A refinement of the crystal structure of luzonite, Cu_3AsS_4[1]

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Auszug

Die Kristallstruktur von Luzonit wurde nach der Methode der kleinsten Quadrate mit Hilfe von 121 photographisch ($CuK\alpha$-Strahlung) vermessenen Reflexen dreidimensional verfeinert. Eine Mikrosondenanalyse ergab die Zusammensetzung $Cu_3(As_{0.64}Sb_{0.36})S_4$. Die Gitterkonstanten sind $a = 5.33_2 \pm 0.005$, $c = 10.57_0 \pm 0.01$ Å und die Raumgruppe ist $D_{2d}^{11}–I\bar{4}2m$. Die Struktur ist vom Zinkblendetypus, mit einer kleinen Abweichung von der Idealstruktur. Die zwischenatomaren Abstände sind (As,Sb)—S = 2,265, Cu(1)—S = 2,304 und Cu(2)—S = 2,337 Å.

Abstract

The crystal structure of luzonite has been refined by means of three-dimensional least-squares methods, utilizing 121 reflection data obtained photographically with $CuK\alpha$ radiation. The chemical composition determined with an x-ray microanalyser is $Cu_3(As_{0.64}Sb_{0.36})S_4$. The lattice constants are $a = 5.33_2 \pm 0.005$ Å, $c = 10.57_0 \pm 0.01$ Å, and the space group is $D_{2d}^{11}–I\bar{4}2m$. The structure is of the zincblende type, having a small deviation from the ideal structure. The interatomic distances are (As,Sb)—S = 2.265, Cu(1)—S = 2.304 and Cu(2)—S = 2.337 Å.

1. Introduction

The crystal structure of luzonite was first studied by SAWADA (1943) and it was found that the structure is of the zincblende type. According to later studies, the unit cell reported by SAWADA is one half of the true unit cell and corresponds to the subcell of the crystal. GAINES (1957) carried out the structure determination referring to the true unit cell

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and confirmed the zincblende-type structure. Though he determined the arrangement of all atoms in the unit cell, no attempt was made to find the distortion of the structure from the ideal zincblende type.

In the zincblende structure all atoms have a tetrahedral coordination. This coordination by four S atoms around an As atom has been reported only in the structures of luzonite and enargite, which is homoeotectic to luzonite. In arsenosulfide crystals the As atoms usually have a trigonal pyramidal coordination by the S atoms. Therefore, the refinement of the structure of luzonite was undertaken, with the intention of determining the distortion from the ideal zincblende structure and at the same time, of confirming the tetrahedral coordination by S around the As atoms.

2. Experimental

Crystals from Cerro de Pasco (Peru), which we obtained through the Naturhistorisches Museum in Vienna (Inv. Nr. J 8894), were used in this investigation. In natural luzonite, part of the As atoms are usually replaced by Sb atoms, although the ideal chemical formula of luzonite is Cu_3AsS_4. Therefore, a chemical analysis of the specimen was carried out with an x-ray microanalyser (type CAMECA MS. 85) by G. BURRI, in order to determine the degree of the replacement. The analysis gave the result: $S = 32$, $Cu = 47.4$, $As = 11.6$, $Sb = 10.5$, total $101.5 \, ^0/_0$. The chemical formula of the specimen derived from these values is to a very good approximation $Cu_3As_{0.644}Sb_{0.356}S_4$.

Oscillation and Weissenberg photographs were taken to determine the space group and the unit-cell dimensions. No certain evidence of a deviation of the x-ray patterns from the tetragonal symmetry could be observed. The unit-cell dimensions obtained from the Weissenberg photographs are

$$a = 5.33_2 \pm 0.005 \text{ Å}, \quad c = 10.57_0 \pm 0.01 \text{ Å},$$

and the space group is $D_{2d}^{11} - I\overline{4}2m$. Though the possible space groups derived from the x-ray diagrams are

$$D_4^9 - I422, \quad C_{4v}^9 - I4mm, \quad D_{2d}^9 - I\overline{4}m2, \quad D_{2d}^{11} - I\overline{4}2m$$

and $D_{4h}^{17} - I4/mmm,$

the space group $D_{2d}^{11} - I\overline{4}2m$ is found to be the true one from the structural similarity to zincblende as stated by GAINES (1957). The unit-cell

dimensions of the specimen used are slightly larger than those obtained by GAINES for a synthetic luzonite owing to the substitution by the Sb atoms. There are two chemical units of $Cu_3(As,Sb)S_4$ in the unit cell.

