

Table 2. Lattice constants of rare earth germanides, antimonides and bismuthides with anti-Th₃P₄ structure type

Germanides	
	<i>a</i>
La ₄ Ge ₃	9.3563 ± 0.0004 Å
Pr ₄ Ge ₃	9.153 ± 0.001
Antimonides	
La ₄ Sb ₃	9.648 ± 0.003
Ce ₄ Sb ₃	9.528 ± 0.002
Pr ₄ Sb ₃	9.458 ± 0.001
Nd ₄ Sb ₃	9.406 ± 0.001
Gd ₄ Sb ₃	9.224 ± 0.005*
Tb ₄ Sb ₃	9.159 ± 0.003
Dy ₄ Sb ₃	9.114 ± 0.001
Ho ₄ Sb ₃	9.072 ± 0.001
Yb ₄ Sb ₃	9.30†
Bismuthides	
La ₄ Bi ₃	9.786 ± 0.001
Ce ₄ Bi ₃	9.672 ± 0.001
Pr ₄ Bi ₃	9.611 ± 0.003
Nd ₄ Bi ₃	9.553 ± 0.001
Gd ₄ Bi ₃	9.383 ± 0.005*
	9.385 ± 0.002
Tb ₄ Bi ₃	9.321 ± 0.001

* Holtzberg, McGuire, Methfessel & Suits (1964).

† Bodnar & Steinfink (1965).

the Nelson–Riley extrapolation equation and the least-squares program by Gvildys (1965).

Fig. 1 shows a plot of the lattice constants of antimonides and bismuthides versus the trivalent ionic radii of the rare earth elements. All data except for Yb₄Sb₃ fall essentially on two straight lines, one for antimonides and one for bis-

muthides. The deviation for Yb₄Sb₃ may be explained by the occurrence of a partly two-valent Yb atom. Data for Eu compounds are missing, but the same deviations may be expected for these.

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Refinement of the crystal structure of euchroite, Cu₂(AsO₄)(OH) · 3H₂O. By J.J. FINNEY, *Department of Geological Engineering, Colorado School of Mines, Golden, Colorado, U.S.A.*

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Introduction

The structure of euchroite was determined by Giuseppetti (1963), using three-dimensional Patterson sections to determine the heavy atom positions, but was completed by means of electron density projections. As part of an overall study of the crystal chemistry of secondary copper minerals a three-dimensional refinement of this structure was considered necessary to portray the structure more accurately and to describe the complex hydrogen bonding which occurs in euchroite.

Experimental

Dr L.G. Berry kindly provided a few crystals of euchroite (USNM 470456) from the sample used in his original work (Berry, 1951). The crystal fragment used in this refinement had the dimensions 0.25 × 0.20 × 0.30 mm.

Euchroite is orthorhombic, space group *P*2₁2₁2₁. The unit-cell dimensions *a* = 10.063, *b* = 10.522 (both ± 0.010), *c* = 6.107 (± 0.005 Å) were obtained from precession films. The unit-cell contents are Cu₈(AsO₄)₄(OH)₄ · 12H₂O. The

density based on the above unit cell is calculated as 3.46 compared with the observed density of 3.389 reported by Giuseppetti.

Data were collected by means of multiple film pack equi-inclination Weissenberg photographs about the *a* and *c* axes with the use of Mo (*K*α) radiation. Intensities were estimated visually.

In each case the zero- and first-layer data were collected. Dr Giuseppetti supplied zero and unpublished upper-level data about the *b* axis taken with Cu *K*α radiation.

Both sets of data were corrected for absorption as well as Lorentz-polarization factors and were placed on an approximately equivalent relative scale by comparison of reflections common to the two sets of data. Absolute scaling was accomplished as a normal part of the least-squares refinement.

Refinement of the structure

The structure was refined with Giuseppetti's atomic positions as a starting point. A full-matrix least-squares program was used in the refinement modified after a program

in use at the Los Alamos Scientific Laboratory. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting system used was: $F_o \leq 60$, $w = 60/F_o$; $F_o \geq 90$, $w = F_o/90$; $60 \leq F_o \leq 90$, $w = 1.0$. A total of 33 positional parameters, 11 isotropic temperature factors and 7 scale factors were allowed to vary simultaneously. After six cycles variations of all parameters were less than the standard deviations and refinement was halted. At this point the overall R value was 0.090 considering only those reflections which were observed. A correlation matrix was calculated after the last cycle. Only five coefficients were found to have values in excess of 0.30 but all were less than 0.40.

The scattering factors employed throughout the refinement were those of Cromer, Larson & Waber (1963) used in five-parameter exponential form. The positional parameters, isotropic temperature factors and standard deviations are listed in Table 1. Table 2 is a list of bond lengths and angles. Giuseppetti's values are included in both tables for reference and his structure determination of euchroite is thus confirmed; the reader is referred to his paper for a description of the structure.

