Zeitschrift für Kristallographie, Bd. 145, S. 334—345 (1977)

Refinement of the crystal structure of α domeykite, a structure related to the $A15$ type*

By J. E. IGLESIAS** and W. NOWACKI

Bern

(Received 7 December 1976)

Auszug

Die Struktur von kubischem (oder α-) Domeykit, Cu_3As, wurde neu untersucht und mittels Zählrohrdaten verfeinert. Das ursprüngliche (1938) und etwas in Mißkredit geratene Modell von STEENBERG konnte voll bestätigt werden. Außer der Ähnlichkeit der Domeykitstruktur mit derjenigen von $Cu_{15}Si_4$, die auch schon von STEENBERG angegeben worden ist, wurde eine Beziehung zwischen der α-Domeykit- und der β-Wolfram-Struktur (A 15-Typ) aufgezeigt.

Abstract

The structure of cubic (or α) domeykite, Cu_3As, has been reexamined and refined from counter data. The original (1938) and somewhat discredited model proposed by STEENBERG has been fully confirmed. In addition to the relation, previously pointed out by STEENBERG, between this structure and the structure of $Cu_{15}Si_4$, a relation is described between the α-domeykite structure and the β-W structure (A 15) type.

Introduction

Several phases have been reported to exist in the Cu—As system (paxite, As_3Cu_2, JOHAN, 1961; koutekite, $AsCu_2$, JOHAN, 1960; algodonite, $Cu_{4-6}As$, MACHATSCHKI, 1929; α and β domeykite, Cu_3As, STEENBERG, 1938; Cu_5As_2, HEYDING and DESPAULT, 1960), but only the structures of algodonite and the α and β modifications of domeykite seem to have been described.

The crystal structure of the two polymorphs of Cu_3As were studied by STEENBERG (1938) from powder x-ray diffraction data. For α do-

* Contribution no. 307a. Part 90 on sulfides and sulfosalts. Department of Crystallography of the University, CH-3012 Bern, Sahlistr. 6.

** Present address: Instituto de Edafología y Biología Vegetal del C.S.I.C., Sección de Físico-Química de Arcillas, Serrano 115 bis, Madrid-6.

meykite he proposed a model based on space group T_d^6—$I\bar{4}3d$ for which he reported a cell edge $a = 9.612$ Å[1] and interatomic distances of 2.57 Å for Cu—Cu and 2.64 Å for Cu—As. This model has been critisized by WYCKOFF (1964) on the basis of producing a Cu—As distance considerably in excess of the sum of the neutral radii. It is perhaps significant that STEENBERG reports a Cu—As distance of 2.36 Å for the hexagonal polymorph (β domeykite), which he considers to be too short, but PAULING (1947) predicts a Cu—As distance of 2.38 Å for covalently bonded atoms, and it would appear that the distance obtained by STEENBERG for the hexagonal modification is in good agreement with the expected value, while the distance obtained in the structure of the cubic form would be too long. On the basis of the similarity that STEENBERG found between the structure of α Cu_3As and that of $Cu_{15}Si_4$, which defines type $D8_6$ of *Strukturbericht* (1937), PEARSON (1958) suggests that perhaps the stoichiometry of α domeykite would correspond to $Cu_{15}As_4$. Since STEENBERG's structure was obtained from powder data it was felt that a study on a single crystal would be justified to clear matters up.

