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The crystal structure of jordanite, $Pb_{28}As_{12}S_{46}$*

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Auszug

Natürlicher Jordanit aus dem Binnatal (Schweiz) ist monoklin, Raumgruppe $P2_1/m$, mit $a = 8{,}918(1)$, $b = 31{,}899(4)$, $c = 8{,}462(1)$ Å und $\beta = 117{,}79(1)°$. Die Elementarzelle ist entlang der a- und der c-Achse ungefähr halbiert. Von der Viertel-Struktur ausgehend wurde die vollständige Struktur mittels einer Art Minimal-Residual-Methode (der Methode der Hauptverschiebungen) gelöst und durch gewöhnliche Fourier- und Kleinste-Quadrate-Methoden bis zu $R = 7{,}0\,^0/_0$ verfeinert.

Die Jordanitstruktur ist ein deformierter PbS-Strukturtyp. Die Elementarzelle enthält 40 Me- und 46 S-Atomlagen. Die 12 unabhängigen Me-Lagen verteilen sich auf drei Schichten $y \approx 0{,}05$, $\approx 0{,}15$ und $\approx 0{,}25$ (die Spiegelebene), mit vier Me-Lagen, 3 Pb + As, in jeder Schicht. Zwischen diesen Me-Schichten befinden sich S-Schichten; drei zusätzliche S-Atome liegen in der dritten Me-Schicht, die eine gemischte (Me—S)-Schicht darstellt. Einige der Lagen sind statistisch besetzt; eine Pb-Lage der ersten Schicht ist von 0,50 Pb + 0,50 As, eine andere Pb-Lage in der dritten Schicht von 0,88 Pb besetzt. Dies ergibt eine Formeleinheit von $Pb_{27,8}As_{12,0}S_{45,8}$ pro Elementarzelle, mit der idealen Formel $Pb_{28}As_{12}S_{46}$.

Die voll besetzten Pb-Lagen der ersten, zweiten bzw. dritten Schicht sind von sechs [mittlerer (Pb—S)-Abstand = 3,01 Å], sieben [3,04 Å] bzw. acht [3,08 Å] S-Atomen koordiniert. Die S-Koordination um die As-Atome ist trigonalpyramidal mit einem mittleren (As—S)-Abstand von 2,25 Å. Die AsS_3-Pyramiden sind voneinander getrennt (Typus I.c$_1$ der Klassifikation von Nowacki).

Abstract

Natural jordanite from Binnatal, Switzerland is monoclinic, space group $P2_1/m$, with $a = 8.918(1)$, $b = 31.899(4)$, $c = 8.462(1)$ Å and $\beta = 117.79(1)°$.

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The unit cell is approximately halved along both the *a* and *c* axes. Starting from the one-fourth substructure, the complete structure was solved by a kind of minimum residual method (the method of key shifts), and was refined by ordinary Fourier and least-squares methods ($R = 7.0\%$).

The structure of jordanite is a deformed PbS-type structure. The unit cell contains 40 metal and 46 sulfur atom sites. The twelve independent metal sites are distributed on three layers at $y \approx 0.05$, ≈ 0.15 and ≈ 0.25 (the mirror plane), with four metal sites, 3 Pb + As, on each layer. These metal layers are interleaved by sulfur layers; three additional S atoms are added to the third metal layer to form a metal-sulfur mixed layer. Some of the sites have statistical nature; one Pb site on the first layer is occupied by 0.50 Pb + 0.50 As, another Pb site on the third layer is occupied by 0.88 Pb. Thus, the unit-cell content is $Pb_{27.8}As_{12.0}S_{45.8}$, with the ideal formula $Pb_{28}As_{12}S_{46}$.

The fully occupied Pb atoms on the first, second and the third layers are coordinated with six (average Pb—S = 3.01 Å), seven (3.04 Å) and eight (3.08 Å) S atoms, respectively. The sulfur coordinations about the As atoms are ordinary trigonal pyramids with an average As—S = 2.25 Å. The AsS_3 pyramids are isolated from each other (type I.c_1 of the classification of NOWACKI).

Introduction

The precise chemical composition of jordanite has been the subject of considerable discussion (SOLLY, 1900; PALACHE, RICHMOND and WINCHELL, 1938; FISHER, 1940; PEACOCK and BERRY, 1940; DOUGLASS, MURPHY and PABST, 1954; WUENSCH and NOWACKI, 1966). The formulae which have been proposed on the basis of the chemical analyses of natural material can be summarized by the range of composition $Pb_{26\text{-}28}As_{14}S_{46\text{-}49}$. On the other hand, ROLAND (1968) proposed a new formula, $Pb_{28-x}As_{12}S_{46-x}$ $[0.8 < x < 1.4]$, from silica-tube quenching experiments and density measurements of synthetic jordanite; moreover, he concluded that jordanite is most probably a high-temperature dimorph of gratonite, $Pb_{27}As_{12}S_{45}$, the structure of which has been established by x-ray work (RIBÁR and NOWACKI, 1969; RÖSCH, 1963). More recently, however, KUTOGLU (1969) proposed an older formula, $Pb_{27}As_{14}S_{48}$, for synthetic jordanite.

Jordanite is a typical superstructure based on the PbS-type substructure. The unit cell is approximately halved along both the *a* and *c* axes. The one-fourth substructure (the average atomic arrangement over four closely related subcells) has been determined by WUENSCH and NOWACKI (1966). The present paper deals with the structure determination of the complete structure of natural jordanite. As described below, the obtained unit-cell content is $Pb_{27.8}As_{12.0}S_{45.8}$, with the ideal formula, $Pb_{28}As_{12}S_{46}$.

Crystal data

A specimen of jordanite (sample code Jord. Nr. 1) from Binnatal, Switzerland was used for the present investigation. A fragment was cut out of the specimen with a razor, and it was made into a sphere with a radius of 0.078 mm by BOND's (1951) method. The powder attached to the surface was dissolved away with a hot aqueous HNO_3 solution. Diffraction patterns showed jordanite to be monoclinic. The lattice constants were obtained from three equatorial Weissenberg photographs (about a, b and [201] axes), taken with a back-reflection double-radius camera. Diffraction patterns of Si powder ($a = 5.43074$ Å) were used for calibration. The wave lengths used were 1.54051 and 1.54433 Å for $\mathrm{Cu}K\alpha_1$ and α_2 radiations, respectively. The results of the least-squares calculations agree fairly well with those given by NOWACKI, IITAKA, BÜRKI and KUNZ (1961) (Table 1)[1].

As was already pointed out by DOUGLASS, MURPHY and PABST (1954), the set of lattice constants given in Table 1 (the reduced cell of jordanite) should carefully be distinguished from another very similar set: $a' = 8.987(1)$ Å, $\beta' = 118.61(1)°$, $b' = b$, $c' = c$ and $V' = V$. The transformation is given by: $\mathbf{a}' = \mathbf{a} + \mathbf{c}$, $\mathbf{b}' = -\mathbf{b}$ and $\mathbf{c}' = -\mathbf{c}$.

The observed systematic absences of reflections were only $0k0$ with k odd. Therefore, permitted space groups are $P2_1$ or $P2_1/m$. Since the mineral is not piezoelectric (NOWACKI *et al.*, 1961) and possesses morphology of symmetry $2/m$, the space group was assumed to be $P2_1/m$[2].

Table 1. *Lattice constants of jordanite*

	Jordanite		Galena*
	Present work	NOWACKI *et al.* (1961)	
a	8.918(1) Å	8.96(4) Å	8.39 Å
b	31.899(4)	31.92(1)	34.24
c	8.462(1)	8.45(3)	8.39
β	117.79(1)°	117°50(10)′	120°
V	2129.5 Å^3	2137.1 Å^3	2085.3 Å^3

* $a = [1\bar{1}0]_{\mathrm{PbS}}$, $b = (10/3)\ [111]_{\mathrm{PbS}}$ and $c = [\bar{1}01]_{\mathrm{PbS}}$, where $a_{\mathrm{PbS}} = 5.93$ Å.

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[1] Throughout the paper, the estimated standard deviations are given in parentheses in an abbreviated form; for example, 8.918(1) means 8.918 ± 0.001.

[2] The results of the present analysis do not rule out the other possible space group $P2_1$. However, even if the correct space group is $P2_1$, deviation from the symmetry of $P2_1/m$ seems to be hardly significant (see also the footnote [4]).

Since chemical and microprobe analyses on natural jordanite from Binnatal have detected at most negligible amount of Sb (cf. Table 7), it was assumed that the crystal used did not contain Sb.

Intensity measurements

The intensities were measured with an automatic diffractometer of the equi-inclination type (Buerger-Supper-Pace) using Ni-filtered Cu$K\alpha$ radiation. The diffracted beams were detected with a proportional counter. The spherical crystal was rotated in the ω-scan mode about the b (0 to 37th layers) and the a (0 to 9th layers) axes. The scanning speed was varied from 0.5° (for higher angles) to 1.0° per minute (for lower angles). The background was measured before and after each Bragg reflection for the time approximately equal to the scan time of the reflection. About 4000 independent reflections were measured, of which 3200 were considered to be observed [$I > 2.33\sigma(I)$]. They were corrected for Lorentz, polarization and absorption (sphere with $\mu r = 9.7$ for Cu$K\alpha$ radiation) effects.

Structure determination

Approximate structure

Starting from the one-fourth substructure of WUENSCH and NOWACKI (1966), an approximate complete structure of jordanite was solved by a kind of minimum residual method (the method of key shifts; ITO, 1973). Since the procedure of key shifts of jordanite is described in detail in the above reference, only the results of the analysis are given in Table 2. The R value at this stage was 33% for all 3200 observed reflections.

Isotropic refinement

The approximate structure was refined by least-squares (block-diagonal approximation) and Fourier methods. In the least-squares calculations, unit weights were given to all reflections, and the atomic scattering factors for the neutral atoms were used[3]. Two cycles of isotropic refinement of the twelve metal atoms of Table 2 reduced R from 33 to 28%. The B value of As(11) showed tendency to diverge and that of Pb(12), which had been considered to be As, became exceptionally low (0.5 Å^2). The corresponding Fourier map also gave a very

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[3] *International tables for x-ray crystallography* (1962), Vol. III, pp. 202 (S and As) and 210 (Pb). Birmingham: Kynoch Press.

