Zeitschrift für Kristallographie, Bd. 124, S. 352—368 (1967)

The crystal structure of nowackiite, $Cu_6Zn_3As_4S_{12}$*

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(Received August 26, 1966)

Auszug

Die Kristallstruktur eines neuen Cu-Zn-Arsensulfosalzes, $Cu_6Zn_3As_4S_{12}$ wurde bestimmt. Der Kristall ist rhomboedrisch mit den Gitterkonstanten $a_{rh} = 8{,}34$ Å, $\alpha_{rh} = 107°20'$, $a_{hex} = 13{,}44$ Å, $c_{hex} = 9{,}17$ Å und der Raumgruppe C_3^4—$R3$. Die Struktur konnte durch Interpretation einer dreidimensionalen, nur mit Überstrukturreflexen berechneten Pattersonsythese gefunden werden. Es war nicht möglich, die Cu- von den Zn-Atomen zu unterscheiden.

Es handelt sich um einen defekten Zinkblendestrukturtyp, wobei die S-Lagen auf den dreizähligen Achsen unbesetzt sind. Vier As-Atome koordinieren die Leerstellen; jedes As hat eine trigonal-pyramidale Koordination von S-Atomen. Die (As—S)-Abstände zwischen 2,24 Å und 2,27 Å befinden sich in guter Übereinstimmung mit dem (As—S)-Abstand bei kovalenter Bindung. Die erhaltenen (Cu, Zn—S)-Abstände liegen zwischen 2,279 Å und 2,355 Å.

Abstract

The crystal structure of a new copper zinc arsenosulfosalt, $Cu_6Zn_3As_4S_{12}$ has been determined. The crystal is rhombohedral, having the unit-cell dimensions $a_{rh} = 8.34$ Å, $\alpha_{rh} = 107°20'$, $a_{hex} = 13.44$ Å, $c_{hex} = 9.17$ Å, and the symmetry C_3^4—$R3$. The structure was solved by interpretation of a three-dimensional Patterson function synthetized with super-lattice reflections only. It was not possible to distinguish between Zn and Cu atoms.

The crystal has a defect zincblende-type structure, the S atom positions on three-fold rotation axes being vacant. Four As atoms surround the vacant sites, each As atom having a trigonal-pyramidal coordination of S atoms. The As—S distances ranging between 2.24 Å and 2.27 Å are in good agreement with the As—S covalent bond length. The Cu—S and Zn—S distances obtained are between 2.279 Å and 2.355 Å.

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1. Introduction

A new copper zinc arsenosulfosalt mineral was found in an old collection of minerals from Lengenbach, Binnatal, Switzerland (MARUMO and BURRI, 1965). There were about ten small crystals of the mineral (ca. $\leqslant$ 0.3 mm), on a zincblende crystal. They are lead-gray to black, granular forms partly with good and partly with rounded faces.

The mineral was identified as a new species from an x-ray powder pattern, single-crystal x-ray diagrams and the chemical composition (by electron microprobe analysis). It is closely related to zincblende.

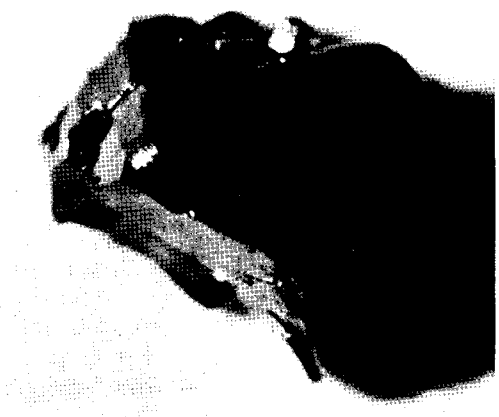


Fig. 1. Crystal of nowackiite, {0001} twin

The name *nowackiite* was proposed by MARUMO and BURRI (1965) for the mineral, in accordance with the suggestion of Mr. J. IMHOF, prospector in Binn, who gave us the specimen for investigation. Recently another crystal of the mineral was found, incorrectly labeled seligmannite. A photograph of the latter is shown in Fig. 1 [Lattice constants (P. ENGEL): $a_{hex} = 13.46 \pm 0.01$, $c_{hex} = 9.18 \pm 0.03$ Å; electron microprobe analysis (G. BURRI, no. 109): Cu 31.2 (30.3), Zn 15.8 (15.5), As 22.7 (23.8), S 30.9 (30.4), Σ 100.6 (100.0, theor. values)]. It is a twin, with {0001} as twinning plane.

In Cu—As—S sulfosalts, there are two possible types of coordinations around the As atoms, trigonal pyramidal and tetrahedral. The As atoms in binnite (WUENSCH, TAKÉUCHI and NOWACKI, 1966) show the former and those in luzonite (MARUMO and NOWACKI, 1967) and

enargite (PAULING and WEINBAUM, 1934) the latter. The structure determination of nowackiite was undertaken to determine the coordination around the As atoms in the mineral, and to clarify the structural relationship to the zincblende type.

2. Experimental

The crystal is rhombohedral. The unit-cell dimensions determined by oscillation and Weissenberg photographs are: $a_{rh} = 8.34 \pm 0.01$ Å, $\alpha_{rh} = 107°20' \pm 10'$, $a_{hex} = 13.44 \pm 0.015$ Å, $c_{hex} = 9.17$ Å ± 0.01 Å,

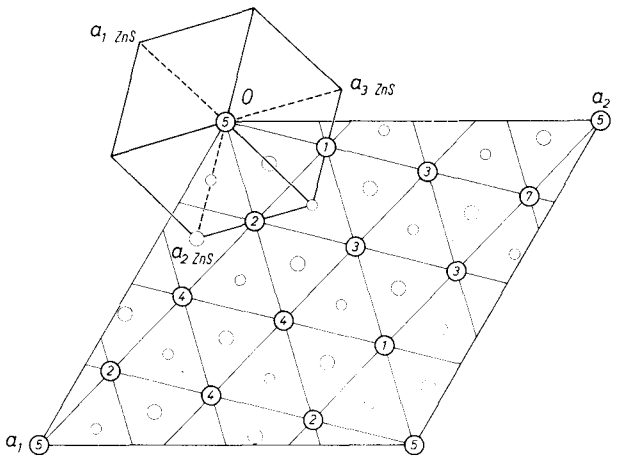


Fig. 2. Arrangement of equivalent points in nowackiite and the relation to zincblende

and the possible space groups obtained from the x-ray diagrams are $C_{3i}^2-R\bar{3}$ and C_3^4-R3. Since it is clear from the diagrams that the crystal has a zincblende-type structure, the crystal should be acentric. Accordingly the true space group is C_3^4R-3. The structure has subcells which are almost equal to the zincblende unit cell. The relation between the true cell and the zincblende unit cell is $a_{hex} \approx \frac{1}{2}[\bar{1}4\bar{3}]_{ZnS}$, $c_{hex} \approx [111]_{ZnS}$, $a_{rh} = \frac{1}{2}[01\bar{3}]_{ZnS}$, $V_{rh} \approx \frac{13}{4} V_{ZnS}$. The relation is also shown in Fig. 2. X-ray powder data obtained with Fe$K\alpha$ radiation are given in Table 1 for comparison with other minerals.