Experimental

Black fragments of α domeykite were obtained from sample AK 304—64 of the mineralogical collection of this laboratory, which originates from Mohawk No. 2 Mine, Keweenaw County, Michigan. The crystal selected for this study was a wedge shaped fragment with approximate dimensions $0.11 \times 0.17 \times 0.04$ mm. Oscillation and Weissenberg photographs showed the crystal to be cubic, Laue class $m3m$. The systematic absences observed were hkl, $h+k+l = 2n+1$, hhl, $2h + l \neq 4n$, which uniquely identify the space group as $I\bar{4}3d$, in agreement with STEENBERG's result. The cell edge was determined with the help of a back-reflection Weissenberg photograph (with nominal camera radius of 57.29 mm) calibrated with the powder pattern of pure silicon, taken at a temperature of 18 °C. A set of 18 θ-values ($65° < \theta < 80°$) was obtained using Cu$K\alpha_1$, Cu$K\alpha_2$, Ni$K\alpha_1$, Ni$K\alpha_2$, Ni$K\beta$ and W$L\alpha_1$ radiations ($\lambda = 1.540562$ Å, 1.544390 Å, 1.657910 Å, 1.661747 Å, 1.500135 Å and 1.47639 Å respectively, *International tables*, 1974). A least-squares fit of these data gave $a = 9.619 \pm 0.001$[2] Å, in good agreement with the value found by STEENBERG.

[1] In all what follows, the distances given in STEENBERG's paper have been multiplied by 1.002056.

[2] The error quoted amounts to ten times the calculated standard deviation.

The intensity data were collected in a Weissenberg geometry diffractometer (Supper-Pace) using Ni-filtered Cu radiation. The crystal was rotated around [010] and the intensities were measured by the moving-crystal—stationary-counter technique, with a wide receiving aperture in front of the Xe-filled proportional counter, and the channel width of the pulse-height analyzer set to accept about 88% of the incident energy. Eleven layers in reciprocal space, $h0l$ to $h\,10\,l$ were explored for a total of 1048 reflections, distributed over the accessible reflections of one quarter of the Cu sphere. The basis for accepting a reflection as statistically non zero was

$$\frac{(P - mb)^2}{P + m^2 b} > 3.881$$

where P is the total integrated peak count, and b is the background count corresponding to $(1/m)$th of the time used to measure P. A general absorption correction based on HOWELLS' method (ALCOCK, 1970) was applied to the data. For the purposes of this correction the crystal was described as a convex polyhedron bounded by six faces. The maximum and minimum values of the calculated transmission factor (on F^2) were respectively 0.3209 and 0.0698. Weights were assigned by the formula (GABE, 1966)

$$w = \frac{1}{\sigma^2(F)} = \frac{4(P - mb)}{K(P + m^2 b)}$$

where K is the product of the absorption, Lorentz and polarization corrections. Symmetry equivalent reflections were then merged by weighted average. The discrepancy between equivalent reflections, estimated by the residual

$$\frac{\sum_j (\sum_i |F_i - \bar{F}|)_j}{\sum_j (\sum_i F_i)_j}$$

was 0.0398 (i runs over all equivalent reflections of a particular set and j runs over all independent reflections). Friedel pairs of the type hkl and $\bar{h}kl$ were considered as independent reflections since the space group is non-centrosymmetric and there was some hope of detecting the small effect of anomalous dispersion. After merging equivalent reflections, a total of 147 independent structure amplitudes was obtained (systematic absences not counted), of which eight were unobserved.

Refinement

The structure was refined by least-squares methods starting from the atomic parameters published by STEENBERG (1938). A few cycles of refinement using isotropic thermal parameters gave $R = 0.076$ for all 147 reflections. In subsequent cycles the eight unobserved reflections were assigned zero weight, and the same was done with the eight strongest reflections, because they were suspected of being affected by extinction (their observed values were much lower than the calculated ones, and their influence was producing ill-behaved thermal parameters). Six cycles of least-squars refinement with anisotropic thermal parameters lowered the discrepancy index to $R = 0.0256$ for the 131 reflections used in the refinement, and $wR = 0.0191$. With the atomic parameters thus obtained, a structure-factor calculation gave $R = 0.0433$ for all 147 reflections, $\{R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)\}$. The standard deviation of an observation of unit weight was 0.7. The atomic scattering factors were taken from CROMER and MANN (1968); those corresponding to neutral atoms were used, corrected for the real and imaginary part of the dispersion term. Separate refinements were carried out with positive and negative signs for f'', and from these the correct absolute orientation was ascertained by means of a statistical test (HAMILTON, 1965) by which it was possible to reject the incorrect one at least at the 0.005 significance level. The R values quoted above correspond to the refinement with $f'' > 0$ but this (ROGERS, 1975) merely indicates how the crystal was mounted in the diffractometer. The final atomic coordinates are listed together with STEENBERG's in Table 2. This table also contains the final values for the anisotropic

