Enfin, les liaisons ioniques de ce cristal (K...O= 2,60; 2,60; 2,75 Å) sont tout à fait comparables à celles que l'on trouve dans les sels de potassium d'acides organiques: acide fumarique: 2,65; 2,89 Å (Gupta, 1956); acide maléique: 2,82; 2,89; 2,87; 3,03 Å (Darlow & Cochran, 1961); acide glycuronique: 2,79; 2,85; 2,97; 2,99 Å (Gurr, 1963).

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The Crystal Structure of Clinoclase, $Cu_3AsO_4(OH)_3$

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The dark bluish green mineral clinoclase, $Cu_3AsO_4(OH)_3$, is monoclinic, space group $P2_1/c$, with $a_o=7{\cdot}24$, $b_o=6{\cdot}46$, $c_o=12{\cdot}38$ Å; $\beta=99°30'$. The heavy atoms were located from three-dimensional Patterson sections, using Buerger's minimum function method. The light atom positions were revealed in the subsequent three-dimensional Fourier synthesis. The atomic parameters were refined by the method of full-matrix least squares, using three-dimensional data.

The coordination of the three independent copper atoms is essentially fivefold distorted tetragonal pyramidal. Cu–O (or OH) distances within the coordination plane average 1·96 Å, while the fifth Cu–O (or OH) bond varies in length from 2·30 to 2·51 Å, and the sixth from 2·84 to 3·32 Å. The copper coordination plane is always curved in a boat shape towards the fifth ligand. Clinoclase contains two sets of $Cu_2(OH)_4O_4$ dimeric groups, each formed by two tetragonal pyramids, sharing an edge of the equatorial plane. One set of dimers forms an infinite chain by sharing two OH corners with two adjacent dimers. These chains, occuring zigzag with respect to each other in the unit cell, sandwich between them isolated $Cu_2(OH)_4O_4$ dimers and AsO_4 tetrahedra, thus giving rise to a complex sheet structure running parallel to the (100) plane. These complex sheets are held to each other through long Cu–O and O–H ... O bonds.

Introduction

As part of a structural study of basic copper arsenates and phosphates, the structure determination of clinoclase, $Cu_3AsO_4(OH)_3$, and cornetite, $Cu_3PO_4(OH)_3$ has been undertaken. In spite of the chemical analogy, these two minerals are not isostructural. Clinoclase crystallizes in the monoclinic system, but cornetite in the orthorhombic system. In contrast, basic copper phosphate–arsenate pairs, like libethenite, $Cu_2PO_4(OH)$, and olivenite, $Cu_2AsO_4(OH)$ (Heritsch, 1938,

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1940; Walitzi, 1963), pseudomalachite, $Cu_5(PO_4)_2(OH)_4$ and erinite, $Cu_5(AsO_4)_2(OH)_4$ (Ghose, 1963; Berry, 1951) are isostructural. The structure of cornetite has been described recently (Fehlmann, Ghose & Finney, 1964). In this paper, the structure determination of clinoclase is reported.

Crystal data and experimental

A very good description of the morphology, as well as the determination of the optical characters, unit-cell dimensions and space group is given by Palache & Berry (1946). Beautifully crystallized dark bluish green needles of clinoclase from Majuba Hill, Nevada (Harvard Museum, No. 100792) have been made available for this study through the courtesy of Prof. Clifford Frondel. The crystals are slender needles, elongated [010] and tabular parallel to [100]. The cell dimensions of clinoclase, determined by Berry (Palache & Berry, 1946), are given below (*a* and *c* interchanged):

Monoclinic, $2/m$
$a_0=7{\cdot}24,\ b_0=6{\cdot}46,\ c_0=12{\cdot}38$ Å; $\beta=99°30'$.
Space group: $P2_1/c$
Cell contents: $4[Cu_3AsO_4(OH)_3]$
$D_m=4{\cdot}38$ g.cm^{-3} . $D_x=4{\cdot}42$ g.cm^{-3}.
μ for Cu $K\alpha=201{\cdot}4$ cm^{-1}.

Optical properties of clinoclase from Majuba Hill, determined by Hurlbut (Palache & Berry, 1946), corresponding to this orientation are as follows:

Orientation	n	Pleochroism	
X	1·756	Pale blue-green	Biaxial (−)
$Y\ b$	1·874	Light blue-green	$2V=50°$ (meas.)
Z near c	1·896	Benzol-green	$r<v$, very strong

It should be noted that the refractive indices along Y and Z directions are approximately the same, while that along X is significantly smaller. This fact, coupled with the negative optic sign, indicates a sheet structure parallel to (100). The perfect (100) cleavage strongly favors this idea, which is ultimately confirmed by the following structure determination.

For the intensity measurements, a crystal measuring approximately $0{\cdot}15\times0{\cdot}5\times0{\cdot}25$ mm was used. Weissenberg multiple-film photographs of zero through the fourth layer about [010] and [100] were taken with Cu $K\alpha$ radiation. The intensities were visually estimated. To correct the intensities for α_1–α_2 splitting, the measured α_1 intensity was multiplied by 1·5, 1·3 and 1·2 for complete, semi-complete and incomplete resolution respectively. Since it was difficult to apply proper absorption corrections to the data taken about [100], they were corrected for Lp factors and were primarily used to normalize data taken about [010]. The $h0l$, $h1l$, $h2l$, $h3l$ and $h4l$ intensities were corrected for Lp factors and absorption, the absorption corrections being made, assuming the crystal to be a cylinder with $\mu R=2{\cdot}0$.

The infrared spectrum of clinoclase was recorded on a Perkin Elmer spectrometer, model 13, with a calcium fluoride prism, the Nujol mull technique being used.

The structure determination

Two Patterson projections along the shorter axes *a* and *b* were first computed. The Patterson projections along *a* showed that almost all the Patterson peaks are located in sections at $v=0$, $\frac{1}{4}$ and $\frac{1}{2}$. As a first approximation to the three-dimensional Patterson function, sharpened Patterson sections along $v=0$, $\frac{1}{4}$ and $\frac{1}{2}$ were computed, with programs written by Shiono (1960). The Patterson function was sharpened by multiplying F^2 with $M(S)$, where

$$M(S)=[\sum_{j=1}^{N}Z_j/\sum_{j=1}^{N}f_{0j}]^2\ .\ \exp\left[-2P\sin^2\theta/\lambda^2\right]\ .$$

P was taken to be equal to 1.

The Harker section at $v=\frac{1}{2}$ (Fig. 1(*c*)) contains many strong peaks which made the correct choice of Harker peaks difficult. However, it was noticed that two sets of three strong peaks made two triangles, *ABC* and *DEF*. These triangles correspond to triangles $A'B'C'$ and $D'E'F'$ occurring on the section at $v=0$ (Fig. 1(*a*)) in dimension, as well as, relative orientation. This fact suggested that these peaks are due to the extra symmetry present in the structure and are not true Harker peaks. Of the remaining smaller peaks, *K*, *L* and *M* are of equal height and have been chosen as possible Harker maxima. The fact that all the strong peaks in [100] Patterson projections are located at $v=0$, $\frac{1}{4}$, $\frac{1}{2}$ indicates that the *y* coordinates of the heavy atoms must be close to either $\frac{1}{8}$ or $\frac{3}{8}$. A peak, corresponding to the vector $(2x, 2y, 2z)$ must occur on the Patterson section at $v=\frac{1}{4}$. A systematic search for peaks of this type in the section corresponding to the Harker peaks *K*, *L*, *M*, led to the peak marked 2*K* (Fig. 1(*b*)). Use of this peak as the point of superposition led directly to the correct choice of origin of the M_2 maps. The minimum function was derived graphically, as described by Buerger (1959), in two stages. The first M_2 map was derived with the use of Patterson sections at $v=0$ and $\frac{1}{4}$, and the second, using sections at $v=\frac{1}{4}$ and $\frac{1}{2}$.

Occurrence of three strong peaks *k*, *l*, *m* on these minimum maps corresponded to the Harker maxima *K*, *L*, *M* respectively. Since the structure contains four heavy atoms, namely three copper and one arsenic, occurrence of only three strong peaks in the minimum maps was surprising. After the structure determination was completed, it was realized that the missing heavy atom corresponds almost exactly in position to that of peak *n* in the minimum maps. This peak was overlooked as a possible heavy atom position because of its lower peak height. A comparison of the M_2 map (superposition of two sections) and the second three-dimensional Fourier synthesis is made in Figs. 2(*a*) and 2(*b*). It will be noticed that they are strikingly similar.

The first structure factor calculation of $h0l$ reflections using the three heavy atom positions found from the M_2 maps (treated as Cu atoms for calculation) yielded an R index of 0·51. The corresponding Fourier projections showed a peak at the l position, twice as high as the other peaks at positions k and m. This high peak at l was considered to be due to two overlapping heavy atoms. The next structure factor calculation including four heavy atoms decreased R to 0·41. Inclusion of some peaks in the structure factor calculation, which appeared in the electron-density projection as oxygen atoms, reduced R further to 0·38. However, it was difficult to separate the two superposing heavy atoms, and this projection did not refine further. This difficulty was overcome through the application of the "Optimal Shift" method (Niggli, Vand & Pepinsky, 1961), using the expressions given below for the plane group $P2$:

$$\Delta x_i = -h\Delta F f_i \sin 2\pi\,(hx_i+ky_i)/4\pi\,(h^2+k^2)\sum_j f_j^2 \sin^2 2\pi(hx_j+ky_j)$$

$$\Delta y_i = -k\Delta F f_i \sin 2\pi\,(hx_i+ky_i)/4\pi\,(h^2+k^2)\sum_j f_j^2 \sin^2 2\pi(hx_j+ky_j)\,.$$