X-ray microanalysis (electron microprobe analysis) was carried out three times to determine the chemical composition (see Table 2). The average values of the composition obtained give with an assumed density of 4.3 $g \cdot cm^{-3}$ a unit-cell content of $Cu_{6.05}Zn_{3.04}As_{3.73}S_{12.46}$,

Table 1. *X-ray powder data of nowackiite collected with* Fe$K\alpha$ *radiation*
The lines with an asterisk are broad

I_0	d	I_0	d	I_0	d
13	3.19_8 Å	11	1.64_1	12	1.10_6*
61	3.12_7	61	1.60_5	20	1.08_5
10	2.69_9	7	1.53_2	75	1.08_1*
4	2.29_3	16	1.32_7	20	1.04_2*
2	1.97_8	7	1.24_4	100	1.01_9*
12	1.93_1	52	1.21_6*	3	0.988
63	1.88_7	12	1.18_5*	3	0.986

Table 2. *Electron microprobe* (CAMECA) *analyses of nowackiite*

	Cu	Zn	As	S	Total
1	31.2	15.9	22.4	31.9	101.4 wt.%
2	31.0	15.9	22.6	32.9	102.4
3	30.9	16.4	22.8	32.0	102.1
4	30.3	15.5	23.8	30.4	100.0

1. Analyst: G. Burri at the Bureau de Recherches Géologiques et Minières in Paris.
2. Same crystal as 1.; analyst G. Bahezre at the same place as 1.
3. The crystal used for the intensity measurements; analyst: G. Burri at the University of Bern.
4. Theoretical values for $Cu_6Zn_3As_4S_{12}$.

indicating an idealized empirical formula $Cu_6Zn_3As_4S_{12-13}$. According to the Grimm-Sommerfeld rule the total number of valence electrons devided by the number of atoms, including vacant sites, should be four if the structure is tetrahedral (Parthé, 1964, pp. 5 and 95). Therefore, the empirical formula of the crystal should be $Cu_6Zn_3As_4S_{12}$ if the structure is tetrahedral ($d_x = 4.38$).

For the intensity measurements, a piece of the crystal with an irregular form was used. The size of the crystal was about $0.12 \times 0.09_5 \times 0.08_8$ mm^3. Integrated Weissenberg photographs up to the eighth layer around the c_{hex}-axis and up to the third layer around the a_{hex} axis were taken with Cu$K\alpha$ radiation. The intensities were measured with a Joyce-Loebl double-beam densitometer and Lorentz-polarization and absorption corrections applied. A sphere with the diameter 0.092 mm was assumed for the absorption correction. Since μr is 1.43 for the sphere, this assumption does not cause serious errors in the observed structure amplitudes, if we measure several equivalent reflections and take the average values.

3. Structure determination

As stated before, the structure is of the zincblende type and one sulfur position in a rhombohedral unit cell is expected to be vacant from the Grimm-Sommerfeld rule. Three types of deviation from the ideal zincblende structure were considered; (1) interchange of metal atoms in the five independent metal-atom sites, (2) shifts of atoms from the ideal positions, and (3) vacancy in sulfur atom positions. The first type was presumed to have only a small influence on the intensities of the super-lattice reflections, since the differences of atomic numbers among the constituent metal atoms are small. Therefore, in the initial stage of the structure determination greater attention was paid to deviations of the second and the third type.

The arrangement of equivalent positions as well as the relation of the subcells to the true unit cell are shown in Fig. 2. The coordinates of ten independent atomic sites of the ideal zincblende-type structure referred to the hexagonal cell are given in Table 3. The origin of the z coordinate was taken at one of the metal atom positions. If one S atom position of the zincblende-type structure is vacant in the rhombohedral unit cell of the crystal, it should be on a three-fold rotation axis, namely at the S(5) position. It is very difficult from the ordinary Patterson function to determine such a small deviation from the average structure. Therefore, a three-dimensional Patterson function was calculated using only super-lattice reflections. This function is a kind of difference Patterson function. It is obvious that the function is more useful for the present purpose than the ordinary Patterson function. If we denote the indices of the main reflections, which corre-

Table 3. *Coordinates of atoms in an ideal zincblende-type structure referred to the hexagonal axes of nowackiite*

The origin of the coordinates is taken at the metal atom (5)

			x	y	z
Metal	(1)	$9b$	3/39	12/39	0
	(2)	$9b$	12/39	9/39	0
	(3)	$9b$	15/39	21/39	0
	(4)	$9b$	21/39	6/39	0
	(5)	$3a$	0	0	0
S	(1)	$9b$	3/39	12/39	3/4
	(2)	$9b$	12/39	9/39	3/4
	(3)	$9b$	15/39	21/39	3/4
	(4)	$9b$	21/39	6/39	3/4
	(5)	$3a$	0	0	3/4

spond to the subcell, by (HKL) and the indices of the super-lattice reflections by $(h'k'l')$, the electron density of the structure $\varrho(r)$ and the electron density of the structure averaged over all subcells $\varrho'(r)$ are respectively

$$\varrho(r) = \sum_H \sum_K \sum_L F(HKL) \exp[-2\pi i (Hx + Ky + Lz)]$$
$$+ \sum_{h'} \sum_{k'} \sum_{l'} F(h'k'l') \exp[-2\pi i (h'x + k'y + l'z)]$$
$$\varrho'(r) = \sum_H \sum_K \sum_L F(HKL) \exp[-2\pi i (Hx + Ky + Lz)].$$

Then, $\varrho(r) - \varrho'(r) = \sum_{h'} \sum_{k'} \sum_{l'} F(h'k'l') \exp[-2\pi i (h'x + k'y + l'z)]$.

The Patterson function $P'(r)$ calculated above is

$$P'(r) = \sum_{h'} \sum_{k'} \sum_{l'} |F(h'k'l')|^2 \cos 2\pi (h'x + k'y + l'z).$$

Therefore, $P'(r)$ is the Patterson function of $\varrho(r) - \varrho'(r)$. If we know $\varrho'(r)$ approximately, we can get $\varrho(r)$ by solving $P'(r)$. Since $P'(r)$ does not contain the experimental and termination errors of the strong reflections (HKL), $P'(r)$ gives more precise knowledge about the deviations. For comparison a section of the difference Patterson map and the corresponding section of the ordinary Patterson map are shown in Fig. 3 (a) and (b). It is clear that the difference Patterson method is much more advantageous for observing small deviations from an average structure. However interpretation of $P'(r)$ is in general rather difficult since the electron distribution around each atom in $\varrho(r)-\varrho'(r)$ depends on the amount of shift of the atom. Fortunately the crystal contains only ten independent atoms, including one vacant site, and the structure was solved with this method, as outlined below.

