Coordination des cations et cohésion cristalline

Les distances interatomiques K–O inférieures à 3,70 Å et Na–O inférieures à 3,50 Å ont été mentionnées dans le Tableau 6. Les trois cations potassium présentent des indices de coordination égaux à huit. Le sodium présente un environnement octaédrique déformé. Les polyèdres de coordination présentent des distortions notables comme l'illustre le domaine important des distances cation–oxygène. Le polyèdre de coordination de K(1) s'enchaîne à celui de K(3^{x}) par la face [O(3^{i}), O(2), W(4^{vi})] et à celui de Na par la face [O(3^{i}), O(5^{i}), W(1)]. Certaines arêtes de polyèdre, W(1^{ii})–O(3^{ix}) dans K(1), W(4)–O(6) et W(2^{i})–O(5^{i}) dans K(2) et W(3^{viii})–O(1^{i}) dans K(3), correspondent à des directions donneur–accepteur de liaisons hydrogène; ceci conduit à des diminutions importantes des angles W–K–O correspondants et implique donc une déformation supplémentaire de l'environnement des cations.

On remarque que l'anion $P_2O_7^{4-}$ joue le rôle de tridentate de deux manières différentes pour les cations K(1) et Na; en effet K(1) est lié à trois oxygènes *trans* [O(3), O(2), O(6)] d'un même groupement $P_2O_7^{4-}$ et Na est lié à deux oxygènes *trans* [O(3^{i}) et O(5^{i})], et à l'oxygène du pont [O(4^{i})] d'un même anion.

Sur la projection de la Fig. 2, on remarque que les cations, les molecules d'eau, les atomes de phosphore, les oxygènes des ponts et les oxygènes terminaux *cis* sont localisés approximativement dans des plans parallèles au plan *ab* aux cotes *x* égales à 0,25 et 0,75. Entre ces plans viennent se placer les oxygènes terminaux *trans* de l'anion $P_2O_7^{4-}$. La cohésion dans les plans de grande densité est assurée essentiellement par les liaisons hydrogène, tandis que la majorité des interactions électrostatiques se développent entre ces plans pour assurer la cohésion de la structure.

Références

BERTAUT, E. F. (1952). *J. Phys. Radium*, **13**, 499–505.
BRUN, G. (1967). Thèse, Montpellier.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
DUMAS, Y. & GALIGNÉ, J. L. (1974). *Acta Cryst.* B**30**, 390–395.
FERRARIS, G. K. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* B**28**, 3572–3583.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B**26**, 274–285.
LARBOT, A. (1971). Thèse, Montpellier.
LEUNG, K. Y. & CALVO, C. (1972). *Can. J. Chem.* **46**, 2521–2526.
MCDONALD, W. S. & CRUICKSHANK, D. W. S. (1967). *Acta Cryst.* **22**, 43–48.
NORBERT, A., MAURIN, M. & LARBOT, A. (1972). *Bull. Soc. Fr. Minéral. Cristallogr.* **95**, 614–617.
TORDJMAN, I. (1976). Communication personnelle.

Acta Cryst. (1978). B**34**, 715–721

Ordering in Olivenite–Adamite Solid Solutions

BY K. TOMAN

Wright State University, Dayton, Ohio 45435, *USA*

(*Received* 13 *July* 1977; *accepted* 23 *September* 1977)

The unit-cell edges of the olivenite–adamite solid solution, $(Cu_x, Zn_{1-x})_2AsO_4(OH)$, show strong positive deviations from Végard's law. The monoclinic distortion of the structure of olivenite disappears if the percentage of adamite in solid solutions is larger than 20 mol%. Atomic coordinates of a solid solution with 42 mol% of olivenite were determined with single-crystal measurements and a least-squares refinement. Analysis of interatomic distances indicates a long-range order with Cu ions in distorted octahedral coordination, CuO_6, and Zn ions in distorted trigonal dipyramidal coordination, ZnO_5.

1. Introduction

Numerous indications that an unlimited solid solubility exists in the olivenite–adamite system are reported in the literature. Guillemin (1956) describes a number of both natural and synthetic members of this series of solid solutions. Minceva-Stefanova, Pantschev, Bonev & Punev (1965) give the dependence of unit-cell edges on the composition.

