OW(4)b–Cu(4)–O(12)b | 100.0(2) |
| <O–O> | 2.990 | <O–Cu(4)–O> | 90.0 |
| As(1) tetrahedron | | | |
| OH(1)–O(1) | 2.737(7) | OH(1)–As(1)–O(1) | 108.8(2) |
| OH(1)–O(2) | 2.684(7) | OH(1)–As(1)–O(2) | 104.2(2) |
| OH(1)–O(3) | 2.753(6) | OH(1)–As(1)–O(3) | 108.8(2) |
| O(1)–O(2) | 2.795(7) | O(1)–As(1)–O(2) | 112.8(2) |
| O(2)–O(3) | 2.739(6) | O(2)–As(1)–O(3) | 108.4(2) |
| O(3)–O(1) | 2.793(6) | O(3)–As(1)–O(1) | 113.4(2) |
| <O–O> | 2.750 | <O–As(1)–O> | 109.4 |
| As(2) tetrahedron | | | |
| OH(2)c–O(4) | 2.692(8) | OH(2)c–As(2)–O(4) | 105.0(2) |
| OH(2)c–O(5) | 2.746(6) | OH(2)c–As(2)–O(5) | 107.4(2) |
| OH(2)c–O(6) | 2.717(7) | OH(2)c–As(2)–O(6) | 104.8(2) |
| O(4)–O(5) | 2.798(7) | O(4)–As(2)–O(5) | 114.0(2) |
| O(5)–O(6) | 2.774(6) | O(5)–As(2)–O(6) | 110.6(2) |
| O(6)–O(4) | 2.820(7) | O(6)–As(2)–O(4) | 114.2(2) |
| <O–O> | 2.758 | <O–As(2)–O> | 109.3 |
| As(3) tetrahedron | | | |
| OH(3)–O(7) | 2.761(7) | OH(3)–As(3)–O(7) | 108.6(2) |
| OH(3)–O(8) | 2.752(7) | OH(3)–As(3)–O(8) | 107.9(2) |
| OH(3)–O(9) | 2.712(7) | OH(3)–As(3)–O(9) | 105.3(2) |
| O(7)–O(8) | 2.747(6) | O(7)–As(3)–O(8) | 110.4(2) |
| O(8)–O(9) | 2.802(6) | O(8)–As(3)–O(9) | 113.2(2) |
| O(9)–O(7) | 2.767(6) | O(9)–As(3)–O(7) | 111.1(2) |
| <O–O> | 2.757 | <O–As(3)–O> | 109.4 |
| As(4) tetrahedron | | | |
| OH(4)–O(10) | 2.740(7) | OH(4)–As(4)–O(10) | 107.8(2) |
| OH(4)–O(11) | 2.742(6) | OH(4)–As(4)–O(11) | 108.3(2) |
| OH(4)–O(12) | 2.673(6) | OH(4)–As(4)–O(12) | 104.1(2) |
| O(10)–O(11) | 2.807(7) | O(10)–As(4)–O(11) | 112.9(2) |
| O(11)–O(12) | 2.729(6) | O(11)–As(4)–O(12) | 108.3(2) |
| O(12)–O(10) | 2.846(6) | O(12)–As(4)–O(10) | 114.9(2) |
| <O–O> | 2.756 | <O–As(4)–O> | 109.4 |

a: $\bar{x}+½$, $\bar{y}+1½$, $\bar{z}+1$; b: x–½, y–½, z; c: x, y+1, z; d: x+½, y–½, z; e: $\bar{x}$, $\bar{y}+1$, $\bar{z}$; f: x, y–1, z; g: $\bar{x}+1$, $\bar{y}+1$, $\bar{z}$; h: x+½, y+½, z; i: $\bar{x}$, $\bar{y}+1$, $\bar{z}+1$; j: $\bar{x}+1$, $\bar{y}+1$, $\bar{z}+1$; k: $\bar{x}+½$, $\bar{y}+½$, $\bar{z}$; l: x–½, y+½, z

groups: there are three oxygen anions and one OH anion, and the As–OH distance is the longest As–$\phi$ distance in each of the tetrahedra (Table 3). The variation in O–As–O bond-angles (Table 3) also falls within the range typical for $AsO_4$ tetrahedra (Griffen & Ribbe 1978).