Because of the very frequent twinning of this mineral, it was impossible to find a single crystal large enough to be ground into a sphere by Bond's method (BOND, 1951), though there were fairly large pieces of the substance. Therefore, s small crystal cube of dimensions of about $0.087 \times 0.087 \times 0.080$ mm³ was used for the intensity measurements. The corners of the cube were cut off before it was x-rayed to make the shape close to a sphere. Intensity data were measured with a double-beam densitometer from equi-inclination integrated Weissenberg photographs taken with $CuK\alpha$ around [110] (zero to 6-th layer) and [111] (zero layer). The intensities were corrected for Lorentz-polarization factors and absorption factors on the assumption of a spherical form with a diameter of 0.085 mm, utilizing programs written by J. A. MINKIN and C. K. JOHNSON for the I.B.M. 1620 calculating machine. The absorption correction factors are 6.04 at $\theta = 0°$ and 3.70 at $\theta = 90°$. Corrections were also made for the splitting of the $CuK\alpha_1$ and $K\alpha_2$ reflections. 121 independent $|F|^2$-values were thus obtained. Since the symmetry is high, equivalent reflections were recorded several times on the same or on different films. All of them were measured and the averaged $|F_o|$-values were used for the refinement of the structure. On an average, the final $|F|$'s are the mean values of 6.4 measurements.

3. Refinement of the structure

Structure amplitudes were calculated with the atomic coordinates of the ideal zincblende type and with an overall temperature factor obtained by the statistical method, allocating to each atom the position proposed by GAINES: As at (000), Cu(1) at $(0\frac{1}{2}\frac{1}{4})$, Cu(2) at $(00\frac{1}{2})$ and S at $(\frac{1}{4}\frac{1}{4}\frac{1}{8})$. At the As atom site 0.644 As and 0.356 Sb atoms were inserted statistically. A fairly good agreement between the calculated and the observed values was obtained, giving an R value of 0.16. In the structure all the atoms, except S, are at fixed positions. There are two positional parameters for the S atoms. Four cycles of refinements of the structure were carried out with isotropic temperature factors, using a program written by D. VAN DER HELM for the I.B.M. 1620. The R value was reduced to 0.065. Then anisotropic temperature factors were introduced and further refinements were undertaken. However,

Table 1. *Final positional parameters, the population of As and Sb atoms, and their standard deviations in luzonite*

	x	y	z	σ_x	σ_z	Population	σ
S	0.2442	0.2442	0.1248	0.0001_7	0.0001_2		
Cu(1)	0	$\frac{1}{2}$	$\frac{1}{4}$	—	—		
Cu(2)	0	0	$\frac{1}{2}$	—			
As	0	0	0	—	—	0.68_5	0.003_5
Sb	0	0	0	—	—	0.31_5	

Table 2. *The final thermal parameters and their standard deviations*

	$\beta_{11} = \beta_{22}$	β_{12}	$\beta_{13} = \beta_{23}$	β_{33}	$\sigma\,(\beta_{11})$	$\sigma\,(\beta_{12})$	$\sigma\,(\beta_{13})$	$\sigma\,(\beta_{33})$	Equivalent isotropic temperature factor
S	0.0086_5	0.00007	−0.00008	0.0023_2	0.0007_8	0.00080	0.0002_5	0.00030	1.00
Cu(1)	0.0136_6	0	0	0.0036_4	0.0005_4	—	—	0.0002_4	1.58
Cu(2)	0.0138_8	0	0	0.0035_2	0.00070	—	—	0.0002_9	1.58
As+Sb	0.0044_1	0	0	0.0014_3	0.0005_4	—	—	0.0001_7	0.55

[Temperature factor $= \exp - (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + kl\beta_{23} + lh\beta_{13})$].

only very small shifts of the thermal parameters were obtained, reducing the R value by 0.002.