The crystal structures of the end members are also known. The crystal structure of adamite, $Zn_2AsO_4(OH)$, was first determined by Kokkoros

(1937) and recently refined by Hill (1976). The crystal structure of olivenite, $Cu_2AsO_4(OH)$, was first determined by Heritsch (1938), who published a set of atomic coordinates based on space group *Pnnm* (the space group of adamite) and showed a close similarity between the adamite and olivenite structures. Unfortunately, his determination, though approximately correct, did not lead to a good agreement between the calculated and observed intensities. Walitzi (1962) reexamined the space group of olivenite and suggested the space group $Pn2_1m$ (as referred to axes used in the present paper). Recently, Toman (1977) showed that the true symmetry of olivenite is $P2_1/n$, and has successfully refined the structure in this space group.

In spite of the considerable amount of previous work on minerals of the olivenite–adamite series, there are some points of interest which deserve further study.

(1) The end members of the olivenite–adamite series have a different space-group symmetry; it is of interest to find out at what concentration of olivenite the mirror planes start to disappear in the structure of adamite and when the *z* coordinates of Cu and Zn ions start to deviate from zero.

(2) In the structures of olivenite and adamite divalent metal ions (*M*) occupy two crystallochemically different positions: they are at the center of a tetragonal dipyramid, MO_6, and at the center of a trigonal dipyramid, MO_5. It is interesting to determine whether, in solid solution, metal ions are randomly distributed over both sites or whether there is a long-range order.

The objective of this paper is to clarify these two points.

2. Unit-cell dimensions in olivenite–adamite solid solutions

The unit-cell dimensions of different members of olivenite–adamite solid solutions were studied by Minceva-Stefanova *et al.* (1965). They indicate only small deviations from Végard's law. Unfortunately, their determination of unit-cell edges for solid solutions with 50 and 60 mol% of olivenite is incomplete. For these compositions they determined only the *c* edges but left the *a* and *b* edges undetermined. In addition, the single-crystal specimen with 42 mol% of olivenite used in the present investigation gave unit-cell dimensions incompatible with unit-cell dimensions indicated in their paper.

These two circumstances prompted a re-examination of the unit-cell dimensions of the olivenite–adamite solid solutions. Material for this study was prepared using a method similar to those used by Guillemin (1956) and Minceva-Stefanova *et al.* (1965). The amorphous precipitate, obtained by adding 10 ml of 0·1 *M* solution of Na_2HAsO_4 in water to 20 ml of a mixture of 0·1 *M* solutions of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ in water, was crystallized by boiling for 10 h in the original liquid. For Cu-rich solid solutions, the time necessary for complete crystallization was short (10–20 min): for Cu-poor solid solutions and for adamite, complete crystallization was achieved only after several hours of boiling. In these preparations every sample was boiled for 10 h to obtain a highly homogeneous, crystalline powder giving sharp diffraction lines. The compositions of the solid solutions were determined by X-ray fluorescence analysis.

The unit-cell dimensions of the solid solutions and of the end-members prepared in this way were determined with least-squares calculations based on 2θ values of 30–40 reflections measured on a powder diffractometer (Cu $K\alpha$ radiation). For indexing of powder patterns, the single-crystal data of olivenite, adamite and of the natural solid solution with 42 mol% of olivenite were used. The 2θ angles were calibrated with a Si standard, with the unit-cell edge of silicon assumed to be 5·4305 Å at 25 °C.

As is shown below, the monoclinic angle of olivenite differs only negligibly from 90°. Therefore, an orthorhombic axial system was used for solid solutions of all compositions; the unit-cell edge which is approximately perpendicular to the bases of the trigonal pyramid, MO_5, is taken to be the *b* edge, and the shortest unit-cell edge is the *c* edge. This is the traditional setting for adamite (Kokkoros, 1937; Hill, 1976) and also for olivenite (Heritsch, 1938; Toman, 1977). This choice has the unfortunate consequence that the unique axis of olivenite is the *a* axis, but it is the usual setting in most structural papers on adamite and olivenite and is used also by Wyckoff (1965) and by Bragg, Claringbull & Taylor (1965).

Considerable effort was spent in determining if there is any deviation of the monoclinic angle α from 90° by comparing the width of reflections 0*kl* with the width of the general *hkl* reflections in the powder diagrams.

