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Crystal structure refinement of arsenian ullmannite

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Abstract

A crystal structure refinement of a pseudo-cubic [a = 5.886(1)Å] arsenian ullmannite $(Ni_{0.97}Co_{0.03})(Sb_{0.91}As_{0.08}Bi_{0.01})(S_{0.98}As_{0.02})$ showed that the arsenic is concentrated in one of the four Sb sites and in one of the four S sites. This ordering reduces the symmetry $P2_13$ to $P1$, and explains why the mineral is anisotropic.

Introduction

The space group of ullmannite has been determined as $P2_13$ by Ramsdell (1925) and confirmed by Peacock and Henry (1948), and Bokii and Tsenokev (1954). The structure of ullmannite has been refined by Takeuchi (1957) and its absolute structure determined. The Sb is ordered into one set of four sites, whereas the S is ordered into the other set of four sites. Optical observations by Klemm (1962) indicated that seven out of eight specimens contained anisotropic areas in a polished section. Since unstrained cubic minerals cannot be anisotropic, an anisotropic specimen of ullmannite has been investigated by single-crystal X-ray diffraction to determine its symmetry.

Experimental

A sample of arsenian ullmannite (BM88503) from Petersbach, Hamm, Westphalia, Germany was obtained from Mr. Peter Embrey of the British Museum. This sample was found to be distinctly weakly anisotropic under reflected light. Then the sample was analyzed by electron microprobe as described by Stout and Bayliss (1975). The analytical results and derived chemical formula based upon a 4 AXY model are presented in Table 1. This 4 AXY model is used, since the synthetic work of Bayliss (1969) shows that As may substitute substantially for Sb and S in the NiSbS formula of ullmannite, although Sb does not substitute for S and vice versa.

A 114.6 mm Debye-Scherrer photograph was taken with Cu radiation/Ni filter. All reflections are indexable on a cubic cell, although the observed reflection 100 violates space group $P2_13$. A unit cell with a = 5.901 Å was calculated by the Nelson and Riley (1945) extrapolation method to θ = 90°. A crystal with dimensions of 68 × 84 × 90 μm was selected because of its well-developed cube form {100}. This crystal was aligned on a precession camera with Cu radiation along an a^* axis. Photographs *hk*0 and *h*0*l* showed no systematic absences or deviation from a cubic cell. Therefore this mineral is pseudo-cubic like cobaltite (CoAsS) as shown by Giese and Kerr (1965), and willyamite (CoSbS) as shown by Cabri *et al.* (1970).

Table 1. Electron microprobe analysis and atomic proportions

Weight	%	Atomic Proportions	
Ni	27.3	0.97	1.00
Co	0.8	0.03	
Sb	52.8	0.91	1.00
Bi	1.0	0.01	
As	3.5	0.08 0.02	1.00
S	15.1	0.98	
Total	100.5		

Table 2. Positional parameters and isotropic temperature factors

Atom	Site Occupancy	x	B (Å^2)
Ni	Ni 0.97 Co 0.03	-.0171(1)	0.65(2)
S	S 0.98 As 0.02	.3817(2)	0.80(3)
Sb	As 0.08 Sb 0.91 Bi 0.01	.6256(1)	0.62(1)