A list of structure factors for this refinement is available upon request.

Hydrogen bonding

The hydrogen bonding in euchroite is somewhat complex in that there are three H₂O atom sets and one OH atom set in the structure. All are involved in hydrogen bonding. Giuseppetti's choice as to which 'oxygen' set was to be assigned as OH is confirmed in light of the hydrogen bonding. Fig. 1 represents the distribution of hydrogen bonds. Atoms not involved in hydrogen bonding are included in this figure for reference. O(1), O(2) and O(6), H₂O molecules, are each

involved in three hydrogen bonds while O(7), hydroxyl, is involved in only one. O(6) however is bonded to two Cu atoms and thus the charge distribution around O(6) is not tetrahedral. However, the bonds O(6)-Cu(1) are 2.365 and 2.479 Å, that is, O(6) is not part of the four coplanar atoms of the Cu(1) polyhedron in which bonds are short. Also to be noted is that fact that the O(6)-O(1) hydrogen bond is longer, 3.052 Å than the other hydrogen bonds in the system.

Discussion

Compositionally, euchroite is a hydrated olivenite. In olivenite, essentially isostructural with libethenite, Cu₂(PO₄)(OH), and its arsenate analogue (Heritsch, 1938, 1940; Walitzi, 1963), both Cu(1), the cation of the polyhedral chain, and Cu(2), the cation of the isolated polyhedron in fivefold coordination, are linked to common oxygen atoms of the AsO₄ group. The same situation exists in euchroite with essentially the same disposition of the Cu(1)-As-Cu(2) atoms relative to each other. Pertinent bond lengths in euchroite are: Cu(1)-As 3.29 Å; Cu(2)-As 3.35 Å and Cu(1)-Cu(2) 3.01 Å. The angle Cu(1)-As-Cu(2) is 54.0°. In olivenite these lengths are: Cu(1)-As 3.33 Å; Cu(2)-As 3.30 Å and Cu(1)-Cu(2) 3.73 Å. The angle Cu(1)-As-Cu(2) is 68.5°. Fig. 2 shows the structural units for these two minerals. It is interesting to note that Cu(2) in olivenite has only five near neighbors and that Cu(2) in euchroite has five neighbors at distances up to 2.397 Å and one additional at a much greater distance, 2.793 Å, forming in effect a fivefold coordination polyhedron.

A comparison of the unit cells of olivenite and euchroite:

$$\begin{aligned} \text{olivenite: } a &= 8.21 \quad b = 8.59 \quad c = 5.94 \text{ \AA;} \\ \text{space group: } &P2_1nm \end{aligned}$$

Table 1. *Positional parameters and temperature factors for euchroite** (with standard deviations in parentheses)

Atom		x	y	z	B
Cu(1)	(F)	0.2431 (2)	0.0082 (3)	0.9698 (3)	0.83 (8)
	(G)	0.245	0.009	0.971	
Cu(2)	(F)	0.1993 (1)	0.2488 (2)	0.6660 (3)	0.90 (7)
	(G)	0.200	0.249	0.665	
As	(F)	0.3910 (2)	0.2358 (2)	0.2172 (3)	0.64 (6)
	(G)	0.390	0.236	0.217	
O(1) H ₂ O	(F)	0.7838 (11)	0.0862 (10)	0.3710 (18)	0.64 (38)
	(G)	0.787	0.082	0.365	
O(2) H ₂ O	(F)	0.0660 (13)	0.3107 (13)	0.2790 (25)	1.86 (49)
	(G)	0.071	0.307	0.283	
O(3)	(F)	0.0461 (10)	0.3183 (10)	0.8232 (17)	0.22 (34)
	(G)	0.045	0.320	0.818	
O(4)	(F)	0.3058 (13)	0.1860 (14)	0.0000 (21)	1.69 (50)
	(G)	0.309	0.180	0.004	
O(5)	(F)	0.3250 (12)	0.1665 (13)	0.4584 (20)	1.08 (43)
	(G)	0.320	0.178	0.454	
O(6) H ₂ O	(F)	0.0713 (10)	0.0511 (10)	0.2234 (20)	0.62 (36)
	(G)	0.067	0.053	0.225	
O(7) OH	(F)	0.1445 (10)	0.0676 (10)	0.7160 (20)	0.58 (35)
	(G)	0.147	0.067	0.713	
O(8)	(F)	0.3927 (11)	0.3883 (10)	0.2485 (21)	0.64 (39)
	(G)	0.389	0.389	0.247	

* (F) Present refinement. - (G) Giuseppetti (1963).