Table 1. *Unit-cell dimensions and unit-cell volume in olivenite–adamite solid solutions*

Composition mol % olivenite	*a*	*b*	*c*	*V*
100	8·630 (8) Å	8·241 (7) Å	5·942 (5) Å	422·6 Å^3
97	8·631 (9)	8·260 (9)	5·945 (6)	423·8
93	8·627 (6)	8·267 (8)	5·948 (7)	424·2
87	8·631 (9)	8·311 (8)	5·963 (6)	427·7
83	8·617 (7)	8·326 (8)	5·964 (9)	427·9
75	8·608 (8)	8·367 (7)	5·961 (10)	429·3
63	8·592 (9)	8·446 (9)	5·977 (8)	433·7
50	8·560 (8)	8·489 (8)	5·993 (7)	435·5
36	8·513 (8)	8·510 (7)	6·007 (8)	435·2
22	8·438 (6)	8·515 (7)	6·020 (6)	432·5
10	8·370 (7)	8·520 (7)	6·040 (8)	430·7
0	8·320 (8)	8·525 (8)	6·055 (7)	429·5

Using this method we were not able to determine any deviation of the angle α from 90° (within an error of 0·1°). A better estimate of the angle α was obtained with a single crystal of olivenite from Cornwall, England,* with a very limited angular misorientation of mosaic blocks. Measurement of angles 2θ, φ and χ for 28 reflections on an automatic four-circle diffractometer provided data for a least-squares calculation of the unit-cell constants, which gave $a = 8{\cdot}629\ (6)$, $b = 8{\cdot}243\ (6)$, $c = 5{\cdot}937\ (3)$ Å and $\alpha = 90{\cdot}11\ (4)°$ (see also Appendix).

The results of the least-squares calculation of unit-cell edges for the olivenite–adamite solid solutions, based on the powder diffractometer measurement mentioned above, are given in Table 1. As can be seen from Table 1 and from Fig. 1, the solid solution exhibits considerable deviations from Végard's law, especially in the a and b unit-cell edges. These deviations are so large that the unit-cell volume goes through a broad maximum in the middle of the composition range. It is difficult to speculate why these results differ so considerably from those of Minceva-Stefanova *et al.* (1965). One reason may be a different degree of order in their samples. On the present powder diffraction records, reflections 440 and 004 are very prominent and do not overlap with other reflections; the variation of the 2θ angle of the 440 reflection with composition gives good qualitative evidence of large positive deviations from linearity in the variation of the a and b unit-cell edges with composition (Table 2).

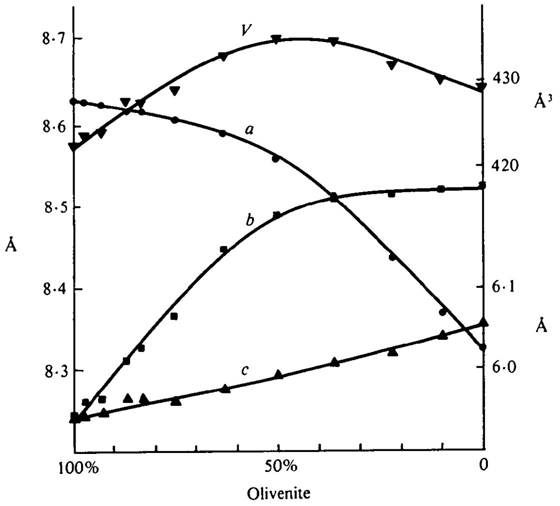

Fig. 1. Unit-cell dimensions and unit-cell volume in olivenite–adamite solid solutions.

3. Symmetry change in olivenite–adamite solid solutions

As previously mentioned, the symmetry of the olivenite–adamite solid solution changes from $P2_1/n$ to $Pnnm$ as Cu ions are replaced by Zn ions. The most direct method of studying this process, the measurement of angle α, is impractical here because of its small deviation from 90°. Also the measurements of the intensity of the pairs of reflections which are equivalent in orthorhombic adamite and independent in monoclinic olivenite (for instance, the 026 and $0\bar{2}6$ or 035 and $0\bar{3}5$ pairs have large intensity differences) cannot be done with powder samples, and even in the case of measurements on single crystals, measurement would be hampered by twinning on (010) which is common in olivenite (Walitzi, 1962; Toman, 1977).