Table 3. Observed and calculated structure factors

l	Fo	Fc
h= 0 k= 0		
1	4	1
2	102	91
3	4	1
4	98	92
5	15	2
6	34	33
7	4	2
8	104	101
h= 0 k= 1		
-8	5	5
-7	47	48
-6	82	81
-5	70	68
-4	3	3
-3	23	22
-2	135	135
-1	50	49
0	3	3
1	47	50
2	135	135
3	21	20
4	3	2
5	69	68
6	81	80
7	47	47
8	5	4
h= 0 k= 2		
-8	19	20
-7	48	50
-6	32	32
-5	37	35
-4	53	53
-3	56	56
-2	81	80
-1	95	94
0	96	91
1	89	93
2	72	75
3	56	57
4	54	52
5	37	36
6	35	32
7	50	47
8	19	19
h= 0 k= 3		
-7	3	2
-6	80	80
-5	17	17
-4	5	4
-3	63	61
-2	113	110
-1	62	61
0	4	2
1	59	61
2	105	109
3	59	61
4	6	6
5	15	15
6	81	77
7	2	2
h= 0 k= 4		
-7	8	8
-6	29	29
-5	19	19
-4	153	156
-3	27	26
-2	53	52
-1	23	22
0	91	91
1	21	20
2	51	52
3	24	24
4	143	151
5	18	18
6	28	27
7	7	7
h= 0 k= 5		
-6	47	48
-5	11	12
-4	9	9
-3	41	39
-2	90	89
-1	37	37
0	12	2
1	40	39
2	86	87
3	38	38
4	9	9
5	11	12
6	46	45
h= 0 k= 6		
-5	48	48
-4	29	29
-3	66	65
-2	31	31
-1	17	17
0	32	32
1	17	17
2	32	32
3	64	62
4	27	28
5	44	43
h= 0 k= 7		
-4	12	11
-3	20	20
-2	70	70
-1	28	28
0	4	2
1	28	27
2	70	68
3	19	18
4	10	10
h= 0 k= 8		
-2	19	20
-1	27	27
0	98	96
1	28	27
2	18	18
h= 1 k=-8		
-1	21	20
0	7	4
1	22	22
h= 1 k=-7		
-4	4	1
-3	53	51
-2	47	44
-1	18	17
0	46	45
1	18	18
2	49	48
3	54	53
4	3	1
h= 1 k=-6		
-5	48	48
-4	61	60
-3	43	41
-2	15	14
-1	51	50
0	77	77
1	52	50
2	14	13
3	44	43
4	63	63
5	50	50
h= 1 k=-5		
-6	44	42
-5	25	25
-4	14	14
-3	23	21
-2	66	64
-1	94	93
0	68	67
1	96	94
2	68	64
3	25	24
4	14	14
5	25	24
6	47	48
h= 1 k=-4		
-7	29	29
-6	54	55
-5	24	25
-4	26	22
-3	36	37
-2	43	43
-1	47	46
0	3	2
1	51	48
2	46	45
3	36	36
4	25	22
5	27	26
6	55	56
7	31	31
h= 1 k=-3		
-7	54	53
-6	50	48
-5	25	24
-4	47	47
-3	26	27
-2	74	78
-1	129	133
0	28	20
1	133	131
2	79	79
3	28	28
4	51	50
5	26	25
6	53	51
7	55	55
h= 1 k=-2		
-7	42	42
-6	27	27
-5	55	54
-4	101	99
-3	83	86
-2	14	12
-1	93	98
0	134	135
1	99	99
2	13	11
3	86	85
4	106	103
5	57	54
6	28	27
7	48	41
h= 1 k=-1		
-8	22	23
-7	16	16
-6	52	51
-5	96	95
-4	52	49
-3	131	130
-2	95	99
-1	46	48
0	52	51
1	41	45
2	100	100
3	137	130
4	54	51
5	97	96
6	53	52
7	17	17
8	21	21
h= 1 k= 0		
-8	28	30
-7	32	30
-6	18	18
-5	39	38
-4	23	22
-3	65	62
-2	97	94
-1	53	47
0	2	3
1	54	50
2	98	94
3	66	61
4	22	20
5	42	39
6	18	17
7	32	29
8	29	29
h= 1 k= 1		
-8	20	21
-7	18	19
-6	51	50
-5	99	97
-4	52	49
-3	135	132
-2	96	97
-1	47	47
0	48	48
1	44	47
2	94	97
