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The crystal structure of fornacite*

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Auszug

Fornacit $Pb_2(Cu,Fe)[CrO_4(As,P)O_4OH]$ hat die Raumgruppe $P2_1/c$ und die Gitterkonstanten $a = 8{,}101$ Å, $b = 5{,}893$ Å, $c = 17{,}547$ Å, $\beta = 110°0'$. Die schwersten Atome wurden durch eine dreidimensionale Patterson-Synthese lokalisiert. Die Lagen der Sauerstoffatome ergaben sich aus sukzessiven Fourier-Synthesen. Die Verfeinerung mittels Differenz-Synthesen und Ausgleichsrechnung führte für 776 beobachtete Reflexe zu $R = 0{,}098$.

Die zwei nicht-äquivalenten Pb-Ionen sind von neun O-Atomen in Abständen von 2,35 bis 3,05 Å umgeben. Das Cu^{+2}-Ion hat wie üblich die Koordination $4 + 2$; die vier O-Atome in den Ecken eines ebenen Quadrats haben als mittleren Abstand vom Cu-Ion 1,97 Å, die beiden übrigen 2,36 und 2,46 Å. (As,P) und Cr sind tetraedrisch von O-Atomen umgeben, die mittleren Abstände sind 1,61 Å für As—O und 1,63 Å für Cr—O. Die Fornacit-Struktur kann als aufgebaut aus dicken Schichten von miteinander verbundenen Polyedern um Pb, parallel zu (001) durch $z \approx 0$ und $c/2$, und aus Zickzackketten von $CuO_4(OH)_2$ längs der Schraubungsachse beschrieben werden. Die AsO_4- und CrO_4-Tetraeder verknüpfen die Pb Schichten und die Cu-Ketten zu dreidimensionalem Netzwerk. Die schlechte Spaltbarkeit erklärt sich aus dem Fehlen von Vorzugsrichtungen.

Abstract

Fornacite, $Pb_2(Cu,Fe)[CrO_4(As,P)O_4OH]$, is monoclinic, with $a = 8.101$ Å, $b = 5.893$ Å, $c = 17.547$ Å, $\beta = 110°00'$, space group $P2_1/c$. After making spherical absorption and Lorentz-polarization corrections, a three-dimensional Patterson synthesis was computed and the heaviest atoms located. The oxygen positions were found by successive Fourier syntheses. The refinement was carried out by difference syntheses and least-squares method. The final discrepancy index R for 776 observed reflections is 0.098.

The two non-equivalent lead ions are surrounded by nine nearest oxygen atoms at distances of 2.35 to 3.05 Å. The Cu^{+2} shows the usual $4 + 2$ coordination. The average bond length in the planar square is 1.97 Å; the two addi-

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tional Cu—O bonds are 2.36 and 2.46 Å. The (As,P)O_4 and CrO_4 tetrahedral complexes show mean distances of 1.61 and 1.63 Å, respectively for As—O and Cr—O.

The fornacite structure can be described in terms of linked Pb polyhedra forming thick sheets parallel to (001) at $z \approx 0$ and $c/2$ and of zig-zag $CuO_4(OH)_2$ chains along the screw axis. The AsO_4 and CrO_4 tetrahedra tightly link the Pb sheets and Cu chain into a three-dimensional network. The absence of preferential directions in the interatomic bonds explains the uneven fracture of the mineral.

Introduction

The mineral fornacite was first described by Lacroix (1915) as a basic copper and lead chromate arsenate belonging to the monoclinic system. The chemical analyses by Guillemin and Prouvost (1951), Smolianinova and Cendrerova (1959), Bariand and Herpin (1962) led to the formula $Pb_2(Cu,Fe)\,[CrO_4\,(As,P)O_4OH]$. According to Guillemin and Prouvost (1951) this mineral is the higher arsenic-content member of an isomorphous series in which vauquelinite is the phosphorous member. Bariand and Herpin (1962) determined the unit cell of fornacite and related its lattice constants to the parameters of vauquelinite (Berry, 1949). It is probable that the structures of the two minerals are closely related. In order to explain better these relations we have undertaken the study of vauquelinite.

Crystal data

Fornacite from Réneville (Congo) was used in this investigation. The chemical analysis for the mineral of this provenance (Bariand and Herpin, 1962) was assumed for the present work.

We refined the lattice parameters by the application of a least-squares method using experimental data from a powder diffractogram. The unit-cell constants are as follows:

$$\begin{aligned} a &= 8.101 \pm .007 \text{ Å} \\ b &= 5.893 \pm .011 \text{ Å} \\ c &= 17.547 \pm .009 \text{ Å} \\ \beta &= 110°0' \pm 2' \end{aligned}$$

The space group is $P2_1/c$, $Z = 4$ and $D_x = 6.30$ g · cm^{-3}; the observed value D is 6.27 g · cm^{-3} (Bariand and Herpin, 1962). The linear absorption coefficient μ is 1019 cm^{-1} for the Cu$K\alpha$ radiation.

Experimental

The choice of a single crystal for x-ray study has shown some difficulties because fornacite consists of polycrystalline aggregates.

Several grains were examined by precession and Weissenberg methods before we could find a fragment of mineral suitable for intensity-data collection. Because of the high absorption, this fragment was ground to an approximately spherical shape with a radius 0.15 mm in order to apply an easier and more accurate correction.

Diffraction effects from $h0l$ to $h4l$ were recorded with the equiinclination Weissenberg method using Ni filtered Cu$K\alpha$ radiation. A total of 1263 independent reflections were collected; of these, 487 were too weak to be evaluated. Intensities were measured with the help of a microdensitometer and the different layers were put on the same relative scale taking into account their exposure time.

Empirical correction for α_1-α_2 doublet resolution was applied; then spherical absorption correction was carried out using a computer program written by the authors for a value $\mu R = 15.3$. The transmission factors at different θ were obtained by graphical interpolation from the values of EVANS and EKSTEIN (1952). Corrections for the Lorentz-polarization factors were made and structure amplitudes were derived.

Structure determination and refinement

In the first stage of the structure determination we remarked the weakness of diffraction effects with l odd. This fact is more evident for the $h1l$ layer, where only 24 weak reflections with l odd were observed against 118 reflections with l even, and it gradually disappears into the upper layers. We were led to think the heaviest atoms in the structure are located at y approximately near to $\frac{1}{4}\,b$ and $\frac{3}{4}\,b$. It was therefore expected that the most useful information in the Patterson synthesis would appear in the planes $v = 0$ and $v = \frac{1}{2}$. Indeed the computed three-dimensional Patterson function shows the highest peaks in these planes.

In this way we could assign two possible sets of coordinates for each of the two Pb ions in the asymmetric unit, because it appeared impossible to distinguish at this stage between the set $x\frac{1}{4}z$ and the other one $x, \frac{1}{4}, z + \frac{1}{2}$. The further interpretation of the Patterson map allowed us to recognize Pb—As, Pb—Cu and Pb—Cr vectors.