Considering these limitations, the only feasible method of studying the change of symmetry in olivenite–adamite solid solutions is the measurement of the intensity of the $h0l$ reflections with $h + l$ odd. These reflections are forbidden by the space group of adamite, but are observable in olivenite. The strongest of them, the 102 reflection, is easily observable even on a powder pattern. In the present study, the integrated intensities of the 102 and 301 reflections were determined from point-by-point measurement with a powder diffractometer (Cu $K\alpha$ radiation). The ratio I_{102}/I_{301}, after corrections for Lorentz and polarization factors were made, was converted into the structure factor F_{102}. The structure factor F_{301} of the solid solution, necessary for the calculation of F_{102} on an absolute scale from the

---

* This sample of olivenite was kindly provided by The National Museum of Natural History, Smithsonian Institution, Washington DC, Division of Mineralogy, sample No. 105178.

Table 2. *Angles* 2θ (°) *of* 440 *and* 004 *reflections in powder diffraction patterns* (Cu $K\alpha$ *radiation*) *of olivenite–adamite solid solutions*

Values for the 004 reflection indicate only a small negative deviation from Végard's law for the c edge; values for the 440 reflection indicate strong positive deviations from Végard's law for both a and b edges.

Composition mol % olivenite	100	97	93	87	75	63	50	34	22	10	0
004	62·57	62·48	62·47	62·42	62·30	62·17	62·00	61·82	61·55	61·33	61·23
440	62·37	62·22	62·20	62·11	61·77	61·50	61·57	61·59	62·05	62·20	62·25

Table 3. *Variation of* $|F_{102}|$ *with composition in olivenite–adamite solid solutions*

Values in brackets indicate the standard deviation. If no peak was observed, the estimated error was up to eight units.

Composition mol % olivenite	100	97	93	87	83	78
$\lvert F_{102}\rvert$	46 (1)	36 (3)	35 (4)	25 (4)	–	–

measured intensity ratio, was obtained by interpolation between the experimental values of F_{301} measured on single crystals of olivenite and those of a solid solution with 42 mol% of olivenite. In both cases the scaling was obtained in the course of a least-squares refinement of the atomic coordinates. The structure factors of the 102 reflection for olivenite–adamite solid solutions are given in Table 3. As can be seen from Table 3, the 102 reflection disappeared when the degree of replacement of Cu by Zn approached 20 mol%. This indicates that the monoclinic structure of olivenite is rather unstable, and that a small amount of Zn stabilizes the common orthorhombic structure.

4. Order in an olivenite–adamite solid solution

For the study of order in the olivenite–adamite solid solution, a crystal of cuprian adamite from Tsumeb, Southwest Africa, was used.* The ratio of Cu/Zn as obtained from X-ray fluorescence analysis corresponds to the formula $(Cu_{0.42}Zn_{0.58})_2AsO_4(OH)$. The crystal used in this study was euhedral, limited by faces {101} and {110}. The size of the crystal was 0·13 × 0·17 × 0·22 mm; the volume was 0·0019 mm³. The unit-cell dimensions determined by a least-squares calculation based on angles 2θ, φ and χ (Mo $K\alpha$ radiation, 16 reflections, automatic four-circle diffractometer) are: $a = 8{\cdot}50$ (2), $b = 8{\cdot}52$ (2) and $c = 5{\cdot}99$ (1) Å. The intensities of 2300 reflections were measured on the same instrument in the 2θ mode in the half sphere with radius 1·28 Å^{-1}. Because the mosaic structure of the crystal was rather coarse and irregular, each reflection was scanned within the range of ±1·9° (2θ). After corrections for absorption, Lorentz and polarization factors (calculated density 4·16 g cm^{-3}, linear absorption coefficient 175·9 cm^{-1}) were made, the intensities of equivalent reflections were averaged. The number of independent reflections was 573. The intensities confirmed the space group as *Pnnm*; no *h*0*l* reflection with $h + l$ odd had a significant intensity.