3	133	133
4	50	47
5	96	95
6	50	51
7	19	18
8	21	21
h= 1 k= 2		
-7	42	42
-6	26	26
-5	56	54
-4	101	101
-3	85	87
-2	16	15
-1	96	98
0	132	134
1	91	99
2	15	15
3	81	84
4	101	100
5	56	54
6	26	25
7	43	41
h= 1 k= 3		
-7	52	53
-6	52	52
-5	25	25
-4	50	51
-3	27	26
-2	78	79
-1	129	130
0	28	23
1	123	129
2	74	79
3	25	27
4	46	48
5	23	23
6	53	50
7	54	52
h= 1 k= 4		
-7	29	31
-6	54	56
-5	25	24
-4	25	21
-3	36	36
-2	44	45
-1	50	49
0	3	3
1	50	49
2	42	43
3	33	35
4	23	22
5	22	23
6	53	53
7	30	31
h= 1 k= 5		
-6	45	46
-5	26	25
-4	13	13
-3	25	24
-2	64	63
-1	94	95
0	65	64
1	94	93
2	62	62
3	24	23
4	13	13
5	25	25
6	43	44
h- 1 k= 6		
-5	49	50
-4	61	61
-3	45	43
-2	12	11
-1	49	49
0	77	78
1	51	50
2	12	12
3	42	40
4	59	60
5	47	48
h= 1 k= 7		
-4	4	2
-3	51	51
-2	48	48
-1	17	17
0	46	45
1	16	15
2	47	46
3	50	50
4	4	2
h= 1 k= 8		
-1	20	20
0	7	5
1	20	19
h= 2 k=-8		
0	22	19
h= 2 k=-7		
-3	45	44
-2	11	6
-1	41	40
0	46	46
1	42	42
2	11	6
3	45	45
h= 2 k=-6		
-5	15	13
-4	22	23
-3	21	18
-2	64	64
-1	26	25
0	35	33
1	27	26
2	65	65
3	23	21
4	24	25
5	15	15
h= 2 k=-5		
-6	11	8
-5	47	48
-4	39	41
-3	55	56
-2	17	13
-1	54	53
0	35	36
1	55	53
2	16	11
3	58	58
4	41	43
5	48	50
6	11	9
h= 2 k=-4		
-6	24	24
-5	63	65
-4	40	38
-3	87	90
-2	47	48
-1	99	99
0	53	52
1	103	101
2	50	50
3	92	94
4	40	38
5	66	67
6	25	25
h= 2 k=-3		
-7	45	44
-6	13	8
-5	57	57
-4	58	61
-3	64	67
-2	20	15
-1	81	83
0	56	57
1	87	86
2	20	16
3	64	65
4	62	63
5	59	58
6	12	7
7	46	47
h= 2 k=-2		
-7	9	6
-6	65	66
-5	13	10
-4	50	50
-3	18	16
-2	107	115
-1	19	15
0	78	74
1	18	13
2	111	116
3	17	15
4	51	51
5	14	12
6	67	67
7	9	7
h= 2 k=-1		
-7	47	48
-6	18	14
-5	66	65
-4	46	45
-3	80	78
-2	23	11
-1	95	100
0	94	93
1	94	97
2	21	14
3	83	81
4	45	44
5	65	64
6	16	13
7	48	50
h= 2 k= 0		
-8	23	21
-7	68	71
-6	34	33
-5	88	90
-4	53	51
-3	111	110
-2	82	78
-1	138	134
0	90	91
1	141	134
2	82	76
3	114	110
4	55	53
5	90	90
6	35	34
7	71	71
8	22	20
h= 2 k= 1		
-7	48	50
-6	17	13
-5	65	64
-4	46	45
-3	80	79
-2	24	14
-1	95	96
0	91	94
1	93	98
2	20	13
3	78	78
4	43	44
5	65	65
6	16	15
7	46	48
h= 2 k= 2		
-7	10	8
-6	65	67
-5	13	11
-4	47	47
-3	17	16
-2	110	114
-1	18	15
0	78	79
1	17	11
2	106	114
3	15	14
4	47	47
5	14	11
6	66	66
7	9	7
h= 2 k= 3		
-7	45	47
-6	15	10
-5	58	59
-4	61	63
-3	64	65
-2	21	16
-1	84	86
0	53	53
1	80	83
2	20	16
3	61	66
4	58	62
5	56	57
6	13	8
7	46	44