Since the structure is a zincblende type and the c_{hex} axis corresponds to [111] of zincblende, all (metal—metal) and (S—S) vectors are nearly in the $z = 0$ and equivalent planes, and (metal—S) vectors are in the $z = \frac{1}{4}$ and equivalent planes. The difference Patterson map near the planes $z = 0$ and $z = \frac{1}{4}$ are shown in Fig. 4 (a) and (b) respectively. If the S atom positions on the trigonal axes are vacant, as it is expected from the Grimm-Sommerfeld rule, the difference Patterson pattern can be explained fairly well by assuming shifts of metal atoms (4) and (5), as shown in Fig. 5. The pattern around the point C in the figure fits the vacancy—metal(5) vector, the pattern around D fits the vacancy—metal(4) vector, the pattern around A can be explained

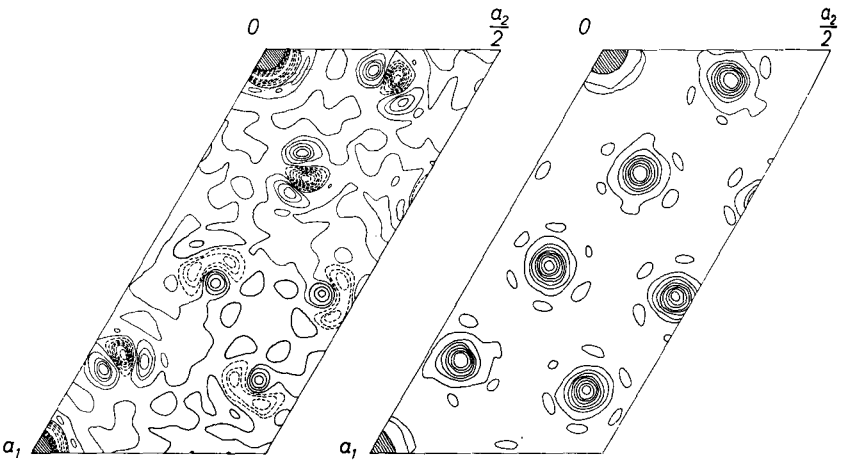


Fig. 3. The $z = 0$ sections of (*a*) the three-dimensional difference Patterson function and (*b*) the ordinary Patterson function. Contours are at equal but arbitrary intervals, negative contours being broken

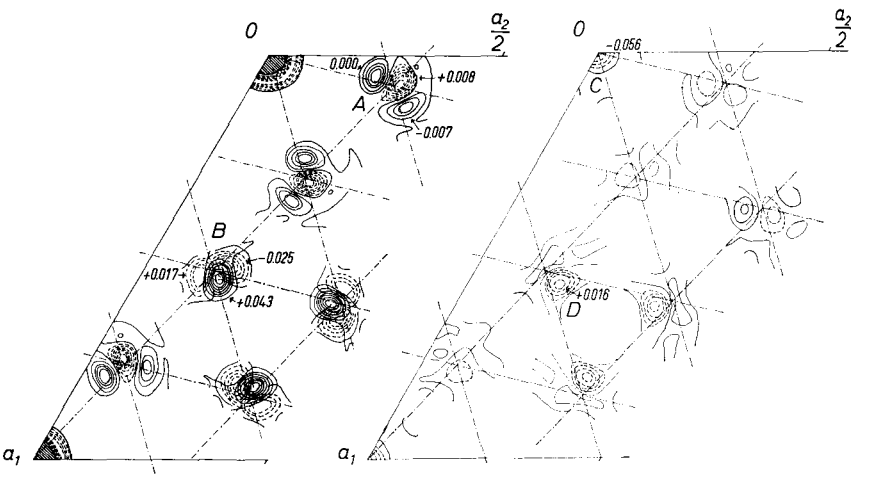


Fig. 4. The difference Patterson map (*a*) near the $z = 0$ plane and (*b*) near the $z = \frac{1}{4}$ plane. Contours are at equal but arbitrary intervals, negative contours being broken. There is a positive peak at 0,0,0.27 which is omitted in the figure, the height corresponding to two contours. The deviations of the maximum (minimum in the case of negative peaks) points from the planes $z = 0$ and $z = \frac{1}{4}$ are given in the figures

fairly well by the metal(4)—metal(4) vector and that around B by the metal(4)—metal(5) vector. The sum of Δz of the negative peaks at C and D is not equal to Δz of the positive peak at B. Presumably this is caused by shifts of other atoms. The structure factors were calculated taking the shifts as $\Delta x = 0.015$, $\Delta y = 0.010$ and $\Delta z = 0.010$ for the metal atom (4), and $\Delta z = -0.010$ for the metal atom (5). All metal

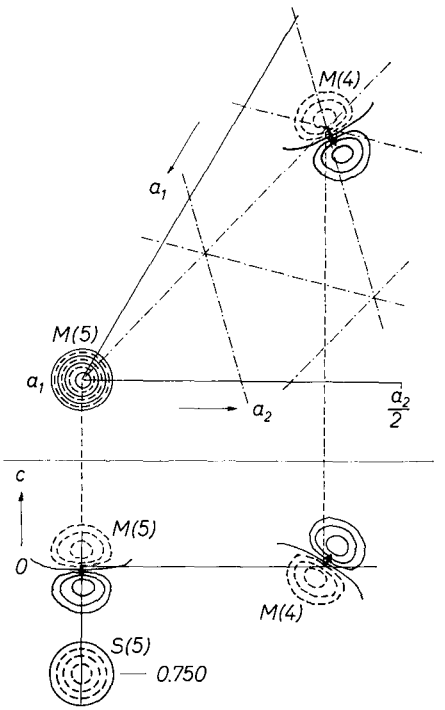


Fig. 5. The presumed shifts of atoms and the expected electron distribution in $\varrho(r)-\varrho'(r)$ near the points A, B, C and D. The direction of the shifts are shown by arrows. Negative contours are in broken lines

atoms were assumed as Cu in the calculation. The discrepancy factor, $R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$, was 0.44. Then a refinement of the structure was carried out by a three-dimensional difference Fourier synthesis. Directions of shifts of whole atoms were found in the difference Fourier map and the metal atoms (4) and (5) were revealed to be As atoms. The height of the peak at B in the difference Patterson map is much larger than the heights of the negative peaks near it. Also the heights of the negative peaks at C and D are much larger than the heights of the

positive peaks near them. Therefore, the difference Patterson pattern is explained better, if the metal atoms (4) and (5) have a larger electron density than the average for all metal atoms. This is the same conclusion as obtained above.

4. Refinement of the structure

Six cycles of refinement including the first mentioned above were carried out by means of the three-dimensional difference Fourier method. During the refinements individual isotropic temperature factors were used. The R factor decreased from the initial value 0.44 to 0.115, indicating the correctness of the model. Then the structure was refined by a least-squares method using anisotropic temperature factors. The program used is for the IBM 1620 computer and consists of two parts. The first part, the structure factor program and the least-squares sum maker, was written by D. VAN DER HELM (Philadelphia), and the second part, the least-squares sum processor, was written by P. ENGEL (Bern). The weighting scheme adopted was $w = |\overline{F}_0|/(|\overline{F}_0| + |F_0| + |F_0|^2/|\overline{F}_0|)$, where $|\overline{F}_0|$ is the mean value of the observed structure amplitudes. For non observed reflections $|F_0|$ was assumed as $2\,|F_{0,\,\mathrm{min}}|$ in the calculation of w. The atomic scattering factors used for neutral Cu and As are the values given by FREEMAN and WATSON and for S, those of DAWSON (International Tables for X-ray crystallography, Volume III). The atomic scattering factors were corrected for anomalous dispersion using the real components given by CROMER (1965). After five cycles of least-squares refinement, all parameter shifts were smaller than their standard deviations and the refinement was terminated. The final R value is 0.088 for all 680 reflections in the calculation and 0.078 for the 637 observed reflections. The final atomic