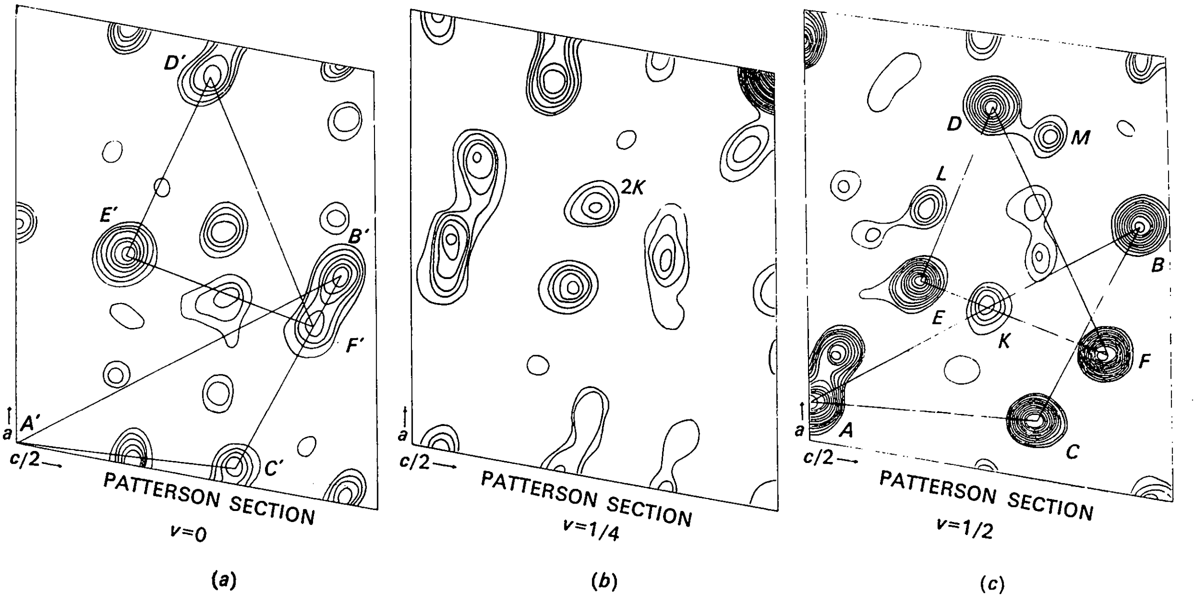

Fig. 1. Sharpened three-dimensional Patterson sections of clinoclase, $Cu_3AsO_4(OH)_3$ at $v=0,\frac{1}{4}$ and $\frac{1}{2}$ respectively.

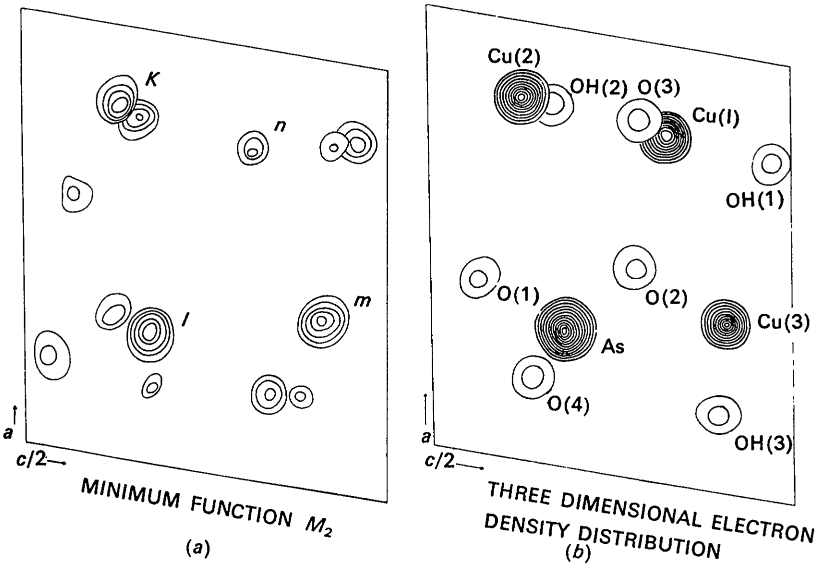

Fig. 2. (a) Superposition of two M_2 maps, derived from Patterson sections of clinoclase at $v=0$ and $\frac{1}{4}$ an $v=\frac{1}{4}$ and $\frac{1}{2}$. (b) Three-dimensional electron density distribution of clinoclase between $y=0$ and $\frac{1}{2}$. Contours are drawn at equal but arbitrary intervals.

The two overlapping heavy atoms were successfully separated and the projection was refined by difference Fourier syntheses till *R* was 0·28.

The first 0*kl* structure factor calculation with the contributions from the heavy atoms only, using the *z* parameters from the [010] projection and *y* parameters as $\frac{1}{8}$ or $\frac{3}{8}$, yielded an *R* index of 0·43. Slight adjustments of the *y* parameters reduced *R* to 0·30. Inclusion of some peaks appearing in the electron-density projection as oxygen atoms reduced *R* further to 0·21. It was found, however, that some of the peaks, which were presumed to be due to oxygen atoms, did not agree in both projections. A three-dimensional Fourier synthesis was computed next, using the signs of structure factors, calculated with the contributions from the four heavy atoms only. All the seven oxygen positions were found readily from the three-dimensional Fourier sections. The first three-dimensional structure factor calculation, including all the non-hydrogen atoms, yielded an *R* index of 0·33. A second three-dimensional Fourier synthesis, followed by a structure factor calculation, reduced *R* to 0·27.

Further refinement was carried out by the full-matrix least-squares method, using the program written by Busing, Martin & Levy (1962), on an IBM 7090 computer. Hughes's (1941) weighting scheme was used. The scattering factors for Cu, As and O were taken from *International Tables for X-ray Crystallography* (1962). 33 positional, 11 isotropic thermal and 5 scale factor parameters were varied simultaneously. Convergence was reached after eight cycles of refinement. The final *R* index is 0·142 for all reflections and 0·137 omitting the unobserved reflections. The final atomic parameters are listed in Table 1 and the observed and calculated structure factors in Table 2. A list of bond lengths and angles is given in Table 3. The average standard deviations of bond lengths are: Cu–Cu, ±0·0038, Cu–As, ±0·0033, Cu–O, ±0·013, As–O, ±0·013 and O–O, ±0·018 Å. Since the absorption corrections could not be properly made, these values may be too low. A more realistic estimate of the standard errors would be to increase these values by 50%.

Description of the structure

The stereochemistry of the cupric ions

The coordination of the three crystallographically different cupric ions in clinoclase is essentially distorted tetragonal pyramidal. Two of them, however, have sixth ligands at much greater distances, completing the distorted tetragonal bipyramid.

The Cu(1) atom is surrounded by two OH groups and two oxygen atoms approximately in a plane at 1·91, 1·91, 1·97 and 2·07 Å. The fifth ligand oxygen, O(4), is at a distance of 2·31 Å, and the sixth ligand, OH(3) at a distance of 2·84 Å. The copper coordination plane is curved in a boat shape towards the fifth ligand, the deviation from planarity being as much as 19°. The fifth ligand, O(4) deviates somewhat from the expected pyramidal position, the angles subtended by O(4) at Cu(1) with the equatorial ligands being 89·4, 113·6, 92·4 and 84·0°. The sixth ligand deviates considerably from the expected octahedral position, as evidenced by the O(4)–Cu(1)–OH(3) angle, which is 161·7°.

The coordination of Cu(2) is tetragonal pyramidal. One oxygen atom and three OH ions surround Cu(2) approximately in a plane at 1·99, 1·95, 1·89 and 1·93 Å. The fifth ligand, O(2) lies at a distance of 2·51 Å. There is apparently no sixth ligand at a reasonable distance, the sixth nearest anion being O(4) at a distance of 3·32 Å. The Cu(2)-coordination plane is slightly curved towards the fifth ligand, the maximum deviation from planarity being about 8°.

The Cu(3) atom forms a planar group with three oxygen atoms and one OH ion at distances of 2·02, 1·99, 1·98 and 1·90 Å. The fifth ligand is an OH(2) group at 2·30 Å and the sixth, OH(1) at 2·99 Å. The Cu(3)-coordination plane is strongly curved in a boat shape towards the fifth ligand, the deviation from planarity being as much as 26°. The fifth ligand, OH(2), deviates from the expected pyramidal position, as shown by the angles subtended by OH(2) at Cu(3) with the equatorial ligands, which are 104·8, 87·2, 99·3 and 88·9°.

There are two sets of dimeric $Cu_2(OH)_4O_4$ ions in clinoclase, each consisting of two tetragonal pyramids, sharing an equatorial edge. The first dimer is formed by tetragonal pyramids around Cu(1) and Cu(2) sharing the equatorial edge O(3)–OH(2). The second dimer is formed by two tetragonal pyramids around two Cu(3) atoms, related by a center of symmetry, sharing the equatorial edge O(1)–O(1). In the first dimer the pyramidal ligands are OH ions, but in the second, oxygen atoms. In both dimers, the pyramidal ligands occur *trans* to each other.

Table 1. *Atomic parameters of clinoclase*, $Cu_3AsO_4(OH)_3$

Cu(1)	0·7877 ± 0·00034	0·1389 ± 0·00052	0·3291 ± 0·00019	0·98 ± 0·078
Cu(2)	0·8150 ± 0·00032	0·3824 ± 0·00048	0·1275 ± 0·00018	0·85 ± 0·077
Cu(3)	0·3872 ± 0·00034	0·3532 ± 0·00052	0·4127 ± 0·00019	0·89 ± 0·075
As	0·3088 ± 0·00021	0·1510 ± 0·00040	0·1796 ± 0·00012	0·24 ± 0·069
O(1)	0·4121 ± 0·00138	0·0667 ± 0·00275	0·0724 ± 0·00082	0·20 ± 0·173
O(2)	0·1623 ± 0·00179	0·3453 ± 0·00265	0·1346 ± 0·00102	0·72 ± 0·217
O(3)	0·1758 ± 0·00148	−0·0568 ± 0·00280	0·2141 ± 0·00087	0·41 ± 0·180
O(4)	0·4728 ± 0·00137	0·2173 ± 0·00248	0·2861 ± 0·00081	0·20 ± 0·176
OH(1)	0·7797 ± 0·00137	0·2026 ± 0·00284	0·4791 ± 0·00081	0·26 ± 0·180
OH(2)	0·1911 ± 0·00158	0·5979 ± 0·00266	0·3209 ± 0·00090	0·48 ± 0·203
OH(3)	0·1780 ± 0·00159	0·1736 ± 0·00246	0·4080 ± 0·00093	0·47 ± 0·200

Table 2. *Observed and calculated structure factors of clinoclase*, $Cu_3AsO_4(OH)_3$.