h= 2 k= 4		
-6	25	25
-5	63	65
-4	41	38
-3	91	92
-2	47	47
-1	98	99
0	51	51
1	98	99
2	46	49
3	87	89
4	37	36
5	60	63
6	23	23
h= 2 k= 5		
-6	12	9
-5	48	49
-4	43	44
-3	58	58
-2	16	12
-1	50	51
0	33	34
1	52	51
2	16	13
3	54	55
4	41	42
5	45	46
6	10	9
h= 2 k= 6		
-5	15	14
-4	25	26
-3	21	19
-2	63	64
-1	26	24
0	32	30
1	27	24
2	62	63
3	20	18
4	24	24
5	14	13
h= 2 k= 7		
-3	45	45
-2	12	8
-1	40	40
0	46	46
1	40	39
2	11	7
3	44	44
h= 2 k= 8		
0	22	19
h= 3 k=-7		
-3	12	10
-2	45	44
-1	51	51
0	2	2
1	51	52
2	46	46
3	13	12
h= 3 k=-6		
-4	53	53
-3	50	49
-2	8	7
-1	50	49
0	76	76
1	49	49
2	8	7
3	53	52
4	54	55
h= 3 k=-5		
-5	55	56
-4	44	45
-3	66	68
-2	57	57
-1	24	23
0	19	15
1	26	25
2	58	57
3	68	69
4	47	48
5	57	60
h 3 k=-4		
-6	19	20
-5	16	16
-4	12	12
-3	20	22
-2	60	62
-1	48	48
0	12	7
1	50	48
2	61	61
3	21	22
4	13	13
5	15	16
6	21	22
h= 3 k=-3		
-7	12	10
-6	52	52
-5	67	67
-4	19	21
-3	85	88
-2	61	66
-1	27	27
0	62	61
1	27	27
2	66	67
3	87	91
4	20	21
5	69	70
6	53	53
7	12	12
h= 3 k=-2		
-7	44	44
-6	21	20
-5	58	56
-4	90	92
-3	63	64
-2	15	15
-1	75	79
0	110	110
1	79	79
2	14	14
3	65	66
4	91	93
5	60	58
6	20	20
7	45	48
h= 3 k=-1		
-7	51	53
-6	42	42
-5	23	23
-4	36	36
-3	29	29
-2	81	83
-1	124	128
0	64	61
1	130	133
2	83	83
3	27	28
4	35	35
5	25	26
6	42	42
7	51	53
h= 3 k= 0		
-7	20	21
-6	63	65
-5	40	40
-4	28	28
-3	61	61
-2	56	55
-1	30	23
0	9	3
1	31	20
2	58	56
3	64	62
4	27	26
5	42	40
6	65	65
7	20	19
h= 3 k= 1		
-7	51	51
-6	44	44
-5	25	24
-4	38	36
-3	27	27
-2	85	87
-1	127	130
0	61	60
1	125	129
2	84	86
3	26	27
4	38	37
5	22	22
6	41	42
7	50	52
h= 3 k= 2		
-7	44	46
-6	20	20
-5	59	57
-4	91	93
-3	64	65
-2	16	16
-1	76	78
0	106	108
1	72	78
2	15	16
3	65	66
4	87	90
5	58	56
6	20	18
7	46	45
h= 3 k= 3		
-7	14	13
-6	51	52
-5	66	68
-4	20	21
-3	88	91
-2	62	63
-1	26	27
0	58	59
1	27	29
2	61	62
3	83	88
4	20	21
5	66	67
6	50	50
7	13	11
h= 3 k= 4		
-6	20	21
-5	15	15
-4	14	14
-3	19	20
-2	60	61
-1	48	50
0	10	3
1	48	48
2	57	60
3	19	20
4	12	13
5	13	14
6	19	20
h= 3 k= 5		
-5	56	58
-4	46	46
-3	66	66
-2	58	58
-1	23	23
0	19	16
1	22	22
2	56	56
3	64	65
4	44	44
5	53	55
h= 3 k= 6		
-4	53	53
-3	50	50
-2	10	9
-1	48	49
0	75	75
1	48	48
2	8	6
3	48	48
4	51	51
h= 3 k= 7		
-3	14	13
-2	43	43
-1	49	50
0	4	2
1	50	50
2	42	42
3	12	10
h= 4 k=-7		
-1	29	30
0	7	7
1	29	29
h= 4 k=-6		
-4	19	18
-3	21	21
-2	23	23
-1	53	53
0	27	28