Table 2. *Approximate coordinates of jordanite as deduced by the method of key shifts*
The overall temperature factor used was $B = 1.7$ Å^2

Designation of atoms		x/a	y/b	z/c
this paper	Ito (1973)			
Pb(1)	Pb(111)	0.440	0.059	0.346
Pb(2)	Pb(112)	440	048	831
Pb(3)	Pb(121)	912	041	322
As(4)	As(122)	912	046	822
Pb(5)	Pb(211)	266	140	001
As(6)	As(212)	266	140	501
Pb(7)	Pb(221)	794	150	017
Pb(8)	Pb(222)	794	150	517
Pb(9)	Pb(311)	131	250	162
Pb(10)	Pb(312)	116	250	677
As(11)	As(321)	543	250	147
Pb(12)	As(322)	543	250	647

low peak for As(11) and a high peak for Pb(12). At the same time, the map revealed ten reasonable sulfur peaks. Therefore, in the next cycle, As(11) was eliminated, the atomic species of Pb(12) was changed from As to Pb and the ten S atoms, S(1) to S(10), were added (altogether 21 atoms). After additional four cycles, R was 17%. In the Fourier map, As(11) disappeared from the mirror plane; instead, three additional sulfur peaks surrounding the absent As(11) position in a triangular arrangement appeared on the plane. In addition, a peak with approximately the same peak height as that of a sulfur atom appeared about 0.7 Å below (by symmetry also above) the As(11) position; the peak together with the above three sulfur peaks formed a trigonal pyramid typical for the AsS_3 pyramid. Therefore, the peak was assigned as As with half occupancy; As(11) now split into two halves and the three S atoms, S(11) to S(13), were added in the next cycle (altogether 25 atoms). A few cycles of least-squares refinement together with the Fourier maps indicated that S(11) had also to be split into two halves, about 0.4 Å above and below the mirror plane. The R value at this stage was 11%.

Refinement of site occupancy

The results of the least-squares refinement ($R = 11\%$) gave abnormally high B values for Pb(2) and Pb(12) (3.9 and 3.2 Å^2, respectively). Both atoms were coordinated with six S atoms. The coordination about Pb(2) was an intermediate one between typical coordinations of Pb and As; the Pb—S distances were about 2.6 and 3.0 Å for the three shorter and three longer bonds, respectively. On the other hand, the coordination about Pb(12) was a typical one for Pb with the six Pb—S distances of about 3.0 Å. Therefore, it was assumed that the Pb(2) site was statistically occupied by Pb and As, and the Pb(12) site was fractionally occupied by Pb. The occupancies of the two sites were then refined in combination with the isotropic temperature factor of each site by a least-squares method (2 × 2 block-diagonal approximation). As for the Pb(2) site, preliminary calculations indicated that the distribution was approximately 0.5 Pb + 0.5 As. Therefore, the number of electrons of the site was refined using a unitary atomic scattering factor, $f = \{f(\mathrm{Pb}) + f(\mathrm{As})\}/(82 + 33)$, in a similar way as was applied to binnite by WUENSCH, TAKÉUCHI and NOWACKI (1966).

Table 3. *Atomic coordinates of jordanite with standard deviations*

Atom	x/a	y/b	z/c
Pb(1)	0.4469(2)	0.05466(4)	0.3504(2)
Pb(2)	4392(2)	05194(8)	8422(3)
Pb(3)	9040(2)	04119(4)	3167(2)
As(4)	9194(4)	05256(10)	8299(4)
Pb(5)	2648(2)	14226(5)	–0028(2)
As(6)	2758(5)	14284(12)	5082(5)
Pb(7)	7904(2)	15071(4)	0176(2)
Pb(8)	7925(2)	15021(4)	5149(2)
Pb(9)	1222(3)	25	1714(3)
Pb(10)	1215(3)	25	6896(3)
As(11)	6158(9)	2265(2)	1766(10)
Pb(12)	5504(4)	25	6395(4)
S(1)	3095(9)	0031(3)	0123(11)
S(2)	3067(10)	0051(3)	5504(12)
S(3)	0460(9)	0862(2)	1005(10)
S(4)	0511(9)	0853(2)	6864(11)
S(5)	6520(9)	0969(3)	2028(10)
S(6)	6733(9)	0910(2)	7073(11)
S(7)	4061(10)	1767(3)	3744(12)
S(8)	4021(11)	1774(3)	7699(11)
S(9)	0307(9)	1791(3)	3838(10)
S(10)	9940(10)	1935(2)	8688(11)
S(11)	3783(17)	2617(4)	055(2)
S(12)	7520(15)	25	032(2)
S(13)	7521(15)	25	455(2)

Table 4. *Thermal parameters of jordanite with standard deviations*

The thermal parameters refer to the expression:

$$T = \exp\{-2\pi^2(b_{11}h^2a^{*2} + \cdots + 2b_{12}hka^*b^* + \cdots)\}$$

B_{eq} is the equivalent isotropic temperature factor.

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	B_{eg}
Pb(1)	0.0203(6)	0.0191(5)	0.0215(6)	0.0032(5)	0.0082(5)	0.0012(5)	1.65 Å^2
Pb(2)	129(9)	469(15)	153(9)	— 70(8)	54(7)	— 111(9)	2.01
Pb(3)	143(5)	232(5)	206(6)	20(5)	43(5)	7(5)	1.65
As(4)	68(14)	93(15)	141(16)	— 4(12)	30(13)	— 28(13)	0.85
Pb(5)	197(6)	361(10)	219(7)	74(6)	79(5)	63(6)	2.10
As(6)	158(17)	.018(2)	.019(2)	24(15)	39(14)	33(15)	1.54
Pb(7)	192(6)	191(5)	190(6)	3(5)	80(5)	2(5)	1.54
Pb(8)	180(6)	165(5)	162(6)	— 1(5)	65(5)	— 1(5)	1.38
Pb(9)	225(9)	258(10)	208(9)	0	80(8)	0	1.88
Pb(10)	233(9)	237(10)	232(9)	0	114(8)	0	1.83
As(11)	.015(3)	.007(4)	.022(4)	.001(3)	.005(3)	— .000(3)	1.25
Pb(12)	.0404(14)	.0160(10)	.0388(14)	0	.0172(12)	0	2.55
S(1)	.003(3)	.022(4)	.018(4)	.001(3)	— .002(3)	— .011(3)	1.34
S(2)	10(3)	11(4)	29(4)	2(3)	12(3)	7(3)	1.22
S(3)	7(3)	12(4)	9(3)	— 4(3)	— 2(3)	— 1(3)	0.89
S(4)	9(3)	11(4)	18(4)	1(3)	9(3)	1(3)	0.88
S(5)	10(3)	16(4)	8(3)	— 7(3)	— 1(3)	— 1(3)	1.04
S(6)	9(3)	9(4)	16(4)	2(3)	6(3)	2(3)	0.87
S(7)	7(4)	37(5)	22(4)	5(4)	8(3)	1(4)	1.71
S(8)	21(4)	17(4)	11(4)	5(3)	5(3)	5(3)	1.38
S(9)	2(3)	16(4)	13(4)	0(3)	2(3)	1(3)	0.86
S(10)	16(4)	8(4)	15(4)	— 1(3)	11(3)	— 4(3)	0.92
S(11)	6(6)	6(8)	15(7)	— 4(4)	2(5)	2(5)	0.79
S(12)	7(5)	38(8)	23(6)	0	7(5)	0	1.79
S(13)	13(5)	17(6)	26(6)	0	6(5)	0	1.56

Table 5. *Observed and calculated structure factors* (0.5)