The y coordinate of lead ions was carefully adjusted by the trial-and-error method, so that the two sets of positions for the heavy atom

Table 1. *Observed and calculated structure factors*

h	k	l	F_o	F_c
0	0	2	86.9	131.2
		4	245.0	-272.8
		6	312.6	-302.4
		8		45.4
		10	242.5	-212.6
		12	99.7	- 86.4
		14	105.2	77.0
		16	218.0	201.2
		18	61.2	59.6
1	0	2	70.9	78.8
		-2		- 22.8
		4	316.3	-340.4
		-4	76.1	82.0
		6	298.0	-277.6
		-6	573.7	641.6
		8	81.9	- 74.2
		-8		- 5.8
		10	277.3	271.4
		-10	310.1	-282.6
		12	60.8	69.2
		-12	327.3	-283.2
		14		- 27.0
		-14	50.1	45.2
		16		1.0
		-16	53.4	- 49.0
		18	161.6	153.2
		-18	83.8	52.8
		20	70.9	- 67.6
		-20	108.2	93.2
2	0	0	200.5	-190.6
		2	211.9	-223.0
		-2	224.3	-263.4
		4		33.0
		-4	191.1	185.4
		6	76.4	-115.0
		-6	122.4	112.6
		8		- 47.6
		-8	168.3	155.0
		10	189.8	183.8
		-10	62.1	- 58.8
		12	351.3	347.2
		-12	306.9	290.0
		14	87.7	- 58.0
		-14	65.4	- 57.8
		16	169.6	-162.6
		-16	310.6	-273.6
		18	98.3	- 95.0
		-18	243.5	-217.2
		-20	95.5	91.2
		-22	64.9	67.4
3	0	0	317.5	-323.2
		2	155.9	-155.2
		-2	43.3	49.0
		4	240.0	270.6
		-4	119.1	-117.2
		6	440.9	528.2
		-6	212.5	-186.4
		8		- 30.2
		-8	51.4	- 50.8
		10	53.1	- 61.2
		-10	267.5	304.0
		12	98.8	- 79.4
		-12	168.3	165.8
		14	62.0	- 53.0
		-14		5.2
		16	147.5	-149.2
		-16	167.9	-160.8
		18		- 0.6
		-18	69.0	84.4
		-20		- 23.4
		-22	117.9	-116.0
4	0	0	506.2	529.2
		2		15.8
		-2	182.6	186.2
		4		35.8
		-4	362.6	-378.4
		6		32.4
		-6	476.3	-518.0
		8		- 25.6
		-8	95.2	95.6
		10	230.4	-219.2
		-10	62.4	65.2
		12	76.4	- 81.2
		-12	66.6	73.0
		14		20.0
		-14	52.5	58.8
		16	82.8	106.8
		-16	237.3	195.2
		-18		38.6
		-20	40.2	- 41.6
		-22	106.6	-126.4
5	0	0	174.5	163.8
		2	77.9	75.8
		-2	189.8	193.2
		4	242.0	-255.2
		-4	66.6	- 58.8
		6	142.0	-147.0
		-6	181.7	202.0
		8	60.8	- 50.6
		-8		43.2
5	0	10	80.3	81.4
		-10	261.8	-276.0
		12	58.3	- 68.4
		-12	334.5	-365.0
		14		- 8.0
		-14	62.5	66.2
		-16	141.4	141.0
		-18	105.8	100.6
6	0	0		- 43.2
		2		- 10.2
		-2	91.7	- 99.2
		4		- 7.6
		-4	142.0	130.6
		6	229.5	-220.4
		-6	173.9	156.6
		8		- 38.2
		-8	133.1	124.2
		10	169.1	163.0
		-10	152.5	-147.2
		12	144.1	166.0
		-12		11.0
		-14		- 20.8
		-16	156.1	-128.2
		-18	225.8	-196.2
		-20	116.8	105.8
7	0	0	331.4	-340.4
		2	110.5	-100.0
		-2		- 13.8
		4	133.1	118.6
		-4	75.5	68.2
		6	156.8	155.0
		-6	73.6	68.2
		8		9.0
		-8		1.8
		10	80.0	77.6
		-10	168.3	162.0
		-12	124.2	105.0
		-14		4.4
		-16	173.7	-160.0
		-18	53.4	- 53.4
8	0	0	64.7	66.0
		2		2.4
		-2	54.6	47.6
		4	130.1	129.8
		-4	129.4	-130.0
		6	69.3	69.8
		-6	303.1	-322.4
		8		- 25.8
		-8		11.2
		-10	182.6	181.0
		-12	125.3	134.4
		-14		- 13.4
		-16	61.2	49.2
9	0	0	105.4	113.0
		2	34.5	33.6
		-2	126.7	128.2
		-4	76.2	- 72.6
		-6	63.5	- 58.8
		-8		- 33.0
		-10	52.5	- 53.4
		-12	166.2	-188.8
		-14	40.2	43.8
		-16	167.1	174.8
10	0	0		42.8
		-2		- 10.4
		-4	44.5	47.8
		-6	68.8	73.4
		-8	48.2	54.0
		-10	78.8	- 79.8
		-12	74.2	- 79.8
0	1	1		- 17.2
		2	216.9	234.0
		3	43.1	57.6
		4	228.0	214.4
		5		30.0
		6	76.8	- 71.2
		7		- 33.8
		8		39.6
		9	70.1	- 53.2
		10	165.0	159.0
		11		12.8
		12	143.9	-119.0
		13		13.2
		14	389.9	-338.6