### *Topology of the structure*

The $Cu\phi_6$ octahedra share edges to form $[Cu\phi_4]$ chains parallel to [010] (Fig. 1a). There are two symmetrically distinct chains, but the chains are topologically identical (Fig. 1a), even to the distribution of the $H_2O$ groups. The $As\phi_4$ groups link along the chain, as shown in Figure 1b. Some of the tetrahedra link to the chain with two vertices, and other tetrahedra link to the chain with one vertex. A view of the structure projected onto (100) (Fig. 2) shows that the chains in Figure 1 link together to form sheets parallel to (001). Adjacent chains within the sheet are topologically identical; tetrahedra share two vertices with one chain, one vertex with the adjacent chain, and the fourth vertex of the tetrahedra does not link to another cation (except H). Figure 1b shows the sheets viewed within the plane; in this view, there is no direct cation–anion linkage between adjacent sheets, and geminite is hence a sheet structure, as its habit and cleavage suggest.

TABLE 4. DETAILS OF H-BONDING (Å,°) IN GEMINITE

| | | | |
|---|---|---|---|
| OH(1)–H(1) | 0.98(7) | H(1)···O(4) | 1.64(7) |
| OH(2)–H(2) | 0.98(5) | H(2)···O(10) | 1.61(6) |
| OH(3)–H(3) | 0.98(6) | H(3)···O(1) | 1.59(6) |
| OH(4)–H(4) | 0.98(8) | H(4)···O(9) | 1.58(8) |
| OH(1)–O(4) | 2.613(7) | OH(1)–H(1)–O(4) | 170(7) |
| OH(2)–O(10) | 2.590(6) | OH(2)–H(2)–O(10) | 174(4) |
| OH(3)–O(1) | 2.541(6) | OH(3)–H(3)–O(1) | 163(8) |
| OH(4)–O(9) | 2.562(7) | OH(4)–H(4)–O(9) | 176(10 |
| OW(1)–H(5) | 0.98(10) | H(5)···OH(4) | 2.2(1) |
| | | H(5)···OH(3) | 2.5(1) |
| OW(1)–H(6) | 0.98(6) | H(6)···O(4) | 1.83(7) |
| OW(2)–H(7) | 0.98(8) | H(7)···OH(1)f | 1.78(9) |
| OW(2)–H(8) | 0.98(7) | H(8)···O(9) | 1.97(7) |
| OW(3)–H(9) | 0.98(7) | H(9)···OW(1)d | 1.82(7) |
| OW(3)–H(10) | 0.98(9) | H(10)···O(9) | 1.70(9) |
| OW(4)–H(11) | 0.98(8) | H(11)···OH(4) | 2.12(7) |
| | | H(11)···OW(2)h | 2.33(8) |
| | | H(11)···O(1) | 2.58(8) |
| OW(4)–H(12) | 0.98(9) | H(12)···O(4) | 1.68(9) |
| OW(1)–OH(4) | 3.033(8) | OW(1)–H(5)–OH(4) | 139(9) |
| OW(1)–OH(3) | 3.241(8) | OW(1)–H(5)–OH(3) | 129(7) |
| OW(1)–O(4) | 2.798(7) | OW(1)–H(6)–O(4) | 171(6) |
| OW(2)–OH(1)f | 2.725(8) | OW(2)–H(7)–OH(1)f | 160(7) |
| OW(2)–O(9) | 2.742(6) | OW(2)–H(8)–O(9) | 134(7) |
| OW(3)–OW(1)d | 2.791(8) | OW(3)–H(9)–OW(1)d | 170(4) |
| OW(3)–O(9) | 2.679(8) | OW(3)–H(10)–O(9) | 173(2) |
| OW(4)–OH(4) | 2.847(6) | OW(4)–H(11)–OH(4) | 129(5) |
| OW(4)–OW(2)h | 2.971(7) | OW(4)–H(11)–OW(2)h | 122(6) |
| OW(4)–O(1) | 3.185(7) | OW(4)–H(11)–O(1) | 120(6) |
| OW(4)–O(4) | 2.653(8) | OW(4)–H(12)–O(4) | 172(7) |
| H(5)–H(6) | 1.6(1) | H(5)–OW(1)–H(6) | 111(8) |
| H(7)–H(8) | 1.4(1) | H(7)–OW(2)–H(8) | 95(8) |
| H(9)–H(10) | 1.7(1) | H(9)–OW(3)–H(10) | 121(5) |
| H(11)–H(12) | 1.5(1) | H(11)–OW(4)–H(12) | 97(8) |