k	$\vert F_o \vert$	F_c
	0 k 0	
8	67	67
10	870	-920
12	110	108
16	33	43
18	150	-155
20	672	656
22	151	143
26	53	-52
28	123	129
30	360	-357
32	80	56
34	92	90
36	67	68
38	93	-110
	1 k 0	
0	36	19
2	99	-92
3	94	88
5	103	-98
6	60	61
7	112	120
8	82	88
12	41	40
14	77	-88
15	172	180
16	143	-143
17	262	-276
18	225	-228
19	96	-88
20	35	17
21	56	59
22	45	-42
23	65	-66
24	109	115
25	179	-191
26	155	161
27	163	180
28	95	97
29	31	25
30	36	-33
31	77	-95
32	27	13
33	56	67
34	71	-66
35	127	139
	2 k 0	
0	91	-96
1	72	57
2	240	229
3	462	443
4	440	429
5	87	-80
6	442	-437
7	584	575
8	472	-456
9	151	141
10	119	122
11	36	-34
12	163	-157
13	391	-384
14	431	-418
16	290	289
17	300	-289
18	238	232
19	49	-21
20	128	-122
21	33	23
22	60	53
23	223	222
24	211	214
25	86	-85
26	166	-170
27	158	163
28	183	-189
29	52	56
31	53	46
33	120	-136
34	94	-104
35	108	106
36	105	112
37	81	-97
	3 k 0	
0	199	-196
1	191	-158
2	78	66
4	64	-52
6	46	42
8	44	-32
9	90	79
10	456	434
11	303	278
13	108	-105
14	54	44
15	58	54
16	38	-18
17	38	- 8
19	53	-45
20	238	-229
21	249	-236
22	178	178
23	28	17
27	30	-23
28	33	-35
29	32	11
30	168	175
31	260	260
32	75	-69
33	62	64
34	16	20
35	50	-46
	4 k 0	
0	84	71
1	178	-167
2	40	-29
3	224	209
4	365	-352
5	529	489
6	293	276
7	230	224
8	53	49
9	192	-186
10	84	-69
11	158	142
13	167	-154
14	368	343
15	448	-423
16	88	-84
17	199	-184
18	81	-84
19	158	149
20	83	80
21	95	-93
23	96	94
24	223	-215
25	227	223
26	55	50
27	38	41
29	170	-166
30	46	-49
31	51	54
32	35	-36
33	38	-41
	5 k 0	
0	35	-19
1	33	-26
2	166	-157
3	340	-317
4	236	-231
5	45	35
6	194	187
7	157	-147
8	87	-74
9	119	101
11	40	-29
12	86	82
13	243	230
14	162	158
15	63	-51
16	130	-128
17	103	90
18	66	57
19	55	-40
21	111	103
22	83	-82
23	254	-245
24	222	-215
25	33	-28
26	82	92
27	23	-19
28	85	-80
29	94	90
30	73	-72
31	26	-20
	6 k 0	
0	301	-304
1	282	266
2	79	-78
3	85	83
4	25	-13
5	98	-91
6	38	20
7	46	45
8	73	64
9	285	276
10	327	321
11	269	-258
12	148	144
13	177	-179
14	41	31
15	87	90
17	22	-26
19	141	-139
20	118	-112
21	290	282
22	99	-96
23	148	151
24	27	-17
25	63	-73
26	53	51
28	45	-42
29	77	86
	7 k 0	
1	100	100
3	147	-148
4	134	130
5	221	-220
6	95	-91
7	175	-178
9	88	92
11	81	-90
12	30	-15
13	95	90
14	70	-61
15	104	102
16	240	235
17	157	157
19	90	-91
20	29	- 6
21	63	68
22	28	18
23	34	-42
24	45	37
25	40	-47
26	153	-159
	8 k 0	
0	84	-90
1	206	-203
2	183	-196
3	128	-133
4	49	38
5	132	129
6	48	-28
7	112	-105
8	152	157
9	146	-151
10	38	38
11	102	106
12	44	31
14	75	-80
15	99	-102
16	37	25
17	64	65
18	153	-158
19	173	186
20	84	-94
	9 k 0	
0	166	183
1	116	-121
2	49	56
3	73	-80
4	69	80
5	26	29
6	45	-54
7	46	-54
8	47	-46
9	128	-136
10	158	-170
11	86	93
12	18	-19
13	60	67
14	72	-78
	-10 k 1	
0	21	-29
1	23	-30
2	31	-37
3	14	2
4	24	29
6	18	-20
	-9 k 1	
1	28	32
2	24	15
3	69	-69
4	26	22
5	57	-63
6	46	43
7	81	-85
8	42	-35
11	25	-21
12	19	-16
13	18	18
14	45	-37
15	46	45
17	70	74
	-8 k 1	
0	98	101
1	47	-35
2	42	-19
3	48	23
4	30	-15
5	76	-71
6	47	44
8	41	36
9	41	-28
10	55	-49
11	33	-17
12	41	-39
13	67	-67
14	31	-39
15	50	37
16	37	-43
17	40	25
18	74	-78
19	40	33
20	29	26
21	61	61
22	41	46
23	38	36
	-7 k 1	
0	128	132
1	17	- 5
2	45	31
3	68	-71
4	33	33
5	42	35
7	54	-51
8	39	-26
10	77	-77
12	70	-65
13	84	92
14	52	-50
18	38	-40
19	25	-23
20	32	33
22	47	49
23	66	-70
24	34	28
25	23	-15
26	42	41
27	27	19
	-6 k 1	
0	48	-51
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23	116	114
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26	85	87
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12	114	-101
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23	132	136
24	47	44
26	118	121
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13	35	-12
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23	45	-38
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13	183	-190
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7	31	-36
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12	40	-39
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14	107	100
15	42	-39
17	37	34
19	112	102
20	244	-241
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22	130	138
25	48	48
26	20	19
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3	328	-317
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5	199	196
6	140	-131
7	273	-276
8	284	-280
9	220	-216
10	43	-30
11	114	119
12	140	-134
13	191	192
14	70	-72
15	173	-174
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17	187	185
18	225	218
19	180	177
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22	54	49
23	146	-148
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26	31	-27
27	93	-92
28	163	-168
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9	60	56
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22	51	-42
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16	39	27
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22	101	101
23	150	150
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29	90	90
30	231	-241
31	128	-129
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34	42	30
35	53	54
-3 k 2		
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4	224	231
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6	107	-115
8	163	161
9	118	112
11	70	-64
13	162	169
14	139	-152
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16	90	91
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21	97	98
23	189	-190
24	214	215
25	159	-160
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27	77	74
28	113	120
29	113	112
30	49	59
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33	118	126
34	115	-111
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36	37	43
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4	453	472
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6	540	-560
7	538	546
8	250	-253
9	132	-141
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11	129	130
12	59	-55
13	302	-312
14	479	-495
15	321	-331
16	221	227
17	255	-262
18	122	129
19	135	139
20	120	-126
21	82	-81
23	175	181
24	269	281
25	85	86
26	195	-202
27	110	119
28	110	-125
29	80	-80
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31	54	63
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34	153	-165
35	31	-26
36	89	95
37	63	-81
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17	37	27
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33	76	80
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6	530	529
7	546	546
8	312	314
9	97	-102
10	162	-172
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12	110	109
13	352	-358
14	491	507
15	264	-265
16	216	-218
17	251	-250
18	157	-162
19	109	115
20	143	145
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22	46	-41
23	219	213
24	283	-281
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26	184	185
27	110	108
28	116	127
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33	113	-122
34	154	162
35	23	-21
36	74	-75
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8	142	-150
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11	85	-72
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14	181	191
15	71	76
16	89	-90
17	51	-48
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19	80	-78
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22	34	15
23	181	-181
24	238	-236
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26	45	-30
27	76	68
28	120	-123
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30	35	-36
31	85	-92
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33	111	118
34	124	123
35	85	88
36	24	-29
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4	36	30
5	85	-95
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10	691	686
11	194	-202
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22	102	-95
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28	89	-94
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18	162	152
19	32	-23
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22	51	48
23	34	-30
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25	85	78
26	185	-185
27	208	-211
28	24	-13
29	42	40
30	52	47
32	38	-31
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6	161	164
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9	192	-193
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13	188	182
14	96	89
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18	239	-231
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21	61	-56
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26	49	47
27	112	-108
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31	21	23
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14	103	-101
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21	82	80
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25	47	48
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22	24	-20
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3	181	191
4	101	106
5	75	-77
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13	198	-204
14	113	-115
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16	79	83
17	102	-102
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6	30	-17
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14	85	-90
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7	71	69
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19	78	-80
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23	27	-17
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19	40	-36
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13	122	-127
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30	56	-53
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33	78	-84
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5	47	-60
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10	31	-27
11	63	-68
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14	105	105
16	22	-24
17	120	130
18	32	-18
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9	183	-181
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13	53	-50
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23	109	108
24	51	47
27	45	37
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35	53	-39
-2 k 3		
1	38	-30
2	89	85
3	121	-123
4	111	124
6	106	-114
7	118	-126
8	33	-31
10	41	-25
11	57	-51
13	38	53
14	98	-115
17	106	109
19	32	-31
20	37	22
21	102	105
23	68	-67
24	108	113
27	45	-31
28	22	20
30	38	-40
31	66	-73
32	37	35
34	23	-22
35	46	-55
-1 k 3		
0	39	31
2	81	66
3	57	64
5	139	-128
7	79	77
8	63	-57
12	87	-84
13	146	-153
14	114	-113
15	45	38
16	152	-154
19	57	59
20	95	-95
22	95	100
23	148	149
24	69	70
25	51	-51
26	109	120
27	31	-18
28	70	74
29	54	-58
30	52	49
31	17	8
32	40	-47
33	81	-90
34	42	-44
0 k 3		
0	221	226
1	66	-56
2	48	65
8	40	27
9	71	76
10	167	-174
11	80	84
13	67	-49
14	69	-54
18	85	-87
19	47	-47
20	73	71
22	47	44
24	105	89
25	33	-35
27	27	27
28	88	88
30	35	-23
31	70	72
33	66	68
35	17	-19
1 k 3		
0	61	-55
1	61	-74
2	96	82
4	45	-31
5	110	111
6	78	77
7	128	137
8	41	21
10	59	55
11	83	67
12	80	-80
15	114	-106
16	161	-155
17	79	-84
18	26	-22
20	82	-74
21	35	-40
22	73	81
23	73	-75
24	52	42
26	120	127
27	56	53
28	48	51
30	71	61
31	39	46
32	44	-39
33	49	53
34	31	-40
2 k 3		
2	49	-27
4	69	72
5	88	93
6	67	-69
7	50	46
8	67	-55
9	97	102
11	44	52
12	42	46
14	98	-94
15	50	-39

