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The Symmetry and Crystal Structure of Olivenite

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The symmetry of the intensity distribution of 1022 reflections of olivenite with $l \geq 0$ was examined and the space group $P2_1/n$ determined. The unit-cell dimensions (with a as a unique axis) are: a = 8·615 (5), b = 8·240 (5), c = 5·953 (4) Å, α = 90·0 (1)°. A least-squares refinement of the structure factors was performed successfully in this space group and the atomic coordinates determined. Weighted R residuals of 0·090 and 0·065 were obtained for refinements where twinning on the (010) plane was ignored and corrected for respectively. The monoclinic structure deviates only moderately from the approximate orthorhombic structure (largest displacement = 0·33 Å) as determined by Heritsch [*Z. Kristallogr.* (1938), **99**, 466–479].

Introduction and preliminary work

The approximate structure of olivenite, $Cu_2AsO_4(OH)$, was published by Heritsch (1938), assuming space group *Pnnm*. In subsequent years the space group of olivenite was redetermined by Richmond (1940) and Berry (1951); these workers proposed space groups $P2_12_12_1$ and *Pnmm* respectively. More recently the problem of the olivenite space group was re-examined by Walitzi (1962). She assigned the structure to space group $Pn2_1m$ based on X-ray data and etching tests.

Our experimental work was carried out on crystals from Chuquicamata, Chile.* Orthorhombic symmetry was assumed and the intensities of 436 independent reflections were measured in one octant of reciprocal space with filtered Mo $K\alpha$ radiation and a manually operated single-crystal diffractometer (Weissenberg geometry, ω scan). The unit-cell dimensions, resulting from a least-squares calculation with 23 measurements of 2θ angles, are: a = 8·615 (5), b = 8·240 (5), c = 5·953 (4) Å. The unit-cell volume is 422·6 Å^3, Z = 4, and the calculated density is 4·45 g cm^{-3}. The intensities were corrected in the usual way for Lorentz and polarization factors. A least-squares refinement of the atomic coordinates based on the space group *Pnnm* and Heritsch's coordinates was computed and an R of 0·24 was obtained (all reflections $h0l$ with $h + l$ odd were omitted from the calculation, in spite of the fact that some have considerable intensity). Another refinement of the structure was attempted in space group $Pn2_1m$, but without success. A difference Fourier map, phased on the atomic coordinates of As, Cu(1) and Cu(2), provided the clue to the symmetry of olivenite. On this map, the z coordinate of the atomic peak of O(1) is not 0 as we expected for an atom in a special position (on a mirror plane), but ±0·06. This indicates that the mirror plane normal to the c axis is absent in olivenite.

The fact that there exists unlimited solid solubility between olivenite and adamite (Minceva-Stephanova, Pantschev, Bonev & Punev, 1965) indicates that the structure of adamite can be changed into the structure of olivenite by a continuous process. This suggests that the space group of olivenite is a subgroup of the space group of adamite; closer consideration shows that space groups $P2_12_12$ and $P2_1/n$ are the most likely. This conclusion was reinforced by our computation of a Patterson map based on reflections $h0l$ with $h + l$ odd. The distribution of maxima and minima on this map strongly indicated the monoclinic space group.

Study of the olivenite structure based on monoclinic space groups

Intensities of 1022 reflections with $l \geq 0$ were collected with a new crystal of dimensions 0·25 × 0·25 × 0·24 mm. All data were obtained by the methods described above. Collected intensities were corrected for absorption with the method of Furnace as described by North, Phillips & Mathews (1968).

The symmetry of olivenite was tested by calculating averages of the absolute values of differences in intensities of pairs of reflections which, in the absence of anomalous scattering, are equivalent in an orthorhombic crystal. If the symmetry of olivenite is orthorhombic and if the anomalous scattering is negligible, all six averages (for example $\langle |I_{hkl} - I_{\bar{h}kl}| \rangle$ among others) must have very similar values, because the differences between intensities are related to errors of measurements and to errors in the absorption correction only.

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* All samples of olivenite used in this study were kindly provided by The National Museum of Natural History, Smithsonian Institution, Washington DC, Division of Mineral Sciences, sample No. 105773-2.

If anomalous scattering is not negligible, the space group $P2_12_12$ requires that the two averages of differences which involve reflections related by the twofold axis ($\langle|I_{hkl} - I_{\bar{h}\bar{k}l}|\rangle$ and $\langle|I_{\bar{h}kl} - I_{hkl}|\rangle$) are small and of a similar value, and that the remaining four averages are larger and also similar.