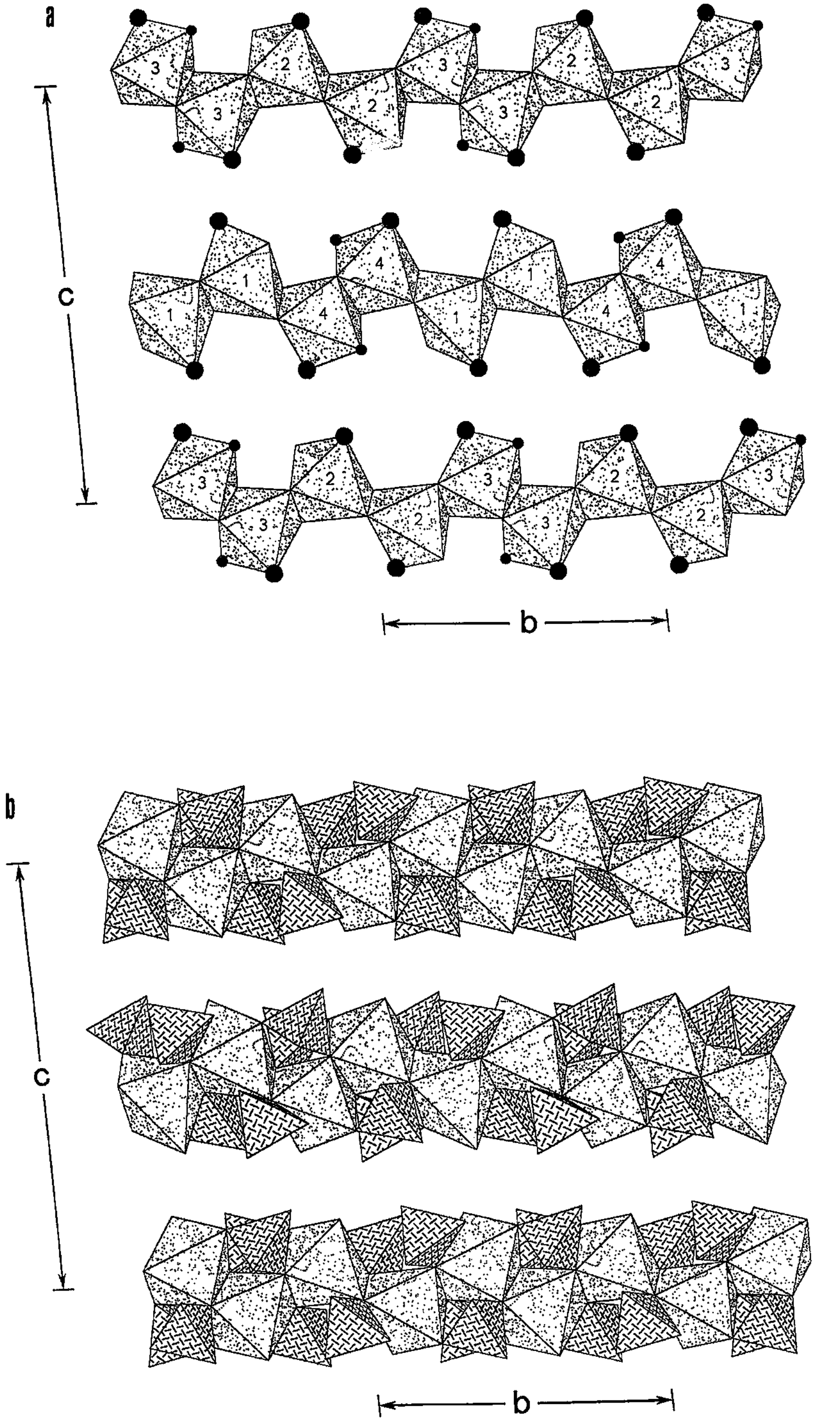

FIG. 1. The crystal structure of geminite projected onto (100); (a) [Cu$\phi_4$] chains extending along the *b* axis; large circles denote $H_2O$ groups, small circles denote OH groups; (b) heteropolyhedral sheets viewed edge-on; Cu$\phi_6$ octahedra are random-dot-shaded, As$\phi_4$ tetrahedra are dash-shaded.