1	54	55
2	25	25
3	20	20
4	18	18
h= 4 k=-5		
-5	34	36
-4	8	9
-3	13	14
-2	65	64
-1	25	24
0	18	18
1	26	25
2	67	65
3	16	17
4	9	10
5	33	36
h= 4 k=-4		
-6	18	17
-5	9	8
-4	65	65
-3	13	13
-2	37	36
-1	23	22
0	150	153
1	24	22
2	41	37
3	13	13
4	65	67
5	11	10
6	19	18
h= 4 k=-3		
-6	54	53
-5	47	47
-4	14	13
-3	20	20
-2	86	90
-1	35	36
0	26	24
1	38	37
2	89	91
3	21	22
4	15	15
5	47	48
6	54	54
h= 4 k=-2		
-6	23	24
-5	42	42
-4	40	36
-3	60	63
-2	48	49
-1	42	44
0	54	53
1	44	44
2	45	46
3	60	64
4	37	37
5	43	44
6	25	26
h= 4 k=-1		
-7	5	3
-6	61	62
-5	19	14
-4	22	22
-3	47	48
-2	98	101
-1	49	49
0	20	21
1	48	47
2	101	100
3	49	48
4	22	23
5	18	14
6	60	62
7	4	3
h= 4 k= 0		
-7	12	11
-6	28	28
-5	9	11
-4	149	152
-3	12	4
-2	53	51
-1	3	2
0	88	90
1	3	1
2	55	52
3	13	7
4	154	153
5	9	11
6	28	28
7	12	10
h= 4 k= 1		
-7	4	2
-6	60	60
-5	19	14
-4	21	21
-3	49	50
-2	99	99
-1	49	49
0	22	23
1	48	48
2	98	98
3	48	48
4	22	21
5	18	15
6	58	61
7	4	1
h= 4 k= 2		
-6	25	25
-5	44	43
-4	39	38
-3	60	62
-2	46	46
-1	44	44
0	49	50
1	42	44
2	47	49
3	59	60
4	39	37
5	41	41
6	24	24
h= 4 k= 3		
-6	54	54
-5	46	47
-4	14	14
-3	20	20
-2	89	91
-1	35	35
0	27	26
1	35	35
2	87	90
3	19	20
4	13	13
5	46	45
6	54	53
h= 4 k= 4		
-6	18	17
-5	10	10
-4	65	65
-3	14	13
-2	41	37
-1	21	19
0	144	149
1	21	20
2	35	35
3	13	12
4	63	63
5	8	8
6	18	17
h= 4 k= 5		
-5	34	36
-4	10	11
-3	15	15
-2	63	62
-1	24	24
0	18	18
1	26	25
2	63	61
3	14	14
4	10	10
5	33	34
h= 4 k= 6		
-4	17	16
-3	20	20
-2	24	24
-1	51	52
0	27	28
1	51	51
2	23	23
3	21	20
4	17	16
h= 4 k= 7		
-1	27	28
0	8	7
1	28	27
h= 5 k=-6		
-2	8	8
-1	45	44
0	47	46
1	44	45
2	9	8
h= 5 k=-5		
-4	34	35
-3	54	55
-2	48	47
-1	26	25
0	19	12
1	25	24
2	50	49
3	56	57
4	36	37
h= 5 k=-4		
-5	32	33
-4	10	10
-3	44	47
-2	42	44
-1	13	13
0	9	9
1	14	14
2	42	43
3	45	47
4	9	9
5	34	36
h= 5 k=-3		
-5	57	57
-4	22	16
-3	65	67
-2	54	55
-1	23	24
0	40	39
1	24	23
2	56	57
3	65	70
4	19	15
5	56	58
h= 5 k=-2		
-6	14	13
-5	48	49
-4	65	63
-3	57	56
-2	19	13
-1	60	62
0	88	87
1	63	64
2	17	12
3	57	56
4	62	64
5	48	50
6	12	13
h= 5 k=-1		
-6	47	48
-5	26	26
-4	26	26
-3	23	22
-2	53	52
-1	90	92
0	41	41
1	91	92
2	55	52
3	24	23
4	25	25
5	24	25
6	47	49
h= 5 k= 0		
-6	46	48
-5	19	10
-4	18	18
-3	20	17
-2	34	36
-1	69	65
0	3	1
1	71	67
2	36	36
3	20	15
4	19	18
5	20	10
6	46	46
h= 5 k= 1		
-6	48	48
-5	26	26
-4	25	24
-3	24	23
-2	55	51