Table 4. *Atomic coordinates in nowackiite*

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
(Cu, Zn) (1)	0.0741	0.2932	0.9987	0.0003	0.0003	0.0003
(Cu, Zn) (2)	0.3088	0.2275	0.9920	0.0003	0.0003	0.0003
(Cu, Zn) (3)	0.3895	0.5539	0.0088	0.0003	0.0003	0.0004
As (1)	0.5533	0.1680	0.0071	0.0002	0.0002	0.0002
As (2)	0	0	0.9808	—	—	0.0002
S (1)	0.3695	0.1026	0.0792	0.0004	0.0004	0.0005
S (2)	0.4380	0.4150	0.0708	0.0004	0.0004	0.0005
S (3)	0.1251	0.1646	0.0909	0.0004	0.0004	0.0006
S (4)	0.2036	0.4750	0.0961	0.0004	0.0004	0.0005

Table 5. *Temperature factors.* The values are the coefficients in the expression exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{13}lh)]$. All values are multiplied by 10^5

	β_{11}	$\sigma(\beta_{11})$	β_{22}	$\sigma(\beta_{22})$	β_{33}	$\sigma(\beta_{33})$	β_{12}	$\sigma(\beta_{12})$	β_{23}	$\sigma(\beta_{23})$	β_{13}	$\sigma(\beta_{13})$	Equivalent isotropic temperature factors
(Cu,Zn)(1)	167	18	87	18	315	30	66	30	−165	38	−86	39	0.89 Å²
(Cu,Zn)(2)	89	16	112	17	252	28	40	27	− 18	35	60	34	0.72
(Cu,Zn)(3)	207	22	229	21	531	39	160	37	10	47	67	47	1.45
As(1)	128	14	145	14	252	24	84	23	− 39	30	−24	29	0.84
As(2)	122	12	122	12	74	20	122	21	0	27	0	27	0.52
S(1)	165	30	175	30	299	50	206	51	− 51	62	44	63	0.91
S(2)	162	30	151	30	288	50	117	50	− 16	65	14	63	0.93
S(3)	193	32	140	31	445	56	186	53	30	68	112	69	1.08
S(4)	90	27	189	30	284	48	152	50	203	62	61	59	0.81

parameters and the standard deviations are given in Tables 4 and 5. The observed and calculated structure amplitudes are given in Table 6 for comparison.

5. Description of the structure

The a_{hex}- and the c_{hex}-axis projections of the structure are shown in Fig. 6(*a*) and (*b*), respectively. The structure is a zincblende type with one vacant sulfur site in a rhombohedral unit cell, containing one chemical unit of $Cu_6Zn_3As_4S_{12}$. The deviations of the atoms from the ideal zincblende structure are very small. They range between 0.09 Å and 0.21 Å (see Table 7). The deviations were calculated by taking the origin of the z coordinates as the mean of the z parameters of those metal atoms which are nearly on the plane $z = 0$, and of the z parameters of the sulfur atoms (minus 0.7500) which are nearly on the plane $z = 0.7500$. Since $[111]_{\text{zincblende}} = 9.36_9$ Å and $\frac{1}{2}[\bar{1}4\bar{3}]_{\text{zincblende}} = 13.79_2$ Å, the unit cell of nowackiite is compressed as compared with zincblende. (This means that $V_{\text{nowackiite}} < 13 \cdot V_{\text{zincblende}}$ because $[111]_{\text{zincblende}} = 9.36_9$ Å $> c_{\text{nowackiite}}$ and $\frac{1}{2}[\bar{1}4\bar{3}]_{\text{zincblende}} = 13.79_2$ Å $> a_{\text{nowackiite}}$). The axial ratio $c_{\text{hex}}/a_{\text{hex}}$ of the crystal is 0.682_3, which is very close to the ratio $9.36_9/13.79_2 = 0.679_3$.

Interatomic distances and bond angles are given in Tables 8 and 9. They are also shown in Fig. 7. The (Cu,Zn—S) distances and the (As—S) distances are in good agreement with those obtained in luzonite

Table 6. *Comparison of the observed and the calculated structure amplitudes of nowackiite*