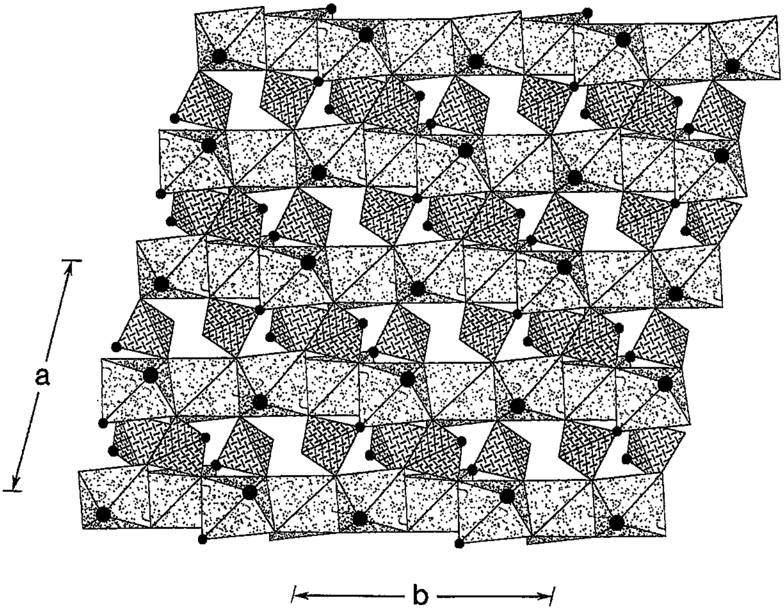

FIG. 2. The crystal structure of geminite projected onto (001), showing the heteropolyhedral sheet of the structural unit; legend as in Fig. 1.

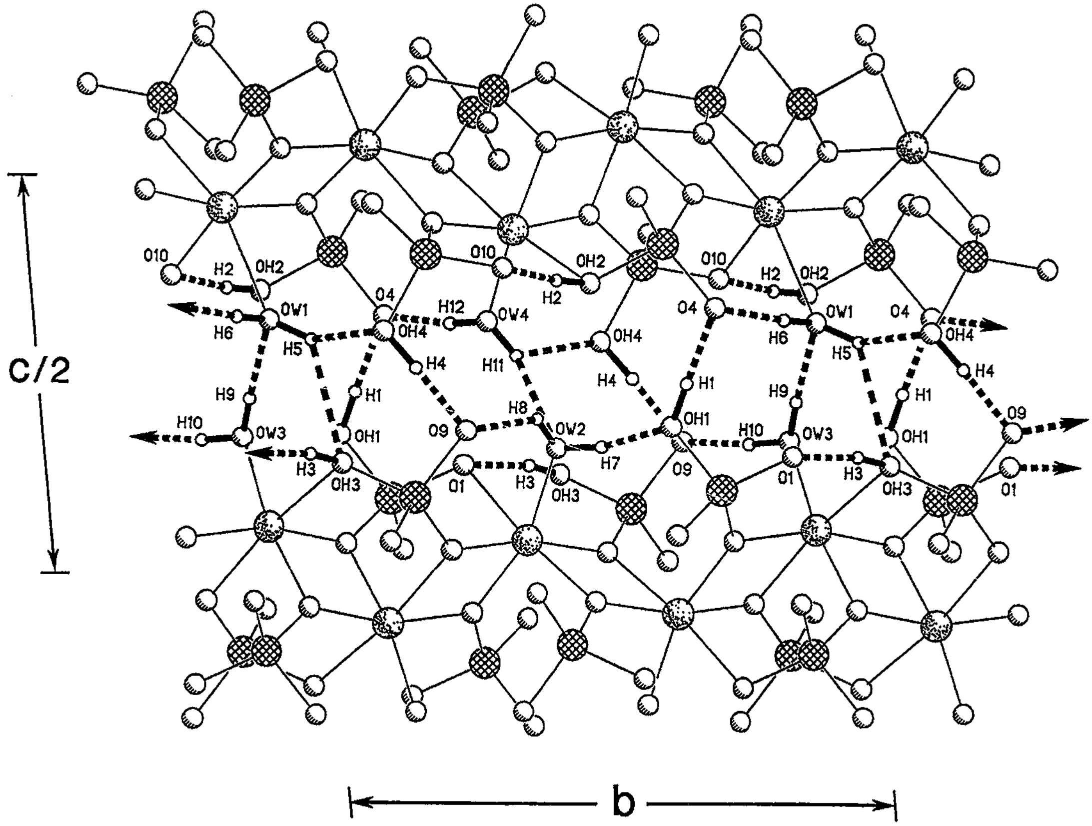

FIG. 3. The hydrogen-bonding arrangement linking the sheets in geminite, projected onto (100); Cu: random dot-shaded circles; As: cross-hatched circles; oxygen: shadowed circles: H; small unshaded circles; O–H bonds: heavy lines; H...O bonds: broken heavy lines.