Table 5. *(Continued)*

k	$\|F_o\|$	F_c
16	57	58
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18	74	72
19	78	-73
20	35	-18
21	36	-40
22	45	-50
23	50	-52
25	50	-44
26	60	-61
27	40	37
29	31	24
30	42	-21
31	63	71
32	44	32
33	82	85
3 k 3		
0	195	-203
1	34	37
4	75	-74
6	74	74
7	33	33
8	47	38
9	165	168
10	82	95
11	41	27
13	40	-31
14	94	93
16	36	-54
17	31	14
19	147	-140
20	62	-54
22	35	-18
23	54	-48
24	36	-29
25	44	-26
26	49	46
27	27	-20
28	20	- 9
29	85	93
30	37	24
31	83	89
4 k 3		
0	57	62
2	84	-81
4	45	-45
7	45	43
8	72	70
10	51	-52
12	60	64
14	98	101
16	92	87
18	36	30
21	29	-29
24	95	-102
26	116	-120
5 k 3		
0	122	-128
1	43	-46
2	77	-75
3	89	-92
4	28	-24
5	46	47
7	89	-93
8	63	57
10	33	28
11	46	29
12	54	48
13	64	67
14	28	20
16	58	46
18	26	18
20	31	-20
21	30	27
22	70	-69
23	76	-80
24	37	-35
25	32	-21
26	56	-63
6 k 3		
0	90	-94
1	24	-28
4	49	56
5	67	-65
6	50	-55
9	53	-53
11	28	-24
13	31	-29
15	30	18
16	62	63
17	43	41
18	72	78
19	68	69
21	66	68
7 k 3		
0	27	18
3	56	-54
5	71	-76
6	20	17
7	87	-89
8	20	18
10	18	-18
14	17	10
-10 k 4		
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1	154	-162
2	151	164
3	93	-100
4	42	-39
5	110	103
6	38	33
7	68	-73
8	122	-124
9	138	-140
10	74	-78
11	76	80
12	46	-42
13	20	25
14	62	65
15	84	-87
-9 k 4		
0	27	-17
1	79	76
2	36	21
3	101	-99
4	103	-96
5	166	-162
6	84	86
7	144	-138
8	26	-26
9	75	76
11	72	-70
13	71	69
15	102	101
16	204	-200
17	106	106
18	23	20
19	88	-88
20	21	- 6
21	55	58
-8 k 4		
0	199	201
1	238	245
2	99	98
3	91	96
4	52	38
5	73	-60
6	49	-35
7	51	51
8	67	-62
9	240	247
10	232	-233
11	227	-223
12	133	-139
13	154	-157
14	47	-39
15	64	67
16	38	32
17	29	-25
18	24	24
19	142	-140
20	84	83
21	221	220
22	82	83
23	126	131
24	33	31
25	45	-49
-7 k 4		
2	113	120
3	226	-221
4	141	145
5	46	49
6	118	-121
7	110	-106
8	50	45
9	89	82
11	39	-13
12	65	-70
13	182	179
14	112	-112
15	60	-52
16	103	99
17	68	67
18	41	-43
19	58	-54
21	55	52
22	91	97
23	205	-204
24	160	157
25	20	- 7
26	83	-90
28	70	70
-6 k 4		
0	52	-43
1	135	-146
3	166	166
4	258	255
5	459	472
6	219	-224
7	164	159
9	144	-155
10	49	31
11	122	120
12	35	33
13	110	-105
14	256	-246
15	365	-365
16	67	59
17	161	-160
18	33	33
19	108	116
20	68	-37
21	73	-79
22	36	-32
23	59	54
24	171	165
25	210	209
26	51	-46
27	55	61
29	141	-141
30	27	22
31	39	41
-5 k 4		
0	134	141
1	100	-79
2	57	-67
3	37	12
4	42	30
5	31	-22
6	37	-30
9	61	61
10	293	-301
11	188	186
12	49	56
13	38	-39
19	47	-46
20	176	176
21	187	-186
22	168	-172
24	26	- 7
25	25	- 7
27	40	-28
28	22	17
29	45	32
30	155	-161
31	194	198
32	79	76
-4 k 4		
0	56	61
2	212	-215
3	345	367
4	300	-320
5	103	-106
6	278	296
7	380	399
8	337	352
9	145	146
10	55	-60
11	58	-51
12	175	177
13	331	-347
14	316	314
15	58	63
16	215	-216
17	223	-222
18	198	-203
19	58	-59
20	82	81
21	44	38
22	63	-59
23	190	196
24	155	-158
25	98	-95
26	115	118
27	142	140
28	147	150
29	46	50
30	27	-20
31	24	26
32	21	23
33	119	-129
-3 k 4		
2	67	73
3	57	49
5	118	-122
6	86	-92
7	78	82
8	41	-43
10	41	18
11	48	-24
12	36	-36
13	40	34
14	96	102
15	155	168
16	120	121
17	189	-194
18	144	145
19	46	-39
20	29	-19
21	45	41
22	51	45
23	45	-39
24	94	-95
25	154	-162
26	151	-157
27	130	132
28	91	-88
29	25	14
30	42	39
31	73	-84
32	35	-24
33	42	41
34	64	57
-2 k 4		
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1	122	-102
4	37	32
6	22	-11
8	47	-57
9	87	-90
10	692	716
11	54	57
12	43	-27
13	40	11
14	53	-52
16	36	-18
18	108	106
19	78	76
20	528	-544
22	104	-102
24	46	50
26	29	26
27	39	20
28	89	-91
29	44	-43
30	279	285
32	64	-49
34	70	-68
-1 k 4		
2	127	118
3	110	-105
5	84	83
6	83	-83
7	151	-151
8	92	-95
12	49	-41
14	74	74
15	140	-141
16	67	66
17	240	247
18	196	192
19	91	88
21	36	-32
22	39	28
23	49	44
24	80	-73
25	152	152
26	94	-92
27	162	-168
28	116	-114
29	47	-38
30	26	9
31	59	71
33	51	-54
34	65	54
0 k 4		
0	106	117
2	135	-137
3	335	-333
4	382	-379
5	42	-34
6	370	370
7	407	-405
8	302	295
9	78	-75
10	102	-109
12	105	98
13	286	284
14	346	343
15	45	34
16	283	-278
17	243	238
18	183	-185
20	108	98
21	51	-25
23	154	-151
24	188	-186
25	50	48
26	173	170
27	165	-159
28	148	159
29	29	-31
30	21	-14
31	26	-25
32	17	- 9
33	92	97
1 k 4		
0	215	222
1	99	105
4	42	33
5	45	43
6	22	-23
10	369	-370
11	240	-229
12	39	-39
13	55	59
14	29	-30
15	47	-40
20	197	194
21	254	244
22	102	-103
23	44	-28
24	28	17
27	37	28
28	40	36
30	142	-142
31	228	-225
32	36	32
2 k 4		
0	79	-86
1	116	126
2	73	66
3	197	-199
4	308	317
5	352	-356
6	253	-264
7	152	-149
8	57	-55
9	142	149
10	78	76
11	102	-108
13	150	147
14	302	-297
14	292	294
16	83	74
17	137	128
18	79	80
19	105	-101
20	72	-73
21	68	65
23	100	-97
24	213	203
25	190	-191
26	44	-40
27	41	-38
28	37	-24
29	148	148
30	57	58
31	38	-36
3 k 4		
0	33	25
1	31	23
2	109	106
3	250	254
4	214	222
6	169	-166
7	126	127
8	40	44
9	50	-39
11	38	28
12	46	-46
13	193	-199
14	188	-187
16	122	127
17	77	-78
18	33	-37
20	38	28
21	81	-79
22	55	54
23	199	196
24	209	205
25	50	47
26	86	-91
28	74	78
29	70	-64
4 k 4		
0	234	249
1	198	-219
2	66	60
3	65	-65
4	35	- 9
5	84	90
7	31	-28
8	24	-23
9	190	-186
10	296	-295
11	228	223
12	125	-131
13	117	121
14	37	27
15	93	-92
16	38	18
17	28	24
19	105	105
20	130	123
21	243	-237
22	67	64
23	117	-121
24	23	-17
25	57	60
26	31	-29
5 k 4		
1	73	-84
2	36	-30
3	124	131
4	126	-124
5	171	174
6	95	97
7	191	196
8	31	31
9	74	-78
10	21	-19
11	81	78
12	40	33
13	79	-83
14	70	64
15	97	-102
16	188	-182
17	164	-167
18	25	-19
19	90	94
20	20	15
21	63	-67
6 k 4		
0	23	27
1	131	151
2	139	147
3	112	121
4	25	-15
5	113	-112
6	20	17
7	81	88
8	119	-131
9	128	130
10	26	-15
11	87	-88
12	32	-24
13	30	-31
14	56	58
15	95	104
-10 k 5		
0	76	-75
1	23	23
2	31	33
4	20	-20
5	55	50
6	22	-22
8	30	-40
9	21	-10
10	64	68
12	36	38
13	68	71
14	41	51
15	31	-31
-9 k 5		
0	80	-90
1	37	-27
2	39	16
3	42	35
4	35	-28
10	80	87
12	59	56
13	73	-77
14	66	55
17	21	16
18	44	45
19	31	30
20	27	-33
-8 k 5		
0	33	25
1	49	51
2	23	-20
4	82	-79
5	89	-63
6	62	-58
7	48	-36
8	42	34
9	32	20
10	31	-29
11	55	-56
12	25	24
13	41	24
14	109	94
16	34	-32
17	40	39
18	24	-19
19	36	19
21	25	28
24	58	-54
-7 k 5		
3	52	-52
4	59	-61
6	57	44
7	31	-40
9	55	-54
11	43	-48
12	39	37
13	37	12
16	42	-27
18	57	-61
19	102	109
20	35	-20
21	88	92
22	23	23
23	59	57
24	24	31
25	28	21
-6 k 5		
1	33	-24
2	42	38
3	103	-104
4	127	136
6	104	-114
7	67	-68
8	39	37
10	39	-26
11	64	-59
12	36	23
13	38	43
14	68	-62
15	63	-51
16	39	30
17	72	70
19	35	40
20	55	41
21	93	94
22	44	-29
23	23	-29
24	71	72
25	23	29
27	57	-59
28	22	7
-5 k 5		
1	53	28
2	52	49
3	35	-11
4	51	27
5	105	-109
7	26	27
8	44	-40
10	54	36
12	49	-48
13	59	-57
14	123	-107
16	121	-113
19	72	69
20	82	-80
22	54	54
23	89	87
24	89	90
25	27	-30
26	81	86
27	79	-79
28	54	52
29	19	-11
30	44	40
31	16	8
-4 k 5		
0	154	166
3	53	40
4	21	26
5	36	-32
8	28	37
9	38	42
10	183	-186
11	47	42
13	62	-62
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18	78	-86
20	79	78
21	28	-10
23	34	31
24	70	69
26	35	-26
28	81	85
30	47	-33
31	44	49
-3 k 5		
1	45	-53
2	44	38
3	35	-14
5	34	32
6	87	90
7	113	121
8	69	72
11	62	63
12	75	-74
13	71	63
14	14	15
15	79	-73
16	111	-112
17	80	-82
19	30	34
20	34	-21
21	65	-74
22	66	66
23	59	-60
26	112	119
27	41	13
28	77	80
29	49	56
30	74	66
31	57	66
32	40	-38
-2 k 5		
0	41	-38
3	43	38
4	42	41
5	46	58
7	94	95
8	74	-85
9	53	51
11	44	46
13	47	-36
14	99	-83
15	39	-41
16	66	49
17	128	-130
18	72	67
20	35	-25
21	48	-57
22	37	-27
23	29	- 9
25	58	-54
26	51	-48
28	22	18
29	27	11
30	27	-18
31	49	50
32	26	22
-1 k 5		
0	214	-222
1	59	54
4	48	-48
5	22	-15
6	48	44
7	29	20
9	175	177
10	89	92
12	51	-47
13	46	31
14	69	55
16	53	-48
18	53	54
19	152	-150
20	80	-79
21	60	-60
23	80	-72
24	52	-57
26	28	33
27	34	-32
28	37	-43
29	123	128
30	43	45
31	76	83
32	22	-25
0 k 5		
0	31	32
2	81	-78
3	62	60
4	57	-55
6	68	67
7	82	78
8	55	46