Table 1. *Diffraction data of α domeykite*

Composition	Cu_3As
Molecular weight	265.54
Z	16
Space group	$I\bar{4}3d$
$F(000)$	1920 electrons
μ	487.3 cm^{-1} (for $\lambda = 1.54178$ Å)
ϱ_x	7.92 g/cm^3

	STEENBERG (1938)	BERRY and THOMPSON (1962)	This work
a	9.612 Å	9.62 Å	9.619(1) Å

thermal parameters. The root-mean-square displacements of the atoms along the thermal ellipsoid axes, and the angles of these with the crystal axes are presented in Table 3.

An electron-density difference map showed negative regions at the atomic positions, an effect not entirely unexpected since the stronger observed structure amplitudes were lower than their calculated values. A second differential density map was computed assigning the strong reflections their calculated amplitudes. This map showed maxima at the atom locations of about 0.6 e/Å^3 and 0.5 e/Å^3 for As and Cu respectively. The map also showed other maxima of about 0.9 e/Å^3, and some of them were at the $12a$ sites which correspond to additional Cu locations in the structure of $Cu_{15}Si_4$. There were however other humps of similar density at other locations in the unit cell, and they

Table 2. *Positional and thermal parameters for α domeykite* (standard deviations in parentheses), the temperature factor being $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + kl\beta_{23})]$.

Atom	Wyckoff position	STEENBERG (1938)	This work	Thermal parameters
Cu	$48e$ 1	$x = -0.03$	$x = -0.0293(1)$	$\beta_{11} = 0.0029(1)$
	xyz	$y = 0.12$	$y = 0.1202(1)$	$\beta_{22} = 0.0023(1)$
		$z = 0.20$	$z = 0.1876(1)$	$\beta_{33} = 0.0044(1)$
				$\beta_{12} = -0.0001(1)$
				$\beta_{13} = 0.0009(1)$
				$\beta_{23} = 0.0001(1)$
As	$16c$ 3	$x = -0.03$	$x = -0.02980(7)$	$\beta_{11} = \beta_{22} = \beta_{33} = 0.00190(6)$
	xxx			$\beta_{12} = \beta_{13} = \beta_{23} = -0.00009(7)$

Table 3. *Data on the thermal ellipsoids of the atoms in α domeykite*

Atom	B isotropic*	Ellipsoid axis	Root-mean-square amplitude	Angle with a	Angle with b	Angle with c
Cu	1.194 Å	1	0.1034 Å	116.22°	149.60°	75.70°
		2	0.1088	37.58	120.27	110.07
		3	0.1511	65.14	87.47	25.01
As	0.703 Å	1	0.0897	54.73	54.73	54.73
		2	0.0966	65.60	65.60	144.25
		3	0.0966	113.80	113.80	34.79

* HAMILTON (1959).

probably represent nothing more than background noise due to series termination (maximum value of $(\sin\theta)/\lambda$ is 0.61).

From these results we conclude that the formula of α domeykite is indeed Cu_3As and not $Cu_{15}As_4$ as suggested by PEARSON (1958) and HEYDING and DESPAULT (1960). The latter authors also conclude from their work and that of BOLFA, PASTANT and ROUBAULT (1950) that α domeykite is exclusively a high-pressure phase. However, α domeykite has been synthesized at atmospheric pressure by WEIL and HOCART (1951), although the lattice parameter they report 9.67 Å, is slightly longer than the values given in Table 1, and also longer than the value (9.60 Å) that these authors finde for a sample of α domeykite from Paracatas (Mexico).