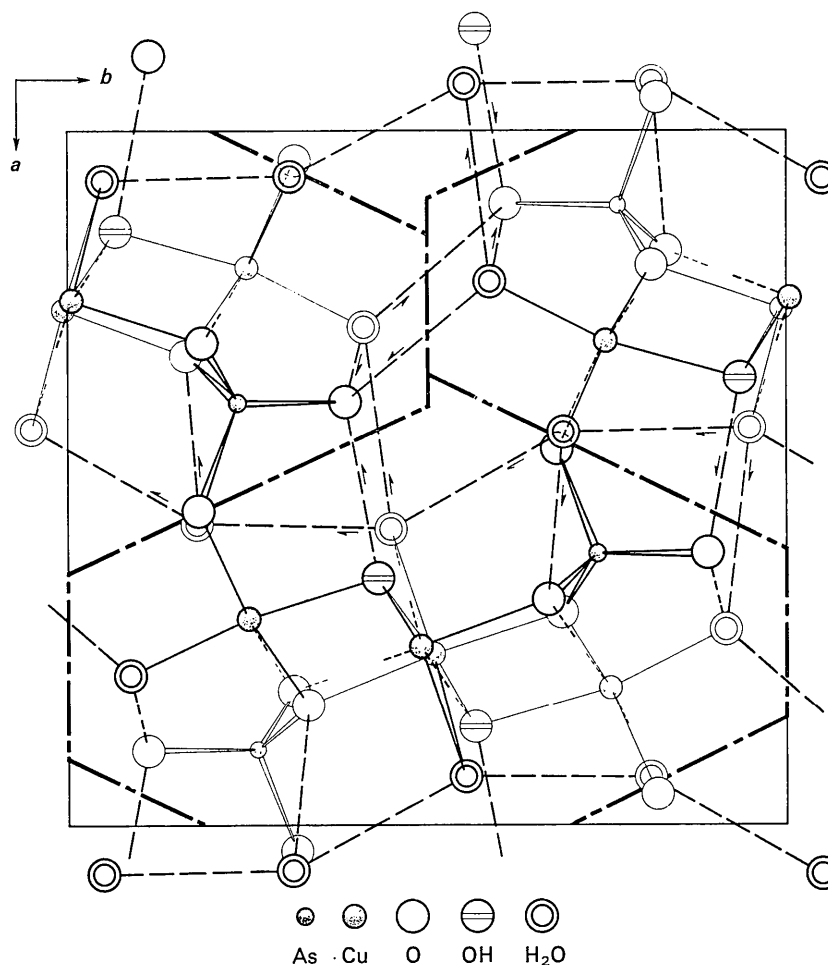


Fig. 1. The crystal structure of euchroite. Heavy alternating long-short-dashed lines indicate postulated cleavage in euchroite, long-dashed lines hydrogen bonds and short-dashed lines copper-oxygen bonds transecting unit-cell boundaries. Arrows along hydrogen bonds indicate hypothesized donor-receptor relationships.

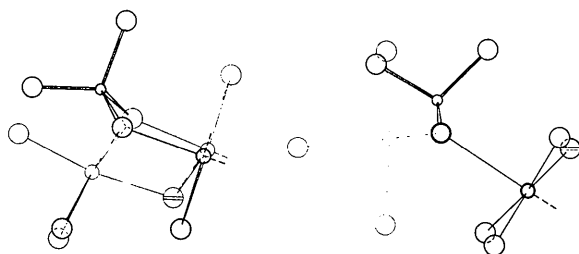


Fig. 2. Schematic representation of structural units of euchroite (left) and olivenite (right). Broad-lined circles in the right hand diagram indicate superimposed oxygen and copper atoms. Small circles are arsenic atoms, larger circles are copper atoms, large open circles are oxygen atoms and large circles with included double lines are hydroxyl groups. Water and oxygen are not differentiated.

euchroite: $a=10.063$ $b=10.522$ $c=6.107 \text{ \AA}$;
space group: $P2_12_12_1$

shows that the $a:b$ axial ratio, 0.956, is the same for both minerals. In addition, the c axis lengths are also nominally

the same. It appears that the structural unit mentioned previously (Fig. 2) is kept intact but rotated somewhat in the structural transition from olivenite to euchroite and that the addition of water to the structure takes place along a plane parallel to (001) enlarging the a and b axes but not the c axis. Euchroite therefore represents, not only compositionally but structurally as well, a hydrated olivenite.

In euchroite the refractive indices are $N_x=1.695$, $N_y=1.698$, $N_z=1.733$ where $X||c$, $Y||a$, $Z||b$. N_x and N_y lie in a plane parallel to the $a-c$ plane. The plane of O(3), O(4) and O(5) of the arsenate group and the plane of the Cu(1) polyhedral linkage also lie nearly parallel to this plane. In effect the structure is isotropic to light in this plane. The N_z value and optic sign (+) can be justified by considering that N_z vibrates parallel to the b axis and the shortest bond of the arsenate group, As-O(8), 1.615 Å, is also parallel to this direction. Additionally the structure parallel to the b axis is more densely packed, *i.e.* the light travels across the structural unit rather than along it.