### *Hydrogen bonding*

Figure 3 shows the details of the hydrogen bonding that links the sheets together. There are 12 distinct H-atom positions in geminite, and the geometrical details of their bonding are given in Table 4. There are four distinct OH anions. The H atoms are 0.98 Å from the associated oxygen atom (as softly constrained in the refinement) and ~1.60 Å from an oxygen atom that acts as a hydrogen-bond acceptor. The H...O distance of ~1.60 Å are quite short, and in line with this fact, the O–H...O angles are close to 180° (Table 4). These H...O distances indicate quite strong H-bonding from the OH anions of the acid arsenate groups to other anions in the structure.

There are four distinct $H_2O$ groups. In each group, the oxygen atom is associated with two H atoms, each at a distance of 0.98 Å; the H–H distances and H–O–H angles (Table 4) are typical for $H_2O$ groups. In the OW(1) group, H(6) forms a H-bond with O(4), and H(5) forms a bifurcated H-bond with OH(3) and OH(4); in accordance with this, the H(6)–O(4) distance is relatively short at 1.83(7) Å, whereas the H(5)–OH(3) and H(5)–OH(4) distances are considerably longer at 2.2(1) and 2.5(1) Å, respectively. It is notable that the OW(1)–H(6)–O(4) angle is large [171(6)°], as is common for most H-bond arrangements, whereas the OW(1)–H(5,6)–OH(3,4) angles are relatively small [139(9) and 129(7)°], although well within the range recorded for H bonds. The OW(2) and OW(3) groups show reasonably strong H-bonds (H–ϕ distances in the range 1.70–1.97 Å) with larger OW–H...O angles (Table 4). The OW(4) group has a similar H-bonding scheme to OW(1): one single strong H-bond and one bifurcated (or possibly trifurcated) H-bond, again with a similar arrangement of OW–H...O angles (Table 4).

Figure 3 shows the H-bond linkage both within and between the sheets. The OH(2) and OH(3) groups H-bond within each sheet, whereas OH(1) and OH(4) H-bond between adjacent sheets. The OW(1) and OW(4) groups belong to the same sheet; in each, the single O...H bond and one of the bifurcated pair of H bonds occurs within the sheet, and the other of the bifurcated pair bonds from one sheet to the other (Fig. 3). The OW(2) and OW(3) groups belong to the other crystallographically distinct sheet; OW(2) H-bonds within the sheet, whereas OW(3) H-bonds both within the sheet and between adjacent sheets. The localized nature of the H bonds is very apparent in Figure 3.

### *Bond-valence arrangement*

The bond-valence arrangement in geminite (Table 5) accords well with the valence-sum rule (Brown 1981, 1992). All the $As\phi_4$ polyhedra show strong bonds to the oxygen anions and slightly weaker