Table 5. *(Continued)*

k	$\|F_o\|$	F_c
11	35	16
12	44	41
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14	82	86
16	87	85
17	48	-41
18	76	66
19	39	42
21	63	-56
23	66	57
24	112	-112
26	91	-91
27	20	-17
28	18	15
31	28	31
1 k 5		
0	74	-83
1	32	-34
2	82	-75
3	127	-128
4	31	-38
5	93	85
6	35	34
7	132	-131
12	61	60
13	129	126
14	48	48
15	60	-38
16	95	95
17	31	22
19	35	-32
22	67	-66
23	131	-130
24	59	-53
25	23	16
26	95	-97
27	38	-19
29	23	25
2 k 5		
0	91	-92
2	63	-64
4	40	43
5	26	-28
6	50	-55
8	33	-11
9	71	-75
10	35	19
11	73	-65
16	39	42
17	51	32
18	65	65
19	80	84
20	34	-24
21	47	42
22	56	-56
23	30	29
24	43	-42
25	42	32
26	35	-36
27	26	-25
28	43	-46
3 k 5		
0	38	44
1	33	35
2	44	-27
3	40	-32
4	35	20
5	94	-96
7	120	-121
9	30	19
10	30	-30
12	39	36
13	34	14
14	33	-28
15	119	114
16	70	75
17	70	66
18	59	57
20	32	30
22	21	-18
23	36	35
24	28	-30
4 k 5		
1	39	-40
3	57	60
5	42	-44
6	54	52
7	30	-26
8	42	36
9	77	-76
10	47	-59
11	31	-29
12	53	-56
13	48	-61
14	24	22
15	40	41
18	35	-35
19	69	67
20	23	23
21	38	35
5 k 5		
0	101	106
1	58	-45
3	24	-14
4	40	42
6	35	-38
7	25	-22
8	42	-44
9	82	-81
10	71	-76
12	28	-29
13	36	36
14	70	-76
15	21	17
6 k 5		
0	39	-42
2	59	70
3	43	53
-10 k 6		
0	25	23
1	59	-63
2	42	-44
3	39	38
4	51	41
5	311	312
6	49	52
7	24	25
8	45	45
9	60	-59
11	46	38
12	37	34
14	37	-36
-9 k 6		
0	189	189
1	50	54
2	39	-36
3	36	12
4	34	30
5	24	-20
6	44	-38
7	33	32
8	42	-34
9	124	125
10	209	-208
11	25	-28
12	61	59
13	50	-24
14	62	-55
16	26	22
17	27	-14
19	72	-71
20	142	151
-8 k 6		
0	29	-31
1	110	115
2	178	-186
3	219	223
4	98	-88
5	144	-143
6	66	65
7	154	156
8	178	181
9	171	169
10	76	77
11	87	-89
12	133	132
13	158	-158
14	44	38
15	153	155
16	63	-59
17	124	-124
18	157	-155
19	146	-149
20	46	-54
21	54	45
22	37	-31
23	100	105
-7 k 6		
1	58	-47
2	28	24
3	93	96
4	95	98
5	39	30
6	106	-104
7	85	89
9	51	-48
13	55	-40
15	38	37
16	220	224
17	154	-153
18	47	49
19	54	51
20	22	-24
21	23	-25
22	33	28
23	31	27
25	48	-44
26	161	-167
-6 k 6		
0	462	-476
1	261	-285
2	86	-83
3	64	-89
4	30	-10
5	50	52
7	40	-44
9	184	-191
10	394	409
11	192	194
13	66	68
14	39	-36
15	52	-49
19	177	177
20	288	-299
21	146	-144
22	56	-54
23	110	-110
24	26	13
25	32	32
28	34	-38
-5 k 6		
0	33	33
1	69	-69
2	27	21
3	100	93
4	123	-121
5	67	61
6	43	41
7	46	-45
8	95	-97
9	57	-61
10	35	- 8
11	31	34
13	116	-115
14	126	108
15	33	-29
16	87	-89
17	50	48
18	108	103
19	93	89
20	41	41
21	45	-32
22	30	-21
23	123	120
24	130	-127
25	100	101
26	27	27
27	65	-65
28	106	-107
29	97	-91
-4 k 6		
0	86	98
1	100	98
3	226	-224
4	307	-316
5	278	-283
6	348	359
7	279	-282
8	97	92
9	101	109
10	76	-90
11	98	-89
13	181	177
14	303	306
15	233	238
16	169	-171
17	165	165
18	72	-70
19	79	-79
20	46	69
21	59	49
22	21	18
23	93	-91
24	192	-190
25	99	-99
26	155	157
27	112	-114
28	73	84
29	72	67
30	36	-31
-3 k 6		
0	57	56
1	77	58
9	83	77
10	50	-31
11	230	-233
12	67	-58
13	71	-45
17	33	-33
18	28	-16
21	275	276
22	57	59
23	34	-30
24	34	20
25	42	-30
27	33	38
28	25	11
29	29	14
30	19	19
-2 k 6		
0	102	-109
1	38	36
2	150	158
3	283	-279
4	313	314
5	87	-79
6	318	-328
7	303	-292
8	191	-197
9	43	44
10	113	116
11	48	-43
12	116	-112
13	264	262
14	324	-322
15	106	105
16	146	149
17	156	147
18	123	123
19	47	-35
20	86	-90
21	42	28
22	43	39
23	166	-163
24	202	199
25	29	-26
26	123	-121
27	91	-93
28	97	-99
29	58	52
30	61	64
-1 k 6		
1	56	-51
2	38	-21
3	127	122
4	190	186
5	166	157
6	52	-46
8	61	60
10	44	-26
13	132	-126
14	193	-178
15	120	-114
16	81	73
17	26	22
18	77	-74
19	40	32
21	65	-58
22	22	-22
23	100	103
24	169	167
25	145	143
26	28	22
27	66	-63
28	105	104
29	69	-69
0 k 6		
0	551	563
1	148	-153
2	35	33
3	39	-42
4	50	-41
5	61	65
6	35	23
8	44	41
10	489	-478
11	121	122
12	59	-61
14	90	90
15	63	-57
18	54	-46
19	45	49
20	353	344
21	123	-122
22	56	44
23	94	-93
24	61	-59
25	31	33
27	19	-27
28	48	51
1 k 6		
0	30	29
1	30	-34
2	107	-98
3	161	157
4	133	-131
5	48	42
6	105	105
7	177	173
8	91	83
9	30	-26
10	28	-27
11	44	30
12	61	60
13	52	-61
14	37	29
15	47	46
16	170	-162
17	244	-239
18	126	-117
19	25	18
20	46	32
21	27	-24
22	51	-46
23	36	34
24	34	-29
25	66	-62
26	99	99
2 k 6		
0	70	-77
1	89	74
2	119	127
3	211	217
4	159	165
5	79	-78
6	124	-127
7	165	168
8	168	-169
9	129	133
10	20	17
11	72	-75
12	79	-78
13	147	-141
14	85	-84
15	118	118
16	146	141
17	160	-155
18	181	182
19	122	-126
21	69	68
22	25	-13
23	76	78
3 k 6		
0	294	-304
1	28	8
2	21	4
3	38	34
4	27	-22
5	59	-57
6	24	20
7	39	37
8	43	30
9	89	83
10	295	302
11	38	26
13	68	-72
14	62	63
15	34	38
17	29	-11
18	25	18
19	42	-36
20	189	-196
4 k 6		
1	69	-69
3	34	36
4	122	-122
5	259	271
6	30	20
7	36	-20
8	22	-11
9	73	-82
11	46	43
14	98	98
-10 k 7		
1	28	-26
2	23	23
4	56	58
5	27	32
6	46	-45
7	54	-53
9	21	16
10	24	23
-9 k 7		
1	24	10
2	23	21
4	48	51
5	23	-26
6	26	24
7	43	-47
9	27	20
10	23	20
12	28	-23
14	57	-61
16	35	-31
17	15	11
-8 k 7		
0	74	74
1	51	-50
2	47	-32
3	31	38
5	47	-39
7	25	19
8	38	38
9	35	31
10	127	-126
12	45	-48
13	66	-74
14	48	-49
15	31	25
17	26	-14
18	64	-70
19	19	5
20	70	67
21	18	17
-7 k 7		
0	65	61
1	28	- 9
3	27	-29
4	25	22
6	34	28
7	39	38
8	56	59
9	46	36
10	55	-50
11	44	34
12	58	-54
13	55	52
16	44	-42
17	50	-48
18	43	-43
20	39	43
21	27	-34
22	20	15
23	39	-40
-6 k 7		
0	27	-32
1	59	-55
3	75	75
4	66	69
7	74	73
11	51	50
13	45	-42
16	62	48
17	94	-99
18	32	25
21	48	-48
22	20	-21
24	33	28
25	30	-31
-5 k 7		
0	159	-162
3	34	27
7	38	25
8	35	-40
9	86	84
10	68	61
12	82	-78
14	40	28
18	62	64
19	98	-102
20	38	-35
21	88	-88
22	46	-40
23	69	-65
24	53	-56
25	27	-13
-4 k 7		
0	30	-30
1	31	22
2	66	-42
3	76	66
4	71	-78
6	70	70
7	59	58
11	39	26
13	36	-36
14	86	84
15	29	14
16	42	14
17	46	-41
18	32	26
19	37	34
21	58	-59
23	63	61
24	92	-92
-3 k 7		
1	37	-16
2	38	-32
3	64	-62
4	38	-37
5	68	68
6	43	33
7	81	-82
8	39	40
12	40	36
13	110	111
14	112	109
15	29	-21
16	74	85
17	36	32
19	51	-45
20	57	57
21	25	7
22	46	-45
23	110	-110
24	73	-73
25	41	46
26	54	-59
-2 k 7		
0	124	-123
2	39	-39
3	29	-22
9	48	-55
10	74	74
11	84	-82
14	24	25
15	25	-20
18	46	50
19	35	36
20	38	-27
21	29	26
22	46	-40
24	62	-57
25	35	28
26	16	10
-1 k 7		
0	23	22
1	71	64
2	44	-41
3	30	-30
4	41	45
5	72	-69
6	63	-62
7	100	-105
8	34	-30
10	41	-33
11	59	-59
12	48	36
13	28	19
14	59	-42
15	75	72
16	102	100
17	75	75
18	29	19
20	52	44
21	38	40
22	53	-58
23	43	42
26	74	-78
0 k 7		
0	54	42
3	48	43
5	60	-61
6	38	30
7	31	-22
8	54	57
9	76	-68
10	29	-12
11	33	-31
12	32	-24
15	37	41
16	38	-21
17	58	55
18	64	-59
19	47	45
20	43	34
22	30	31
23	51	53
24	33	35
1 k 7		
0	147	159
2	28	- 8
4	49	48
6	53	-53
7	22	-18
8	27	-13
9	121	-119
10	95	-94
13	35	27
14	60	-65
16	36	39
17	21	-13
18	29	-26
19	88	86
20	59	58
21	28	-26
2 k 7		
0	39	-41
1	41	-15
2	47	44
3	32	31
4	23	21
5	18	16
8	50	-49
10	36	31
12	46	-49
13	30	13
14	70	-75
15	17	9
16	75	-75
17	19	-22
3 k 7		
0	72	72
1	31	37
2	67	67
3	79	81
4	19	20
5	30	-31
7	70	77
8	48	-49
9	16	14
11	22	-15
12	36	-30
-10 k 8		
0	70	-67
1	158	-164
-9 k 8		
2	51	-52
3	100	96
4	66	-66
5	31	-30
6	53	54
7	55	53
8	18	-13
9	37	-30
10	29	-16
12	36	37
13	108	-103
14	72	74
-8 k 8		
0	23	26
1	89	89
2	26	22
3	99	-106
4	142	-130
5	355	-339
6	141	133
7	59	-57
8	39	-43
9	96	97
11	72	-69
12	35	-31
13	48	45
14	124	119
15	216	214
16	37	-29
17	87	89
-7 k 8		
0	69	-69
1	39	15
2	54	35
7	25	6
9	28	-10
10	154	152
11	87	-83
12	58	-60
13	30	-24
19	32	29
20	95	-100
-6 k 8		
0	36	-30
1	39	-46
2	138	140
3	224	-224
4	188	182
5	76	74
6	150	-146
7	193	-186
8	194	-189
9	105	-102