		15		4.4
		16	102.0	- 90.4
		17		- 0.8
		18	152.8	144.6
		19		26.0
		20	80.0	80.0
1	1	0		- 32.0
		1		- 31.2
		-1	66.5	48.2
		2	236.4	284.6
		-2	77.5	- 82.6
		3		- 57.0
		-3	77.5	92.0
		4	452.8	496.8
		-4	56.0	- 57.0
		5		- 21.6
1	1	-5		9.6
		6	178.9	-164.4
		-6	189.6	179.4
		7		- 18.6
		-7		- 14.6
		8	456.6	-474.0
		-8	400.2	353.6
		9		- 14.4
		-9		10.4
		10	199.3	-193.0
		-10	165.7	143.0
		11		- 13.6
		-11		8.0
		12	83.9	71.0
		-12	114.4	- 97.0
		13		40.4
		-13	57.5	- 45.0
		14		14.8
		-14	142.2	-115.6
		15		21.8
		-15	57.5	- 32.0
		16	69.2	50.2
		-16	34.6	37.0
		17		0.6
		-17		18.2
		18	137.4	130.2
		-18		34.6
		19	30.3	- 24.8
		-19		23.6
		-20	140.8	-149.6
2	1	0		- 51.0
		1		- 59.0
		-1		28.6
		2	413.8	-447.6
		-2	498.0	-656.4
		3		- 49.4
		-3		- 39.6
		4	140.1	-149.4
		-4	326.6	-409.2
		5		- 18.4
		-5		- 33.8
		6		- 20.8
		-6	157.4	160.0
		7	67.9	81.6
		-7		34.6
		8	125.7	-117.8
		-8	151.4	148.2
		9		18.6
		-9	82.4	73.8
		10		5.6
		-10		- 32.0
		11		- 0.4
		-11		- 13.2
		12	207.3	185.4
		-12	161.9	142.0
		13		- 17.6
		-13	60.4	- 52.6
		14	181.6	169.4
		-14	175.1	150.0
		15		16.4
		-15		- 10.4
		16	36.8	22.6
		-16		- 3.8
		17		- 14.8
		-17		15.2
		18	69.4	- 81.8
		-18	147.5	-130.8
		-19		- 8.2
		-20	104.7	-103.6
3	1	0		- 22.6
		1	80.4	76.4
		-1	64.4	- 72.4
		2	310.5	-307.8
		-2		12.0
		3		20.6
		-3	73.7	- 84.0
		4	140.8	-144.8
		-4	74.4	79.6
		5		- 13.2
		-5		- 11.4
		6	104.3	104.8
		-6		42.8
		7		- 5.8
		-7	58.0	67.4
		8	186.8	188.2
		-8	401.2	-504.6
		9	69.4	69.0
		-9		0.6
		10	77.3	63.8
		-10	262.3	-286.8
		11		- 14.0
		-11		7.4
		12	57.5	- 60.0
		-12	233.6	231.4
		13		- 26.0
		-13		15.6
		14	67.9	67.0
		-14	238.9	230.6
		15		- 24.0
		-15		33.2
3	1	16	57.5	67.6
		-16	86.9	65.2
		-17		- 19.6
		-18		- 26.0
		-19		- 30.4
		-20		- 26.2
4	1	0		- 5.0
		1		- 12.6
		-1		16.2
		2	62.2	69.6
		-2	252.6	256.4
		3	75.2	81.0
		-3		- 13.2
		4		1.4
		-4	253.1	256.6
		5		3.6
		-5		34.2
		6		- 31.4
		-6		0.8
		7		- 11.6
		-7		- 47.0
		8	224.1	236.2
		-8	132.0	-143.8
		9	46.7	- 45.2
		-9		- 19.4
		10	174.3	179.2
		-10		47.6
		11		12.6
		-11		- 15.2
		12	146.6	-136.6
		-12		- 9.6
		13		- 16.4
		-13		32.0
		14	171.3	-186.2
		-14	260.2	227.4
		15		- 5.2
		-15		13.0
		16	34.6	- 41.4
		-16	141.9	114.6
		-17		12.6
		-18	235.5	-182.2
		-19		1.6
		-20	210.9	-186.2
5	1	0	92.9	- 84.2
		1		24.0
		-1		- 22.6
		2	330.9	356.4
		-2	197.2	206.6
		3		- 14.0
		-3	54.6	51.8
		4	268.8	287.2
		-4	48.3	52.2
		5		14.0
		-5		4.2
		6	83.1	- 80.4
		-6	61.6	63.8
		7		- 44.0
		-7		- 14.4
		8	141.0	-145.6
		-8	144.1	149.0
		9		- 4.8
		-9	52.0	- 57.4
		10		- 38.4
		-10	83.7	- 88.8
		11		- 13.6
		-11		21.8
		12	67.4	- 65.6
		-12	134.8	121.0
		13	27.6	31.6
		-13		- 11.8
		14	64.0	- 76.4
		-14	213.2	171.0
		-15		- 8.2
		-16	50.2	40.8
		-17		- 3.8
		-18	72.2	- 69.8
		-19	56.0	41.6
6	1	0		8.2
		1	57.8	- 64.4
		-1		50.2
		2		- 5.6
		-2	279.7	288.2
		3		- 29.4
		-3		6.8
		4		10.8
		-4	350.2	348.0
		5		- 15.0
		-5		18.2
		6	109.2	-103.8
		-6	161.2	157.6
		7		39.6
		-7		- 15.4
		8	161.0	-167.8
		-8	273.1	302.8
		9		- 15.6
		-9	67.0	69.2
		10		- 19.2
		-10	99.9	109.2
		11		10.8
		-11		- 17.0