h	k	l	F_{obs}	F_{calc}
0	0	2	102.3300	112.1871
0	0	4	178.3400	221.7947
0	0	6	99.0600	88.4909
0	0	8	102.5600	95.0014
0	0	10	58.1700	61.2093
0	0	12	69.8300	74.2130
0	0	14	56.4600	53.7680
1	0	-14	38.6700	25.3182
1	0	-12	0	3.1985
1	0	-10	133.9600	161.1996
1	0	-8	176.2500	211.1493
1	0	-6	191.5100	235.7696
1	0	-2	9.9400	1.7254
1	0	0	51.4200	57.8929
1	0	2	53.8500	46.1592
1	0	6	82.5400	77.7082
1	0	8	54.3400	48.0672
1	0	10	61.4900	66.7633
1	0	12	97.1100	101.8600
1	0	14	25.7000	23.0883
2	0	-14	128.2100	146.8240
2	0	-12	53.7000	53.2117
2	0	-10	11.0800	11.1105
2	0	-8	24.6800	22.9295
2	0	-6	148.7300	152.9650
2	0	-4	167.1700	185.0011
2	0	-2	78.9400	77.4330
2	0	2	106.5100	110.2885
2	0	4	46.0500	34.8624
2	0	6	154.4700	186.6779
2	0	8	89.1600	96.4507
2	0	10	14.2300	12.4742
2	0	12	14.5600	12.1483
3	0	-14	102.6200	108.1266
3	0	-12	33.1000	23.7795
3	0	-10	106.2200	128.4474
3	0	-8	109.1100	113.9539
3	0	-6	87.6300	85.1972
3	0	-4	116.8700	119.5500
3	0	-2	81.5000	81.9598
3	0	0	126.1000	118.1216
3	0	2	119.6500	135.4671
3	0	4	0	3.4556
3	0	6	40.9700	30.2989
3	0	8	81.8000	96.4208
3	0	10	43.4300	48.4978
4	0	-14	73.2600	73.7060
4	0	-12	41.6700	37.7232
4	0	-10	45.7200	41.3241
4	0	-8	40.1300	37.2020
4	0	-6	83.3400	81.8443
4	0	-4	24.3400	21.3481
4	0	-2	58.0600	50.2776
4	0	0	35.6100	27.6138
4	0	2	165.7900	177.7615
4	0	4	83.0800	84.1131
4	0	6	108.7100	142.9205
4	0	8	12.5800	7.3819
4	0	10	17.4900	13.2662
4	0	12	52.0700	58.2021
5	0	-14	54.8400	57.5486
5	0	-12	29.7200	21.2457
5	0	-10	13.4000	9.3394
5	0	-8	47.8500	52.2690
5	0	-6	98.2800	101.9746
5	0	-4	61.4200	60.7665
5	0	-2	113.4400	112.3530
5	0	0	150.0600	155.7254
5	0	2	11.4000	5.3964
5	0	4	124.2700	138.3747
5	0	6	25.2000	23.7442
5	0	8	45.0200	48.4635
5	0	10	8.7900	7.4096
6	0	-12	78.9600	74.3090
6	0	-10	43.9400	35.1468
6	0	-8	66.4500	56.9097
6	0	-6	93.1100	100.5753
6	0	-4	75.1500	70.4276
6	0	-2	133.9500	150.5542
6	0	0	81.3100	83.0193
6	0	2	25.6100	18.6524
6	0	4	16.9700	17.5478
6	0	6	25.8500	20.4533
6	0	8	23.9700	24.1505
6	0	10	19.1300	21.0351
7	0	-12	25.5800	30.7832
7	0	-10	85.4300	86.5318
7	0	-8	25.5400	23.4458
7	0	-6	43.7900	35.7787
7	0	-4	15.5700	12.5618
7	0	-2	42.9300	27.1475
7	0	0	44.4700	37.7840
7	0	2	32.3300	30.8078
7	0	4	45.6300	39.9519
7	0	6	55.4600	56.4525
8	0	-10	27.1100	30.2693
8	0	-8	15.2900	6.0868
8	0	-6	86.5200	79.9055
8	0	-4	42.8300	35.7658
8	0	-2	44.1900	32.6085
8	0	0	100.3600	99.5772
8	0	2	90.2200	91.7522
8	0	4	43.8700	44.8181
9	0	-4	72.5200	93.5197
9	0	-2	50.9900	53.1905
9	0	0	22.9800	25.2824
0	1	1	0	5.4694
0	1	2	10.6100	1.6752
0	1	3	22.7400	28.3493
0	1	4	107.1600	89.6303
0	1	5	49.3800	28.9700
0	1	6	84.0900	52.9824
0	1	7	158.8000	121.1830
0	1	8	77.6400	65.7897
0	1	9	30.7900	25.8577
0	1	10	37.1900	28.4863
0	1	11	77.2500	77.6807
0	1	12	5.0800	5.1273
0	1	13	16.7400	13.7726
0	1	14	96.7400	82.9122
0	1	15	13.1600	14.3733
1	1	-15	28.8600	28.8178
1	1	-14	17.8900	17.3191
1	1	-13	58.0700	44.4567
1	1	-12	67.1200	61.2472
1	1	-11	12.6400	7.0908
1	1	-10	18.7300	15.2510
1	1	-9	29.9900	30.4878
1	1	-8	21.1100	14.8992
1	1	-7	25.2600	19.6156
1	1	-6	47.0800	35.7032
1	1	-5	67.3700	43.5278
1	1	-4	68.1400	54.9153
1	1	-3	49.6000	41.4614
1	1	-2	49.5100	36.1414
1	1	-1	66.0500	65.8044
1	1	0	8.7100	3.5711
1	1	1	87.7300	132.8294
1	1	2	51.9600	54.8840
1	1	3	47.8400	46.6475
1	1	4	37.7300	43.5729
1	1	5	73.5200	70.7739
1	1	6	102.3100	100.9621
1	1	7	31.9200	28.0796
1	1	8	114.8800	117.7891
1	1	9	0	7.2470
1	1	10	66.6600	75.3084
1	1	11	59.9800	64.7396
1	1	12	26.1200	26.5570
1	1	13	33.7600	29.3967
1	1	14	8.9200	11.4360
1	1	15	20.4700	27.7673
2	1	-15	39.9300	40.6812
2	1	-14	16.9200	11.8186
2	1	-13	23.2500	19.1800
2	1	-12	41.5700	33.8379
2	1	-11	14.0700	9.7125
2	1	-10	24.4500	21.0436
2	1	-9	22.9300	22.3242
2	1	-8	37.8000	31.4076
2	1	-7	89.0800	65.7735
2	1	-6	56.2100	40.5225
2	1	-5	46.6600	32.2087
2	1	-4	23.6100	27.2753
2	1	-3	63.8600	53.3773
2	1	-2	83.8700	82.5138
2	1	-1	57.7800	55.5342
2	1	1	60.2700	64.1781
2	1	2	24.1400	18.9451
2	1	3	71.9100	84.2370
2	1	4	96.3800	102.8550
2	1	5	91.8500	92.1365
2	1	6	10.7100	4.9829
2	1	7	114.1800	141.6846
2	1	8	62.3300	70.4905
2	1	9	7.1500	3.6381
2	1	10	36.8100	40.8345
2	1	11	49.6500	50.7885
2	1	12	45.9100	46.8562
2	1	13	38.5700	39.5588
2	1	14	52.1300	61.3839
3	1	-15	7.2800	5.6403
3	1	-14	16.7600	11.9069
3	1	-13	14.6400	15.8403
3	1	-12	24.3600	22.0364
3	1	-11	11.5600	11.9794
3	1	-10	101.8000	89.7654
3	1	-9	16.3500	5.4471
3	1	-8	40.3700	35.4153
3	1	-7	101.3700	87.1920
3	1	-6	143.8700	132.4315
3	1	-5	52.2100	34.6104
3	1	-4	66.2800	67.5309
3	1	-3	131.6200	144.0285
3	1	-2	18.7000	16.4341
3	1	-1	105.6000	97.8661
3	1	0	143.3900	174.6806
3	1	1	103.0400	118.8068
3	1	2	35.9000	34.9268
3	1	3	61.5900	67.9006
3	1	4	114.8500	142.2361
3	1	5	22.2400	19.7044
3	1	6	66.4800	72.1993
3	1	7	7.1200	6.5485
3	1	8	30.4600	33.7639
3	1	9	30.0800	31.9995
3	1	10	52.0600	59.7794
3	1	11	43.6200	45.0937
3	1	12	56.9800	61.0695
3	1	13	15.2500	13.3159
4	1	-15	11.0900	14.4831
4	1	-14	87.7000	76.9756
4	1	-13	73.7500	58.2583
4	1	-12	7.5300	6.2511
4	1	-11	88.0900	73.1486
4	1	-10	19.2500	18.6763
4	1	-9	42.7600	46.2841
4	1	-8	20.2800	18.6773
4	1	-7	133.1900	138.3569
4	1	-6	151.3400	152.7629
4	1	-5	33.2300	23.0271
4	1	-4	109.4900	109.4988
4	1	-3	29.7200	24.2059
4	1	-2	98.1700	85.2972
4	1	-1	17.1400	12.4037
4	1	0	136.7300	124.5511
4	1	1	87.2300	87.1986
4	1	2	65.1600	63.1742
4	1	3	53.7500	52.2586
4	1	4	17.6300	17.8018
4	1	5	49.9300	48.1370
4	1	6	78.7900	103.9677
4	1	7	53.4400	63.1853
4	1	8	62.1900	81.9174
4	1	9	47.0800	54.9428
4	1	10	27.5500	25.9151
4	1	11	7.5000	5.5841
4	1	12	21.3300	20.5155
5	1	-14	87.4700	80.3223
5	1	-13	40.7400	36.5037
5	1	-12	23.4200	22.3530
5	1	-11	13.1000	12.9110
5	1	-10	115.9900	121.5958
5	1	-9	23.1400	23.4318
5	1	-8	39.2100	39.2757