Table 5. *(Continued)*

k	|F_o|	F_c
10	37	9
11	60	53
12	142	-140
13	221	222
14	168	-164
15	85	-86
16	129	129
17	124	121
18	133	129
19	66	73
20	26	-25
21	37	-35
22	40	36
-5 k 8		
0	25	23
1	31	-17
2	64	-58
4	24	14
5	107	102
6	97	100
7	38	-33
9	33	31
12	31	25
14	83	-79
15	133	-133
16	61	-65
17	98	95
18	56	-35
21	22	-16
22	33	-32
-4 k 8		
0	525	525
1	105	96
3	20	20
4	31	-30
6	27	19
7	28	13
8	26	25
9	103	101
10	411	-400
11	59	-55
12	30	-34
13	35	-29
14	56	56
16	31	- 7
18	39	-35
19	85	-82
20	329	332
21	27	22
22	45	42
-3 k 8		
1	53	47
2	106	-110
3	83	78
5	74	-69
6	73	77
7	124	121
8	81	76
12	37	30
13	27	20
14	60	-53
15	80	83
17	148	-153
18	118	-111
19	59	-58
21	20	8
22	29	-25
23	15	- 9
-2 k 8		
0	88	-96
1	30	-16
2	67	52
3	174	172
4	244	242
5	90	83
6	206	-207
7	193	191
8	140	-139
9	34	34
10	67	68
11	30	- 9
12	55	-57
13	158	-158
14	212	-207
15	43	-38
16	208	204
17	138	-136
18	119	119
19	24	-17
20	63	-60
21	42	32
23	62	61
-1 k 8		
0	171	-174
1	55	-50
2	32	-21
5	34	-27
9	47	-42
10	222	222
11	139	135
12	34	31
15	25	14
17	21	16
18	23	17
19	24	7
20	107	-113
0 k 8		
0	67	68
1	71	-65
2	70	-69
3	139	143
4	200	-200
5	192	193
6	199	203
7	71	62
8	30	30
9	95	-94
10	61	-60
11	55	58
12	26	24
13	98	-96
14	178	176
15	134	-136
16	50	-44
17	56	-57
18	40	-40
1 k 8		
0	19	-14
2	47	-50
3	129	-133
4	136	-140
5	56	-52
6	109	107
7	79	-82
9	21	-11
10	22	- 6
11	26	-17
12	16	10
13	112	115
14	143	148
2 k 8		
0	132	-142
1	129	145
2	41	-42
3	40	46
4	28	18
5	52	-59
6	18	- 9
7	18	12
-9 k 9		
0	17	-18
1	18	-12
2	13	- 8
3	24	28
4	27	28
6	33	-16
-8 k 9		
0	28	-29
2	24	-21
3	65	67
4	75	-79
6	52	50
7	34	34
8	21	-26
9	18	-15
10	20	13
11	34	38
12	20	-14
-7 k 9		
2	21	-18
4	39	-41
5	30	32
6	32	31
7	20	-18
12	17	17
13	40	39
14	85	85
16	52	53
-6 k 9		
0	85	-80
1	24	19
3	28	-29
4	17	-16
5	25	27
7	32	-36
9	28	-28
10	103	99
11	28	-30
14	34	37
15	18	- 8
-5 k 9		
0	34	-33
1	46	46
2	20	- 5
3	26	-21
6	65	-61
7	81	-79
8	58	-57
11	43	-47
12	23	18
14	22	-24
15	19	21
16	57	57
17	64	65
-4 k 9		
0	46	45
2	25	-20
3	20	-18
7	56	-58
8	50	44
10	21	-16
11	27	-27
15	26	20
16	31	-20
17	78	80
18	46	-40
-3 k 9		
0	141	146
1	29	-22
4	30	34
5	28	20
6	36	-30
8	30	34
9	82	-84
10	86	-84
14	21	-22
16	32	30
-2 k 9		
2	23	20
4	26	29
6	31	-25
8	25	-22
9	22	-22
12	20	-20
14	62	-67
16	49	-50
-1 k 9		
0	32	32
2	43	39
3	82	89
4	41	41
5	35	-37
6	34	-37
7	76	79
8	28	-24
9	17	- 5
12	32	-30
13	90	-89
0 k 9		
0	22	20
1	23	12
2	41	42
3	17	14
4	32	-30
6	36	41
7	26	25
-7 k 10		
0	41	-44
1	47	48
2	36	-33
4	61	61
5	38	-40
6	13	-12
-6 k 10		
0	68	-58
1	54	-52
2	18	12
3	100	105
4	160	160
5	197	196
6	171	-172
7	112	115
8	24	-19
9	65	-67
-5 k 10		
0	66	-53
1	27	-19
2	27	-24
7	23	-19
8	18	16
9	75	-76
10	20	17
-4 k 10		
0	57	56
2	98	-104
3	144	153
4	156	-160
5	33	23
6	163	171
7	132	130
8	97	100
9	19	-16
-3 k 10		
1	25	31
2	25	26
3	41	-42
4	91	-94
5	114	-116
6	17	8

The least-squares calculations converged properly after four cycles to give the results: 57.4(1.0) electrons and 88(2)$^0/_0$ for Pb(2) and Pb(12), respectively ($R = 9.7\,^0/_0$). If we assume that the Pb(2) site is fully occupied by Pb and As, the obtained number of electrons corresponds to the distribution, 0.50(2) Pb + 0.50(2) As[4].

Anisotropic refinement

Anisotropic temperature factors were then introduced to all 25 atoms. After several cycles, the R value converged to 7.0$^0/_0$. The final atomic coordinates and the thermal parameters are given in Tables 3 and 4, respectively. The observed and calculated structure factors are compared in Table 5.

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[4] The almost exact half-and-half distribution of Pb and As may be an indication that the correct space group of jordanite is not $P2_1/m$ but $P2_1$, and the Pb and As atoms of the Pb(2) site occupy crystallographically independent sites. However, three cycles of least-squares refinement with the space group $P2_1$, in which the Pb(2) site was divided into Pb(2) and As(2) (altogether 50 independent atoms), led to essentially the same structure as obtained with $P2_1/m$; although the isotropic temperature factors of Pb(2) and As(2) converged to reasonable values (1.8 and 1.7 Å^2, respectively), the other atomic parameters of the structure changed very little.

Discussion of the structure

Unit-cell content

The distribution of Pb, As and S atoms in the unit cell of jordanite is given in Table 6. It should be noted that the following five sites on the special positions (the mirror plane) have multiplicity of 2: Pb(9), Pb(10), Pb(12), S(12) and S(13). As is evident from the table, the unit cell of jordanite contains 40 metal and 46 sulfur atom sites; the 40 metal sites are occupied by 27.8 Pb and 12.0 As atoms. If we assume the balance of valency, the number of S atoms should be 45.8, although it was not experimentally confirmed. Thus, the unit-cell content of jordanite is $Pb_{27\cdot8}As_{12\cdot0}S_{45\cdot8}$ with the ideal formula $Pb_{28}As_{12}S_{46}$. These formulae are in fairly good agreement with that of ROLAND (1968), $Pb_{28\text{-}x}As_{12}S_{46\text{-}x}$ $(0.8 < x < 1.4)$, for synthetic jordanite.

The calculated density of jordanite with the formula $Pb_{27\cdot8}Ss_{12\cdot0}S_{45\cdot8}$ is 6.34 g · cm^{-3}, in agreement with the observed densities for natural material: 6.38(1) (FISHER, 1940), 6.44 (PEACOCK and BERRY, 1940), 6.32 (PALACHE *et al.*, 1938) and 6.413 g · cm^{-3} (SOLLY, 1900). It is, however, significantly higher than 6.15(3) g · cm^{-3} reported by ROLAND (1968) for synthetic jordanite. The difference between the higher values and the lower one is probably not caused by the experimental errors,

Table 6. *Distribution of atoms in the unit cell of jordanite*

Site	Pb	As	Site	S
Pb(1)	4		S(1)	4
Pb(2)[1]	2.0	2.0	S(2)	4
Pb(3)	4		S(3)	4
As(4)		4	S(4)	4
Pb(5)	4		S(5)	4
As(6)		4	S(6)	4
Pb(7)	4		S(7)	4
Pb(8)	4		S(8)	4
Pb(9)	2		S(9)	4
Pb(10)	2		S(10)	4
As(11)[2]		2	S(11)[2]	2
Pb(12)[3]	1.8		S(12)	2
			S(13)	2
Total	27.8	12.0		46

[1] The statistically occupied site.

[2] The split-atom sites; 0.5 × 4 = 2.

[3] The fractionally occupied site; 0.88 × 2 = 1.76.

Table 7. *Chemical composition* (weight percent) *of jordanite*
All results are adjusted to 100% total

		Pb	As	S	Sb
I	$Pb_{27\cdot8}As_{12\cdot0}S_{45\cdot8}$ (Present work)	70.87	11.06	18.07	—
II	Chemical analysis (SOLLY, 1900) no. 29	69.22	12.42	18.36	—
III	Chemical analysis (SOLLY, 1900) no. 30	69.03	12.50	18.47	—
IV*	Chemical analysis (NOWACKI and BAHEZRE, 1963)	67.06	12.58	19.10	1.25
V	Microprobe analysis (NOWACKI and BAHEZRE, 1963)	66.8	11.7	21.5	—

* The water content (0.83%) was ignored.

but is an indication of the real difference in the chemical composition of natural and synthetic jordanite.

In Table 7, the calculated composition of formula $Pb_{27\cdot8}As_{12\cdot0}S_{45\cdot8}$ is compared with the results of chemical and microprobe analyses. It should be noted that the calculated composition (I) gives significantly lower As content than the chemically obtained results (II, III and IV); the As content of I is in better agreement with that of the microprobe analysis (V). The above difference in As content is reflected on the number of As atoms in the unit cell; since most of the older formulae have been derived from the results of the chemical analyses (II and III), they contain 14 As atoms, whereas the present formula and that of ROLAND (1968) contain only 12 As atoms.

This point must be clarified by future work. On one hand, the difference may be attributed to the experimental errors in the chemical analyses. On the other hand, it may have been caused by some syste-

Fig. 1. Atomic arrangements in jordanite, viewed along the b axis: (a) the first metal layer ($y \approx 0.05$), (b) the second metal layer ($y \approx 0.15$) and (c) the third metal-sulfur mixed layer ($y \approx 0.25$). The Pb(2) site is statistically occupied by 0.50 Pb + 0.50 As, the Pb(12) site is fractionally occupied by 0.88 Pb, and the As(11) and S(11) sites are split into two halves above and below the mirror plane at $y = 1/4$

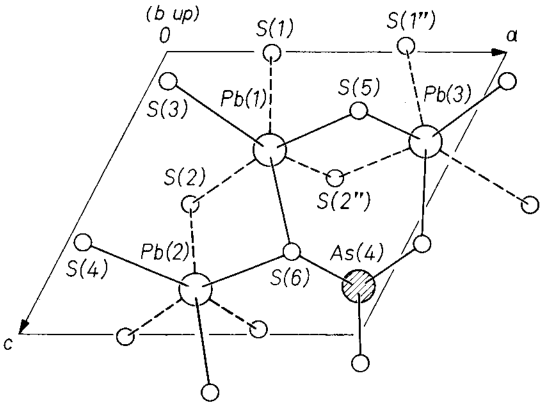

Fig. 1a

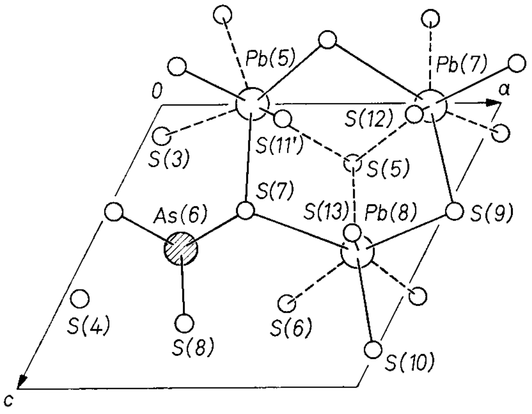

Fig. 1b

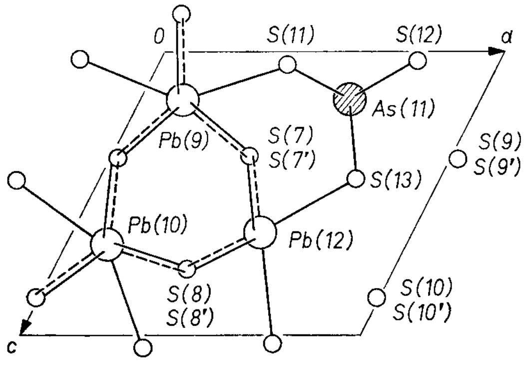

Fig. 1c

matic errors in the present analysis; for example, it is difficult to conclude definitely that the Pb(12) site is never occupied by As, although the site was assumed to be fractionally occupied by only Pb from the coordination of S atoms.