-1	93	94
0	36	37
1	90	92
2	54	51
3	24	23
4	24	25
5	24	25
6	47	49
h= 5 k= 2		
-6	15	14
-5	49	49
-4	64	63
-3	58	57
-2	17	11
-1	61	62
0	83	86
1	60	63
2	16	10
3	57	55
4	65	63
5	48	49
6	14	14
h= 5 k= 3		
-5	56	56
-4	21	16
-3	64	65
-2	55	55
-1	24	23
0	38	39
1	22	22
2	54	55
3	64	65
4	21	17
5	55	55
h= 5 k= 4		
-5	34	35
-4	10	10
-3	46	47
-2	42	43
-1	12	12
0	8	9
1	12	12
2	39	41
3	45	46
4	9	8
5	33	34
h= 5 k= 5		
-4	34	34
-3	55	56
-2	47	46
-1	24	24
0	18	11
1	25	24
2	46	46
3	54	55
4	31	32
h= 5 k= 6		
-2	9	9
-1	43	42
0	44	43
1	44	43
2	9	8
h= 6 k=-5		
-2	13	12
-1	49	48
0	44	45
1	49	48
2	14	14
h= 6 k=-4		
-4	16	16
-3	51	52
-2	23	24
-1	61	60
0	27	28
1	62	61
2	24	23
3	53	53
4	17	17
h= 6 k=-3		
-4	21	21
-3	48	49
-2	18	18
-1	41	40
0	63	64
1	42	41
2	18	19
3	48	50
4	19	21
h= 6 k=-2		
-5	9	9
-4	23	23
-3	7	6
-2	62	65
-1	13	11
0	34	32
1	14	13
2	63	65
3	8	8
4	23	24
5	10	10
h= 6 k=-1		
-5	45	45
-4	53	53
-3	50	49
-2	26	26
-1	50	50
0	17	17
1	49	49
2	25	25
3	52	50
4	53	54
5	42	45
h= 6 k= 0		
-5	45	45
-4	28	28
-3	76	75
-2	33	31
-1	79	76
0	31	31
1	81	76
2	36	32
3	77	75
4	28	27
5	48	45
h= 6 k= 1		
-5	44	43
-4	55	55
-3	50	48
-2	26	25
-1	49	47
0	17	18
1	49	48
2	26	26
3	49	47
4	54	54
5	43	43
h= 6 k= 2		
-5	10	9
-4	25	25
-3	11	9
-2	62	64
-1	13	10
0	31	29
1	12	12
2	62	64
3	9	8
4	25	24
5	9	8
h= 6 k= 3		
-4	19	19
-3	49	49
-2	19	19
-1	44	42
0	60	62
1	41	40
2	19	19
3	49	49
4	18	18
h= 6 k= 4		
-4	17	16
-3	52	51
-2	24	23
-1	59	57
0	27	27
1	60	58
2	22	21
3	52	49
4	16	16
h= 6 k= 5		
-2	15	14
-1	45	46
0	45	45
1	46	45
2	14	13
h= 7 k=-4		
-1	3	3
0	10	9
1	2	2
h= 7 k=-3		
-3	11	11
-2	44	45
-1	50	50
0	18	18
1	51	51
2	44	45
3	12	12
h= 7 k=-2		
-3	43	43
-2	9	7
-1	45	46
0	68	67
1	45	46
2	7	5
3	45	45
h= 7 k=-1		
-4	29	29
-3	51	50
-2	39	38
-1	17	17
0	30	27
1	19	19
2	40	38
3	51	50
4	30	30
h= 7 k= 0		
-4	8	6
-3	3	3
-2	47	46
-1	47	46
0	3	2
1	48	46
2	47	45
3	4	2
4	7	5
h= 7 k= 1		
-4	29	28
-3	51	49
-2	41	40
-1	17	17
0	30	28
1	16	16
2	41	40
3	52	49
4	28	28
h= 7 k= 2		
-3	44	43
-2	9	7
-1	47	46
0	67	66
1	43	45
2	6	5
3	43	43
h= 7 k= 3		
-3	14	13
-2	43	42
-1	49	48
0	19	20
1	49	49
2	42	41
3	10	11
h= 7 k= 4		
-1	1	2
0	12	11
1	1	2
h= 8 k=-2		
0	21	17
h= 8 k=-1		
-1	20	20
0	28	26
1	22	20
h= 8 k= 0		
-2	22	18
-1	6	4
0	94	92
1	7	5
2	19	18
h= 8 k= 1		
-1	21	20
0	27	26
1	23	22
h= 8 k= 2		
0	22	19