Discussion

The result of the above analysis confirm that STEENBERG's (1938) model for the structure of α domeykite was correct, and considering the experimental method used and the time of its publication, very accurate. The position of the As atom is almost exactly the same in both models (the displacement amounts to 0.003 Å) and that of the Cu atom is very similar, the difference between both positions being only 0.12 Å. This however, considerably changes some of the interatomic distances, as can be appreciated in Table 4, in particular some among the Cu—Cu distances. Our shortest Cu—As distance of 2.414 Å agree very well with the corresponding distance found in lautite, AsCuS (2.417 Å, MARUMO and NOWACKI, 1964; 2.416 Å, CRAIG and STEPHENSON, 1965), and is not very different from PAULING's (1947) predicted value for covalently bonded atoms (2.383 Å). This distance corresponds to 2.39 Å in STEENBERG's paper; for unknown reasons STEENBERG quoted 2.64 Å as the (shortest) Cu—As distance, while his model in fact contains also shorter distances of 2.39 Å and 2.60 Å. The error has propagated into reference books (*Strukturbericht*, 1941; WYCKOFF, 1964), and the validity of the structure has even been questioned for that reason (see above).

The Cu—Cu distances are in good agreement with the distance found in the metal (2.55 Å, *International tables for x-ray crystallography*, vol. III), and their spread is smaller in our model than in STEENBERG's version. It should be noted that STEENBERG's coordinates produce Cu—Cu distances of 2.50 Å, 2.55Å, 2.57 Å and 2.75 Å (Table 4) of which only the last two are mentioned in his paper and in the subsequent literature.

Table 4. *Interatomic distances* less than 4 Å in α domeykite*

	This work		STEENBERG**	
As—Cu	3 ×	2.414 Å	3 ×	2.39 Å
	3 ×	2.540	3 ×	2.64
	3 ×	2.605	3 ×	2.60
	3 ×	3.404	3 ×	3.29
	next As—Cu = 4.155			
Cu—As		2.414		2.39
		2.540		2.64
		2.605		2.60
		3.404		3.29
Cu—Cu		2.562		2.57
	2 ×	2.604	2 ×	2.55
		2.604		2.50
	2 ×	2.615	2 ×	2.75
	2 ×	2.922	2 ×	2.94
	2 ×	3.941	2 ×	4.04

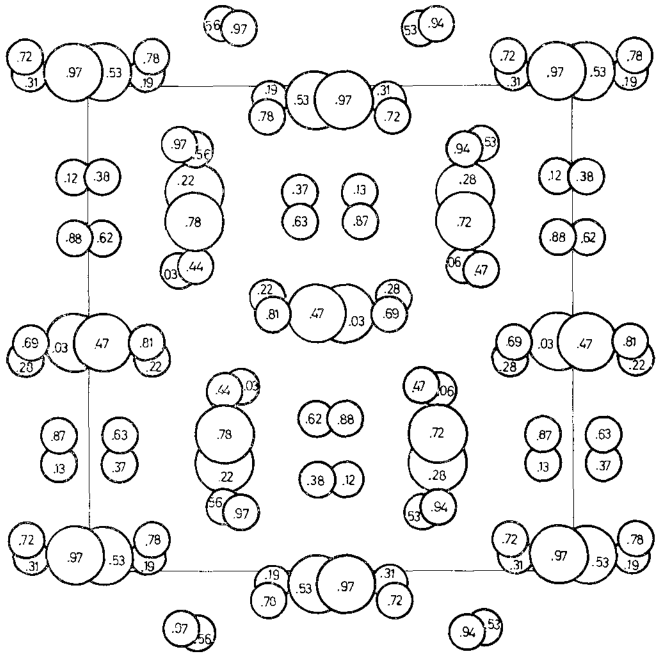
* All distances in this work have an estimated standard deviation of 0.001 Å (error in cell dimensions not included in the estimation).