Table 1. *(Continued)*

h	k	l	F_o	F_c
6	1	12	59.1	74.4
		-12		23.8
		-13		- 43.0
		-14		- 17.2
		-15		- 43.4
		-16		22.8
		-17		31.6
		-18	141.9	115.2
		-19		3.6
		-20	96.7	86.8
7	1	0	72.1	- 66.0
		1		46.0
		-1		- 32.6
		2	175.6	-177.8
		-2	103.7	- 99.2
		3		- 24.6
		-3		- 27.8
		4	75.2	- 80.8
		-4	115.2	-109.8
		5		2.8
		-5		- 27.4
		6		34.8
		-6		1.8
		7		4.2
		-7	60.6	62.6
		8	33.5	42.4
		-8	128.9	-128.2
		9		40.8
		-9		5.6
		10		- 26.4
		-10	152.8	-163.2
		-11		11.6
		-12	154.3	-146.0
		-13		- 17.6
		-14	284.2	-263.2
		-15		20.4
		-16	61.6	- 51.0
		-17		- 18.6
		-18	112.9	101.6
		-19		- 9.4
		-20	66.8	56.0
8	1	0		- 9.2
		1		- 5.8
		-1		1.6
		2		- 44.2
		-2	63.7	64.4
		3		38.4
		-3		- 45.0
		4	124.4	-124.6
		-4	98.3	98.4
		-5		14.8
		-6		19.6
		-7		- 18.2
		-8	150.7	-143.4
		-9		14.8
		-10	97.8	-109.2
		-11		- 20.2
		-12		- 26.4
		-13		34.4
		-14		- 23.8
		-15		8.4
		-16	51.3	43.4
		-17		17.4
		-18	103.7	- 93.0
9	1	0		- 14.6
		1		27.6
		-1		- 21.0
		2	148.8	164.6
		-2	186.3	-191.4
		-3		23.2
		-4	86.2	- 94.4
		-5		- 3.6
		-6		28.2
		-7		3.4
		-8		15.8
		-9	54.0	- 48.8
		-10		- 14.4
		-11		12.4
		-12	56.2	- 60.8
		-13		2.8
		-14	98.4	87.2
		-15		11.2
		-16	46.2	44.4
0	2	1		- 20.4
		2	276.9	-252.0
		3		18.2
		4	272.7	241.8
		5	153.0	131.8
		6	109.0	83.6
		7	119.2	99.4
		8	177.4	151.4
		9	79.8	- 72.6
		10	112.8	89.8
		11	100.9	- 89.4
		12	161.1	144.0
		13		- 17.0
		14	179.2	-141.8
		15		17.2
		16	122.1	-116.4
		17		- 32.8
0	2	18	116.2	-111.6
		19		- 5.2
		20	65.6	70.6
1	2	0	170.8	-126.8
		1	132.5	118.8
		-1	96.6	107.0
		2	144.6	133.6
		-2	178.9	194.2
		3	79.4	- 82.0
		-3		- 18.2
		4	200.6	152.6
		-4	213.8	-217.6
		5	77.8	- 73.2
		-5	101.7	-104.2
		6	288.1	284.8
		-6	498.9	-475.0
		7		17.2
		-7		- 10.0
		8	92.5	- 76.8
		-8	176.3	-164.0
		9		0.4
		-9		- 8.6
		10	87.7	- 71.4
		-10	468.0	423.0
		11	92.9	- 78.2
		-11	55.9	- 46.0
		12	142.2	-114.6
		-12	223.2	192.4
		13		- 24.6
		-13		- 35.0
		14	56.2	58.6
		-14		14.2
		15	57.0	51.6
		-15	59.3	53.2
		16	92.1	- 78.6
		-16	63.1	- 47.2
		17	52.8	44.6
		-17	73.8	63.6
		18	64.1	- 80.8
		-18		17.6
		-19		- 0.6
		-20	120.5	-114.2
2	2	0	497.6	447.2
		1	96.8	98.2
		-1		18.8
		2	65.2	50.8
		-2	72.7	84.8
		3		17.4
		-3		- 10.6
		4		0.4
		-4	128.6	-124.4
		5	124.1	-126.6
		-5	79.4	87.0
		6	64.3	- 46.4
		-6	245.3	-271.4
		7	60.0	- 58.0
		-7	81.0	81.2
		8	183.8	173.0
		-8	56.3	57.0
		9		23.8
		-9	57.3	- 56.4
		10	243.7	-230.2
		-10	59.3	- 48.4
		11	58.6	43.6
		-11	117.1	-106.6
		12	246.3	-232.0
		-12	181.7	-165.4
		13		- 5.4
		-13		- 27.2
		14		- 8.4
		-14		- 32.4
		15		20.2
		-15		7.4
		16	177.8	184.6
		-16	324.6	298.8
		17	36.4	36.0
		-17		1.4
		-18	124.8	122.8
		-19		- 6.4
		-20	25.4	- 28.4
3	2	0	177.6	161.0
		1	61.5	- 57.6
		-1	67.5	-120.8
		2	293.0	291.4
		-2	116.4	122.6
		3		5.6
		-3		27.4
		4	336.8	-341.2
		-4		- 20.2
		5		4.0
		-5	86.0	108.8
		6	373.6	-395.8
		-6	180.8	205.8
		7		- 18.0
		-7		57.2
		8	73.5	- 77.2
		-8	97.7	-113.0
		9		36.8
		-9		- 42.4
		10	169.7	160.6
3	2	-10	89.8	- 95.0
		11	83.5	75.8
		-11		31.4
		12		26.4
		-12	191.2	-195.2
		13		25.2
		-13		39.0
		14	83.9	82.6
		-14		39.0
		15	46.9	- 45.8
		-15		- 31.6
		16	66.7	77.2
		-16	56.8	42.6
		-17	69.9	- 63.2
4	2	0	270.2	-259.2
		1	104.0	-101.2
		-1		- 53.2
		2	102.0	-117.4
		-2	233.6	-257.6
		3		22.6
		-3		0.6
		4		6.8
		-4	319.4	360.0
		5	85.5	88.8
		-5		- 20.2
		6	125.9	-121.2
		-6	250.5	296.0
		7		42.4
		-7		- 52.4
		8	134.5	117.0
		-8	60.0	76.6
		9	43.0	- 44.8
		-9		45.6
		10	155.3	143.6
		-10	113.0	-125.0
		11		- 10.8
		-11	124.5	112.2
		12	106.5	119.8
		-12		14.6
		13		11.2
		-13		30.4
		14	62.9	- 59.2
		-14	125.0	-132.6
		-15	90.3	- 61.2
		-16	113.0	-106.2
		-17		- 24.8
		-18	91.1	- 93.0
		-19		8.8
		-20	79.0	84.0
5	2	0	224.6	-208.8
		1	54.1	43.2
		-1	75.8	92.6
		2		40.4
		-2	55.5	- 61.4
		3		- 22.0
		-3		- 4.8
		4	135.2	127.4
		-4	51.2	- 60.8
		5		26.2
		-5	101.5	-122.0
		6	159.3	164.2
		-6	104.4	-109.4
		7		44.4
		-7		- 57.0
		8		- 13.6
		-8	119.3	-137.8
		9		- 29.0
		-9		4.4
		10		- 3.8
		-10	351.3	358.8
		11	66.4	- 61.6
		-11		18.4
		12	46.2	26.2
		-12	282.1	262.4
		-13		- 18.8
		-14		- 14.2
		-15		31.0
		-16	199.8	-205.6
		-17	49.6	50.8
		-18	34.5	- 30.2
		-19		10.2
		-20	53.9	- 62.0
6	2	0	152.4	141.6
		1	66.7	64.6
		-1		60.2
		2	42.1	- 44.4
		-2		13.4
		3		- 7.8
		-3		- 28.0
		4		47.0
		-4	76.1	- 66.0
		5	41.9	- 56.6
		-5		- 4.4
		6	120.3	129.4
		-6	220.3	-233.8
		7		- 11.0
		-7		34.0
		8	82.1	83.2
		-8		- 20.2
		9		4.8
6	2	-9		- 8.4
		10	152.8	-168.4
		-10	63.1	66.8
		-11	63.9	- 70.2
		-12		58.0
		-13		- 26.6
		-14		- 46.2
		-15		34.8
		-16	170.8	161.4
		-17	38.7	37.6
		-18	124.1	123.6
		-19		2.4
		-20	40.1	- 49.6
7	2	0	120.0	259.0
		1		0.2
		-1		- 22.0
		2	139.9	145.8
		-2	69.4	77.8
		3		- 12.4
		-3		4.4
		4	153.7	-160.2
		-4	119.2	-132.8
		5	35.8	- 45.2
		-5	61.2	74.4
		6	89.8	-108.8
		-6		- 15.2
		-7	41.7	61.8
		-8	61.8	- 65.2
		-9		- 35.0
		-10	52.6	- 60.0
		-11		- 41.6
		-12	132.9	-128.0
		-13		2.0
		-14		32.8
		-15		3.0
		-16	78.7	78.0
		-17	43.7	- 41.2
		-18	78.7	90.6
8	2	0		- 4.6
		1	44.8	- 53.4
		-1		- 53.4
		2		- 36.0
		-2	67.5	- 77.6
		3		20.6
		-3		- 3.0
		4	84.6	- 90.8
		-4	144.0	152.0
		-5		28.2
		-6	228.0	223.6
		-7		- 7.2
		-8		40.6
		-9		5.0
		-10	171.1	-191.8
		-11		42.6
		-12	38.7	- 71.2
		-13		26.0
		-14	46.0	- 42.6
9	2	0	92.7	-111.4
		-1		14.8
		-2	70.6	- 77.4
		-3		3.6
		-4		9.8
		-5		- 49.0
		-6	43.5	76.0
		-7		- 39.0
		-8		1.4
		-9		22.2
		-10	69.3	94.0
		-11	32.0	45.2
		-12	106.9	133.2
0	3	1		18.4
		2	241.6	-204.8
		3	158.5	-133.2
		4	201.2	-168.2
		5	71.1	- 64.8
		6	46.9	44.2
		7	146.4	118.6
		8		- 28.4
		9	134.8	111.0
		10	137.3	-124.6
		11		- 15.0
		12	104.1	86.4
		13	63.2	- 49.4
		14	282.6	257.8
		15		0.6
		16	74.3	70.4
		17		- 12.8
		18	101.3	-104.8
		19	35.4	- 41.8
1	3	0		16.6
		1	142.9	119.4
		-1	144.0	-141.4
		2	218.2	-204.6
		-2	59.0	- 60.0
		3	124.1	110.2
		-3	174.9	-204.8
		4	366.6	-330.8
		-4		- 22.4
		5	53.1	39.4
		-5		- 14.6