However, in spite of the possible ambiguities about the exact distribution of Pb and As on the 40 metal sites, the present analysis has clearly shown that most of the older formulae which contain more than 40 metal atoms and/or more than 46 sulfur atoms are improbable.

Description of the structure

The unit cell of jordanite consists of ten metal layers along the *b* axis; the ten metal layers are interleaved by ten sulfur layers. The atomic arrangements in the asymmetric unit ($y = 0$—$1/4$) are shown in Fig. 1. The twelve independent metal sites are distributed on the three layers at $y \approx 0.05$, ≈ 0.15 and ≈ 0.25 (the mirror plane) (Fig. 1a, b and c, respectively). There are four metal sites, 3 Pb + As, on each layer. Another one-fourth unit cell ($y = 1/4$—$1/2$) is related to the asymmetric unit by the mirror plane at $y = 1/4$; the remaining half cell ($y = 1/2$—1) is related to the other half by the center of inversion and also by the screw diad along the *b* axis.

Some of the atomic sites have statistical nature (Table 6). The Pb(2) site on the first metal layer is occupied by 0.50 Pb and 0.50 As. The Pb(12) site on the third metal layer is fractionally ($88^0/_0$) occupied by Pb. On the same layer, the As(11) site is split into two halves, 0.75 Å above and below the mirror plane; instead, three additional S atoms, S(11) to S(13), are approximately on the mirror plane and coordinate to the split As atoms[5]. The S(11) site is also split into two halves, 0.37 Å above and below the mirror plane.

As was already pointed out by WUENSCH and NOWACKI (1966), the structure of jordanite within the asymmetric unit ($y = 0$—$1/4$) can be correlated to the PbS structure by taking the *b* axis of jordanite parallel to the [111] axis of PbS (Table 1). However, the displacements of the atoms from the ideal PbS-type structure, especially those of the S atoms, are so large (Table 8), that the sulfur coordinations about the metal atoms are essentially different from those in PbS.

The displacements of the metal atoms are approximately 0.3 Å. However, that of the split As(11) atom is exceptionally large; the atom is displaced along the *b* axis by 0.75 Å, almost one half (0.80 Å)

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[5] In fact, the third metal layer is a metal-sulfur mixed layer.

Table 8. *Displacements of the atoms of jordanite from the ideal PbS-type structure*

Layer number	Atom	Ideal coordinates			Displacements (Å)			
		x/a	y/b	z/c	Δx	Δy	Δz	Δr
1st metal	Pb(1)	5/12	1/20	2/6	+ 0.270	+ 0.149	+ 0.144	0.282
	Pb(2)	5/12	1/20	5/6	+ 0.201	+ 0.062	+ 0.075	0.189
	Pb(3)	11/12	1/20	2/6	− 0.112	− 0.281	− 0.140	0.311
	As(4)	11/12	1/20	5/6	+ 0.025	+ 0.082	− 0.029	0.094
2nd metal	Pb(5)	3/12	3/20	0	+ 0.132	− 0.247	− 0.023	0.286
	As(6)	3/12	3/20	3/6	+ 0.230	− 0.228	+ 0.069	0.308
	Pb(7)	9/12	3/20	0	+ 0.360	+ 0.023	+ 0.149	0.320
	Pb(8)	9/12	3/20	3/6	+ 0.379	+ 0.007	+ 0.126	0.339
3rd metal*	Pb(9)	1/12	5/20	1/6	+ 0.347	0	+ 0.040	0.330
	Pb(10)	1/12	5/20	4/6	+ 0.340	0	+ 0.194	0.303
	As(11)	7/12	5/20	1/6	+ 0.290	− 0.751	+ 0.084	0.795
	As(11′)	7/12	5/20	1/6	+ 0.290	+ 0.751	+ 0.084	0.795
	Pb(12)	7/12	5/20	4/6	− 0.294	0	− 0.230	0.276
1st sulfur	S(1)	3/12	0	0	+ 0.531	+ 0.099	+ 0.104	0.501
	S(2)	3/12	0	3/6	+ 0.506	+ 0.161	+ 0.427	0.513
2nd sulfur	S(3)	1/12	2/20	1/6	− 0.333	− 0.440	− 0.560	0.666
	S(4)	1/12	2/20	4/6	− 0.287	− 0.470	+ 0.167	0.613
	S(5)	7/12	2/20	1/6	+ 0.613	− 0.099	− 0.306	0.552
	S(6)	7/12	2/20	4/6	+ 0.802	− 0.286	+ 0.344	0.766
3rd sulfur	S(7)	5/12	4/20	2/6	− 0.094	− 0.744	+ 0.347	0.845
	S(8)	5/12	4/20	5/6	− 0.130	− 0.722	− 0.536	0.872
	S(9)	11/12	4/20	2/6	+ 1.017	− 0.666	+ 0.427	1.120
	S(10)	11/12	4/20	5/6	+ 0.689	− 0.208	+ 0.300	0.644
4th sulfur*	S(11)	3/12	6/20	0	+ 1.144	− 1.220	+ 0.467	1.587
	S(11′)	3/12	6/20	0	+ 1.144	− 1.969	+ 0.467	2.215
	S(12)	9/12	6/20	0	+ 0.018	− 1.595	+ 0.266	1.616
	S(13)	9/12	6/20	3/6	+ 0.018	− 1.595	− 0.385	1.643

* 3rd metal and 4th sulfur layers are mixed up to form a metal-sulfur mixed layer.

of the average metal-sulfur interlayer separation. The displacements of the S atoms along the *b* axis are generally systematic; the magnitudes increase with increasing layer numbers. In fact, the fourth sulfur layer is displaced as much as one interlayer separation (1.59 Å), and, there-

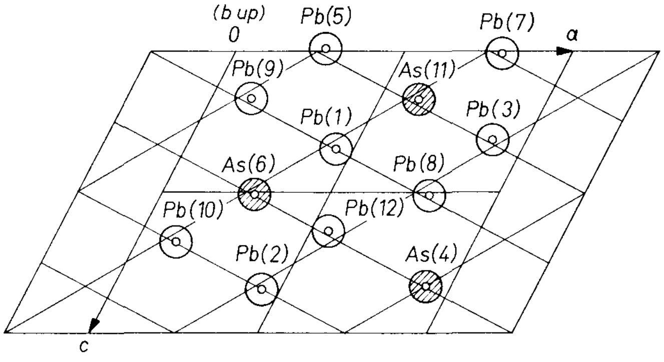

Fig. 2a

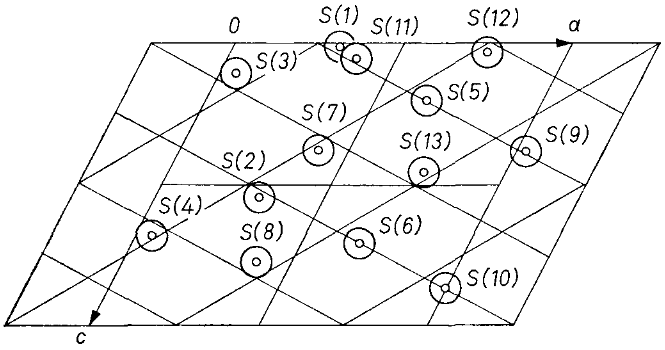

Fig. 2b

Fig. 2. Displacements of (a) the metal and (b) the sulfur atoms in jordanite from the ideal PbS-type structure

fore, is mixed up with the third metal layer to form the metal-sulfur mixed layer. The displacements of the atoms perpendicular to the *b* axis can be seen from Fig. 2; most of the atoms are displaced along the [201] direction.

If we denote the idealized atomic arrangements in the first, second and third sulfur layers as *a*, *b* and *c*, and those in the metal layers as *B*, *A* and *C*, respectively (in an analogous way as in the face-centered cubic packing scheme), the stacking sequence along the *b* axis of jordanite is given by

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
a	*B*	*c*	*A*	*b*	*C'*	*b*	*A*	*c*	*B*	*a*	*C*	*b*	*A*	*c*	*B'*	*c*	*A*	*b*	*C*

The two layers, C' and B', are on the mirror planes of the structure; the primes are added because these layers are not pure metal but metal-sulfur mixed layers. If the above sequence is compared with that in the PbS-type structure, $|aBcAbC|$, it is evident that the correspondence

Table 9. *Bond distances in jordanite*

Notation of the symmetry operations: single primed: mirror reflection; double primed: inversion. The estimated standard deviations are about 0.008 and 0.010 Å for metal-sulfur and sulfur-sulfur distances, respectively

Pb(1)—S(2″)	2.728 Å
—S(5)	2.975
—S(6)	2.976
—S(2)	2.984
—S(1)	3.020
Mean(5)	(2.937)
—S(3)	3.349
Mean(6)	(3.005)
Pb(2)—S(2)	2.647
—S(1″)	2.655
—S(1)	2.718
—S(6)	3.072
—S(5)	3.094
Mean(5)	(2.837)
—S(4)	3.255
Mean(6)	(2.907)
Pb(3)—S(5)	2.668
—S(1″)	2.904
—S(2″)	2.991
—S(3)	3.028
—S(4)	3.107
Mean(5)	(2.940)
—S(2)	3.393
Mean(6)	(3.015)
Pb(5)—S(10)	2.690 Å
—S(8)	2.941
—S(4)	3.030
—S(7)	3.038
—S(3)	3.059
Mean(5)	(2.952)
—S(11′)	3.191
—S(5)	3.383
Mean(7)	(3.047)
Pb(7)—S(3)	2.903 Å
—S(5)	2.954
—S(9)	2.971
—S(10)	2.979
—S(6)	3.008
Mean(5)	(2.963)
—S(12)	3.194
—S(8)	3.216
Mean(7)	(3.032)
Pb(8)—S(5)	2.889
—S(4)	2.932
—S(9)	2.965
—S(6)	2.993
—S(10)	3.014
Mean(5)	(2.959)
—S(7)	3.190
—S(13)	3.217
Mean(7)	(3.029)
Pb(9)—S(10)	2.895
—S(10′)	2.895
—S(11)	2.901
—S(12)	2.942
Mean(4)	(2.908)
—S(9)	3.222
—S(9′)	3.222
—S(7)	3.283
—S(7′)	3.283
Mean(4)	(3.253)
Mean(8)	(3.080)