** Distances calculated using $a = 9.612$ Å and the atomic parameters given in STEENBERG's paper.

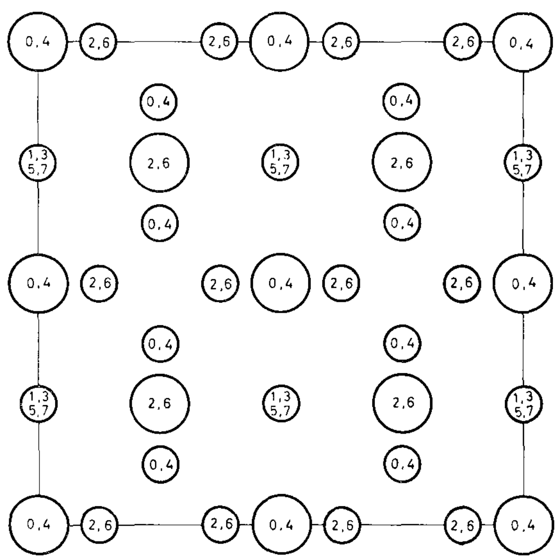
The structure can be described as a distortion of the β-W structure type (*A*15, *Strukturbericht*, 1937, p. 6). The As atoms are approximately at the nodes of a body-centered lattice with a cell edge equal to half that of the crystal, occupying positions homologous to those of W_I in the *A*15 type. The Cu atoms are not far from the array of sites which define the $\frac{1}{4}\frac{1}{4}\frac{1}{4}W_2$ lattice complex[3] (FISCHER, BURZLAFF, HELLNER and DONNAY, 1973, p. 37); these are the positions occupied by W_{II} in the *A*15 type. The distance from the As atoms to their ideal position amounts to only 0.052 Å; the corresponding distance for Cu atoms is larger, 0.665 Å. The α-domeykite structure and the *A*15 structure (cell edges doubled) are depicted together in Fig. 1. The cell edge of the *A*15 structure has been taken (after doubling) as equal to that of α domeykite, in order to facilitate direct comparison.

In the ideal structure, the As atom would be icosahedrally surrounded by 12 Cu atoms at a distance of $\sqrt{5}\,a/8 \simeq 2.689$ Å. In the real structure,

[3] Kind information of Prof. W. FISCHER, Münster.

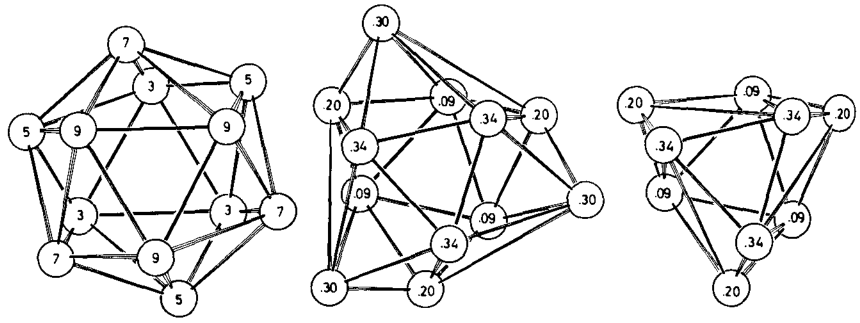


(a)



(b)

Fig. 1. (a) Projection of the structure of α domeykite in the [001] direction. Large circles are As atoms, smaller circles are Cu Atoms. (b) Projection of the idealized structure (β-W = *A* 15 type) in the [001] direction. Symbols as in (a)



(a) (b) (c)

Fig. 2. Projections in the [111] direction of the Cu polyhedra around As atoms (central atoms not shown); heights in fractions of the length of the body diagonal (a) Idealized structure, heights in 1/24ths. Central atom at 6/24. (b) Distorted icosahedron observed in actual structure. Central atom at 0.22. (c) Coordination polyhedron which results if only the nine shortest Cu—As distances are considered. Central atom at 0.22. Distances from central atom: 2.414 Å to atoms at 0.20, 2.540 Å to atoms at 0.34 and 2.605 Å to atoms at 0.09