h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
3 0 0	16.1	16.7	-1 10 1	160.8	160.9	-4 12 2	27.7	26.3	-13 14 3	27.4	30.7
6	34.4	35.4	-4	0	7.8	-7	47.3	46.4	-3 15 3	10.2	6.6
9	8.5	8.9	-7	41.9	40.4	-10	0	7.0	-6	44.1	41.8
12	15.4	10.9	0 11 1	43.9	43.7	0 13 2	39.0	34.7	-9	8.9	7.4
1 1 0	9.6	12.2	3	13.1	9.7	-3	0	2.4	-12	21.6	24.5
4	50.4	43.3	-3	10.3	13.5	-6	54.0	51.3	-5 16 3	38.4	40.3
7	27.4	28.3	-6	0	7.5	-9	34.4	34.8	-8	26.7	29.8
10	18.9	17.0	-9	20.8	17.0	-12	15.6	14.6	-11	14.1	17.0
13	19.4	20.2	1 12 1	10.2	7.3	1 14 2	25.6	27.3	1 0 4	47.5	44.1
2 2 0	15.4	13.7	4	78.3	80.2	-2	22.8	21.3	4	20.1	16.2
5	261.4	322.9	-2	62.7	60.8	-5	17.8	15.4	7	35.9	34.9
8	0	6.4	-5	25.7	24.6	-8	31.7	31.4	10	16.7	16.1
11	36.6	37.1	-8	19.9	17.9	-11	23.4	21.9	13	124.6	116.7
3 3 0	33.9	24.9	-11	32.3	36.0	-1 15 2	40.8	44.4	2 1 4	41.2	34.3
6	54.6	52.6	2 13 1	15.6	16.8	-4	30.1	28.6	5	35.9	32.6
9	43.7	41.8	-1	21.9	20.2	-7	28.3	25.8	8	25.0	24.7
12	20.3	19.2	-4	24.5	25.5	-10	18.3	17.1	11	33.9	32.2
1 4 0	16.5	15.4	-7	40.8	38.0	-13	16.1	13.4	0 2 4	12.3	8.3
4	47.0	43.9	-10	25.2	24.9	-3 16 2	22.1	28.0	3	15.8	15.6
7	19.2	16.6	0 14 1	17.4	16.6	-6	16.1	20.2	6	41.2	38.9
10	152.8	144.5	-3	29.0	29.2	-9	25.0	21.2	9	0	3.1
2 5 0	15.6	16.1	-6	41.3	40.1	-12	22.1	25.2	12	32.5	37.8
5	10.3	6.3	-9	28.3	27.9	-8 17 2	13.4	15.3	1 3 4	290.6	326.0
8	31.2	31.4	-12	11.2	9.2	0 0 3	240.9	320.9	4	33.0	32.2
11	43.1	44.4	-2 15 1	26.5	25.4	3	28.8	26.5	7	44.1	43.8
3 6 0	19.0	17.9	-5	25.7	25.5	6	39.7	37.6	10	16.1	17.1
6	20.7	19.7	-8	114.9	97.7	9	27.0	24.9	-2	31.4	28.1
9	41.3	40.5	-11	0	2.9	12	35.7	33.5	2 4 4	23.4	26.0
1 7 0	17.6	16.5	-14	16.1	15.2	1 1 3	17.8	14.0	5	34.8	29.7
4	49.3	46.7	-4 16 1	0	10.0	4	36.3	32.5	8	20.7	18.3
7	13.6	12.0	-7	22.5	20.8	7	37.7	37.1	11	21.0	24.0
10	6.5	6.4	-10	24.5	24.8	10	38.4	38.0	-1	7.8	5.0
2 8 0	41.5	35.6	-13	0	5.4	13	13.6	13.9	0 5 4	45.0	43.6
5	26.5	23.9	-9 17 1	33.7	36.7	2 2 3	24.5	20.4	3	15.2	13.7
8	14.9	17.2	2 0 2	7.3	8.6	5	188.6	212.4	6	181.8	185.2
3 9 0	172.2	183.3	5	54.0	53.5	8	15.4	16.4	9	20.1	20.7
6	16.1	15.3	8	26.1	25.8	11	44.6	44.6	-3	18.7	15.2
1 10 0	35.7	35.8	11	33.9	33.2	-1	21.2	21.6	1 6 4	21.9	19.7
4	41.2	39.0	14	28.3	29.4	0 3 3	34.3	28.5	4	25.6	25.0
7	24.7	27.0	0 1 2	17.2	15.6	3	21.8	16.7	7	37.2	38.3
2 11 0	52.8	49.1	3	37.3	37.7	6	45.9	44.3	10	19.6	23.2
5	12.7	12.1	6	31.2	29.4	9	35.9	35.7	-2	28.8	25.6
3 12 0	6.9	5.4	9	73.2	66.2	12	24.8	25.9	-5	41.7	36.6
1 13 0	20.7	21.8	12	21.0	19.2	1 4 3	19.9	14.1	2 7 4	7.8	7.3
1 0 1	8.3	6.2	1 2 2	14.9	12.7	4	28.3	25.2	5	46.6	48.2
4	8.9	10.4	4	31.2	26.8	7	23.6	23.2	8	11.4	13.4
7	48.4	46.5	7	14.9	13.5	10	107.1	97.2	-1	37.7	37.3
10	25.7	24.5	10	55.1	54.3	-2	47.1	43.4	-4	36.3	32.7
13	108.1	95.7	13	15.6	20.1	2 5 3	21.8	19.2	0 8 4	49.0	49.0
2 1 1	23.9	23.5	2 3 2	41.5	40.9	5	36.8	36.0	3	14.3	15.8
5	8.7	3.1	5	6.7	11.3	8	14.1	14.5	6	13.2	14.1
8	9.6	9.6	8	35.0	36.1	11	34.8	39.1	-3	41.2	40.3
11	35.5	36.8	11	27.2	27.3	-1	41.5	38.5	-6	226.4	238.3
14	36.3	37.5	-1	4.4	6.6	-4	44.1	43.1	1 9 4	25.9	27.0
0 2 1	15.4	12.9	0 4 2	16.1	16.3	0 6 3	18.7	18.0	4	28.3	28.8
3	8.9	4.8	3	20.5	18.3	3	46.8	45.7	7	7.3	9.5
6	30.3	28.2	6	0	5.8	6	14.1	13.5	-2	25.6	22.8
9	0	8.2	9	33.9	36.0	9	18.1	16.9	-5	28.3	26.0
12	41.3	43.7	12	15.6	14.4	-3	21.2	18.0	-8	37.7	36.2
1 3 1	273.2	321.8	-3	140.7	135.7	1 7 3	23.9	22.6	2 10 4	30.3	30.9
4	15.6	12.7	1 5 2	23.4	22.6	4	48.4	48.4	5	36.3	38.8
7	18.9	17.7	4	14.9	14.8	7	8.0	8.5	-1	176.9	184.8
10	0	3.9	7	40.8	42.6	-2	185.1	211.6	-4	23.0	22.6
13	13.6	17.0	10	15.6	11.3	-5	33.5	30.7	-7	39.7	40.6
-2	14.3	12.8	-2	26.7	27.0	2 8 3	42.4	39.8	0 11 4	22.5	25.2
2 4 1	51.1	51.2	2 6 2	102.8	95.2	5	18.5	16.0	3	24.7	21.5
5	30.8	26.7	5	0	4.4	8	28.8	33.5	-3	27.4	26.3
8	0	3.3	8	22.1	22.4	-1	12.0	6.9	-6	0	4.1
11	22.5	27.1	-1	14.9	11.0	-4	46.8	45.7	-9	15.8	14.3
-1	14.3	15.5	-4	47.9	48.6	-7	0	3.5	1 12 4	9.6	8.9
0 5 1	58.9	59.5	0 7 2	24.5	26.9	0 9 3	14.1	11.4	-2	53.1	50.7
3	21.4	18.3	3	48.8	47.9	3	125.3	121.1	-5	15.8	14.4
6	157.2	159.3	6	27.7	29.2	6	10.7	10.3	-8	25.6	25.6
9	8.9	9.3	9	15.6	15.5	-3	51.7	50.0	-11	35.4	33.7
-3	23.4	24.9	-3	17.2	13.7	-6	32.3	29.4	-1 13 4	8.7	6.5
1 6 1	16.1	12.1	-6	17.2	15.1	1 10 3	29.6	31.7	-4	0	5.3
4	23.9	20.3	1 8 2	58.4	58.6	4	25.4	24.1	-7	43.1	39.3
7	52.2	53.2	4	16.7	16.0	-2	21.6	19.6	-10	33.9	30.7
10	17.4	21.9	7	35.0	34.1	-5	19.4	18.2	0 14 4	7.8	11.5
-2	23.9	20.2	-2	30.1	29.7	-8	27.0	23.9	-3	25.6	27.3
-5	40.2	35.1	-5	33.4	29.8	2 11 3	41.5	36.5	-6	33.9	33.9
2 7 1	20.8	19.6	2 9 2	30.1	32.4	5	9.8	12.2	-9	33.9	31.8
5	58.2	62.7	5	0	8.3	-1	23.6	24.2	-12	28.8	29.8
8	16.1	15.0	8	29.9	37.2	-4	37.7	35.6	-5 15 4	28.3	30.4
-1	26.5	26.2	-1	20.5	20.2	-7	27.0	27.3	-8	130.0	116.1
-4	43.3	37.7	-4	25.0	23.8	-10	14.1	12.8	-11	21.0	20.5
0 8 1	35.0	34.2	-7	36.8	34.1	0 12 3	13.2	11.2	-7 16 4	15.8	17.4
3	20.8	17.5	0 10 2	39.7	41.7	3	22.3	25.5	-10	26.5	30.1
6	19.9	23.9	3	26.1	20.7	-3	39.9	38.0	2 0 5	13.6	15.0
9	22.5	27.5	6	37.3	39.1	-6	31.4	28.9	5	34.3	34.9
-3	21.9	22.7	-3	18.3	15.1	-9	131.3	122.8	8	26.3	25.8
-6	220.5	212.9	-6	18.3	18.5	1 13 3	31.0	33.7	11	21.8	18.8
1 9 1	32.8	32.4	-9	23.4	22.0	-2	14.9	13.2	0 1 5	12.1	12.2
4	32.8	33.3	1 11 2	19.9	21.1	-5	33.9	31.1	3	40.4	39.4
7	14.3	11.1	4	14.9	13.1	-8	31.0	29.9	6	0	4.9
-2	16.7	9.3	-2	19.4	20.1	-11	54.0	49.4	9	136.2	127.7
-5	27.2	26.8	-5	73.4	66.4	-1 14 3	15.8	13.4	12	11.6	10.0
-8	47.1	46.6	-8	23.4	19.7	-4	115.7	93.9	1 2 5	27.2	25.5
2 10 1	24.5	22.8	2 12 2	17.2	16.3	-7	21.8	20.4	4	10.5	9.5
5	18.9	19.4	-1	30.1	25.3	-10	44.1	41.9	7	26.8	26.5