However, if the symmetry of olivenite is $P2_1/n$ (with *a* as a unique axis), then the averages of differences involving reflections related by the mirror plane ($\langle|I_{\bar{h}kl} - I_{hkl}|\rangle$ and $\langle|I_{h\bar{k}l} - I_{\bar{h}\bar{k}l}|\rangle$) should be small and of a similar value, whereas the remaining four differences should be larger but also similar.

Numerical values of all six averages of intensity differences are given in Table 1; they indicate decisively the $P2_1/n$ symmetry of olivenite (the space group $Pn2_1m$, which is not excluded by this test if anomalous scattering is appreciable, is ruled out by arguments presented in the preceding section).

After the monoclinic symmetry of olivenite was established, the intensities of olivenite reflections were reduced to a unique set of 488 by averaging. Averaged intensities were corrected for Lorentz and polarization factors and were then converted into structure factors and used in a least-squares calculation of atomic coordinates, space group $P2_1/n$ being assumed.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968) together with corrections for anomalous scattering of As and Cu atoms. Weighting was according to the formula $w^{1/2} = 1{\cdot}2/\max(0{\cdot}006|F_o|, \sigma_F)$, where σ_F is the standard deviation of a structure factor as obtained from counting statistics. This weighting scheme led to an acceptable variation of $w(F_o - F_c)^2$ *vs* F_o (variation less than ±30%).

Final atomic coordinates are shown in Table 2. Atomic coordinates refer to Heritsch's original axes, which are used throughout this paper. This setting has the disadvantage that the unique axis of our monoclinic structure is the *a* axis, but this is compensated for by the fact that the structures of olivenite and adamite, $Zn_2AsO_4(OH)$ (Kokkoros, 1937), are described with respect to the same system of axes. This is useful because both structures are very similar and form extensive solid solutions (Minceva-Stephanova *et al.*, 1965).

The weighted *R* obtained was 0·090.* Differences between the calculated and observed structure factors have a systematic trend. If within a pair of reflections (hkl, $\bar{h}\bar{k}l$) one reflection is considerably weaker than the other, the calculated value of the stronger reflection agrees fairly well with the measured value. However, the measured value of the weaker reflection is frequently higher than that calculated. This behavior can be explained by the presence of twinning with the twin plane (010), as reported by Walitzi (1962).

If we accept the hypothesis of microtwinning in our specimen, the measured intensity I^m_{hkl} is the sum of contributions from crystal I and from crystal II composing the twin: $I^m_{hkl} = (1-\alpha)I_{hkl} + \alpha I_{h\bar{k}l}$, where I_{hkl} and $I_{h\bar{k}l}$ are the intensities of reflections superimposed in the twin and α is the volume fraction of crystal II. The corrected intensity of a reflection *hkl*, I^c_{hkl}, is, therefore, $I^c_{hkl} = [(1-\alpha)I^m_{hkl} - \alpha I^m_{h\bar{k}l}]/(1-2\alpha)$. To test this, the measured intensities of reflections were corrected for twinning with different values of α, and

Table 1. *Averages of intensity differences* $\langle|I_{hkl} - I_{h'k'l'}|\rangle/\langle|I_{hkl} + I_{h'k'l'}|\rangle$

hkl	$\bar{h}kl$	0·067	hkl	$h\bar{k}l$	0·171
hkl	$\bar{h}\bar{k}l$	0·151	$\bar{h}kl$	$\bar{h}\bar{k}l$	0·129
$\bar{h}kl$	$h\bar{k}l$	0·146	$\bar{h}\bar{k}l$	$h\bar{k}l$	0·060

Table 2. *Atomic coordinates in olivenite as determined by Heritsch* (1938) *for the structure in Pnnm and in this work in* $P2_1/n$ (*the a axis is the unique axis*)

Atomic coordinates of a general position are: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$.