5	1	-7	88.0500	93.2388
5	1	-6	44.7100	41.9785
5	1	-5	16.8500	16.7864
5	1	-4	28.9300	24.8556
5	1	-3	107.6800	102.3459
5	1	-2	81.2300	71.9382
5	1	-1	64.8600	57.3239
5	1	0	44.9100	41.5204
5	1	1	0	3.1921
5	1	2	79.5400	84.1415
5	1	3	66.7000	72.9031
5	1	4	51.3900	52.8694
5	1	5	59.1300	67.6354
5	1	6	58.4500	62.3141
5	1	7	38.7400	45.5468
5	1	8	17.2700	15.0953
5	1	9	35.9000	36.1361
5	1	10	78.1400	84.8090
6	1	-13	82.3300	76.8939
6	1	-12	25.0700	22.6762
6	1	-11	23.2900	58.0218
6	1	-10	33.3700	27.3976
6	1	-9	32.0400	28.7547
6	1	-8	13.2600	4.1260
6	1	-7	75.7100	72.6102
6	1	-6	100.1500	97.8451
6	1	-5	107.1700	93.1637
6	1	-4	48.5600	41.7855
6	1	-3	16.9600	8.4926
6	1	-2	0	.8970
6	1	-1	99.1900	86.1108
6	1	0	94.5600	87.7006
6	1	1	27.8600	26.3469
6	1	2	104.4000	134.5577
6	1	3	13.8100	13.0292
6	1	4	17.7200	19.0833
6	1	5	35.3800	47.6949
6	1	6	94.4600	115.4008
6	1	7	40.4500	43.7881
6	1	8	47.0100	47.4354
6	1	9	62.4400	71.4138
7	1	-12	13.7700	16.9081
7	1	-11	41.5600	35.4702
7	1	-10	56.2700	46.4922
7	1	-9	63.6300	47.7491
7	1	-8	76.9600	65.5176
7	1	-7	0	1.2507
7	1	-6	42.1400	28.4320
7	1	-5	8.1500	6.9199
7	1	-4	87.3100	76.9693
7	1	-3	15.2200	13.4584
7	1	-2	96.2000	92.3318
7	1	-1	91.8500	87.5313
7	1	0	11.8100	7.7184
7	1	1	38.8100	34.5447
7	1	2	13.1000	13.8723
7	1	3	55.3800	64.6793
7	1	4	7.4300	5.6309
7	1	5	39.1000	43.9914
7	1	6	60.5800	70.2631
7	1	7	14.0000	14.8891
7	1	8	11.5200	13.8193
8	1	-10	19.7600	21.2576
8	1	-9	32.9700	29.2136
8	1	-8	27.4800	21.9797
8	1	-7	59.1000	47.4743
8	1	-6	14.9000	12.9138
8	1	-5	106.4000	80.6803
8	1	-4	63.8600	48.7849
8	1	-3	0	1.2601
8	1	-2	87.7700	76.3556
8	1	-1	48.4800	44.5730
8	1	0	57.3300	55.0287
8	1	1	5.3100	3.4664
8	1	2	61.0300	62.1200
8	1	3	20.7500	16.7920
8	1	4	3.4100	1.3641
8	1	5	30.1500	41.4833
9	1	-6	19.8100	21.6906
9	1	-5	8.7800	9.2425
9	1	-4	38.5200	37.8924
9	1	-3	15.6000	13.7469
9	1	-2	8.8400	6.7259
9	1	-1	44.6300	44.8790
0	2	2	8.6600	3.8050
0	2	3	130.8200	157.4199
0	2	4	27.3600	11.6475
0	2	5	70.4600	63.9241
0	2	6	31.6900	25.9945
0	2	7	226.6200	252.0437
0	2	8	29.0000	23.5388
0	2	9	89.1000	79.9922
0	2	10	21.0500	22.4263
0	2	11	68.5400	63.2180
0	2	12	29.6400	27.8890
0	2	13	118.5900	112.3459
0	2	14	24.3600	23.2903
0	2	15	48.8600	66.3306
1	2	-15	54.2300	59.2570
1	2	-14	0	6.3908
1	2	-13	66.3100	64.2346
1	2	-12	29.5100	29.5428
1	2	-11	98.7500	107.2006
1	2	-10	34.4400	29.7147
1	2	-9	28.9700	23.3117
1	2	-8	93.5600	72.8014
1	2	-7	81.3200	66.4883
1	2	-6	0	6.2851
1	2	-5	30.5300	26.3318
1	2	-4	74.3000	65.6649
1	2	-3	182.8100	236.6669
1	2	0	34.0100	38.0527
1	2	2	20.2300	14.9752
1	2	3	121.1800	136.3976
1	2	4	50.7300	48.2621
1	2	5	70.1200	63.5774
1	2	6	14.1400	3.0431
1	2	7	18.8700	14.0012
1	2	8	51.9900	48.7356
1	2	9	106.6500	111.6615
1	2	10	0	7.1132
1	2	11	59.0300	58.7141
1	2	12	26.2400	20.8481
1	2	13	20.3200	18.9448
2	2	-15	7.4700	9.4414
2	2	-14	40.2400	32.9547
2	2	-13	93.5400	95.1334
2	2	-12	44.5400	38.4343
2	2	-11	125.4800	160.2659
2	2	-10	0	5.4386
2	2	-9	63.8600	63.9636
2	2	-8	14.5800	11.8879
2	2	-7	230.8400	267.7278
2	2	-6	58.3000	48.8963
2	2	-5	45.1300	33.2279
2	2	-4	63.2800	52.5978
2	2	-3	17.6200	21.6909
2	2	-2	0	.1953
2	2	-1	10.2900	15.7436
2	2	0	29.2500	30.8065
2	2	2	68.5300	51.2979
2	2	3	62.1900	54.8724
2	2	4	26.5200	24.9849
2	2	5	71.9000	64.7455
2	2	6	29.7100	18.1096
2	2	7	42.0000	35.9719
2	2	8	25.4400	23.5546
2	2	9	96.2600	107.5203
2	2	10	0	1.3136
2	2	11	43.8900	45.8249
2	2	12	17.6200	16.2629
2	2	13	104.6200	126.8765
2	2	14	14.3700	16.1964
3	2	-15	59.0600	74.1904
3	2	-14	30.9000	27.6246
3	2	-13	95.4900	88.0056
3	2	-12	0	4.7600
3	2	-11	38.9800	37.7876
3	2	-10	31.7700	29.0016
3	2	-9	0	1.7019
3	2	-8	26.2000	20.7586
3	2	-7	99.6500	91.1568
3	2	-6	10.4100	9.5053
3	2	-5	37.4900	31.5524
3	2	-4	16.0700	11.7348
3	2	-3	99.8300	114.0460
3	2	-2	80.0400	76.3240
3	2	-1	62.6400	57.4030
3	2	0	14.9000	15.6339
3	2	1	65.6700	56.3953
3	2	2	35.4700	31.2100
3	2	3	79.2800	85.8032
3	2	4	9.1900	10.0852
3	2	5	134.2500	180.6409
3	2	6	27.8400	28.3501
3	2	7	56.5200	68.9524
3	2	8	27.9400	20.6558
3	2	9	78.4000	88.4285
3	2	10	12.3900	11.6684
3	2	11	42.4600	38.7714
3	2	12	19.9800	18.6178
3	2	13	7.1300	3.4560
4	2	-14	8.6200	4.7713
4	2	-13	72.8500	66.0957
4	2	-12	0	4.2690
4	2	-11	80.5900	74.7769
4	2	-10	27.5700	26.7863
4	2	-9	9.8100	6.1389
4	2	-8	41.7100	38.0466
4	2	-7	60.9100	61.7395
4	2	-6	57.8800	52.0551
4	2	-5	115.9600	118.7207
4	2	-4	15.5200	12.4312
4	2	-3	75.6800	64.0207
4	2	-2	14.3800	10.1689
4	2	-1	125.3100	139.7506
4	2	0	17.0600	15.8404
4	2	1	54.7500	43.8074
4	2	2	42.1300	36.9537
4	2	3	43.5900	40.1406
4	2	4	32.6000	35.0986
4	2	5	61.0800	72.5224
4	2	6	12.1700	5.4415
4	2	7	38.4400	42.4809
4	2	8	26.3300	21.7048
4	2	9	67.1300	68.9970
4	2	10	19.1300	18.8452
4	2	11	39.9700	41.3226
4	2	12	11.8400	13.0488
5	2	-14	10.7300	14.1212
5	2	-13	0	3.6522
5	2	-12	23.3500	18.7313
5	2	-11	40.3700	31.0876
5	2	-10	13.7300	1.5563
5	2	-9	44.6900	43.2085
5	2	-8	19.3800	18.3982
5	2	-7	34.3100	40.9791
5	2	-6	24.4100	17.3974
5	2	-5	0	3.8951
5	2	-4	0	8.9219
5	2	-3	72.4800	68.6069
5	2	-2	38.0500	36.7929
5	2	-1	68.3900	62.2608
5	2	0	19.6800	15.5483
5	2	1	88.4100	93.3790
5	2	2	38.6400	37.6550
5	2	3	36.6800	40.7734
5	2	4	23.2500	19.7878
5	2	5	47.7400	48.0489
5	2	6	18.7900	17.4460
5	2	7	34.7500	39.3962
5	2	8	16.0100	21.4998
5	2	9	8.5000	10.2766
5	2	10	0	1.7307
5	2	11	27.7200	31.8752
6	2	-12	6.3100	1.1226
6	2	-11	9.0600	6.3528
6	2	-10	23.3900	25.6782
6	2	-9	102.9600	100.8136
6	2	-8	0	1.4126
6	2	-7	32.7300	29.4603
6	2	-6	10.4500	6.9403
6	2	-5	84.7700	88.8767
6	2	-4	14.7400	13.8060
6	2	-3	13.9500	4.6814
6	2	-2	29.6800	17.4162
6	2	-1	48.5000	56.2799
6	2	0	0	10.2478
6	2	1	60.7900	70.1307
6	2	2	9.6500	6.6040
6	2	3	24.0800	28.1772
6	2	4	0	1.8877
6	2	5	50.9100	51.2716
6	2	6	0	.4162
6	2	7	51.0500	47.3677