Table 6. *(Continued)*

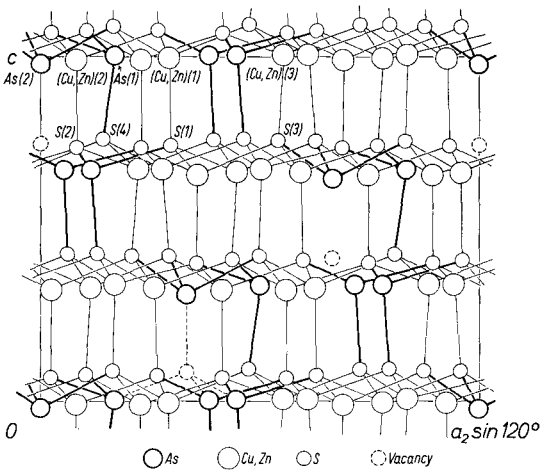
h k l	$\|F_o\|$	$\|F_c\|$
10 2 5	41.3	39.9
2 3 5	34.6	34.5
5	7.6	8.4
8	50.4	48.7
11	0	7.1
-1	7.6	6.5
0 4 5	34.6	35.2
3	20.1	18.5
6	18.1	16.2
9	13.6	12.0
-3	210.3	219.4
1 5 5	0	6.5
4	0	5.8
7	27.7	30.0
10	4.0	3.2
-2	25.7	27.8
2 6 5	161.9	165.2
5	27.2	27.7
8	11.1	11.5
-1	13.6	11.3
-4	36.3	37.0
0 7 5	0	2.8
3	42.8	45.0
6	15.6	15.1
-3	12.7	9.7
-6	18.1	18.7
1 8 5	58.6	58.6
4	0	3.7
7	81.0	82.9
-2	0	6.5
-5	27.2	26.8
2 9 5	15.6	14.3
5	17.6	19.0
-1	14.1	14.5
-4	32.8	30.5
-7	35.7	35.5
0 10 5	31.2	30.4
3	0	3.2
-3	27.7	28.1
-6	28.6	27.4
-9	13.6	12.2
1 11 5	21.2	22.0
4	9.1	11.7
-2	36.3	36.3
-5	141.2	128.8
-8	0	7.0
2 12 5	20.7	23.9
-1	14.1	7.9
-4	30.3	28.5
-7	22.7	22.6
-10	0	7.0
0 13 5	87.2	84.2
-3	13.1	9.7
-6	48.4	44.4
-9	7.6	6.4
-12	15.2	18.2
-2 14 5	0	7.3
-5	11.6	11.0
-8	12.1	11.6
-11	28.1	30.0
-4 15 5	8.7	4.1
-7	22.7	24.1
-10	24.1	26.6
0 0 6	102.3	102.1
3	14.3	16.3
6	21.6	21.2
9	21.6	20.5
12	23.6	26.3
1 1 6	18.3	20.2
4	21.6	24.1

h k l	$\|F_o\|$	$\|F_c\|$
7 1 6	21.6	22.8
10	39.9	37.0
2 2 6	9.4	8.2
5	83.9	71.6
8	0	3.5
11	23.6	26.2
-1	23.0	23.3
0 3 6	19.0	16.6
3	0	2.2
6	39.9	39.0
9	25.7	28.2
1 4 6	0	5.6
4	35.9	34.0
7	15.0	13.1
10	23.6	28.2
-2	35.2	33.3
2 5 6	8.0	7.5
5	30.5	30.6
8	0	8.0
-1	19.0	15.9
-4	39.9	38.0
0 6 6	8.0	6.9
3	42.6	42.8
6	0	7.3
-3	19.4	21.3
1 7 6	23.0	23.1
4	23.6	22.9
7	0	4.6
-2	85.0	71.7
-5	20.8	19.0
2 8 6	31.9	30.9
5	0	4.8
-1	23.6	27.7
-4	28.3	29.2
-7	0	6.7
0 9 6	0	5.5
3	37.7	38.3
-3	44.8	42.1
-6	16.9	18.1
1 10 6	11.1	9.4
4	31.2	29.2
-2	20.8	20.9
-5	10.2	11.0
-8	19.0	17.6
2 11 6	37.7	38.0
-1	16.1	15.5
-4	35.9	33.1
-7	19.4	20.1
-10	21.6	17.7
0 12 6	12.9	12.7
-3	20.8	20.1
-6	35.2	29.9
-9	43.3	37.9
-2 13 6	12.1	11.4
-5	27.7	22.6
-8	26.3	25.7
-11	33.7	33.9
-4 14 6	26.3	29.2
-7	15.0	12.4
-10	29.0	29.4
1 0 7	46.2	44.8
4	20.1	18.8
7	6.9	6.9
10	22.8	24.1
2 1 7	31.9	31.9
5	36.1	34.1
8	38.6	38.0
11	15.2	20.1
0 2 7	12.9	13.1
3	11.6	14.0

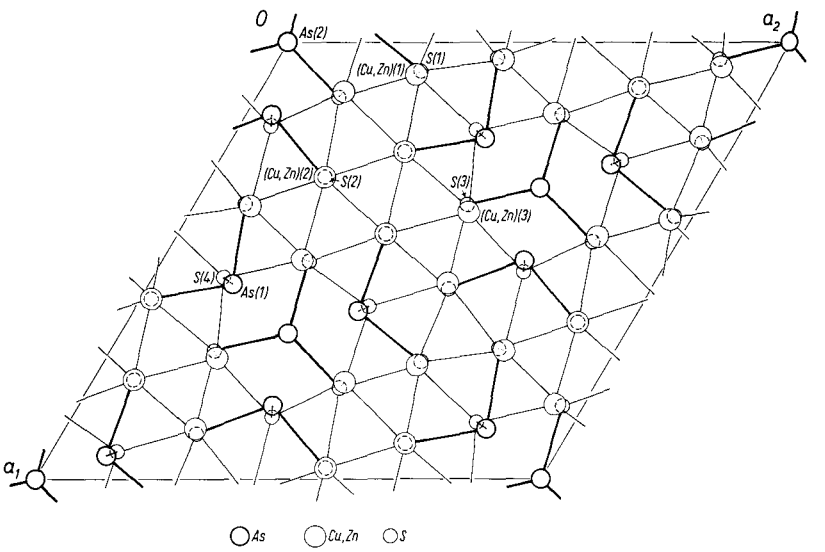
h k l	$\|F_o\|$	$\|F_c\|$
6 2 7	49.0	48.5
9	0	1.5
1 3 7	155.2	161.4
4	27.0	25.1
7	45.5	45.1
10	14.7	17.1
-2	31.9	31.6
2 4 7	8.0	5.9
5	29.9	31.9
8	18.3	16.9
-1	12.9	10.2
0 5 7	20.8	21.2
3	19.8	20.8
6	102.6	97.2
-3	21.6	21.5
1 6 7	29.9	32.3
4	14.0	15.0
7	16.7	20.1
-2	23.2	22.1
-5	29.4	29.3
2 7 7	14.0	13.9
5	16.7	19.4
-1	45.5	46.6
-4	20.8	22.4
0 8 7	44.8	43.4
3	14.0	11.9
-3	39.9	38.5
-6	132.5	124.5
1 9 7	13.6	12.1
4	36.1	40.5
-2	27.0	27.3
-5	29.0	28.3
-8	25.2	25.2
2 10 7	19.0	18.5
-1	104.4	95.8
-4	28.3	27.8
-7	33.0	30.3
0 11 7	8.0	4.5
-3	21.6	21.6
-6	12.1	13.5
-9	16.0	15.7
-2 12 7	32.5	31.6
-5	22.8	24.0
-8	31.2	29.2
-11	22.1	25.0
-4 13 7	16.0	13.5
-7	30.6	31.3
-10	34.3	34.3
2 0 8	23.9	25.9
5	9.8	11.9
8	24.8	21.8
11	15.8	18.5
0 1 8	29.6	29.6
3	19.0	20.9
6	25.4	23.5
9	129.1	119.8
1 2 8	38.3	41.6
4	31.2	31.9
7	27.2	27.7
2 3 8	47.0	47.3
5	17.6	17.2
8	28.6	32.3
-1	8.2	7.3
0 4 8	43.0	45.9
3	39.0	39.7
6	28.6	26.8
-3	192.7	189.9
1 5 8	6.9	9.3
4	13.4	12.2
7	30.3	34.5