Olivenite with indices: $N_x=1.772$, $N_y=1.810$, $N_z=1.863$, optic sign (+) and $X||b$, $Y||c$, $Z||a$ has higher indices than euchroite. The euchroite structure is an expanded and hence less densely packed olivenite owing to the presence of water

Table 2. *Interatomic distances and angles for euchroite*

Within the Cu(1) polyhedron			Within the Cu(2) polyhedron		
	(F)	(G)		(F)	(G)
Cu(1)–O(4)	1.983	1.92	Cu(2)–O(1)	1.946	1.99
–O(5)	1.963	2.08	–O(2)	2.795	2.74
–O(6)	2.365	2.42	–O(3)	1.958	1.97
–O(6')	2.479	2.51	–O(4)	2.397	2.47
–O(7)	1.943	1.96	–O(5)	1.989	1.92
–O(7')	2.044	2.01	–O(7)	2.008	2.01
O(4)–Cu(1)–O(6)	89.5°	90°	O(1)–Cu(2)–O(2)	84.5°	86°
O(4)–Cu(1)–O(6')	93.1	93	O(1)–Cu(2)–O(3)	93.9	93
O(4)–Cu(1)–O(7)	86.2	88	O(1)–Cu(2)–O(4)	98.6	98
O(4)–Cu(1)–O(7')	97.1	96	O(1)–Cu(2)–O(5)	92.1	90
O(5)–Cu(1)–O(6)	86.9	88	O(2)–Cu(2)–O(3)	87.1	87
O(5)–Cu(1)–O(6')	90.3	89	O(2)–Cu(2)–O(5)	82.4	79
O(5)–Cu(1)–O(7)	95.5	96	O(2)–Cu(2)–O(7)	102.6	102
O(5)–Cu(1)–O(7')	81.6	80	O(3)–Cu(2)–O(4)	92.2	94
O(6)–Cu(1)–O(7)	95.0	95	O(3)–Cu(2)–O(7)	93.6	95
O(6)–Cu(1)–O(7')	89.8	90	O(4)–Cu(2)–O(5)	74.4	73
O(6')–Cu(1)–O(7)	89.0	89	O(5)–Cu(2)–O(7)	81.8	84
O(4)–Cu(1)–O(5)	176.2	—	O(1)–Cu(2)–O(7)	170.0	—
O(6)–Cu(1)–O(6')	175.3	—	O(2)–Cu(2)–O(4)	176.9	—
O(7)–Cu(1)–O(7')	174.2	—	O(3)–Cu(2)–O(5)	167.3	—
Within the arsenate tetrahedron					
As–O(3)	1.680	1.68	O(3)–As–O(4)	104.8°	103°
–O(4)	1.664	1.65	O(3)–As–O(5)	109.3	111
–O(5)	1.773	1.73	O(3)–As–O(8)	110.1	112
–O(8)	1.615	1.61	O(4)–As–O(5)	109.9	109
Hydrogen bond distances			O(4)–As–O(8)	114.4	116
O(1)–O(6)	3.052	2.95	O(5)–As–O(8)	108.3	105
O(1)–O(8)	2.583	2.61			
O(1')–O(8)	2.834	2.77			
O(2)–O(6)	2.753	2.94			
O(2')–O(6)	2.882	2.70			
O(7)–O(8)	2.585	2.63			
O(2)–O(5)	2.918	2.96			

The average standard deviations of the bond lengths for this refinement are: Cu–O 0.012; As–O 0.012. That of the angles is 0.50°.

molecules. The difference in birefringence may be partly caused by the rotation of the structural unit into a plane parallel to (010) in euchroite.

It has been stated (Palache, Berman & Frondel, 1951) that euchroite possesses a {110} and {101} cleavage in traces. Fig. 1 shows the hypothesized {110} cleavage developed by breaking hydrogen bonds between O(1) and O(8) and between O(7) and O(8). Also one stronger bond need be broken between Cu(2) and O(3). The {101} cleavage cannot be accounted for in any simple manner.

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The similarity of atomic radius of palladium (II) and palladium (IV). By J. D. BELL, D. HALL and T. N. WATERS, *Chemistry Department, University of Auckland, New Zealand*

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A number of apparently trivalent complexes of palladium and platinum have been investigated crystallographically (Brosset, 1948; Cohen & Hughes, 1954; Hall & Williams,

1958; Craven & Hall, 1961, 1966; Ryan & Rundle, 1961; Wallen, Brosset & Vannerberg, 1962), and invariably the structures have proved to be based on chains in which