Table 1. *(Continued)*

h	k	l	F_o	F_c
1	3	6	120.2	107.2
		-6	127.9	127.6
		7		11.6
		-7	67.9	66.4
		8	377.5	368.4
		-8	231.6	203.8
		9	94.7	90.8
		-9		-20.0
		10	155.9	149.6
		-10	91.7	85.4
		11		-5.4
		-11		-29.6
		12	71.1	-59.4
		-12	61.5	-53.4
		13	114.7	-100.0
		-13	109.2	91.4
		14		-23.2
		-14	88.4	-75.8
		15	78.1	-76.2
		-15	85.7	69.6
		16	53.3	-44.8
		-16		18.2
		17	34.5	39.0
		-17		-24.2
		18	87.3	-99.8
		-18		-30.2
		-19	51.4	-57.4
		-20	81.1	-112.2
2	3	0		20.0
		1		44.0
		-1		8.4
		2	301.5	274.4
		-2	419.8	-427.2
		3	152.3	142.6
		-3		53.4
		4	121.1	112.0
		-4	222.4	-286.2
		5	46.1	38.4
		-5	43.7	58.8
		6	57.9	50.8
		-6	80.1	84.0
		7	128.5	-123.0
		-7	96.0	-106.4
		8	112.2	95.4
		-8	93.9	98.4
		9	129.0	-116.0
		-9	119.5	-118.8
		10		-15.2
		-10	67.5	52.0
		11		32.2
		-11		9.0
		12	146.2	-141.6
		-12	128.7	118.6
		13		20.6
		-13	120.0	104.6
		14	112.2	-119.6
		-14	115.4	106.2
		-15		19.6
		-16		-3.8
		-17		-15.0
		-18	96.3	-98.2
		-19	26.0	28.6
		-20	65.5	-84.4
3	3	0	51.0	52.4
		1	61.2	-61.8
		-1	54.7	52.0
		2	225.0	205.2
		-2		8.2
		3	96.3	-82.8
		-3	174.9	185.4
		4	81.7	82.6
		-4	69.2	84.6
		5		38.8
		-5		27.4
		6	87.7	-81.6
		-6		-30.8
		7		-46.2
		-7		-58.6
		8	130.4	-119.4
		-8	313.1	-377.0
		9	78.7	-72.4
		-9		-54.6
		10	61.4	-53.2
		-10	212.8	-220.8
		11		-13.4
		-11		-5.6
		12		35.6
		-12	199.1	180.8
		13	78.3	75.6
		-13	63.9	-61.0
		14	46.1	-54.0
		-14	191.1	181.8
		15	30.5	29.6
		-15	71.1	-63.8
		16	29.1	-46.4
		-16	61.8	49.2
		-17		35.2
		-18		19.4
		-19	85.4	94.0
4	3	0		10.2
4	3	1	90.5	-89.0
		-1	61.5	73.4
		2	55.3	-57.4
		-2	196.6	190.6
		3	140.6	-136.2
		-3		-6.0
		4		-7.8
		-4	182.8	176.4
		5		-29.4
		-5		-56.6
		6		31.2
		-6		-11.4
		7	95.5	93.0
		-7		48.4
		8	176.1	-176.0
		-8	94.7	-114.2
		9		22.6
		-9	124.4	149.6
		10	131.2	-137.2
		-10		-33.2
		11		17.4
		-11		-9.6
		12	94.9	95.0
		-12		3.2
		13		17.4
		-13	86.8	-90.2
		14	108.4	142.4
		-14	165.1	-166.8
		-15	69.5	-62.8
		-16	82.9	-86.6
		-17		19.4
		-18	133.6	143.0
		-19		-13.0
		-20	118.1	142.4
5	3	0	70.9	62.2
		1	70.9	65.0
		-1	74.8	-67.8
		2	281.8	-278.8
		-2	156.2	147.8
		3		-14.2
		-3	119.8	-110.6
		4	226.3	-226.0
		-4		55.4
		5		-1.8
		-5		-40.4
		6	65.3	55.6
		-6	44.4	52.0
		7		44.0
		-7	124.8	143.6
		8	112.6	121.2
		-8	91.2	99.8
		9	86.8	95.4
		-9		47.2
		10		37.6
		-10		47.8
		11		-16.6
		-11		-20.6
		12	50.3	56.8
		-12	72.1	-74.0
		-13		-0.6
		-14	113.5	-117.4
		-15	63.0	56.0
		-16	40.5	-41.2
		-17	31.6	-28.0
		-18	40.5	41.6
		-19	58.8	-64.8
6	3	0		-12.4
		1	44.8	45.8
		-1		-23.2
		2		-0.6
		-2	207.7	-201.4
		3	128.2	129.6
		-3	61.8	-68.4
		4		-6.0
		-4	225.2	-250.4
		5		6.0
		-5		-4.2
		6	95.5	94.0
		-6	121.4	115.6
		7	35.8	-37.6
		-7		-43.8
		8	114.9	123.8
		-8	197.3	218.0
		9	38.4	-36.4
		-9		-49.6
		-10	74.6	90.0
		-11		-11.8
		-12		-10.2
		-13	103.2	104.8
		-14		11.0
		-15	51.2	57.4
		-16		-31.4
		-17		-7.6
		-18	80.6	-86.4
		-19	24.9	-32.0
7	3	0	57.2	59.6
		1		-6.8
		-1		-15.8
		2	134.8	121.4
		-2	59.0	-67.6
7	3	3		11.2
		-3	83.6	98.8
		4	46.1	59.4
		-4	84.9	-83.0
		5		26.0
		-5		23.8
		6		-19.6
		-6		-18.4
		7	52.3	-63.2
		-7		-47.0
		-8	91.4	-101.6
		-9	89.3	-99.6
		-10	129.5	-127.2
		-11		8.0
		-12	125.0	124.8
		-13		2.6
		-14	201.4	207.4
		-15		-1.0
		-16	43.2	41.8
		-17		-1.4
		-18	63.4	-79.6
8	3	0		7.6
		1	60.3	-66.8
		-1	46.9	66.8
		2		32.0
		-2	38.8	53.6
		3		-39.2
		-3	38.6	57.6
		4	95.2	86.8
		-4	55.8	67.8
		-5		8.4
		-6		-12.4
		-7		-27.6
		-8	97.2	-107.8
		-9	63.4	60.0
		-10	74.1	-83.2
		-11		-4.2
		-12		15.6
		-13	63.2	-69.0
		-14		21.0
		-15	63.0	-70.4
		-16	43.4	-37.0
0	4	1		4.8
		2	65.0	57.4
		3		-6.4
		4	168.0	-120.6
		5	209.2	-182.2
		6	193.1	-162.6
		7	128.4	-110.0
		8		-0.4
		9	88.8	79.2
		10	147.9	-123.4
		11	153.8	139.8
		12		-15.6
		13		11.4
		14	64.8	48.0
		15		-14.8
		16	89.8	110.2
		17	27.5	38.2
1	4	0		-31.0
		1	167.8	-140.4
		-1	164.0	-173.0
		2	33.3	22.8
		-2		27.0
		3	61.8	63.2
		-3		36.8
		4	219.0	-185.2
		-4	61.6	56.6
		5	122.6	107.2
		-5	117.0	110.6
		6	122.2	-106.6
		-6	354.7	349.8
		7		-32.8
		-7	59.4	41.6
		8	48.2	-46.0
		-8		-1.0
		9		19.0
		-9		4.2
		10	143.8	127.4
		-10	171.2	-163.0
		11	107.6	93.4
		-11	98.2	86.2
		12	37.9	38.8
		-12	182.2	-177.6
		13	49.3	47.2
		-13		36.8
		14		-1.6
		-14		9.4
		15	71.0	-76.0
		-15	60.1	-74.0
		16		2.2
		-16	44.9	-37.6
		17	39.6	-56.6
		-17	92.4	-108.8
		-18	50.5	44.4
2	4	0	81.7	-79.4
		1	151.3	-146.4
		-1		-0.6
		2	133.1	-115.6
		-2	135.6	-127.4
2	4	3		10.0
		-3		11.4
		4		34.6
		-4	92.9	84.6
		5	185.0	163.0
		-5	111.0	-101.6
		6	63.2	-54.4
		-6	57.3	52.4
		7	99.3	90.8
		-7	129.6	-138.0
		8		-11.6
		-8	94.9	85.8
		9	60.5	-52.6
		-9	69.0	91.8
		10	103.4	96.4
		-10		-25.0
		11	58.5	-47.0
		-11	141.2	138.2
		12	191.4	204.0
		-12	167.8	166.6
		13		-6.0
		-13	57.3	49.6
		14	45.1	-36.6
		-14		-30.8
		15		-25.4
		-15		-28.6
		16	50.4	-93.8
		-16	134.8	-151.4
		-17		5.8
		-18	105.5	-130.4
3	4	0	206.5	-193.2
		1	114.8	109.0
		-1	159.5	150.2
		2	104.2	-93.2
		-2		7.4
		3		-26.8
		-3		-30.8
		4	145.1	132.2
		-4	94.5	-86.2
		5		10.4
		-5	165.2	-182.6
		6	303.8	293.8
		-6	43.8	-48.6
		7		24.4
		-7	50.1	-55.0
		8		-7.8
		-8		-8.4
		9	38.6	-40.8
		-9	41.5	45.6
		10		-28.8
		-10	143.6	158.0
		11	116.3	-127.8
		-11		-25.2
		12	53.4	-53.6
		-12	66.7	76.6
		13		-30.0
		-13	54.6	-61.8
		14	39.9	-42.4
		-14		21.6
		-15	64.6	60.8
		-16	84.9	-90.2
		-17	67.3	81.2
		-18	39.5	43.8
4	4	0	292.6	286.4
		1	109.6	109.0
		-1	87.2	84.2
		2		21.2
		-2	100.5	94.0
		3		-13.0
		-3		1.2
		4	56.9	44.4
		-4	191.9	-189.2
		5	144.6	-142.2
		-5	45.2	50.0
		6		-0.6
		-6	256.0	-279.4
		7	61.1	-61.4
		-7	49.0	44.6
		8	35.6	-34.8
		-8		28.8
		9	44.0	50.4
		-9	53.2	-48.8
		10	115.9	-130.8
		-10		12.8
		11	30.1	30.8
		-11	173.9	-158.8
		12	20.9	-35.8
		-12	45.5	50.0
		-13	36.3	-34.6
		-14	42.8	44.6
		-15	56.2	66.2
		-16	86.7	105.2
		-17	39.6	43.6
5	4	0	82.2	73.2
		1	46.9	-39.2
		-1	125.0	-126.6
		2	45.1	28.2
		-2	130.9	118.6
		3		9.4
		-3		13.0