h k l	$\|F_o\|$	$\|F_c\|$
-2 5 8	23.0	23.8
2 6 8	144.3	149.8
5	30.3	31.5
-1	26.3	30.6
-4	25.4	23.7
0 7 8	0	9.3
3	19.9	20.9
-3	22.3	22.4
-6	35.0	29.9
1 8 8	35.7	37.1
4	18.3	18.2
-2	23.0	20.8
-5	43.9	37.5
2 9 8	16.7	19.8
-1	23.0	20.6
-4	40.6	38.8
-7	47.0	42.0
0 10 8	34.3	34.1
-3	23.9	23.3
-6	19.9	21.5
-9	28.6	30.9
-2 11 8	37.3	37.0
-5	137.1	119.3
-8	31.2	29.3
-4 12 8	18.3	18.8
-7	12.7	12.7
0 0 9	136.0	133.8
3	33.2	32.6
6	14.3	11.7
9	21.0	23.0
1 1 9	17.2	16.6
4	14.9	13.8
7	16.0	12.2
2 2 9	19.8	18.4
5	110.4	106.2
8	21.9	23.4
-1	18.7	18.6
0 3 9	16.1	17.0
3	12.7	11.1
6	27.6	27.6
1 4 9	18.9	18.0
2 5 9	24.3	23.6
0 6 9	15.4	11.8
3	28.3	29.0
1 7 9	33.7	35.9
2 8 9	11.6	12.4
0 9 9	15.6	15.0
1 0 10	24.8	26.5
4	0	5.6
7	15.6	13.4
2 1 10	16.0	14.4
5	18.9	18.9
0 2 10	16.5	16.7
3	9.4	8.5
6	28.1	32.2
1 3 10	45.9	44.1
4	17.9	16.4
-2	11.2	9.5
2 4 10	17.6	16.2
0 5 10	20.5	17.9
3	0	3.0
1 6 10	14.3	15.3
2 0 11	22.1	24.8
0 1 11	16.0	19.5
3	0	3.4
1 2 11	27.7	26.9
4	24.8	28.5
2 3 11	35.9	38.0
-1	10.9	10.3
0 4 11	28.6	29.5

(Marumo and Nowacki, 1967), lautite (Marumo and Nowacki, 1964; Craig and Stephenson, 1965), binnite (Wuensch, Takéuchi and Nowacki, 1966) and zincblende. All As atoms have a trigonal pyramidal coordination of S atoms. The As-S_3 pyramids are not connected to each other by sharing S atoms. Arsenic atoms are shifted towards the vacant position as compared to the ideal zincblende structure, yielding shorter As—As distances than the normal. The other metal and sulfur positions have tetrahedral coordination, the tetrahedron around the (Cu,Zn)(2) position being the most regular. Owing to the nature of the As—S bonds, the S—As—S bond angles are smaller than the tetrahedral angle.



(a)



(b)

Fig. 6. The projections of the structure of nowackiite (a) along the a_{hex} axis and (b) along the c_{hex} axis

Each S atom is coordinated to one As atom. We can consider the structure as a close packing of As_4S_{12} groups with Cu and Zn atoms in tetrahedral interstices of S atoms.

Table 7. *The deviations of the atoms in nowackiite from the atomic positions in the ideal zincblende-type structure*

(Cu,Zn)(1)	(Cu,Zn)(2)	(Cu,Zn)(3)	As(1)	As(2)	S(1)	S(2)	S(3)	S(4)
0.18_0	0.09_4	0.19_8	0.20_4	0.18_1	0.14_7	0.13_1	0.19_4	0.19_0 Å

Table 8. *Atomic distances in nowackiite* (Å)

(a) Metal—sulfur and sulfur—sulfur distances

	(Cu,Zn)(1)	(Cu,Zn)(2)	(Cu,Zn)(3)	As(1)	As(2)	S(1)	S(2)	S(3)	S(4)
S(1)	2.32_2	2.34_4		2.26_7		3.70_7	3.55_5	3.77_3	3.54_6
	2.33_9					3.70_7	3.82_3	3.90_0	3.64_3
							3.83_0	3.93_4	3.87_5
S(2)		2.33_4	2.33_5	2.27_0		3.55_5	3.77_6	3.66_0	3.45_9
		2.34_8				3.82_3	3.77_6	3.85_9	3.62_9
						3.83_0		3.91_2	3.77_6
S(3)	2.31_4	2.35_5	2.31_2		2.24_1	3.77_3	3.66_0	3.46_5	3.68_5
					2.24_1	3.90_0	3.85_9	3.46_5	3.75_7
					2.24_1	3.93_4	3.91_2		3.87_2
S(4)	2.35_5		2.27_9	2.26_1		3.54_6	3.45_9	3.68_5	3.94_4
			2.31_5			3.64_3	3.62_9	3.75_7	3.94_4
						3.87_5	3.77_6	3.87_2	
Mean	2.33_3	2.34_5	2.31_0	2.26_6	2.24_1	3.75_4	3.73_2	3.75_3	3.73_9
σ		0.006_7		0.006_0			0.007_6		

(b) Metal—metal distances

	(Cu,Zn)(1)	(Cu,Zn)(2)	(Cu,Zn)(3)	As(1)	As(2)
(Cu,Zn)(1)	3.84_7	3.60_6	3.72_0	3.67_3	3.55_3
	3.84_7	3.67_7	3.80_7	4.00_0	3.55_3
		3.75_7	3.92_4	4.01_9	3.55_3
Cu,Zn)(2)	3.60_6	3.78_5	3.69_0	3.64_0	3.72_8
	3.67_7	3.78_5	3.96_1	3.67_3	3.72_8
	3.75_7		3.97_4	3.75_3	3.72_8
(Cu,Zn)(3)	3.72_0	3.69_0	3.46_9	3.61_3	3.87_2
	3.80_7	3.96_1	3.46_9	3.65_0	3.87_2
	3.92_4	3.97_4		3.94_9	3.87_2
As(1)	3.67_3	3.64_0	3.61_3	3.40_9	3.43_5
	4.00_0	3.67_3	3.65_0	3.40_9	3.43_5
	4.01_9	3.75_3	3.94_9		3.43_5
As(2)	3.55_3	3.72_8	3.87_2	3.43_5	
Mean	3.78_6	3.75_3	3.75_8	3.68_5	3.64_7
σ		0.003_8	$\sim 0.005_7$		