At this stage a least-squares program was written to refine the populations of the As and Sb atoms together with the positional, thermal and scaling parameters. The sum of the populations of the As and Sb atoms was assumed to be one. The refinements, obtained with this program, also resulted in quite inconsiderable changes of the parameters, yielding an R value of 0.0507. The weighting scheme used is $w = 76/(38 + |F_o| + \frac{1}{38} |F_o|^2)$ [38 = mean $|F_o|$ value], which gives $w = 0.050$ for the strongest reflection ($|F_o| = 218.3$), $w = 1.404$ for the weakest reflection ($|F_o| = 12.2$) and $w = 0.667$ for the reflections of medium strength. The R value is 0.049 for the reflections corresponding to the subcell ($a' = a$, $c' = \frac{1}{2} c$) and 0.074 for the super-lattice reflections. These values should be reasonable, since the relative error is larger for the weaker than for the stronger reflections.

Table 3. *Observed and calculated structure amplitudes of luzonite*

h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$
0	0	2	19.6	21.7	0	4	10	15.6	16.3	1	4	5	17.5	17.7	2	5	3	24.0	23.3
		4	94.7	84.7	0	5	1	25.5	25.0			7	20.3	18.9			5	24.0	22.4
		6	19.4	19.9			3	13.9	12.4			9	19.8	18.2			7	12.9	11.8
		8	160.1	168.3			5	12.7	12.2	1	5	0	19.8	18.8	2	6	0	94.9	99.9
		10	19.8	18.7			7	24.1	21.6			2	100.2	95.7			2	15.4	16.3
		12	26.6	26.4			9	17.5	19.5			4	17.5	17.4			4	19.6	23.3
0	1	1	22.4	24.3	0	6	0	30.2	29.0			6	84.4	80.9	3	3	0	17.1	20.3
		3	17.1	18.6			2	17.1	16.7			8	16.2	16.2			2	109.5	116.4
		5	17.5	18.6			4	96.4	99.6	1	6	1	19.0	16.4			4	19.4	18.3
		7	20.3	21.2			6	14.5	15.9			3	19.8	17.9			6	104.6	96.1
		9	17.9	19.6	1	1	0	17.1	21.3			5	18.4	18.4			8	18.8	17.5
		11	16.4	15.5			2	198.7	211.4	2	2	0	218.3	221.5	3	4	1	15.6	15.2
		13	13.9	14.0			4	20.0	20.7			2	17.5	20.7			3	24.5	22.0
0	2	0	95.1	85.6			6	148.1	146.7			4	69.0	63.3			5	22.1	21.8
		2	20.2	20.7			8	17.3	19.4			6	18.3	19.1			7	16.4	14.6
		4	212.0	220.5			10	100.6	93.6			8	127.4	138.4			9	12.2	12.8
		6	18.4	20.4			12	16.9	15.9			10	18.6	17.4	3	5	0	17.5	16.4
		8	48.9	45.8	1	2	1	16.9	18.8			12	17.3	21.4			2	90.5	81.4
		10	18.1	16.9			3	21.1	22.6	2	3	1	22.1	25.6			4	19.4	17.5
		12	96.8	97.2			5	20.3	22.4			3	14.1	16.1			6	67.3	67.4
0	3	1	13.5	15.3			7	16.4	18.3			5	14.3	15.0	3	6	1	17.5	19.9
		3	24.0	25.5			9	16.9	16.5			7	23.4	21.9	4	4	0	120.4	117.4
		5	21.7	24.2			11	18.6	17.1			9	21.5	20.2			2	20.5	17.4
		7	14.8	14.7	1	3	0	18.1	20.2			11	13.5	12.8			4	29.1	28.7
		9	13.5	14.0			2	145.1	148.1	2	4	0	52.7	47.6			6	17.1	16.0
		11	18.6	18.7			4	19.2	20.3			2	19.6	19.1	4	5	1	22.4	21.9
0	4	0	158.2	170.8			6	112.9	115.5			4	141.7	139.7			3	12.5	12.8
		2	17.5	19.8			8	19.6	17.9			6	19.6	18.1					
		4	49.1	47.2			10	82.3	79.7			8	31.0	27.8					
		6	17.9	18.1	1	4	1	20.5	22.6			10	14.1	14.9					
		8	117.5	115.9			3	17.5	19.6	2	5	1	12.9	12.3					

The refinements gave the value 0.685 for the population of the As atoms, which is in excellent agreement with the value 0.644 obtained by x-ray microanalysis. The final atomic parameters and their standard deviations are given in Table 1 and Table 2, the calculated and observed structure amplitudes in Table 3. In the final stage of the refinement, atomic scattering factors of the form $f_0 = f + \Delta f' + i\Delta f''$ were used for As, Sb and Cu, of $f_0 = f + \Delta f'$ for S on the assumption that $\Delta f'$ and $\Delta f''$ do not depend on the scattering angle θ and are equal to the values at $\theta = 0°$.