	Heritsch (1938)			This work (α – 0·00)			This work (α = 0·23)		
	x	y	z	x	y	z	x	y	z
As	0·244	0·264	0	0·2496 (4)	0·2626 (5)	−0·0103 (4)	0·2500 (3)	0·2622 (5)	−0·0115 (4)
Cu(1)	−0·122	0·362	0	−0·1180 (6)	0·3624 (6)	0·0172 (6)	−0·1178 (5)	0·3627 (5)	0·0219 (5)
Cu(2)	0	0	$\frac{1}{4}$	0·0006 (5)	0·0003 (6)	0·2510 (5)	0·0007 (5)	0·0005 (7)	0·2511 (4)
O(1)	0·114	0·375	0	0·105 (3)	0·398 (3)	-0·060 (3)	0·111 (3)	0·398 (3)	−0·058 (3)
O(2)	0·394	0·353	0	0·420 (3)	0·368 (3)	0·006 (3)	0·419 (2)	0·370 (3)	0·001 (3)
O(3)	-0·097	0·120	0	-0·102 (2)	0·134 (2)	0·025 (2)	−0·099 (2)	0·131 (3)	0·013 (2)
O(4)	0·236	0·139	$\frac{1}{4}$	0·223 (3)	0·158 (3)	0·240 (3)	0·222 (2)	0·161 (3)	0·240 (2)
O(5)	0·236	0·139	$-\frac{1}{4}$	0·246 (3)	0·136 (3)	−0·217 (3)	0·248 (2)	0·132 (3)	-0·215 (3)

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32536 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Dependence of R (unit weights) on the assumed twinning ratio*

α	R	α	R
0·00	0·107	0·25	0·092
0·10	0·102	0·30	0·096
0·20	0·094	0·35	0·104

were then used in the least-squares calculations. The dependence of R (constant weights) on α is shown in Table 3. The best R obtained was for $\alpha = 0{\cdot}23$ (interpolated); the corresponding weighted R was 0·065. The atomic coordinates from this refinement are shown in Table 2.

Most of the crystallographic calculations performed in this work were carried out with the XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

In concluding this part of the paper we would like to summarize our results as follows: (i) The symmetry of the intensity distribution of X-ray reflections supports the conclusion that olivenite is monoclinic. (ii) Good agreement is obtained between the observed and calculated structure factors with space group $P2_1/n$, especially if partial microtwinning is assumed. (iii) No deviation of the axial angles from 90° was observed (experimental error 0·1°).

Discussion

As can be seen from Table 2, the monoclinic structure of olivenite differs only slightly from the original orthorhombic structure proposed by Heritsch (1938). The largest difference is in the z coordinate of O(1), which is displaced by 0·33 Å. The interatomic distances calculated from the coordinates obtained in a least-squares refinement based on structure factors corrected for twinning are given in Table 4. The AsO_4 tetrahedron in olivenite is less regular than the tetrahedron in adamite (Bingman, Getz, Hillock, Shock & Toman, 1976). The average As–O distance in olivenite is 1·681 compared with 1·693 Å in adamite. The average Cu–O distance in the basal plane of the trigonal bipyramid CuO_5 is 2·07 Å; the average apical Cu–O distance is 1·95 Å. These values can be compared with 2·076 and 1·930 Å, which are corresponding average values for six CuO_5 groups listed by Shannon & Calvo (1973). If they are compared with similar distances in the ZnO_5 group in adamite (Bingman *et al.*, 1976) (2·013 and 2·07 Å) and in tarbuttite, $Zn_2PO_4(OH)$ (Cocco, Fanfani & Zanazzi, 1966) (1·972 and 2·11 Å), we observe that the trigonal bipyramid ZnO_5 is expanded in the apical direction (the average ratio of apical Zn–O distance to basal Zn–O distance is 1·049), whereas the trigonal bipyramid CuO_5 is compressed in that direction (average ratio 0·930). The average Cu–O distance in the distorted octahedron CuO_6 is 2·12 Å with a distortion of 0·0076.[*] This is very close to the values for clinoclase, $Cu_3AsO_4(OH)_3$ (2·118 Å and 0·0103) (Ghose, Fehlmann & Sundaralingam, 1965), and for euchroite, $Cu_2AsO_4(OH).3H_2O$ (2·129 Å and 0·0099) (Finney, 1966).

The O atom of the hydroxyl group in the structure of adamite was identified by Kokkoros (1937); in our notation it is O(3). Neither the original structure of olivenite (Heritsch, 1938), nor its distorted version presented in this paper departs sufficiently from that of adamite to cast any doubt on the identification of O(3) as the O atom of the OH group in olivenite. The nearest O eligible for hydrogen bonding is O(1) at a distance of 3·69 Å, which is too long to attribute much significance to hydrogen bonding in this structure.

In comparing the structure of adamite with the structure of olivenite, the major difference is in the symmetry of all the O polyhedra. In adamite the groups AsO_4, ZnO_5 and ZnO_6 have symmetry m, m and 2 respectively. In olivenite all polyhedra have symmetry

Table 4. *Interatomic distances (Å) in the oxygen polyhedra of olivenite*

Values are based on coordinates obtained in the least-squares calculation with $\alpha = 0{\cdot}23$.