there are 9 Cu atoms at distance between 2.414 Å and 2.605 Å of the As atom, and the remaining three Cu atoms which would complete the icosahedron are at 3.404 Å. The average distance is then 2.741 Å, not very different from the theoretical value. The ideal icosahedron, the distorted icosahedron, and the actual coordination polyhedron that results of only considering a coordination number of 9 are shown in projection parallel to [111] in Fig. 2. The observed ninefold coordination polyhedron can be regarded as a distorted version of the vertex figure of the semiregular four-dimensional polytope $S\{3, 4, 3\}$ (COXETER, 1973, p. 151—152), which has been reported as a structural feature in R-105 elemental boron (see, for instance, DONOHUE, 1974, p. 61—78). In that structure, the polyhedron results of the condensation of three empty boron icosahedra. It is also possible to interpret the coordination polyhedron of As in α domeykite as the result of the condensation of three Cu-filled icosahedra made up of Cu and As atoms, but since the 12 Cu vertex distances in these icosahedra are not the 12 shortest observed distances around a Cu atom, and these icosahedra are very distorted, we prefer not to carry on the analogy any further.

The coordination of a Cu atom in the ideal $A15$ structure would be to 8 Cu atoms at a distance $a/4\sqrt{3/2} \sim 2.945$ Å, to two Cu atoms

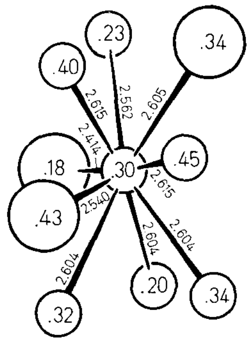


Fig. 3. Coordination polyhedron around a Cu atom, projected in the [111] direction. Large circles are As, smaller circles are Cu. Indicated distances are in Å

at $a/4 \simeq 2.405$ Å, and to four As atoms at a distance of $a\sqrt{5}/8 \simeq 2.688$Å. The resulting average Cu—Cu distance would be 2.873 Å. The average distance in the observed structure for the ten shortest Cu—Cu distances is 2.933 Å. The actual coordination polyhedron around the Cu atoms is not easy to define (Fig. 3). There are three As atoms at 2.414 Å, 2.540 Å and 2.605 Å, and six Cu atoms at distances ranging between 2.562 Å and 2.615 Å. Two more Cu atoms are at 2.922 Å from the central atoms; but these can be perhaps considered as nonbonded, since their distances interrupt an otherwise smooth sequence of Cu—Cu separations. We can calculate the average Cu—Cu separation by PAULING's (1947) equation.

$$\Delta R(n) = 0.3 \cdot \log n$$

by puting

$$n = \frac{1}{m} (5.44—3)$$

where m is the number of Cu atoms bonded to the central atom, and 5.44 and 3 are the metallic valence of Cu and As respectively. If we assume there are six Cu atoms bonded to the central atom, the average Cu—Cu separation is calculated as 2.580 Å, while the observed average value for the six shortest distances is 2.601 Å; if the assumption is made that eight Cu atoms are bonded to the central Cu, the calculated distance is 2.655 Å. and the observed value is 2.681 Å. Therefore it is not absolutely clear that the last two atoms should be excluded from the coordination sphere. The polyhedron formed by 3 As + 6 Cu atoms could be described as a distorted triangular antiprism formed by

5 Cu + 1 As, plus 2 As + 1 Cu lying close to its equator, *i.e.* the plane through the central Cu atom parallel to the two triangular faces.

In view of the relations between the structure of α domeykite and the *A* 15 type, and the apparently well-established fact that α domeykite is a low-pressure phase (1—1000 bars), one can speculate with the possibility that this compound would perhaps undergo a second-order phase transition to the *A*15 type at sufficiently high pressures.

Acknowledgement

We extend our thanks to Dr. V. DIVJAKOVIĆ, Dr. A. EDENHARTER and PD Dr. P. ENGEL for their help with experimental and computing techniques. The work was supported by Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (project no. 2.228-0.74) and Stiftung Entwicklungsfonds Seltene Metalle.