Table 1. *(Continued)*

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
5	4	4	129.4	-127.0	5	4	-12	193.5	-212.2	6	4	5	66.7	75.8	7	4	1		14.0
		-4		- 21.2			-13		7.6			-5		19.4			-1	37.5	32.6
		5		- 30.6			-14	39.7	46.0			6	102.8	-132.4			2	54.6	- 62.6
		-5	133.9	141.2			-15	24.8	- 35.8			-6	85.5	78.2			-2		- 6.8
		6	59.2	- 65.4			-16	65.5	79.8			-7	76.4	- 69.6			3		5.2
		-6	103.3	115.8			-17	71.9	- 86.0			-8	93.7	87.8			-3		- 4.6
		7	57.5	- 63.4			-18	54.1	69.6			-9		26.4			4	50.5	67.2
		-7	92.8	101.6	6	4	0		- 18.8			-10	62.0	- 68.8			-4	31.9	32.2
		8	36.5	- 36.0			1	103.2	-108.5			-11	98.1	108.8			5	46.5	70.0
		-8		11.2			-1	75.4	- 83.2			-12		5.6			-5	114.6	-125.4
		9	45.3	51.0			2		- 24.2			-13	46.5	51.6			-6	38.7	42.8
		-9		- 15.2			-2	36.1	- 44.2			-14		- 19.8			-7	80.2	- 73.4
		10	38.5	47.6			3		29.0			-15	50.4	- 68.4			-8		8.8
		-10	170.2	-155.6			-3		31.4			-16	55.0	- 77.2			-9	54.3	50.0
		11	41.9	76.0			4		- 6.2			-17	36.0	- 49.8			-10	94.2	87.8
		-11		- 20.8			-4	71.3	75.4	7	4	0	173.8	-198.8					

were no longer equivalent and we could choose the more satisfactory arrangement in comparing observed and computed $|F|$'s.

A three-dimensional Fourier synthesis computed with the phases given by the heavy atoms revealed oxygen locations. A first refinement was carried out by difference syntheses; the discrepancy index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.15.