Table 2 (*cont.*)

h	k	l	F_{obs}	F_{calc}
6	2	8	20.2600	23.3467
6	2	9	30.6700	37.1648
7	2	-11	30.0700	25.2574
7	2	-10	34.1300	31.0161
7	2	-9	7.8600	8.6051
7	2	-8	15.2000	10.9431
7	2	-7	101.7800	92.9368
7	2	-6	0	2.7171
7	2	-5	48.8700	35.4405
7	2	-4	0	9.2421
7	2	-3	102.2200	83.9493
7	2	-2	17.8500	13.0496
7	2	-1	0	.3381
7	2	0	0	10.0472
7	2	1	0	1.6518
7	2	2	33.4300	34.2369
7	2	3	46.7100	46.1398
7	2	4	0	5.8604
7	2	5	52.4400	56.0447
7	2	6	13.5900	14.0674
7	2	7	27.4100	36.8742
8	2	-9	59.3600	72.0626
8	2	-8	12.8600	10.9917
8	2	-7	33.5900	33.4604
8	2	-6	26.1200	24.7485
8	2	-5	34.8600	37.0772
8	2	-4	11.4900	12.5596
8	2	-3	20.3400	17.6322
8	2	-2	0	1.4403
8	2	-1	53.6200	54.2144
8	2	0	0	2.4245
8	2	1	42.9700	44.7455
8	2	2	19.4600	18.6211
8	2	3	16.5000	19.1706
8	2	4	15.1400	16.5120
9	2	-3	28.8100	42.2951
9	2	-2	16.7200	22.0841
0	3	1	0	15.4450
0	3	2	54.3200	66.0485
0	3	3	27.3100	22.1247
0	3	4	24.7700	11.4122
0	3	5	0	.8400
0	3	6	32.7300	31.0221
0	3	7	85.2000	88.8105
0	3	8	27.5580	19.1020
0	3	9	34.8100	36.9319
0	3	10	44.6100	44.1796
0	3	11	93.0100	101.8601
0	3	12	0	2.9631
0	3	13	0	4.7033
0	3	14	46.8400	44.2286
1	3	-13	26.2600	14.8893
1	3	-12	31.6000	27.5314
1	3	-11	22.1700	21.0705
1	3	-10	0	.4189
1	3	-9	17.7600	13.6842
1	3	-8	41.1400	35.7673
1	3	-7	20.2700	16.7226
1	3	-6	13.5400	10.7682
1	3	-5	0	4.5838
1	3	-4	27.9900	23.3560
1	3	-2	46.4000	41.3673
1	3	-1	66.9600	90.6388
1	3	0	45.1600	69.4115
1	3	1	76.1800	104.8665
1	3	2	60.3300	75.1839
1	3	3	82.3200	95.9190
1	3	4	72.4800	84.7147
1	3	5	74.9200	77.2227
1	3	6	82.5700	85.8098
1	3	7	0	2.4717
1	3	8	34.8800	34.6830
1	3	9	11.4900	7.4390
1	3	10	38.1100	30.5480
1	3	11	76.4800	76.6367
1	3	12	40.6700	37.9836
1	3	13	14.0500	9.1620
1	3	14	9.2900	5.9199
2	3	-14	21.0100	16.3805
2	3	-13	0	2.4134
2	3	-12	0	5.5418
2	3	-11	18.2300	17.6106
2	3	-10	14.5300	12.1735
2	3	-9	13.3700	11.7494
2	3	-8	38.5000	29.7906
2	3	-7	87.0500	95.5346
2	3	-6	50.2700	45.2295
2	3	-5	28.2600	17.2823
2	3	-4	87.0900	87.9351
2	3	-3	103.5100	116.4469
2	3	-2	48.4300	50.4168
2	3	-1	24.2000	21.3500
2	3	0	96.4200	141.9301
2	3	1	75.6900	88.9866
2	3	2	18.7700	15.9664
2	3	3	107.9700	130.5626
2	3	4	69.0900	53.8258
2	3	5	93.3400	115.3437
2	3	6	40.3800	40.7482
2	3	7	119.5200	167.0025
2	3	8	0	1.3672
2	3	9	26.6300	27.3247
2	3	10	35.0800	33.5155
2	3	11	42.4200	35.8874
2	3	12	28.9100	28.0240
2	3	13	39.1900	39.7158
3	3	-14	17.0800	16.8890
3	3	-13	32.4600	27.0239
3	3	-12	0	7.9539
3	3	-11	69.6000	64.0438
3	3	-10	58.8100	54.1131
3	3	-9	20.9200	20.1351
3	3	-8	30.7900	27.7815
3	3	-7	57.5400	56.7680
3	3	-6	72.1900	73.7614
3	3	-5	0	2.4461
3	3	-4	17.1300	12.4484
3	3	-2	47.8800	47.4284
3	3	-1	96.5100	112.9526
3	3	1	119.0700	168.7885
3	3	2	42.4300	39.4851
3	3	3	80.6000	85.4927
3	3	4	70.6000	87.9018
3	3	5	40.8800	38.0474
3	3	6	41.9500	39.9609
3	3	7	33.3300	37.2753
3	3	8	9.0900	6.0224
3	3	9	64.9500	72.8475
3	3	10	56.7200	50.9799
3	3	11	54.9100	58.0430
3	3	12	28.9500	26.9748
4	3	-14	27.3600	31.0201
4	3	-13	63.0400	60.5094
4	3	-12	33.0500	24.8632
4	3	-11	90.7800	87.6732
4	3	-10	9.6300	7.3350
4	3	-9	66.2700	65.0422
4	3	-8	30.9900	30.0325
4	3	-7	112.2300	158.7685
4	3	-6	54.9000	50.0413
4	3	-5	39.3300	30.6592
4	3	-4	67.6000	71.5132
4	3	-3	24.0900	16.0207
4	3	-2	73.8000	71.4180
4	3	-1	51.2500	40.7668
4	3	0	101.8400	108.1701
4	3	1	126.4100	154.7032
4	3	2	62.2900	62.9820
4	3	3	49.9200	46.3470
4	3	4	32.1900	32.2892
4	3	5	60.5900	62.3850
4	3	6	54.9300	63.8740
4	3	7	74.9800	86.7059
4	3	8	26.8100	23.8805
4	3	9	69.7200	66.5404
4	3	10	15.4200	12.7457
4	3	11	7.7400	2.3069
5	3	-13	23.4200	21.2686
5	3	-12	0	2.6722
5	3	-11	30.4500	25.4842
5	3	-10	54.2800	58.1012
5	3	-9	65.0000	59.3099
5	3	-8	18.6500	15.2414
5	3	-7	88.2700	96.0333
5	3	-6	41.8100	42.7954
5	3	-5	57.5600	60.5992
5	3	-4	47.9900	45.8584
5	3	-3	112.5100	128.2316
5	3	-2	18.9700	11.7101
5	3	-1	71.4600	72.3010
5	3	0	0	5.5207
5	3	1	31.4900	25.4631
5	3	2	13.3700	9.3332
5	3	3	88.4800	111.0475
5	3	4	31.2000	29.3759
5	3	5	83.7900	113.2024
5	3	6	48.2000	45.7797
5	3	7	23.1100	19.9617
5	3	8	34.4600	28.0960
5	3	9	59.3600	58.1595
5	3	10	34.6100	40.2553
6	3	-12	13.2900	12.6131
6	3	-11	77.5700	69.6710
6	3	-10	12.3600	7.2108
6	3	-9	32.2000	21.8929
6	3	-8	0	2.9794
6	3	-7	96.8300	77.3989
6	3	-6	36.4000	24.0441
6	3	-5	91.5000	98.4935
6	3	-4	60.4800	58.4475
6	3	-3	20.3600	16.1613
6	3	-2	15.8300	9.0743
6	3	-1	98.8700	116.4631
6	3	0	57.0600	44.3224
6	3	1	64.5600	74.1399
6	3	2	71.9800	79.1945
6	3	3	11.9500	7.5940
6	3	4	8.0000	11.7219
6	3	5	40.8600	40.1970
6	3	6	77.1300	72.4865
6	3	7	65.1100	68.1712
6	3	8	19.7200	14.3893
7	3	-10	30.2300	29.5352
7	3	-9	92.1800	93.1970
7	3	-8	34.1800	29.4321
7	3	-7	30.0800	25.3793
7	3	-6	20.5000	15.8030
7	3	-5	42.1500	36.5136
7	3	-3	20.5500	11.2507
7	3	-2	31.2900	21.2487
7	3	-1	90.5600	106.2071
7	3	0	62.5900	58.1445
7	3	1	46.5400	50.4048
7	3	2	23.9200	13.7389
7	3	3	87.2700	96.7602
7	3	4	18.9100	13.9051
7	3	5	61.6900	68.3723
7	3	6	29.5900	27.7991
8	3	-7	43.1100	43.0723
8	3	-6	21.3800	22.2036
8	3	-5	111.7400	106.9505
8	3	-4	17.4400	15.6512
8	3	-3	0	4.8356
8	3	-2	33.6900	38.4344
8	3	-1	33.7400	41.1143
8	3	0	33.2900	28.6107
8	3	1	10.3800	8.0875
8	3	2	50.9000	50.4278
0	4	1	42.9000	70.5799
0	4	2	43.3900	52.4368
0	4	3	56.1100	58.2667
0	4	4	125.9600	156.9453
0	4	5	41.6900	44.3908
0	4	6	65.3100	60.5689
0	4	7	64.3700	68.9876
0	4	8	47.0700	47.4228
0	4	9	0	.8093
0	4	10	24.4000	18.0708
0	4	11	25.6400	21.0888
0	4	12	55.7600	55.7403
0	4	13	23.7800	22.9806
1	4	-13	15.3800	14.1683
1	4	-12	11.5800	8.7418
1	4	-11	68.8100	67.1504
1	4	-10	93.9800	119.4459
1	4	-9	28.8600	25.2258
1	4	-8	98.3900	112.4898
1	4	-7	20.2100	17.8829
1	4	-6	103.9500	112.2868
1	4	-5	51.8800	48.4299
1	4	-4	118.3100	137.4667
1	4	-3	92.8100	108.9377
1	4	-2	24.7600	25.6490
1	4	-1	30.6700	35.8954
1	4	0	17.0300	8.4818
1	4	1	36.8800	43.9838
1	4	2	26.2300	25.6482
1	4	4	109.4800	126.3512
1	4	5	98.4800	99.2163
1	4	6	47.0900	44.5436
1	4	7	38.0200	43.3616
1	4	8	33.3200	38.9508
1	4	9	51.6500	52.8215
1	4	10	62.6100	65.7441
1	4	11	45.2900	46.8667
1	4	12	61.0500	70.8977
1	4	13	5.3300	5.1247
2	4	-13	38.9600	42.8899
2	4	-12	33.9900	27.0046
2	4	-11	45.8800	41.1562
2	4	-10	38.1900	30.6988
2	4	-9	28.1100	19.3404
2	4	-8	9.7800	2.5517
2	4	-7	43.0600	38.4006
2	4	-6	88.6600	89.9615
2	4	-5	24.1500	15.5761
2	4	-4	108.6200	138.0393
2	4	-3	49.2500	49.5915
2	4	-2	55.8200	68.2464
2	4	-1	26.2700	20.9445
2	4	0	110.4100	155.381[illegible]
2	4	1	73.7800	93.7662
2	4	2	73.4100	91.0648
2	4	3	11.1900	13.5298
2	4	4	15.9300	5.9426
2	4	5	47.7300	52.9475
2	4	6	76.7500	93.5172
2	4	7	31.9800	36.2648
2	4	8	58.2600	65.7280
2	4	9	24.6600	22.0724
2	4	10	33.9800	31.8000
2	4	11	23.6100	26.1012
3	4	-13	6.9000	7.3638
3	4	-12	11.2900	12.0417
3	4	-11	7.7100	5.1149
3	4	-10	99.9100	122.3597
3	4	-9	35.5500	33.4930
3	4	-8	70.1900	73.6204
3	4	-7	48.0900	55.9585
3	4	-6	41.8900	42.3160
3	4	-5	26.5900	21.6596
3	4	-4	81.3600	84.5245
3	4	-3	55.8000	54.9195
3	4	-2	64.4900	68.5542
3	4	-1	14.3400	8.6665
3	4	0	26.5400	19.3495
3	4	1	19.4900	16.7322
3	4	2	55.9600	61.5513
3	4	3	11.0100	1.4340
3	4	4	30.8100	32.5216
3	4	5	68.0800	68.1239
3	4	6	11.2400	3.7552
3	4	7	29.8000	35.7722
3	4	8	56.3100	67.3680
3	4	9	27.4500	22.7405
3	4	10	35.2900	36.9019
3	4	11	19.4300	20.7382
4	4	-13	25.7200	30.3505
4	4	-12	34.9600	32.9430
4	4	-11	24.0500	23.4858
4	4	-10	26.3900	22.0166
4	4	-9	18.6600	5.9245
4	4	-8	26.7400	21.3496
4	4	-7	0	3.6143
4	4	-6	48.9300	43.3968
4	4	-5	0	10.4414
4	4	-4	0	2.1819
4	4	-3	57.3500	66.4247
4	4	-2	44.8900	40.1588
4	4	-1	23.6900	14.3792
4	4	0	31.2000	26.2579
4	4	1	58.5400	54.1112
4	4	2	102.3200	111.4807
4	4	3	17.0000	5.3986
4	4	4	31.8300	26.2895
4	4	5	9.5200	4.0068
4	4	6	69.4900	80.1315
4	4	7	8.5300	1.0673
4	4	8	16.0500	7.4423
4	4	9	25.6900	30.0120
4	4	10	24.2500	23.3950
5	4	-12	11.8700	4.0231
5	4	-11	32.3900	28.1332
5	4	-10	0	.9139
5	4	-9	52.4000	46.9163
5	4	-8	31.4800	22.4837
5	4	-7	56.4900	47.2270
5	4	-6	57.9800	51.2804
5	4	-5	17.3600	13.9637
5	4	-4	62.5400	67.1448
5	4	-3	25.7300	20.1492
5	4	-2	61.2100	55.0317
5	4	-1	34.2600	32.1378
5	4	0	74.3900	81.0061
5	4	1	34.4100	32.5337
5	4	2	22.0400	18.9122
5	4	3	0	.6985
5	4	4	72.4000	71.9069
5	4	5	16.3000	7.5044
5	4	6	22.7000	17.9382
5	4	7	9.8800	7.4575
5	4	8	49.4600	46.1702
5	4	9	37.1700	43.2392
6	4	-10	18.4900	6.6337
6	4	-9	52.6700	50.3110
6	4	-8	54.1400	46.5268
6	4	-7	20.1700	12.6515
6	4	-6	61.1300	50.3616
6	4	-5	21.8500	13.9951
6	4	-4	59.7400	46.3459
6	4	-3	0	3.1168
6	4	-2	95.2200	81.9815
6	4	-1	35.6300	24.5505
6	4	0	62.3300	46.8363
6	4	1	45.1200	50.9511
6	4	2	54.1100	38.2476
6	4	3	25.5300	24.1569
6	4	4	30.5100	20.8795
6	4	5	7.7100	6.2743
6	4	6	30.0000	29.5619
6	4	7	8.5800	7.2422
7	4	-9	15.9400	15.9303
7	4	-8	20.4700	15.4617
7	4	-7	0	2.4942
7	4	-6	42.4000	39.1476
7	4	-5	61.6200	55.5605
7	4	-4	11.2700	8.5781
7	4	-3	19.6100	14.9573
7	4	-2	31.1400	24.9783
7	4	-1	12.2800	12.0135
7	4	0	27.6200	20.5550
7	4	1	10.1100	7.1237
7	4	2	23.7400	19.2614
7	4	3	36.5700	31.1442
7	4	4	35.2300	34.1223
7	4	5	28.8500	36.3511
8	4	-5	11.8200	13.1036
8	4	-4	36.4800	39.4534
8	4	-3	6.9700	4.6990
8	4	-2	14.7300	11.2924
8	4	-1	26.6000	31.9680
8	4	0	45.8900	62.9725