Table 9. *Bond angles in nowackiite*

S(3)—(Cu,Zn)(1)—S(1)	$114.5° \pm 0.4_8°$	As(1)—S(1)—(Cu,Zn)(1)	$106.3° \pm 0.4_6°$
S(3)—(Cu,Zn)(1)—S(1)	115.4	As(1)—S(1)—(Cu,Zn)(1)	121.5
S(3)—(Cu,Zn)(1)—S(4)	107.2	As(1)—S(1)—(Cu,Zn)(2)	109.0
S(1)—(Cu,Zn)(1)—S(1)	105.4	(Cu,Zn)(1)—S(1)—(Cu,Zn)(1)	111.3
S(1)—(Cu,Zn)(1)—S(4)	111.9	(Cu,Zn)(1)—S(1)—(Cu,Zn)(2)	107.3
S(1)—(Cu,Zn)(1)—S(4)	101.8	(Cu,Zn)(1)—S(1)—(Cu,Zn)(2)	100.7
S(2)—(Cu,Zn)(2)—S(1)	110.0	As(1)—S(2)—(Cu,Zn)(2)	104.5
S(2)—(Cu,Zn)(2)—S(2)	107.5	As(1)—S(2)—(Cu,Zn)(3)	118.1
S(2)—(Cu,Zn)(2)—S(3)	113.1	As(1)—S(2)—(Cu,Zn)(2)	105.4
S(1)—(Cu,Zn)(2)—S(2)	109.2	(Cu,Zn)(2)—S(2)—(Cu,Zn)(3)	104.5
S(1)—(Cu,Zn)(2)—S(3)	106.8	(Cu,Zn)(2)—S(2)—(Cu,Zn)(2)	107.9
S(2)—(Cu,Zn)(2)—S(3)	110.3	(Cu,Zn)(3)—S(2)—(Cu,Zn)(2)	115.5
S(4)—(Cu,Zn)(3)—S(3)	115.0	As(2)—S(3)—(Cu,Zn)(3)	116.5
S(4)—(Cu,Zn)(3)—S(4)	118.3	As(2)—S(3)—(Cu,Zn)(1)	102.5
S(4)—(Cu,Zn)(3)—S(2)	109.9	As(2)—S(3)—(Cu,Zn)(2)	108.4
S(3)—(Cu,Zn)(3)—S(4)	105.5	(Cu,Zn)(3)—S(3)—(Cu,Zn)(1)	107.1
S(3)—(Cu,Zn)(3)—S(2)	104.0	(Cu,Zn)(3)—S(3)—(Cu,Zn)(2)	116.7
S(4)—(Cu,Zn)(3)—S(2)	102.6	(Cu,Zn)(1)—S(3)—(Cu,Zn)(2)	103.9
S(4)—As(1)—S(1)	$103.1° \pm 0.4_1°$	As(1)—S(4)—(Cu,Zn)(3)	105.5
S(4)—As(1)—S(2)	99.6	As(1)—S(4)—(Cu,Zn)(3)	105.8
S(1)—As(1)—S(2)	103.2	As(1)—S(4)—(Cu,Zn)(1)	120.1
S(3)—As(2)—S(3)	101.3	(Cu,Zn)(3)—S(4)—(Cu,Zn)(3)	98.1
S(3)—As(2)—S(3)	101.3	(Cu,Zn)(3)—S(4)—(Cu,Zn)(1)	110.5
S(3)—As(2)—S(3)	101.3	(Cu,Zn)(3)—S(4)—(Cu,Zn)(1)	114.4

It was not possible to distinguish between the Cu and Zn atoms during the course of the refinement. Also, it is generally impossible to distinguish them from coordinations and bond distances. However, from the temperature factors and the interatomic distances it is certain that the Zn atom is at either the (Cu,Zn)(1) or (Cu,Zn)(2) position. If we take into account only metal atoms, the structure is almost centrosymmetric and these two metal atoms are related by a pseudo-center of symmetry. Therefore very accurate intensity data would be necessary to allocate the Zn atom to one of these positions. The (Cu,Zn)(2) atom is more probable for the Zn atom than (Cu,Zn)(1), since a smaller temperature factor was obtained for (Cu,Zn)(2).

Acknowledgements. — The author wishes to thank Prof. W. NOWACKI for his continuous encouragement and advice, Mr. J. IMHOF for providing the crystals and Dr. N. D. JONES for his helpful advice and

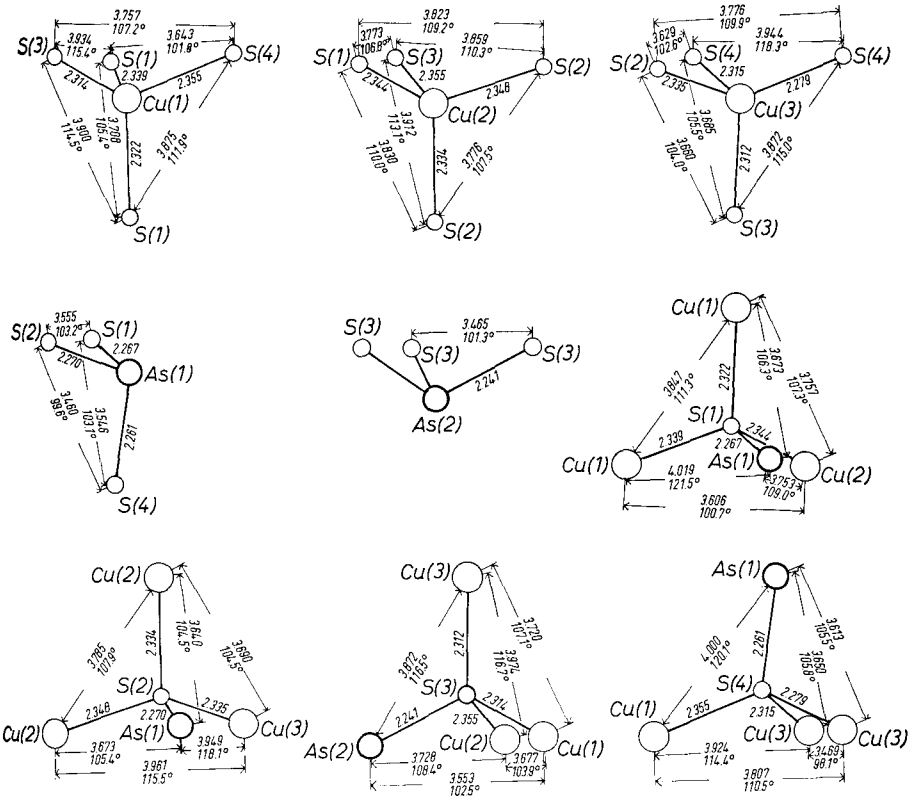


Fig. 7. The coordinations, the atomic distances and the bond angles in nowackiite. Cu stands for a (Cu,Zn) atom

criticism. The investigation was supported by Schweizerischer Nationalfonds (project no. 2337), Kommission zur Förderung der wissenschaftlichen Forschung (projects nos. 384/386) and Stiftung Entwicklungsfonds Seltene Metalle.

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