Table 4. *Atomic coordinates and thermal parameters in an olivenite–adamite solid solution with* 43 mol% *of olivenite*

A general atomic position in space group *Pnnm* has coordinates: x,y,z; $-x,-y,-z$; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$; $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$; $x,y,-z$; $-x,-y,z$; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$. The anisotropic temperature coefficients (Cruickshank's formula) U_{11}, U_{22}, U_{33}, U_{12} should be divided by 100 to be in Å².

	x	y	z	U
As	0·2522 (2)	0·2618 (2)	0	
Zn	−0·1276 (2)	0·3621 (2)	0	
Cu	0	0	0·2487 (4)	
O(1)	0·106 (1)	0·394 (1)	0	1·0 (2)
O(2)	0·424 (1)	0·367 (1)	0	0·7 (2)
O(3)	−0·104 (2)	0·119 (2)	0	1·6 (2)
O(4)	0·237 (1)	0·144 (1)	0·224 (2)	1·6 (2)

	U_{11}	U_{22}	U_{33}	U_{12}
As	0·59 (8)	1·19 (8)	0·73 (7)	−0·03 (6)
Zn	0·65 (9)	1·44 (9)	1·14 (9)	0·09 (7)
Cu	1·18 (9)	1·65 (9)	0·75 (9)	0·73 (7)

The first cycle of the least-squares refinement was started with the atomic coordinates of olivenite (Toman, 1977). The monoclinic distortion was removed by setting the *z* coordinates of atoms As, Cu(1), O(1)–O(3) and the *x* and *y* coordinates of atom Cu(2) equal to zero and by averaging the absolute values of all the coordinates of O(4) with O(5); in the structure of adamite there are only four independent O atoms. Refinement progressed smoothly toward R = 0·08 (anisotropic temperature factors for As and Zn, isotropic for O; constant weights); the same atomic scattering factor (Zn) was used for both sites. Analysis of the interatomic distances clearly indicated at this stage that most of the Cu was concentrated in the site with sixfold coordination (tetragonal dipyramid) and most of the Zn was concentrated in the site with fivefold coordination (trigonal dipyramid). The refinement was repeated with appropriate atomic scattering factors. The final R was 0·064 for a refinement with mixed temperature factors (anisotropic temperature factors for heavy atoms, isotropic for O) and with the weighting scheme $w^2 = 1 + (F_o - 70)^2/1600$. In all calculations, the atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1968) (including correction for anomalous scattering) were used.

Table 4 gives the atomic coordinates and temperature coefficients.* In Table 5, the interatomic distances are listed. All calculations described in this

---

* This crystal and the crystal of libethenite from Ray, Arizona, mentioned in the Appendix, were kindly provided by Mr R. L. Sohn, curator of the Mineral collections of Wright State University, Dayton, Ohio.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33040 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Interatomic distances* (Å) *in* AsO_4, ZnO_5 *and* CuO_6 *polyhedra in an olivenite–adamite solid solution with* 42 mol% *of olivenite*

Tetrahedron AsO_4

As—O distances

As—O(1)	1·68 (1)	As—O(2)	1·72 (1)	As—O(4)	1·68 (1)
Average:	1·689 (9)				

O—O distances

O(1)—O(2)	2·72 (1)	O(1)—O(4)	2·76 (1)
O(2)—O(4)	2·82 (1)	O(4)—O(4)	2·67 (1)

Trigonal dipyramid ZnO_5

Zn—O distances

Zn—O(1)	2·00 (1)	Zn—O(4)	2·01 (1)
Zn—O(1)	2·08 (1)	Zn—O(3)	2·08 (1)
Average basal:	2·011 (9)	Average apical:	2·081 (9)

O—O distances

O(1)—O(4)	3·56 (2)	O(4)—O(4)	3·29 (2)
O(1)—O(1)	2·55 (2)	O(1)—O(4)	3·01 (2)
O(1)—O(3)	2·95 (2)	O(3)—O(4)	2·85 (2)
Average basal:	3·47 (2)	Average apical:	2·87 (2)

Tetragonal dipyramid CuO_6

Cu—O distances

Cu—O(2)	1·99 (1)	Cu—O(3)	2·01 (1)	Cu—O(4)	2·37 (1)
Average basal:	1·999 (9)		Average apical:	2·37 (1)	

O—O distances

O(2)—O(3)	2·99 (2)	O(2)—O(2)	2·61 (2)	O(3)—O(3)	2·70 (2)
O(2)—O(4)	3·20 (2)	O(2)—O(4)	3·13 (2)		
O(3)—O(4)	2·86 (2)	O(3)—O(4)	3·20 (2)		
Average basal:	2·77 (2)		Average apical:	3·10 (2)	

section were performed with the XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