In the Cu(1)–Cu(2) dimer, the shared edge, OH(3)–OH(3) (2·59 Å) is much shorter than the unshared edges, which average 2·81 Å. The Cu(1)–Cu(2) distance within the dimer is 2·984 Å and the coordination planes around Cu(1) and Cu(2) make an angle of about 173° with each other. These dimers polymerize to form an infinite chain, running parallel to the *c* axis, by sharing two OH(1) groups with two adjacent dimers. The equatorial planes of the dimers lie zigzag, roughly parallel to (100). The edges of two adjacent dimers, namely, OH(3)–OH(1) and OH(1)–O(2) make an angle of 61·1° with each other within the dimeric chain (Fig. 5).

Within the isolated Cu(3)–Cu(3) dimer, the shared edge, O(1)–O(1) (2·52 Å) is much shorter than the unshared edges, which average 2·89 Å. The Cu(3)–Cu(3) distance, 3·127 Å is considerably longer than the corresponding distance in the Cu(1)–Cu(2) dimer.

The arsenate group

The tetrahedral arsenate group deviates considerably from regularity. The As–O distances may be grouped into two classes, namely, As–O(1), As–O(3) averaging 1·73 Å and As–O(2), As–O(4) averaging 1·68 Å. The difference in these two sets of bond lengths ($\Delta/\sigma = 2{\cdot}5$) is probably significant. Qurashi & Barnes (1963) have

Table 3. *Interatomic distances and angles in clinoclase,* $Cu_3AsO_4(OH)_3$

(I)	x, y, z
(II)	$-x, -y, -z$
(III)	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
(IV)	$x, \frac{1}{2}-y, \frac{1}{2}+z$
(V)	$1+x, y, z$
(VI)	$1-x, 1-y, -z$
(VII)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
(VIII)	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(IX)	$x, -1+y, z$
(X)	$1+x, -1+y, z$
(XI)	$1-x, 1-y, 1-z$
(XII)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$
(XIII)	$1+(1-x), -\frac{1}{2}+y, \frac{1}{2}-z$
(XIV)	$-1+x, y, z$

Within the Cu(1) polyhedron

Cu(1)(I)–OH(1)(I)	1·913 Å	OH(1)–Cu(1)(I)–O(2)(VIII)	91·1°
–O(2)(VIII)	1·969	O(2)(VIII)–Cu(1)(I)–OH(2)(VII)	92·7
–OH(2)(VII)	1·906	OH(2)(VII)–Cu(1)(I)–O(3)(VII)	81·2
–O(3)(VII)	2·066	O(3)(VII)–Cu(1)(I)–OH(1)(I)	94·1
–O(4)(I)	2·310	O(4)(I)–Cu(1)(I)–OH(1)(I)	89·4
–OH(3)(V)	2·842	O(4)(I)–Cu(1)(I)–O(2)(VIII)	113·6
OH(1)(I)–O(2)(VIII)	2·771	O(4)(I)–Cu(1)(I)–OH(2)(VII)	92·4
O(2)(VIII)–OH(2)(VII)	2·805	O(4)(I)–Cu(1)(I)–O(3)(VII)	84·0
OH(2)(VII)–O(3)(VII)	2·586	OH(3)(V)–Cu(1)(I)–OH(1)(I)	80·6
O(3)(VII)–OH(1)(I)	2·915	OH(3)(V)–Cu(1)(I)–O(2)(VIII)	82·1
O(4)(I)–OH(1)(I)	2·984	OH(3)(V)–Cu(1)(I)–OH(2)(VII)	96·3
O(4)(I)–O(2)(VII)	3·586	OH(3)(V)–Cu(1)(I)–O(3)(VII)	81·5
O(4)(I)–OH(2)(VII)	3·055	OH(1)(I)–Cu(1)(I)–OH(2)(VII)	174·8
O(4)(I)–O(3)(VII)	2·934	O(2)(VIII)–Cu(1)(I)–O(3)(VII)	161·7
OH(3)(V)–OH(1)(I)	3·156	O(4)(I)–Cu(1)(I)–OH(3)(V)	161·7
OH(3)(V)–O(2)(VIII)	3·227		
OH(3)(V)–OH(2)(VII)	3·593		
OH(3)(V)–O(3)(VII)	3·256		

Within the Cu(2) polyhedron

Cu(2)(I)–O(3)(VII)	1·990 Å	O(3)(VII)–Cu(2)(I)–OH(2)(VII)	82·1°
–OH(2)(VII)	1·949	OH(2)(VII)–Cu(2)(I)–OH(1)(XII)	92·2
–OH(1)(XII)	1·894	OH(1)(XII)–Cu(2)(I)–OH(3)(VII)	93·8
–OH(3)(VII)	1·934	OH(3)(VII)–Cu(2)(I)–O(3)(VII)	92·0
–O(2)(V)	2·513	O(2)(V)–Cu(2)(I)–O(3)(VII)	96·6
–O(4)(VII)	3·320	O(2)(V)–Cu(2)(I)–OH(2)(VII)	88·6
O(3)(VII)–OH(2)(VII)	2·586	O(2)(V)–Cu(2)(I)–OH(1)(XII)	88·9
OH(2)(VII)–OH(1)(XII)	2·769	O(2)(V)–Cu(2)(I)–OH(3)(VII)	92·1
OH(1)(XII)–OH(3)(VII)	2·795	O(3)(VII)–Cu(2)(I)–OH(1)(XII)	172·0
OH(3)(VII)–O(3)(VII)	2·822	OH(2)(VII)–Cu(2)(I)–OH(3)(VII)	174·0
O(2)(V)–O(3)(VII)	3·379	O(2)(V)–Cu(2)(I)–O(4)(VII)	136·8
O(2)(V)–OH(2)(VII)	3·142		
O(2)(V)–OH(1)(XII)	3·116		
O(2)(V)–OH(3)(VII)	3·227		