For the structure-factor calculations, we used the scattering-factor values given for Pb^{+2} ion by CROMER and WEBER (1965) and for As[1], Cu^{+2}, Cr and O^- by International Tables (1962). Correction for the real part of anomalous dispersion was applied for Pb, As and Cu with the

Table 2. *Fractional atomic coordinates, isotropic temperature factors and their standard deviations*

Atom	x	$10^3\sigma(x)$	y	$10^3\sigma(y)$	z	$10^3\sigma(z)$	B	$\sigma(B)$
Pb(1)	.2194	.2	.2197	.3	.3757	.1	1.92	.02
Pb(2)	.2225	.2	.7731	.3	.0589	.1	1.67	.02
As	.4865	.4	.2595	.9	.0814	.2	1.61	.06
Cu	.4859	.7	.5082	1.1	.2486	.3	1.33	.08
Cr	.0504	.6	.2597	1.3	.1589	.3	1.05	.08
O(1)	.5409	3.9	.0282	6.3	.1377	1.7	2.50	—
O(2)	.4723	3.9	.4779	6.3	.1322	1.7	2.50	—
O(3)	.2901	3.7	.2088	6.4	.0149	1.6	2.50	—
O(4)	.6377	3.9	.3153	6.5	.0476	1.7	2.50	—
O(5)	.9941	3.7	.0316	6.5	.1019	1.7	2.50	—
O(6)	.0044	3.5	.4726	6.7	.0944	1.6	2.50	—
O(7)	.2501	3.5	.2478	6.4	.2135	1.6	2.50	—
O(8)	.9271	3.5	.2889	6.4	.2182	1.6	2.50	—
OH	.3440	3.4	.7607	6.7	.2192	1.5	2.50	—

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[1] Because of isomorphous replacement of As by P, on the basis of the chemical analysis, we used for the scattering factor of "As" a value $f(\theta) = 0.925\, f(\theta)_{As} + 0.075\, f(\theta)_P$. No correction was apported to the Cu^{+2} scattering factor for the insignificant Fe content.

values $\Delta f'$ reported for Cu$K\alpha$ radiation by Cromer (1965). An isotropic temperature factor $B = 1.0$ Å^2 for heavy atoms and $B = 2.0$ Å^2 for oxygen atoms was assumed, based upon results from similar structures.

The refinement of the structure was performed using a block-diagonal approximation. The program, written for the IBM 1620 computer, applies the weighing scheme suggested by Cruickshank *et al.* (1961)[2]. Seven cycles of least-squares were completed, until the atomic positions remained virtually unchanged. We did not refine the individual temperature factor of oxygen atoms because of their erratic behaviour, caused by the dominant role of the heavy atoms in the structure. To the oxygen therefore, an overall thermal parameter $B = 2.5$ Å^2 was imposed.

The final R value for all observed structure factors was 0.098. The observed and calculated structure factors are listed in Table 1. The atomic coordinates and isotropic vibrational parameters with their standard deviations are given in Table 2.

Discussion

The atomic arrangement in the unit cell projected along b and a axis is respectively shown in Fig. 1 and 2.

The lists of bond lengths and bond angles with their standard deviations are included in Tables 3 and 4. The standard deviations are estimated with the Cruickshank formula (1953) for bond lengths, and with the Darlow formula (1961) for bond angles.

Because of the location of Pb_1, Pb_2, As and Cr at y about $\frac{1}{4}b$ and $\frac{3}{4}b$ and of Cu at y about 0 and $\frac{1}{2}b$, close to the screw axis, the unit cell seems halved along c axis. The presence of the same well-marked pseudo-cell with half the volume of the true cell, was observed also in vauquelinite (Berry, 1949).

Similar arrangement of oxygen atoms occur around each of the two non-equivalent lead ions. Both Pb(1) and Pb(2) have nine nearest oxygen neighbours at distances of 2.35 to 3.03 Å and 2.55 to 3.05 Å, respectively. These values are in agreement with those reported for linarite (Bachmann and Zemann, 1961) and pyrobelonite (Donaldson

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[2] We are grateful to Prof. V. Scatturin, Dr. V. Albano, Dr. P. L. Bellon and Dr. F. Pompa, who have supplied us with all the IBM 1620 computer programs employed in this work.

and BARNES, 1955). Two larger distances occur between Pb_1—O(4,IV) (3.69 Å) and Pb_2—O(3,I)′ (3.49 Å). The closest approaches of oxygen atoms within these irregular polyhedra are 2.51 Å [between O(2,III)

Table 3. *Bond lengths and their standard deviations*
(I: x, y, z; II: $\bar{x}, \bar{y}, \bar{z}$; III: $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; IV: $x, \frac{1}{2}-y, \frac{1}{2}+z$;
the label indicates atoms of adjacent cells)

Pb(1,I)—O(1,III)	2.73 Å	± .03 Å	Cu(I)—O(1,III)	2.08 Å	± .02 Å
O(2′,III)	2.92	.03	O(2,I)	2.02	.02
O(3, IV)	2.35	.02	OH(I)	1.84	.03
O(4′,III)	2.78	.03	OH(III)	1.95	.03
O(5,III)	2.64	.03	O(7,I)	2.36	.03
O(6,III)	2.51	.03	O(7,III)	2.46	.03
O(7,I)	2.95	.02			
O(8′,I)	2.99	.02	As(I)—O(1,I)	1.65 Å	± .03 Å
O(8′,III)	3.03	.03	O(2,I)	1.59	.03
			O(3,I)	1.65	.03
Pb(2,I)—O(1′,I)	2.89 Å	± .03 Å	O(4,I)	1.57	.03
O(2,I)	2.64	.03			
O(3′,I)	2.78	.03	Cr(I)—O(5′,I)	1.64 Å	± .03 Å
O(4′,II)	2.55	.02	O(6,I)	1.64	.03
O(5′,I)	2.69	.03	O(7,I)	1.57	.03
O(5′,II)	3.00	.02	O(8′,I)	1.68	.02
O(6,I)	2.72	.03			
O(6′,II)	3.05	.03	OH(I)—O(8,III)	2.78 Å	± .03 Å
OH(I)	2.64	.02			

Table 4. *Bond angles and their standard deviations in* $CuO_4(OH)_2$, AsO_4 *and* CrO_4 *coordination polyhedra*

O(1,III)—Cu(I)—O(7,I)	86.9°	± 1.0°	O(1,I)—As(I)—O(2,I)	112.6°	± 1.3°
O(7,III)	94.3°	1.0°	O(3,I)	105.7°	1.6°
OH(I)	87.9°	1.1°	O(4,I)	108.4°	1.6°
OH(III)	93.4°	1.1°	O(2,I)—As(I)—O(3,I)	107.8°	1.6°
O(2,I) —Cu(I)—O(7,I)	85.4°	1.0°	O(4,I)	105.0°	1.7°
O(7,III)	93.8°	1.0°	O(3,I)—As(I)—O(4,I)	117.4°	1.2°
OH(I)	88.6°	1.1°			
OH(III)	90.9°	1.1°	O(5,I)—Cr(I)—O(6,I)	104.6°	± 1.4°
O(7,I) —Cu(I)—OH(I)	94.6°	1.3°	O(7,I)	110.4°	1.7°
OH(III)	91.0°	1.3°	O(8,I)	111.2°	1.5°
O(7,III)—Cu(I)—OH(I)	90.8°	1.3°	O(6,I)—Cr(I)—O(7,I)	113.4°	1.6°
OH(III)	83.6°	1.3°	O(8,I)	107.8°	1.5°
			O(7,I)—Cr(I)—O(8,I)	109.4°	1.1°
O(1,III)—Cu(I)—O(2,I)	171.2°	1.2°			
O(7,I) —Cu(I)—O(7,III)	174.5°	2.3°			
OH(I) —Cu(I)—OH(III)	174.3°	2.8°			

and O(4,III)] and 2.60 Å [between O(5,I) and O(6,II)]. The shortest distance Pb—Pb is 4.13 Å.