TABLE 5. BOND-VALENCE* TABLE FOR GEMINITE

| | Cu(1) | Cu(2) | Cu(3) | Cu(4) | As(1) | As(2) | As(3) | As(4) | H(1) | H(2) | H(3) | H(4) | H(5) | H(6) | H(7) | H(8) | H(9) | H(10) | H(11) | H(12) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| O(1) | | 0.12 | | | 1.33 | | | | | | 0.28 | | | | | | | | 0.05 | | 1.78 |
| O(2) | | 0.35 | 0.45 | | 1.21 | | | | | | | | | | | | | | | | 2.01 |
| O(3) | | | 0.44<br>0.37 | | 1.26 | | | | | | | | | | | | | | | | 2.07 |
| O(4) | | | | | | 1.33 | | | 0.25 | | | | | 0.18 | | | | | | 0.23 | 1.99 |
| O(5) | 0.48 | | | 0.15 | | 1.28 | | | | | | | | | | | | | | | 1.91 |
| O(6) | 0.43<br>0.44 | | | | | 1.21 | | | | | | | | | | | | | | | 2.08 |
| O(7) | | 0.47 | 0.22 | | | | 1.30 | | | | | | | | | | | | | | 1.99 |
| O(8) | | 0.49<br>0.18 | | | | | 1.29 | | | | | | | | | | | | | | 1.96 |
| O(9) | | | | | | | 1.25 | | | | | 0.28 | | | | 0.14 | | 0.22 | | | 1.89 |
| O(10) | 0.44 | | | | | | | 1.23 | | 0.27 | | | | | | | | | | | 1.94 |
| O(11) | 0.12 | | | 0.48 | | | | 1.27 | | | | | | | | | | | | | 1.87 |
| O(12) | | | | 0.44<br>0.44 | | | | 1.24 | | | | | | | | | | | | | 2.12 |
| OH(1) | | | | | 1.18 | | | | 0.75 | | | | | | 0.19 | | | | | | 2.12 |
| OH(2) | | | | 0.13 | | 1.10 | | | | 0.73 | | | | | | | | | | | 1.96 |
| OH(3) | | | 0.16 | | | | 1.11 | | | | 0.72 | | 0.05 | | | | | | | | 2.04 |
| OH(4) | | | | | | | | 1.19 | | | | 0.72 | 0.09 | | | | | | 0.10 | | 2.10 |
| OW(1) | 0.10 | | | | | | | | | | | | 0.86 | 0.82 | | | 0.18 | | | | 1.96 |
| OW(2) | | 0.41 | | | | | | | | | | | | | 0.81 | 0.86 | | | 0.07 | | 2.15 |
| OW(3) | | | 0.46 | | | | | | | | | | | | | | 0.82 | 0.78 | | | 2.06 |
| OW(4) | | | | 0.50 | | | | | | | | | | | | | | | 0.78 | 0.77 | 2.09 |
| | 2.01 | 2.02 | 2.10 | 2.14 | 4.98 | 4.92 | 4.95 | 4.93 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | |

* calculated with the curves of Brown & Altermatt (1985)

TABLE 6. CELL DIMENSIONS FOR GEMINITE

| | *C*-centered | Primitive | Sarp & Perroud (1990) |
|---|---|---|---|
| *a* (Å) | 9.841(2) | 6.434(1) | 6.395(3) |
| *b* | 10.818(2) | 8.096(2) | 8.110(3) |
| *c* | 15.733(3) | 15.733(3) | 15.732(9) |
| $\alpha$ (°) | 95.71(2) | 86.77(2) | 92.01(5) |
| $\beta$ | 90.94(2) | 84.48(2) | 93.87(5) |
| $\gamma$ | 103.11(2) | 84.44(2) | 95.02(4) |

bonds to the acid OH groups, as would be predicted from bond-valence theory. Of particular interest are the oxygen atoms O(4) and O(9), both of which bond only to one As atom and no Cu atoms. Both of these anions are acceptors for three H-bonds, which emphasizes the key role that H-bonding plays in the structure of geminite; without these strong H-bonding arrangements, the O(4) and O(9) arsenate ligands would not accord with the valence-sum rule, and the structure would not be stable.

### *Cell dimensions*

The cell dimensions we obtained differ somewhat from those of Sarp & Perroud (1990). The values for the axial lengths of the primitive cell are virtually identical (Table 6); on the other hand, the interaxial angles of Sarp & Perroud (1990) are for a Type-II triclinic cell, whereas our values indicate a Type-I primitive cell.

### *Pseudo-symmetry*

As is apparent from Figure 1b, adjacent sheets are topologically identical and geometrically very similar. The sheets are, in fact, related by a pseudo-*b*-glide plane at $z = \pm\frac{1}{4}$. In addition, there are pseudo-two-fold and two-fold-screw axes orthogonal to the sheet. These elements of pseudosymmetry indicate pseudo-*C*112/*b* symmetry. True monoclinic symmetry in this orientation would require that $\alpha = \beta = 90°$, whereas $\beta$ deviates significantly from 90°. The magnitude of $\alpha$ is dictated by the relative displacement of adjacent sheets. These sheets are only linked by H bonds, and hence interact only very weakly. It is feasible that a slightly different H-bonding arrangement, perhaps at a higher temperature, could allow monoclinic symmetry.

The presence of pseudosymmetry *and* extensive polysynthetic twinning (Sarp & Perroud 1990) suggests the presence of a phase transition at higher temperatures. Allowing for the difference in setting, the transition $C2/c \rightarrow P\bar{1}$ is a proper ferroelastic (Stokes & Hatch 1988). We note that such transitions seem to be fairly common in minerals, particularly where stereochemical effects (*e.g.*, Jahn–Teller distortion, stereoactive lone-pair behavior) are present.

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