Table 4. Positional parameters, anisotropic temperature factors (× 10^4) and extinction parameter

Atom	Site Occupancy	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni_1	Ni 0.97 Co 0.03	-.0174(4)	-.0162(4)	-.0179(4)	60(5)	39(5)	50(5)	4(4)	7(4)	7(4)
Ni_2	Ni 0.97 Co 0.03	.5165(4)	.0184(4)	.4841(4)	50(5)	38(5)	55(5)	-2(4)	2(4)	5(4)
Ni_3	Ni 0.97 Co 0.03	.4811(4)	.5170(4)	.0164(4)	51(5)	45(5)	47(5)	-2(4)	2(4)	9(4)
Ni_4	Ni 0.97 Co 0.03	.0163(4)	.4833(4)	.5171(4)	54(5)	36(5)	47(5)	-2(4)	4(4)	2(4)
S_1	S 0.99(1) As 0.01	.3818(8)	.3829(8)	.3815(8)	73(11)	47(10)	52(10)	-13(8)	3(8)	8(8)
S_2	S 1.00(1) As 0.	.1200(8)	.6200(8)	.8816(8)	69(11)	40(10)	50(10)	-11(8)	0(8)	-4(8)
S_3	S 0.95(1) As 0.05	.8816(8)	.1193(8)	.6186(8)	76(10)	63(10)	65(10)	11(8)	4(8)	12(8)
S_4	S 1.00 As 0.	.6189(8)	.8835(8)	.1185(8)	73(11)	41(10)	49(10)	9(8)	6(8)	1(8)
Sb_1	As 0.04(1) Sb 0.96 Bi 0.00(1)	.6249(3)	.6266(3)	.6259(3)	48(3)	39(3)	49(3)	0(2)	6(2)	6(2)
Sb_2	As 0.06(1) Sb 0.91 Bi 0.03(1)	.8736(3)	.3744(3)	.1255(3)	50(3)	40(3)	48(3)	1(2)	3(2)	4(2)
Sb_3	As 0.03(1) Sb 0.96 Bi 0.01(1)	.1256(3)	.8748(3)	.3743(3)	52(3)	38(3)	48(3)	-1(2)	3(2)	6(2)
Sb_4	As 0.20 Sb 0.80 Bi 0.00	.3744(3)	.1262(3)	.8745(3)	46(3)	32(3)	42(3)	-1(2)	5(2)	3(2)