Within the Cu(3) polyhedron

Cu(3)(I)–O(1)(IV)	2·023 Å	O(1)(IV)–Cu(3)(I)–O(1)(VII)	77·6°
–O(1)(VII)	1·990	O(1)(VII)–Cu(3)(I)–O(4)(I)	93·5
–O(4)(I)	1·983	O(4)(I)–Cu(3)(I)–OH(3)(I)	93·3
–OH(3)(I)	1·901	OH(3)(I)–Cu(3)(I)–O(1)(IV)	97·4
–OH(2)(I)	2·296	OH(2)(I)–Cu(3)(I)–O(1)(IV)	104·8
OH(1)(I)	2·988	OH(2)(I)–Cu(3)(I)–O(1)(VII)	87·2
O(1)(IV)–O(1)(VII)	2·516	OH(2)(I)–Cu(3)(I)–O(4)(I)	99·3
O(1)(VII)–O(4)(I)	2·894	OH(2)(I)–Cu(3)(I)–OH(3)(I)	88·9
O(4)(I)–OH(3)(I)	2·824	O(1)(IV)–Cu(3)(I)–O(4)(I)	153·7
OH(3)(I)–O(1)(IV)	2·948	O(1)(VII)–Cu(3)(I)–OH(3)(I)	172·6
OH(2)(I)–O(1)(IV)	3·427	OH(2)(I)–Cu(3)(I)–OH(1)(I)	147·4
OH(2)(I)–O(1)(VII)	2·964		
OH(2)(I)–O(4)(I)	3·268		
OH(2)(I)–OH(3)(I)	2·953		

Table 3 (*cont.*)

Within the $\mathrm{AsO_4}$ group			
As(I)–O(1)(I)	1·716 Å	O(1)(I)–As(I)–O(2)(I)	108·2°
–O(2)(I)	1·678	O(1)(I)–As(I)–O(3)(I)	105·9
–O(3)(I)	1·746	O(1)(I)–As(I)–O(4)(I)	110·3
–O(4)(I)	1·677	O(2)(I)–As(I)–O(3)(I)	108·2
O(1)(I)–O(2)(I)	2·750	O(2)(I)–As(I)–O(4)(I)	113·4
O(1)(I)–O(3)(I)	2·762	O(3)(I)–As(I)–O(4)(I)	110·5
O(1)(I)–O(4)(I)	2·785		
O(2)(I)–O(3)(I)	2·774		
O(2)(I)–O(4)(I)	2·804		
O(3)(I)–O(4)(I)	2·814		
Copper–copper distances			
Cu(1)(I)–Cu(2)(I)	2·984 Å	Cu(3)(I)–Cu(2)(VII)	3·376 Å
Cu(1)(I)–Cu(2)(XIII)	3·286	Cu(3)(I)–Cu(3)(XI)	3·127
Cu(2)(I)–Cu(3)(VII)	3·376		
Copper–arsenic distances			
As(I)–Cu(1)(VII)	3·226 Å	As(I)–Cu(3)(VIII)	3·268 Å
As(I)–Cu(3)(I)	3·132		
Hydrogen bond distances and angles			
OH(1)(I)–O(1)(VII)	2·752 Å*		
Cu(2)(IV)–OH(1)(I)–O(1)(VII)	117·0°	Cu(1)(I)–OH(1)(I)–Cu(2)(IV)	149·2°
O(1)(VII)–OH(1)(I)–Cu(1)(I)	93·1		
OH(2)(I)–O(3)(V)	2·804 Å		
O(3)(V)–OH(2)(I)–Cu(1)(I)	97·2°	Cu(1)(I)–OH(2)(I)–Cu(2)(I)	101·4°
O(3)(V)–OH(2)(I)–Cu(2)(I)	108·3	Cu(1)(I)–OH(2)(I)–Cu(3)(VIII)	115·8
O(3)(V)–OH(2)(I)–Cu(3)(VIII)	108·9	Cu(2)(I)–OH(2)(I)–Cu(3)(VIII)	122·2
OH(3)–O(2)(IV)	2·828 Å		
O(2)(IV)–OH(3)(I)–Cu(1)(XIV)	97·9°	Cu(1)(XIV)–OH(3)(I)–Cu(2)(VIII)	84·7°
O(2)(IV)–OH(3)(I)–Cu(2)(VIII)	101·0	Cu(1)(XIV)–OH(3)(I)–Cu(3)(I)	143·2
O(2)(IV)–OH(3)(I)–Cu(3)(I)	99·1	Cu(2)(VII)–OH(3)(I)–Cu(3)(I)	123·3

* See text.

suggested that in the $\mathrm{AsO_4}$ distorted tetrahedra of arsenates, bond lengths of about 1·64 ± 0·04 Å represent essentially covalent double bonds, while those of about 1·74 ± 0·03 Å represent covalent single bonds. It is most likely that As–O(2) and As–O(4) bonds in clinoclase possess considerable double bond character. The difference in the As–O bond lengths can be explained on the basis of bonding schemes of the oxygens concerned. Thus, O(1) and O(3) are involved in two further short Cu–O bonds, while O(2) and O(4) are involved in one short and one long Cu–O bond. It is interesting to note that the bonds with considerable double bond character, As–O(2) and As–O(4), subtend the largest angle (O(2)–As–O(4)), 113·4°, consistent with the largest bond-pair/bond-pair interaction.

The complex sheet structure

Two sets of Cu(1)–Cu(2) dimeric chains are arranged in a zigzag fashion with respect to each other in the unit cell. These chains sandwich between them isolated Cu(3)–Cu(3) dimers and $\mathrm{AsO_4}$ tetrahedra. The complex sheet structure thus formed runs parallel to the (100) plane. The first set of chains, occurring at $x \simeq 0{\cdot}2$, $y \simeq 0{\cdot}75$ in neighboring cells, are bonded to each other through the $\mathrm{AsO_4}$ tetrahedra and the Cu(3)-tetragonal pyramids. The $\mathrm{AsO_4}$ tetrahedron shares corners O(2), O(3) with two Cu(1)-coordination planes, while the Cu(3)-tetragonal pyramid shares corners OH(2), OH(3) with two Cu(2)-coordination planes, belonging to two adjacent dimeric chains (Fig. 4). The Cu(3)–Cu(3) dimers are connected to each other through $\mathrm{AsO_4}$ groups, sharing corners, O(1) and O(4). Two sets of dimeric chains, occurring at $x \simeq 0{\cdot}2$, $y \simeq 0{\cdot}75$ and $x \simeq 0{\cdot}8$, $y \simeq 0{\cdot}25$, are cross linked by the Cu(3)–Cu(3) dimeric groups, sharing one OH(3) corner each with two Cu(2)-coordination planes, belonging to two different dimeric chains (Fig. 5). The chains are further joined together by long Cu–O bonds between Cu(1) and O(4) (2·31 Å). The complex sheets are held together by long Cu–O bonds, namely Cu(1)–OH(3), 2·84 Å, Cu(2)–O(2), 2·51 Å, and a hydrogen bond O–H(2) $\cdots$ O(3), 2·80 Å (Fig. 3). These long bonds are naturally weak and the perfect (100) cleavage breaks just these bonds.

The hydrogen bonds

The infrared spectrum of clinoclase at the 3μ region consists of a sharp peak at 3530 cm^{-1} and a broad band, presumably due to superimposition of two separate peaks, at 3325 cm^{-1}. The sharp peak at 3530 cm^{-1}

indicates a practically free OH group, while the broad band at 3325 cm^{-1} indicates that the other two OH groups are hydrogen bonded.

The hydrogen bond between OH(3) and O(2) (O–H(3) · · · O(2) = 2·83 Å) binds two adjacent Cu(1)–Cu(2) dimers closer together, while that between OH(2) and O(3) (O–H(2) · · · O(3) = 2·80 Å) helps bind the complex sheets to each other. The distance between OH(1) and O(1) (2·75 Å) is a reasonable hydrogen bonding distance. However, if OH(1) is really hydrogen bonded to O(1), the configuration of the OH(1) oxygen would be highly distorted trigonal planar. In view of this fact, as well as the infrared evidence, it is suggested that the OH(1) group is virtually free. In contrast, all the three OH groups in the structure of cornetite, $Cu_3PO_4(OH)_3$ are involved in hydrogen bonding.

Discussion

The stereochemistry of the copper(II) ions in the structure of clinoclase, though essentially tetrahedral pyramidal, shows a transitional state between tetragonal bipyramidal on the one hand, as evidenced by a sixth ligand at a much greater distance, and a trigonal bipyramidal on the other, by means of a curvature of the coordination plane in a boat shape towards the fifth ligand. A similar stereochemistry of the copper(II) ions has previously been noted in the structure of

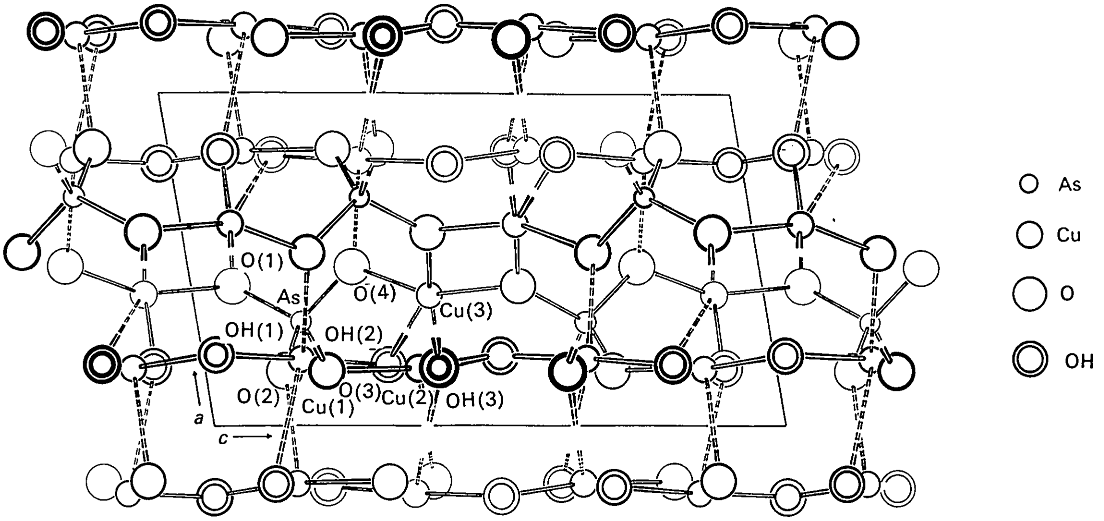

Fig. 3. A view of the clinoclase structure down the *b* axis, showing the complex sheet structure.