AsO_4 tetrahedron

As–O(1)	1·66 (3)	O(1)–O(4)	2·81 (3)
As–O(2)	1·71 (2)	O(1)–O(5)	2·66 (3)
As–O(4)	1·73 (2)	O(2)–O(4)	2·81 (3)
As–O(5)	1·62 (2)	O(2)–O(5)	2·77 (3)
O(1)–O(2)	2·69 (3)	O(4)–O(5)	2·73 (2)

CuO_5 trigonal bipyramid		CuO_6 octahedron	
Cu(1)–O(1)	2·05 (2)*	Cu(2)–O(2)	1·96 (2)*
Cu(1)–O(4)	1·99 (2)*	Cu(2)–O(2′)	1·95 (2)*
Cu(1)–O(5)	2·16 (2)*	Cu(2)–O(3)	1·97 (2)*
Cu(1)–O(3)	1·92 (2)	Cu(2)–O(3′)	2·09 (2)*
Cu(1)–O(1′)	1·98 (2)	Cu(2)–O(4)	2·32 (2)
O(1)–O(1′)	2·64 (3)†	Cu(2)–O(5)	2·41 (2)
O(1)–O(4)	3·88 (3)*	O(2)–O(2′)	2·55 (3)*
O(1)–O(5)	3·42 (3)*	O(2)–O(3′)	3·06 (3)*
O(1)–O(3)	2·88 (3)	O(2)–O(4)	3·10 (3)
O(1′)–O(4)	2·86 (3)	O(2)–O(5)	3·31 (3)
O(1′)–O(5)	3·05 (3)	O(2′)–O(3)	2·90 (3)*
O(3)–O(4)	2·74 (3)	O(2′)–O(4)	3·04 (3)
O(3)–O(5)	2·92 (3)	O(2′)–O(5)	3·09 (3)
O(4)–O(5)	3·26 (3)*	O(3)–O(3′)	2·75 (3)*
		O(3)–O(4)	3·08 (3)
		O(3)–O(5)	2·79 (3)
		O(3′)–O(4)	3·03 (3)
		O(3′)–O(5)	3·28 (3)

* Distances in the basal plane.
† Shared edge.

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[*] Defined in Shannon & Calvo (1973) as $\langle(\Delta R/R)^2\rangle$, where R is the average Cu–O distance and ΔR are corresponding deviations.

1. It is tempting to attribute the lowering of the symmetry of O polyhedra in olivenite to the Jahn–Teller effect associated with the Cu^{2+} ion. The difference in the shape of the ZnO_5 and CuO_5 trigonal bipyramids is probably related to the same cause. In connection with the structure of olivenite, a revision of the symmetry of libethenite, $Cu_2PO_4(OH)$ (Walitzi, 1963), seems to be desirable. According to Walitzi, the symmetry of libethenite is *Pnnm*, the same as the symmetry of adamite.

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On the Binding in Phases of T^{10}–B^6 Mixtures

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The two-correlations model for electrons in crystal structures allows the binding of a phase to be described by two correlation types and two commensurabilities. Since empirical rules are valid for the occupancy of the correlations, predicting whether or not a compound will appear at a certain composition may be possible. Therefore, the two-correlations model is a valence model giving new insights and explaining more facts than older valence models. The model is crystallographic in character, as it assumes the existence of lattice-like spatial correlations of electrons in crystal structures. Applied to T^{10}–B^6 mixtures the model yields three main types of binding: CuZn, In and PtS binding. These main types undergo certain modifications in order to stabilize a phase at a simple composition. Certain rules are valid for transformations in a compound or for morphotropics of it, *i.e.* structural changes when the homologous representative is changed.

Introduction

A T^{10} element is defined as an element in the same homologous class as Ni, a B^6 element is either S, Se or Te, and T^{10}–B^6 represents alloys between a T^{10} element and a B^6 element, in other words, a set of homologous mixtures. [The term 'mixture', common in thermodynamic literature (*e.g.* Guggenheim, 1950), replaces the 'system' which has in its original sense, and in its major present day use, a different meaning.] It is of interest to have a chemical valence model for T^{10}–B^6 mixtures, which indicates whether or not a compound is formed at a given composition. (The term 'compound' is used in the sense of 'intermediary phase'.) Such a valence model does not yet exist; however, since the two-correlations model (Schubert, 1976) helped to better understand brass-like mixtures, it seems possible that it could also help to better understand T^{10}–B^6 mixtures.

Reviews of T^{10}–B^6 mixtures have been given by Hulliger (1968) and Jellinek (1968); these should be consulted for original references and structure draw-