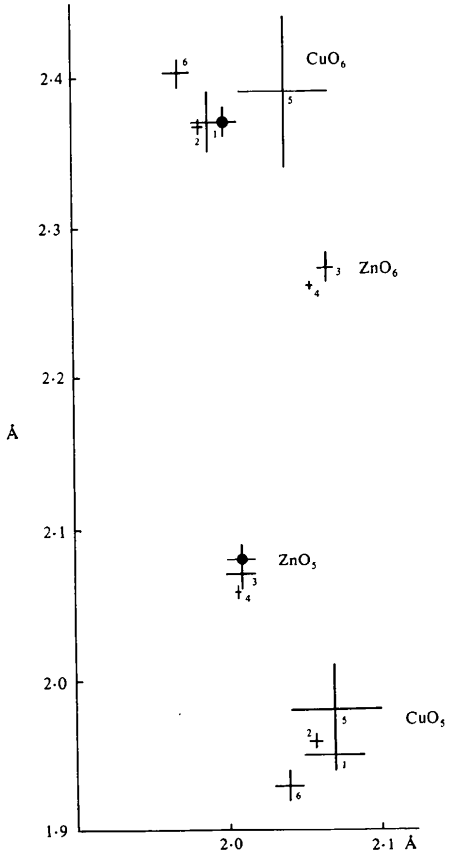

Fig. 2. *M*—O distances in MO_5 and MO_6 polyhedra in olivenite, libethenite, adamite and in a solid solution with 42 mol% of olivenite. Horizontal axis, average basal distances; vertical axis, average apical distances. Size of crosses corresponds to ±one standard deviation. Olivenite: (1) Toman (1977), (2) present paper, Appendix; adamite: (3) present paper, Appendix, (4) Hill (1976); libethenite: (5) Walitzi (1963), (6) present paper, Appendix; solid solution, 42 mol% of olivenite: large dots.

5. Discussion

First, let us discuss the validity of the claim that there is a long-range order in the olivenite–adamite solid solution and of the assignment of the Cu ions to the tetragonal dipyramidal coordination and the Zn ions to the trigonal dipyramidal coordination. Fig. 2 and Table 6 show the *M*—O distances in MO_5 and MO_6 polyhedra, averaged separately in the basal plane and in the apical direction, for structures closely related to the solid solution: olivenite (Toman, 1977; Toman, unpublished), libethenite, $Cu_2PO_4(OH)$, (Walitzi, 1963; Toman, unpublished) and adamite (Hill, 1976; Toman, unpublished) – a brief review of the unpublished refinements of minerals of the olivenite group is given in the Appendix. It is to be observed that the apical distance in the MO_5 group is larger if the central ion is Zn and that the opposite is true for the basal distance. On the other hand, the apical distance in the MO_6 group is larger if the central ion is Cu and the opposite holds for the basal distance. It can be seen from Fig. 2 that the distances in the MO_6 group of the solid solution correspond very closely to distances in CuO_6 groups in olivenite and libethenite, whereas the distances in the MO_5 group of the solid solution correspond very closely to distances in the ZnO_5 group of adamite. These facts are the basis for the claim that the solid solution is ordered, with Cu ions in CuO_6 groups and Zn ions in ZnO_5 groups. The same sort of argument is used to deduce the Al,Si order in network silicates; in both cases the differences in the atomic scattering factors are so small that the indication of the existence of order in the structure cannot be based on them.

The structure of the present olivenite–adamite solid solution is similar to that of stranskiite, $CuZn_2(AsO_4)_2$, where the Cu ions are in the center of a group of six O atoms, forming an elongated tetragonal dipyramid, and

Table 6. *M*—O *distances* (Å) in *M*O_5 *and M*O_6 *polyhedra in olivenite, libethenite, adamite and in the solid solution with* 42 mol% *of olivenite*