Table 9. *(Continued)*

Pb(10)—S(11)	2.889 Å
—S(10)	2.906
—S(10′)	2.906
—S(13)	2.949
Mean(4)	(2.913)
—S(8)	3.241
—S(8′)	3.241
—S(9)	3.242
—S(9′)	3.242
Mean(4)	(3.242)
Mean(8)	(3.077)
Pb(12)—S(13)	2.882
—S(12)	2.945
—S(7)	3.077
—S(7′)	3.077
—S(8)	3.114
—S(8′)	3.114
Mean(6)	(3.035)
—S(10)	3.938
—S(10′)	3.938
As(4)—S(3)	2.293
—S(4)	2.297
—S(6)	2.297
Mean(3)	(2.296)
S(3)—S(6)	3.439
S(4)—S(6)	3.461
S(3)—S(4)	3.526
Mean(3)	(3.475)
As(6)—S(7)	2.242 Å
—S(8)	2.250
—S(9)	2.253
Mean(3)	(2.248)
S(7)—S(8)	3.364
S(7)—S(9)	3.387
S(8)—S(9)	3.399
Mean(3)	(3.383)
As(11)—S(11)	2.186
—S(13)	2.215
—S(12)	2.222
Mean(3)	(2.208)
S(11)—S(12)	3.451
S(11)—S(13)	3.488
S(12)—S(13)	3.580
Mean(3)	(3.506)
As(11)—As(11′)	1.502
As(11)—S(11′)	1.912
Pb(2)—S(2)	2.647
—S(1″)	2.655
—S(1)	2.718
Mean(3)	(2.673)
S(1)—S(1″)	3.505
S(2)—S(1″)	3.696
S(1)—S(2)	3.898
Mean(3)	(3.700)

between the two structures is limited only within the first six layers, because the mirror planes at $y = 1/4$ and $3/4$ in the former are absent in the latter.

Sulfur coordinations about the metal atoms

The sulfur coordinations about the metal atoms in jordanite can be seen from Fig. 1. The bond distances and angles are given in Tables 9 and 10, respectively.

The fully occupied Pb atoms in the first metal layer, Pb(1) and Pb(3), are coordinated with six S atoms in distorted octahedral arrangements with an average Pb—S distance of 3.01 Å. The statistically occupied Pb(2) site (0.50 Pb + 0.50 As) is also coordinated with six sulfur atoms. However, the coordination is an intermediate one between typical coordination of Pb and As; three Pb—S distances are short (average 2.67 Å) and the other three are long (average 3.14 Å). The large mean-square amplitude of vibration of the site, 0.0469 Å^2 along the *b* axis (Table 4), is probably an indication of positional disorder of the site; the true coordinations of the 0.50 Pb and 0.50 As atoms are probably more Pb and As like, respectively, than the averaged coordination given in Tables 9 and 10.

Table 10. *Bond angles in jordanite*

The estimated standard deviations are about 0.3 degrees. For the Pb atoms, only the angles between the four or five shortest Pb—S bonds are given

S(2″) —	Pb(1)	—S(5)	83.2°	S(10) —	Pb(5)	—S(8)	94.2°
		—S(6)	83.8			—S(4)	86.0
		—S(2)	86.9			—S(7)	93.4
		—S(1)	79.9			—S(3)	84.2
S(5) —		—S(6)	89.5	S(8) —		—S(4)	86.9
		—S(2)	168.6			—S(7)	117.0
		—S(1)	84.6			—S(3)	157.7
S(6) —		—S(2)	84.1	S(4) —		—S(7)	156.1
		—S(1)	163.2			—S(3)	70.8
S(2) —		—S(1)	99.0	S(7) —		—S(3)	85.3
S(2) —	Pb(2)	—S(1″)	88.4°	S(3) —	Pb(7)	—S(5)	86.3°
		—S(1)	93.2			—S(9)	82.0
		—S(6)	88.2			—S(10)	82.1
		—S(5)	169.6			—S(6)	71.1
S(1″) —		—S(1)	81.4	S(5) —		—S(9)	84.3
		—S(6)	82.4			—S(10)	167.9
		—S(5)	81.5			—S(6)	92.0
S(1) —		—S(6)	163.7	S(9) —		—S(10)	90.9
		—S(5)	87.7			—S(6)	153.1
S(6) —		—S(5)	88.1	S(10) —		—S(6)	87.3
S(5) —	Pb(3)	—S(1″)	85.0°	S(5) —	Pb(8)	—S(4)	86.7°
		—S(2″)	83.9			—S(9)	85.5
		—S(3)	89.1			—S(6)	90.8
		—S(4)	87.2			—S(10)	168.9
S(1″) —		—S(2″)	82.8	S(4) —		—S(9)	82.5
		—S(3)	85.6			—S(6)	71.5
		—S(4)	165.0			—S(10)	82.2
S(2″) —		—S(3)	166.9	S(9) —		—S(6)	153.9
		—S(4)	83.6			—S(10)	91.7
S(3) —		—S(4)	107.1	S(6) —		—S(10)	87.0

Table 10. *(Continued)*

S(10) — Pb(9)—S(10')	77.0°	S(3) — As(4) —S(4)	100.4°
—S(11)	80.2	—S(6)	97.0
—S(12)	74.8	S(4) — —S(6)	97.8
S(10')— —S(11)	70.7	Mean(3)	(98.4)
—S(12)	74.8		
S(11) — —S(12)	140.9	S(7) — As(6) —S(8)	97.0°
		—S(9)	97.8
S(11) — Pb(10) —S(10)	80.2°	S(8) — —S(9)	98.0
—S(10')	70.7	Mean(3)	(97.6)
—S(13)	143.2		
S(10) — —S(10')	76.7	S(11)— As(11)—S(13)	104.8°
—S(13)	76.5	—S(12)	103.1
S(10')— —S(13)	76.5	S(13)— —S(12)	107.6
		Mean(3)	(105.2)
S(13) —Pb(12) —S(12)	113.8°		
—S(7)	76.1		
—S(7')	76.1		
S(12) — —S(7)	130.5		
—S(7')	130.5		
S(7) — —S(7')	99.0		

The Pb atoms in the second metal layer, Pb(5), Pb(7) and Pb(8), are coordinated with seven S atoms with an average Pb—S distance of 3.04 Å; in addition to the six distorted octahedral S atoms, the seventh S atom, S(11')[6], S(12) or S(13), respectively, comes into the coordination sphere.

The fully occupied Pb-atom sites in the third metal layer (the metal-sulfur mixed layer on the mirror plane), Pb(9) and Pb(10), are coordinated with eight S atoms with an average Pb—S distance of 3.08 Å. Six of the eight S atoms around each Pb atom occupy the corners of a distorted trigonal prism along the *b* axis, whereas the other two S atoms belonging to the same metal-sulfur mixed layer coordinate to the Pb atom through two sides of the prism. The fractionally occupied Pb(12) atom is coordinated with six S atoms with an average Pb—S distance of 3.04 Å; two other S atoms, S(10) and S(10'), are far apart (3.94 Å) from Pb(12) (Fig. 1c).

The sulfur coordinations about the As atoms are ordinary trigonal pyramidal. The average As—S distances are 2.296, 2.248 and 2.208 Å for As(4), As(6) and As(11)[7], respectively.

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[6] The other half atom S(11) is much apart (3.915 Å) from Pb(5).

[7] Between the two possible bonds, As(11)—S(11) or As(11)—S(11'), the former (2.186 Å) was considered to be the real bond, because the latter (1.912 Å) was too short for an As—S bond (see, for example, Nowacki, 1969).

The AsS_3 pyramids are isolated from each other in the structure; even the half-occupied $Pb(2)S_3$ pyramid does not share S atoms with the other AsS_3 pyramids (type $I.c_1$ of the classification of NOWACKI, 1969).

Relation of jordanite and gratonite

From heating experiments on natural gratonite, ROLAND (1968) concluded that gratonite is most probably a low-temperature dimorph of jordanite. On the other hand, the unit cell content of jordanite obtained in this study, $Pb_{27.8}As_{12.0}S_{45.8}$, is appreciably different from that of gratonite ($3\,Pb_9As_4S_{15} = Pb_{27}As_{12}S_{45}$); jordanite has 0.8 PbS in excess of gratonite. However, because of the statistical nature of the atomic distributions in jordanite, the difference does not seem to be so definite as to rule out the possible dimorphism of the two minerals. For example, if we assume that the Pb(12) site is occupied by 0.50 Pb in synthetic jordanite (instead of 0.88 Pb as found for natural material in the present work), the unit-cell content will be exactly the same as that of gratonite.

The crystal structure of gratonite has already been established (RIBÁR and NOWACKI, 1969; RÖSCH, 1963). The crystal is rhombohedral, space group $R3m$, with $a_{\text{hex}} = 17.758(14)$ and $c_{\text{hex}} = 7.807(6)$ Å. There are no statistical sites in the structure.

It seems hardly possible to find any simple relationship between the atomic arrangements in jordanite and gratonite. As far as the metal atoms are concerned, the structure of gratonite can also be correlated to the PbS structure, when the c axis of gratonite is taken as the [111] axis of PbS[8]. However, the correspondence is only formal.

Table 11

Displacements of the metal atoms of gratonite from the ideal PbS-type structure

Atom	Ideal coordinates			Displacements (RIBÁR and NOWACKI, 1969)			
	x/a	y/b	z/c	Δx	Δy	Δz	Δr
Pb(1)	3/4	3/4	0	+ 0.451 Å	+ 0.114 Å	+ 0.003 Å	0.406 Å
Pb(2)	3/4	1/4	0	+ 0.069	− 0.069	+ 1.234	1.240
As(1)	1/2	1/2	0	+ 0.400	− 0.400	+ 0.920	1.152
As(2)	0	0	0	0	0	− 0.444	0.444

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[8] In fact, the approximate structure of gratonite was first solved by RÖSCH (1963) starting from the ideal PbS-type arrangements of the metal atoms; afterwards, one of the two As positions and all S positions have been corrected and the whole structure has been refined by RIBÁR and NOWACKI (1969).

The ideal structure of gratonite itself is very much deformed from the PbS structure; the average separation of the metal layers ($c/3 = 2.60$ Å) is considerably shorter than those in PbS ($[111]/3 = 3.42$ Å) and jordanite ($b/10 = 3.19$ Å). Moreover, the displacements of the metal atoms from the ideal coordinates are much larger (Table 11) than those in jordanite (Table 8). The sulfur positions in gratonite are completely different from the ideal positions; they can hardly be correlated to those in PbS or jordanite. Thus, it is evident that considerable rearrangements of both the metal and sulfur atoms should take place in the transition from gratonite to jordanite.

Calculations

The main part of the numerical calculations was performed on the Bull-Gamma 30 S computer and the IBM 370/155 computer at the Rechenzentrum der Universität Bern with the program system, "Kristallographische Programme, 1970 and 1972" written by P. ENGEL (Bern). The lattice-parameter refinement, key shifts and site-refinement programs used were written by one of the authors (T.I.).

Acknowledgements

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