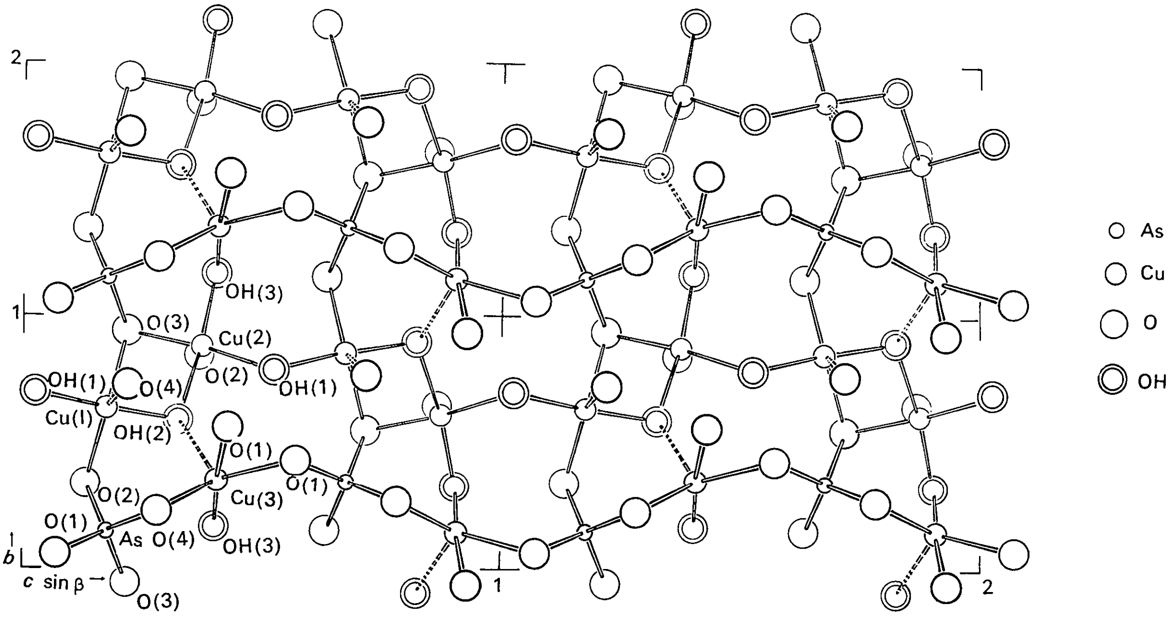

Fig. 4. A part of the complex sheet structure in clinoclase viewed down the *a* axis between $x=0$ and $\frac{1}{2}$, showing the linkage of the Cu(1)–Cu(2) dimeric chains through AsO_4 groups and Cu(3)-tetragonal pyramids.

cornetite, $Cu_3PO_4(OH)_3$ (Fehlmann, Ghose & Finney, 1964). Cornetite, however, possesses a three-dimensional network structure. In both of these structures, the cupric ions occur in two sets of dimers, one set of which polymerizes further into an infinite chain. The dimeric chain found in clinoclase is apparently a new type, while that found in cornetite is similar in principle to the chain found in euchroite, $Cu_2AsO_4(OH) . 3H_2O$ (Giuseppetti, 1963).

The tendency of the cupric ions to form isolated dimers by sharing an edge of the coordination plane or a pyramidal edge has been noted recently in a number of inorganic, as well as metal-organic, cupric complexes; *e.g.* libethenite, $Cu_2PO_4(OH)$ and olivenite, $Cu_2AsO_4(OH)$ (Heritsch, 1938, 1940; Walitzi, 1963), callaghanite, $Cu_2Mg_2CO_3(OH)_6 . 2H_2O$ (Brunton, Steinfink & Beck, 1962), dolerophanite, $CuOSO_4$ (Flügel-Kahler, 1963), $LiCuCl_3 . 2H_2O$ (Vossos, Fitzwater & Rundle, 1963), $KCuCl_3$ and NH_4CuCl_3 (Willet, Dwiggins, Kruh & Rundle, 1963), $Cu_2Cl_4(CH_3CN)_2$ and $Cu_3Cl_6(CH_3CN)_2$ (Willet & Rundle, 1964), acetylacetone-mono-(*o*-hydroxyanil) copper(II) (Barclay & Hoskins, 1963), anhydrous copper formate (Barclay & Kennard, 1961), *N*,*N'*-ethylenebis(salicylidemineiminato)copper(II) (Hall & Waters, 1960), copper bis-8-hydroxyquinoline (Bevan, Graddon & MacConnell, 1963), *etc.* The polymerization of the dimers to form an infinite chain is known so far in the structures of clinoclase, $Cu_3AsO_4(OH)_3$, cornetite, $Cu_3PO_4(OH)_3$ and euchroite, $Cu_2AsO_4(OH) . 3H_2O$.

The complex sheet structure found in clinoclase is a new type, in contrast to the simple distorted-octahedral sheet structures, found so far in basic cupric compounds (Ghose, 1963). The arsenate group forms an integral part of the sheet in clinoclase, while in erinite, $Cu_5(AsO_4)_2(OH)_4$ it binds the distorted octahedral sheets together into a three-dimensional network.

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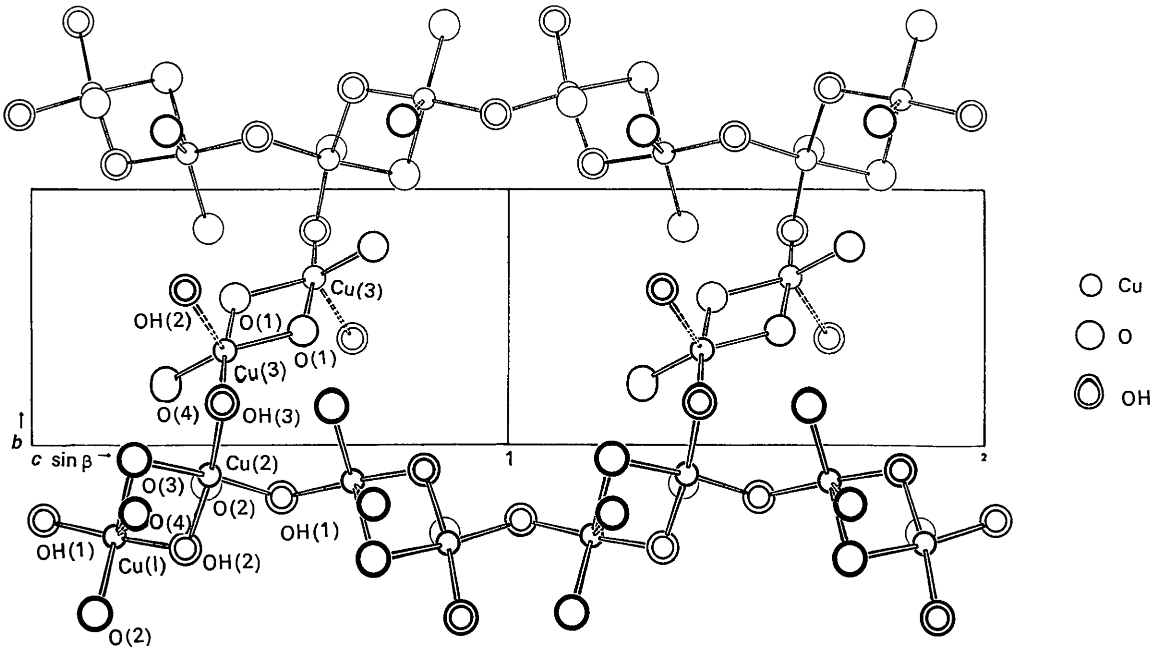

Fig. 5. A partial view of the clinoclase structure down the *a* axis, showing the cross-linkage of two Cu(1)–Cu(2) dimeric chains through Cu(3)–Cu(3) dimers.

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The Crystal Structure of γ-Dicalcium Silicate

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Least-squares analysis of three-dimensional single-crystal data confirms that γ-Ca_2SiO_4 is isostructural with olivine, Mg_2SiO_4. The relative positions of the SiO_4 tetrahedra and half the Ca atoms are similar to those in the β and α′ forms. The remaining Ca atoms are surrounded by corresponding tetrahedra but considerably displaced. The γ form hydrates less rapidly than the β and α′ forms because of the greater strength and uniformity of Ca–O bonding.

Introduction

The polymorphism of dicalcium silicate has been the subject of many investigations because of its importance to portland cement clinker and slag chemistry. Bredig (1950), Nurse (1952), Roy (1958), Smith, Majumdar & Ordway (1961) and others have agreed that four distinct crystalline modifications of Ca_2SiO_4 do exist. These forms, designated α, α′, β, and γ in order of decreasing temperatures of stability, exhibit complex equilibrium phase relations which are still not established beyond doubt. The presently accepted schematic free energy–temperature diagram (Smith, Majumdar & Ordway, 1961) is shown in Fig. 1.

Several authors discuss possible structure types for the various modifications and their interrelations. O'Daniel & Tscheischwili (1942) proposed the olivine-type structure for γ-Ca_2SiO_4 by its analogy with Na_2BeF_4. Greer (1932) apparently reached the same conclusion, from a study of $(Ca,Mg)_2SiO_4$ solid solutions. The α-Ca_2SiO_4 unit-cell dimensions were determined by Bredig (1950) and Douglas (1952) from the high temperature X-ray data of Van Valkenburg & McMurdie (1947), by showing an analogy with glaserite, $Na_3K(SO_4)_2$. The cell dimensions for the α′ form, based on analogy with the K_2SO_4 structure, were determined by Bredig (1950) from the data of Trömel and verified by Douglas (1952). Although similarities between the α′ and α forms were obvious from a com-

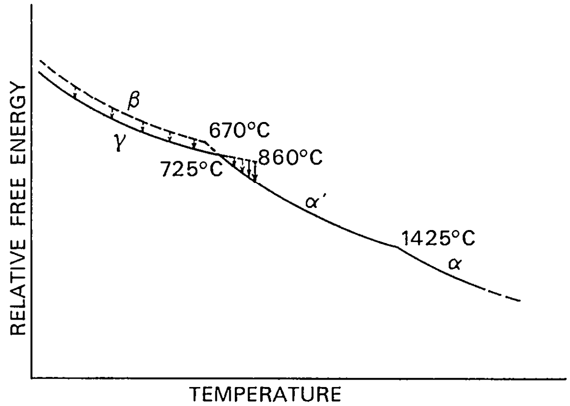

Fig. 1. The schematic free energy–temperature diagram for the polymorphs of Ca_2SiO_4. The solid lines indicate regions of apparent stability; the dotted lines, of apparent metastability.

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