Polyhedron	Basal distance	Apical distance	Mineral	Reference
CuO_6	1·993 (15)	2·37 (2)	olivenite	Toman (1977)
	1·984 (5)	2·37 (1)	olivenite	Present paper, Appendix
	2·035 (50)	2·39 (5)	libethenite	Walitzi (1963)
	1·972 (12)	2·40 (1)	libethenite	Present paper, Appendix
	1·999 (9)	2·37 (1)	solid solution	Present paper
ZnO_6	2·057 (3)	2·261 (4)	adamite	Hill (1976)
	2·067 (15)	2·27 (2)	adamite	Present paper, Appendix
CuO_5	2·067 (17)	1·950 (17)	olivenite	Toman (1977)
	2·057 (8)	1·959 (7)	olivenite	Present paper, Appendix
	2·070 (50)	1·975 (50)	libethenite	Walitzi (1963)
	2·044 (12)	1·933 (9)	libethenite	Present paper, Appendix
ZnO_5	2·008 (4)	2·058 (4)	adamite	Hill (1976)
	2·001 (20)	2·069 (22)	adamite	Present paper, Appendix
	2·011 (9)	2·081 (9)	solid solution	Present paper

the Zn ions are in the center of the group of five O atoms forming a trigonal dipyramid (Plieth & Sänger, 1967).

If the Cu ions in olivenite are gradually replaced by Zn ions, the Zn ions enter preferentially into fivefold coordination. If this result is compared with the observation described in §3 of this paper, it becomes evident that the Cu ions in fivefold coordination are responsible for the lowering of the symmetry in the olivenite–adamite series.

The change in unit-cell dimensions with the composition of the olivenite–adamite solid solutions can be qualitatively explained with our concept of order. In the olivenite structure, the trigonal dipyramid CuO_5 is oriented with its apical direction parallel to the *b* axis. The apical direction of the CuO_6 tetragonal dipyramid is in the *ab* plane, at 33·2° from the *a* axis. If the Cu ions are gradually replaced by Zn ions in olivenite, the Cu ions in the CuO_5 polyhedra are the first to be replaced by Zn ions. As can be seen in Fig. 2, for the CuO_5 polyhedra, contraction of the basal *M*—O distances is about $\frac{1}{2}$ of the expansion of apical *M*—O distances if Cu is replaced by Zn. Therefore, the unit-cell edge *b* should increase faster than the unit-cell edge *a* would decrease if Cu is being replaced by Zn olivenite. As can be seen from Fig. 1, this is confirmed by the experimental data. When the concentration of olivenite in the solid solution drops below 50 mol%, Zn ions start to replace the Cu ions in the CuO_6 tetragonal dipyramids. If a CuO_6 group changes into a ZnO_6 group its apical distance decreases about twice as fast as its basal dimension increases. As a result of the orientation of the apical direction in the *ab* plane, the decrease of the *a* edge in this case should be larger than the increase in the *b* edge. Again, this is in agreement with observation.

The author wishes to express his thanks to Mr W. W. Adams from the Air Force Materials Laboratory of WPAFB Dayton, Ohio, who made it possible to perform a large number of intensity measurements on a Picker automatic diffractometer and took great interest in this work. He is also indebted to Miss A. Kowalski and Miss C. Tateman who assisted with the determination of the unit-cell dimensions and the symmetry of the olivenite–adamite solid solutions. Finally, without the help of Dr D. J. Schaefer from the Wright State University Computing Center, extensive computations which were necessary to prepare this paper could not have been completed.

APPENDIX

Additional information is given here on the unpublished refinements of the atomic coordinates in some minerals of the adamite group referred to in Fig. 2 of this paper.

(i) *Olivenite.* In addition to the calculations based on measurements made on olivenite crystal from Chuquicamata, Chile (Toman, 1977), a crystal from Cornwall, England, was recently measured and a refinement of the atomic coordinates was completed; 4105 reflections were measured with Mo *K*α radiation on a four-circle diffractometer. After correction for absorption, they were reduced to 2035 independent intensity values. The crystal was twinned to the same extent as the crystal from Chuquicamata. A least-squares refinement (the heavy atoms with anisotropic temperature factors) led to the final weighted $R = 0{\cdot}065$. The average standard deviation of the *M*—O distances is 0·007 Å. The refinement was in $P2_1/n$. Unit-cell dimensions are quoted in §2 of this paper.

(ii) *Libethenite.* A crystal of libethenite from Ray, Arizona, was measured on the four-circle diffractometer. Mo *K*α radiation was used; 3471 reflections were measured in the whole sphere; a check of orthorhombic symmetry was performed; averaging gave 533 independent intensity values after a correction for absorption was made. A least-squares refinement (the heavy atoms having anisotropic temperature factors) gave the weighted $R = 0{\cdot}068$. The average standard deviation of the M—O distances is 0·009 Å. The unit-cell dimensions are $a = 8{\cdot}425$ (9), $b = 8{\cdot}084$ (8) and $c = 5{\cdot}909$ (7) Å.