The Cu^{+2} atom has two O and two OH as nearest neighbours in approximately square array at an average distance 1.97 Å. Two oxygen atoms, one above and one below the plane of the square, complete the coordination to form the usual pseudo-octahedron with bond lengths of 2.36 Å and 2.47 Å.

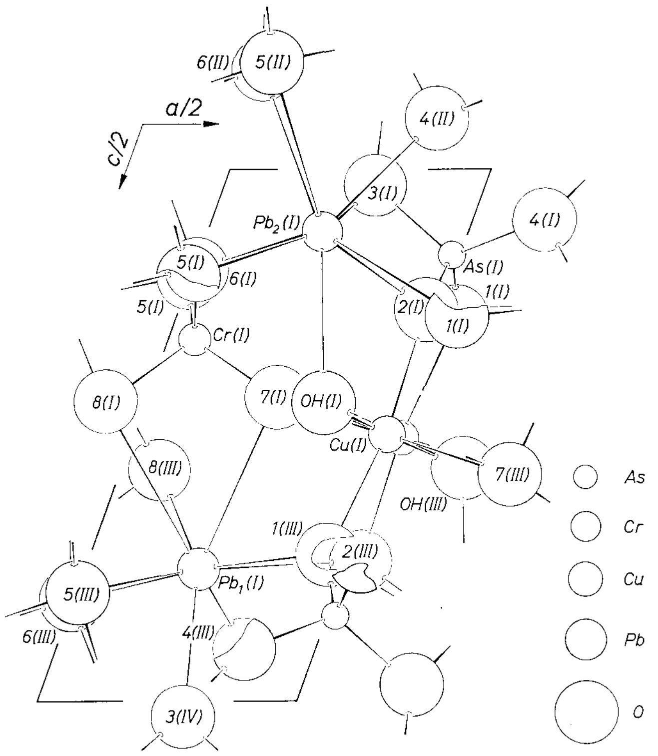

Fig. 1. Fornacite structure projected along the *b* axis

The tetrahedral arsenate group deviates considerably from regularity. As—O bond lengths have an average value 1.61 Å. The most reliable data of arsenate minerals show a remarkable dispersion of the bond lengths As—O: in clinoclase (Ghose, Fehlmann and Sundaralingam, 1965) the shortest As—O distance is 1.68 Å, the largest one is 1.75 Å (mean value 1.70 Å); in conichalcite (Qurashi and Barnes, 1963) the As tetrahedron appears very irregular with As—O bonds 1.60

to 1.74 Å long (mean value 1.68 Å); in eucroite (GIUSEPPETTI, 1963) and brandtite (DAHLMAN, 1952) the mean As—O value is 1.67 Å (from 1.61 to 1.76 Å); in liroconite (GIUSEPPETTI, CODA, MAZZI and TADINI, 1962) the mean bond length is 1.65 Å (shortest distance is 1.60 Å). The shorter value of As—O distance in fornacite can be partially explained by the isomorphous replacement of arsenic by phosphorous.

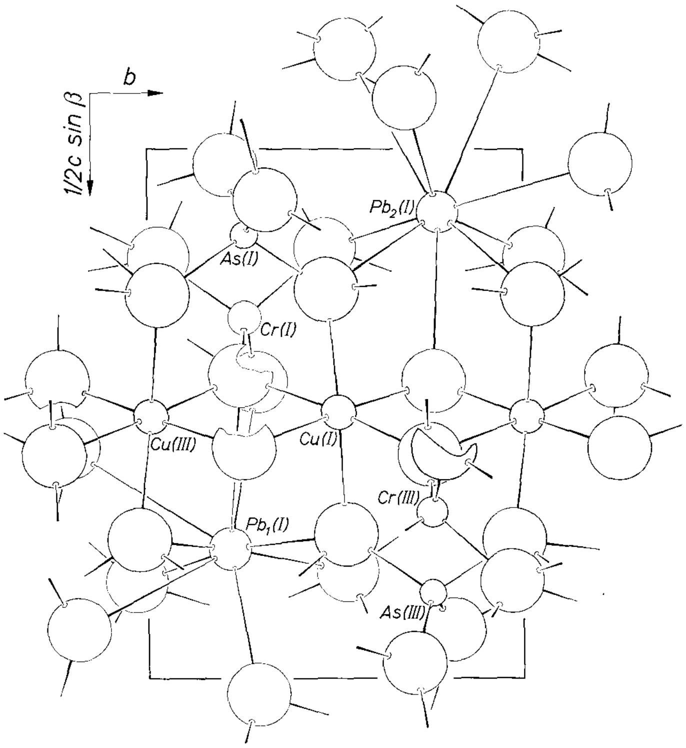

Fig. 2. Projection along *a* axis

The chromate ion has a distorted tetrahedral configuration with a mean Cr—O distance of 1.63 Å, in agreement with the value 1.64 Å found for crocoite (NARAY-SZABO and ARGAY, 1964).

Considerations of distances between OH and surrounding oxygen atoms have led us to locate an hydrogen bond between OH and O(8) (distance 2.78 Å). Therefore all the oxygen atoms show a tetrahedral coordination, according to the following scheme:

O(1) binds 1 Cu + 1 As + 1 Pb(1) + 1 Pb(2)
O(2) 1 Cu + 1 As + 1 Pb(1) + 1 Pb(2)
O(3) 1 As + 1 Pb(1) + 1 Pb(2) [+ 1 Pb(2)]
O(4) 1 As + 1 Pb(1) + 1 Pb(2) [+ 1 Pb(1)]
O(5) 1 Cr + 1 Pb(1) + 2 Pb(2)
O(6) 1 Cr + 1 Pb(1) + 2 Pb(2)
O(7) 2 Cu + 1 Cr + 1 Pb(1)
O(8) 1 Cr + 2 Pb(1) (+ H bond)
OH 2 Cu + 1 Pb(2)

The coordination polyhedra of Pb an Cu ions and AsO_4 and CrO_4 tetrahedra share edges and corners to form a very tightly knit three-dimensional network.

The $CuO_4(OH)_2$ pseudo-octahedron shares two opposite edges O—OH with adjacent Cu polyhedra. The arrangement of these linked complexes appears as a zig-zag chain along the screw axis. The distance Cu—Cu is 2.95 Å.

Each Pb(1) coordination polyhedron links four Pb(2) polyhedra by four different edges, while each one of these last polyhedra links four Pb(1) and two other Pb(2) by six different edges. Two infinite sets of these bonds occur at $z = 0$ and $\frac{1}{2}c$ along a and b axes, so that the Pb resultant array consists of two thick sheets parallel to (001). One of these sheets is linked to the other one by the Cu chains. The AsO_4 and CrO_4 tetrahedra confer steadiness to the three-dimensional structure both with bonds among different Pb polyhedra in the same sheet, and among two sheets and the Cu polyhedra.

The absence of preferential directions in the interatomic bonds explains the lack of good cleavage and the uneven fracture of the mineral.

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