References

N. W. ALCOCK (1970), The analytical method for absorption correction, in *Crystallographic computing*, F. R. AHMED (editor), Munksgaard, Copenhagen, p. 271—278.

L. G. BERRY and R. M. THOMPSON (1962), *X-ray powder data for ore minerals: The Peacock atlas.* Geol. Soc. Amer., New York, p. 30.

J. BOLFA, R. PASTANT et M. ROUBAULT (1950), Réalisation de la synthèse des arséniures de cuivre par frittage. C. R. Acad. Sci. [Paris] **230**, 103—104.

H. S. M. COXETER (1973), *Regular polytopes*, 3rd edition, Dover Publ. Inc., New York, p. 163.

D. C. CRAIG and N. C. STEPHENSON (1965), The crystal structure of lautite, CuAsS. Acta Crystallogr. **19**, 543—547.

D. T. CROMER and J. B. MANN (1968), X-ray scattering factors computed from numerical Hartree-Fock wave functions. Acta Crystallogr. A **24**, 321—324.

J. DONOHUE (1974), *The structures of elements.* John Wiley and Sons, New York, p. 68 and foll.

W. FISCHER, H. BURZLAFF, E. HELLNER and J. D. H. DONNAY (1973), Space groups and lattice complexes. Natl. Bureau Standards, Washington, p. 73.

E. J. GABE (1966), 1620 programs from the Institute for Cancer Research Dept. of Molecular Structure (Physics Dept.) I.C.R. 16, Data reduction.

W. C. HAMILTON (1959), On the isotropic temperature factor equivalent to a given anisotropic temperature factor. Acta Crystallogr. **12**, 609—610.

W. C. HAMILTON (1965), Significance tests on the crystallographic *R* factor. Acta Crystallogr. **18**, 502—510.

R. D. HEYDING and G. J. G. DESPAULT (1960), The copper-arsenic system and the copper arsenide minerals. Canad. J. Chem. **38**, 2477—2481.

International tables for x-ray crystallography (1962), Vol. III. The Kynoch Press, Birmingham.

International tables for x-ray crystallography (1974), Vol. IV. The Kynoch Press, Birmingham.

Z. Johan (1960), Koutekit—Cu_2As, ein neues Mineral. Chemie Erde **20**, 217—226.

Z. Johan (1961), Paxite, Cu_2As_3, a new copper arsenide from Černý Důl in the Giant Mts. (Krkonoše). Acta Univer. Carolinae, Geologica 1961 (2), 77—86. [in Czech; English abstract: Amer. Min. **47** (1962) 1484—1485.

F. Machatschki (1929), Algodonit und Whitneyit. N. Jahrb. Min. **59** A, 137—158.

F. Marumo and W. Nowacki (1964), The crystal structure of lautite and of sinnerite, a new mineral from the Lengenbach quarry. Schweiz. Min. Petr. Mitt. **44**, 439—454.

L. Pauling (1947), Atomic radii and interatomic distances in metals. J. Amer. Chem. Soc. **69**, 542—553.

W. B. Pearson (1958), A handbook of lattice spacings and structures of metals and alloys. Pergamon Press, London, p. 395.

D. Rogers (1975), Some fundamental problems of relating tensorial properties to the chirality or polarity of crystals, in *Anomalous scattering*, S. Ramaseshan and S. C. Abrahams (editors), I.U.Cr., Munksgaard, Copenhagen, p. 231—250.

B. Steenberg (1938), The crystal structure of Cu_3As and Cu_3P. Arkiv Kemi Min. Geol. **12** A, no. 26, 1—15.

Strukturbericht (1937), Band II (1928—1932), p. 6.

Strukturbericht (1941), Band VI (1938), p. 66—67.

R. Weil and R. Hocart (1951), Synthèse simultanée de la domeykite cubique et de la domeykite héxagonale, en milieu liquide et à la pression ordinaire. C.R. Acad. Sci. [Paris] **233**, 880—882.

R. Wyckoff (1964), *Crystal structures*. 2nd. edition, vol. 2. Interscience Publishers, New York, p. 110.