(iii) *Adamite.* A crystal of adamite from Durango, Mexico, was measured on a Weissenberg-type diffractometer with Mo $K\alpha$ radiation. Altogether, 692 reflections were measured; they gave 330 independent reflections after averaging. An absorption correction was applied; the least-squares refinement with anisotropic temperature factors for the As and Zn atoms was used; final weighted $R = 0{\cdot}045$. The average standard deviation of the M—O distances is 0·012 Å. The unit-cell dimensions are $a = 8{\cdot}32$ (1), $b = 8{\cdot}53$ (1) and $c = 6{\cdot}05$ (1) Å; refinement was in *Pnnm*.

Publication of the full details of items (i) and (iii) is not contemplated because the atomic coordinates obtained agree within one or two standard deviations with previously published data (Toman, 1977; Hill, 1976). Details of item (ii) will be published in a paper on libethenite solid solutions.

References

Bragg, L., Claringbull, G. F. & Taylor, W. H. (1965). *Crystal Structures of Minerals.* Ithaca: Cornell Univ. Press.

Guillemin, G. (1956). *Bull. Soc. Fr. Minéral. Cristallogr.* **79**, 7–95.

Heritsch, H. (1938). *Z. Kristallogr.* **99**, 466–479.

Hill, R. J. (1976). *Am. Mineral.* **61**, 979–986.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed. Birmingham: Kynoch Press.

Kokkoros, P. (1937). *Z. Kristallogr.* **96**, 417–433.

Minceva-Stefanova, J., Pantschev, B., Bonev, I. & Punev, L. (1965). *Izv. Geol. Inst. Bulg. Akad. Nauk.* **14**, 91–106.

Plieth, K. & Sänger, G. (1967). *Z. Kristallogr.* **124**, 91–100.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Toman, K. (1977). *Acta Cryst.* B**33**, 2628–2631.

Walitzi, E. M. (1962). *Tschermaks Mineral. Petrogr. Mitt.* **8**, 275–280.

Walitzi, E. M. (1963). *Tschermaks Mineral. Petrogr. Mitt.* **8**, 614–624.

Wyckoff, R. W. G. (1965). *Crystal Structures.* Vol. III, 2nd ed. New York, London, Sydney: Interscience.

Acta Cryst. (1978). B**34**, 721–724

The Crystal Structure of $ZrIr_3B_{\sim 4}$

By P. Rogl

*Institut für Physikalische Chemie, Universität Wien, A-*1090 *Währingerstrasse* 42, *Wien, Austria*

(*Received* 4 *July* 1977; *accepted* 3 *October* 1977)

$ZrIr_3B_{\sim 4}$ crystallizes in the hexagonal space group $P6_3/m$, with $a = 7{\cdot}560$ (2), $c = 3{\cdot}512$ (2) Å, $Z = 2$. $HfIr_3B_4$ is isotypic. The structure was determined and refined from single-crystal counter data: $R = 0{\cdot}038$ for 237 reflections. The structure contains two different types of boron atoms: B(1), isolated, in distorted trigonal prisms, and B(2), at the centres of Ir octahedra, forming linear chains with B—B = 1·756 Å. The Zr atoms have tetrakaidecahedral metal coordination. The crystal structure of $ZrIr_3B_{\sim 4}$ is related to the Fe_2P-type structure.

Introduction

The ternary compound $ZrIr_3B_{\sim 4}$ was found in the course of an X-ray investigation of the Zr–Ir–B system at 1100 °C (P. Rogl, unpublished results). The corresponding phase of the homologous system Hf–Ir–B reported by Brukl & Rudy (1967) has been recognized as being isotypic with the former. The purpose of the present work is the determination of the crystal structures of both these phases.

Experimental

Powders of the elements* were compacted in steel dies (without the use of binders or lubricants). The pellets (0·5–1 g) were presintered in vacuum on a boronitride substrate (5×10^{-6} Torr, 1000 °C, 2 h) and finally

---

* Zr: Koch Light Laboratories, Colnbrook, England; 99·9% Zr. Hf: Wah Chang, Albany, Oregon, USA; 3% Zr, 600 ppm O. Ir: Englehard Industries Inc., Newark, NJ; 99·9% Ir. B: crystalline, Koch Light Laboratories; 99% B.