Extinction parameter -0.000002

This crystal was aligned along an *a** axis on a four-circle diffractometer with reflections 800, $\bar{8}00$ and 080. A least-squares analysis of 20 high 2θ reflections gave a cubic cell of 5.886(1)Å. Integrated intensities of all reflections from four quadrants were collected with Mo$K\alpha$ radiation and a graphite 002 monochromator. A scanning speed of 1/2° 2θ per minute was used in the ω-2θ scan mode within a 6° to 60°2θ range. Twenty-second background counts were made before and after each reflection. A standard reflection was measured after every 50 reflections.

Since the space group $P2_13$ requires the systematic absences of *h*00 with *h* odd, 0*k*0 with *k* odd, and 00*l* with *l* odd, the possibility that these reflections were observed because of the Renninger effect was investigated. The intensity and background of four reflections (0*k*0 with *k* odd from $k = 1$ to $k = 7$) were measured as the crystal was rotated about the scattering vector. This test confirmed that these reflections are not caused by the Renninger effect.

Background, Lorentz polarization, and absorption corrections were made following the method of Wuensch and Prewitt (1965). The linear absorption coefficient of arsenian ullmannite is 239 cm^{-1} and results in transmission factors between 0.14 and 0.27. The extinction factor described by Zachariasen (1967) and extended by Coppens and Hamilton (1970) was calculated. From four quadrants, 1186 symmetry-independent reflections were measured and 1185 were observed above the 1σ level. All reflections, except if $|F_o-F_c|$ is greater than 8, were included in the refinement of the crystal structure by the least-squares program (REFINE 2) of Finger (Carnegie Institution, unpublished report, 1972). All observations were weighted according to $w = 1/\sigma_F^2$, where σ_F is the standard deviation based on counting statistics. Initial positional parameters were taken from Takeuchi (1957). The neutral atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* (1974). The data was first refined in space group $P2_13$ to an *R* factor of 0.041. The atomic coordinates and temperature factors are listed in Table 2.

This *R* factor indicates that the structure is basically correct, but space group $P2_13$ requires systematic absences. From this group all 12 reflections were recorded above the 2σ level. The only space group which allows all reflections to be observed with this crystal structure is $P1$. This is similar to the crystal structure of gerdorffite, NiAsS (Bayliss and Ste-

Table 5. Interatomic distances and angles

Atom	Distance (Å)	Atom	Angle (°)
Ni - S	2.35 - 2.39	S - Ni - S	100
Ni - Sb	2.53 - 2.54	S - Ni - Sb	83 and 86
S - Sb	2.49 - 2.51	Sb - Ni - Sb	91
		Ni - S - Ni	117
		Ni - Sb - Ni	117
		Ni - S - Sb	101
		Ni - Sb - S	101

Table 6. R_w for different crystal structure models

	$P2_13$	P1 (isotropic temperature factors)	P1 (anisotropic temperature factors)
Number of variables	8	65	125
Number of Reflections	1167	1171	1176
R_w	4.3	4.1	3.8

phenson, 1968). The data were then refined in this space group initially with isotropic temperature factors. The Co was distributed uniformly over the four Ni sites, because of their similar size and scattering characteristics. The occupancies of the four S sites were varied within the restraints imposed by the chemical composition. The S content of three sites was varied with the S content of the fourth site reset so that the total S content remained constant. In addition the As content of these four S sites was reset so that each site had an occupancy of exactly one, which also meant that the total As content remained constant. Similarly the occupancies of the four Sb sites were varied within the restraints composed by the chemical composition.

Finally anisotropic temperature factors were used with a series of site occupancy least-squares cycles. The data was finally refined to an R factor of 0.034. Table 3 contains the observed and calculated structure factors; Table 4 contains the atomic coordinates and temperature factors; and Table 5 contains the interatomic distances and angles.

Discussion

Of the twelve reflections listed in Table 3 which violate the systematic absences of space group $P2_13$, ten have $F_o > F_c$ whereas only two have $F_o < F_c$. If this systematic trend is real, there appears to be no logical explanation.

Table 6 gives a list of R_w (weighted R factor), number of observed reflections, and number of parameters in order to use the significance test described by Hamilton (1965). The reduction of R_w is significant at the 0.005 level between the cubic crystal structure and the triclinic crystal structure.

Evidence which supports the conclusion that this arsenian ullmannite is triclinic (pseudo-cubic) includes (1) optical anisotropy, (2) presence of forbidden reflections for $P2_13$ ($h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd), (3) a greater than 3σ movement of some atomic coordinates from the cubic crystal structure to the triclinic crystal structure, and (4) a significant reduction of R_w at the 0.005 level.

The decrease in symmetry is attributed directly to the preferential occupancy of As in sites S_3 and Sb_4 (Table 4). There are no significant variations of interatomic angles between the cubic crystal structure and the triclinic crystal structure, and only small variations of interatomic distances (Table 5).

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