4. Discussion

The structure is of the zincblende type as has already been described by SAWADA (1943) and GAINES (1957) (Fig. 1). The unit cell is slightly shrunk as compared with that of zincblende ($a = 5.409$ Å), and the shrinkage is larger along the c axis than along the a axis, though the difference is very small. All the metal atoms at special positions have exactly the same coordinates as the Zn atoms in zincblende if referred to the sub-cell. The shift of the S atoms from the centre of the tetra-

Fig. 1. Projection of the structure along the a axis. The shaded As and Cu atoms are on the plane $x = \frac{1}{2}$ and the unshaded ones are on $x = 0$. The shaded S atoms are nearly on the plane $x = \frac{1}{4}$ and the unshaded S are nearly on $x = \frac{3}{4}$.

hedron formed by 2 Cu(1), Cu(2) and (As,Sb) atoms is about 0.044 Å, which is also very small. Accordingly the structure is very close to the ideal zincblende-type structure.

The inter-atomic distances and the bond angles are given in Table 4 and Table 5 respectively, and are shown also in Fig. 1. The (As,Sb)—S distance of 2.265 Å is almost equal to the length of the As—S covalent bond. The Cu—S distances, 2.304 Å and 2.337 Å, are in good agreement with the Cu—S distances of tetrahedrally coordinated Cu atoms in

Table 4. *Interatomic distances in luzonite*

Atoms	distance	standard deviations σ
(As,Sb)—S	2.265 Å	0.001_5 Å
Cu(1) —S	2.304	0.001_5
Cu(2) —S	2.337	0.001_5
S —S	3.683	0.002_8
	3.707	0.002_5
	3.757	0.002_4
	3.771	0.002_8
	3.795	0.002_6
	3.858	0.002_9

Table 5. *Bond angles in luzonite*

Atoms	angle	σ
S—(As,Sb)—S	108° 47'	9'
S—(As,Sb)—S	109° 50'	8'
S—Cu(1)—S	109° 51'	9'
S—Cu(1)—S	109° 15'	8'
S—Cu(2)—S	111° 14'	9'
S—Cu(2)—S	108° 34'	8'
As—S—Cu(1)	111° 13'	8'
As—S—Cu(2)	110° 01'	8'
Cu(1)—S—Cu(1)	109° 49'	8'
Cu(1)—S—Cu(2)	108° 40'	8'

other Cu sulfosalt structures. The distances are for example 2.289 Å and 2.304 Å in lautite (MARUMO and NOWACKI, 1964) and 2.342 Å in tetrahedrite (WUENSCH, 1964). Though all bond angles are very close to the tetrahedral bond angle, 109.5°, the tetrahedron around the Cu(2) atom has the largest and that around the Cu(1) atom the least distortion.

The trigonal-pyramidal coordinations by S atoms are most common for As atoms in arsenosulfide crystals, each As atom having p^3 bonds. Another kind of coordination around an As atom is the tetrahedral one. In this case, however, the four atoms at the apices of the tetrahedron are not always S atoms only. They are three Fe and one S in arseno-pyrite, three Co and one As in cobaltite, two As, one S and one Cu in lautite. Beside luzonite, enargite (Cu_3AsS_4) is the only known example, in which each of the As atoms is tetrahedrally surrounded by four S atoms. The nature of the chemical bond in arsenopyrite-group mine-rals is somewhat different from that in luzonite, enargite and lautite.

Each atom is supposed to have sp^3 hybrid bonds in the latter three minerals, while As atoms form As—S and As—As groups in arsenopyrite and in cobaltite respectively.

The tetrahedral coordination around the As (Sb) atom is inevitable from the structural similarity to zincblende when we assume a tetragonal space group for luzonite, since four As—S atomic distances are always equal under these conditions. As stated at the beginning, it was impossible to obtain definite evidence of deviation from tetragonal symmetry. Moreover the final R value of 0.057 indicates that the proposed structure should be very close to the true structure, even if the symmetry of the crystal is lower than tetragonal. It suggests also that the tetragonal symmetry is not caused by twinning of crystals of lower symmetry as in the cases of bornite (MORIMOTO, 1964) and digenite (MORIMOTO and KULLERUD, 1963). This is also supported by the very small anisotropy of the temperature factors.

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