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The crystal structure of picropharmacolite, $\text{Ca}_4\text{Mg}(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 11\text{H}_2\text{O}$

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Abstract

X-ray diffraction intensities were measured by single-crystal diffractometry (MoK α radiation) on picropharmacolite from Sainte-Marie-aux-Mines (Alsace), and the following structure parameters were determined: $a = 13.547(3)$, $b = 13.500(3)$, $c = 6.710(1)\text{\AA}$, $\alpha = 90.85(1)$, $\beta = 96.41(2)$, $\gamma = 91.60(1)^\circ$; $Z = 2$, space group $P\bar{1}$. The structure was solved by direct methods; the mixed isotropic (oxygen atoms) and anisotropic (heavier atoms) refinement converged to $R = 0.087$ (1611 reflections). As, Ca, and Mg coordination polyhedra sharing edges and vertices form corrugated (100) layers, which are linked by hydrogen bonding only. Four independent water molecules are sandwiched between adjacent layers, and build up [001] hydrogen-bonded chains. The Mg coordination octahedron and the Ca polyhedra show typical bond distances, so that no significant Ca/Mg substitution should occur in any cation site. The formula of picropharmacolite can then be written as $\text{Ca}_4\text{Mg}(\text{H}_2\text{O})_7(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$. A close relationship is observed between this structure and those of the two dimorphs guerinite and ferrarisite, $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 9\text{H}_2\text{O}$; in these minerals the layers of polyhedra are also present, but are linked by Ca-O bonds in addition to hydrogen bonds. Cleavage and possible twinning are discussed on structural grounds.

Introduction

Picropharmacolite is a member of a family of mineral acid arsenates of divalent cations (Pierrot, 1964), and occurs as globular crusts of tiny crystals whose poor quality prevented a crystal structure determination until now. The known phases of the family, whose chemical formula can be written as $\text{M}_2^+\text{H}_2(\text{AsO}_4)_4 \cdot n\text{H}_2\text{O}$, can be divided into two groups: species such as sainfeldite, $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$, the dimorphs guerinite and ferrarisite, $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$ (Bari *et al.*, 1980), and chudobaite, $(\text{Mg,Zn})_5\text{H}_2(\text{AsO}_4)_4 \cdot 10\text{H}_2\text{O}$, with only one type of M^{2+} (except for isomorphous substitution); minerals such as irhtemite, $\text{Ca}_4\text{MgH}_2(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$ (Pierrot and Schubnel, 1972), and picropharmacolite, $\text{Ca}_4\text{MgH}_2(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$ where two different, and presumably ordered, types of M^{2+} are present. The Ca and Ca/Mg phases often occur together as accessory minerals which originated by reactions of arsenic ores with surrounding calcareous rocks. The crystal structures of sainfeldite (Ferraris and Abbona, 1972), guerinite (Catti and Ferraris, 1974), ferrarisite (Catti *et al.*, 1980), and chudobaite (Dorner and Weber, 1976) have been determined.

Different crystallochemical formulae have been proposed for picropharmacolite (Abbona and Ferraris, 1976). In most chemical analyses, the CaO/As₂O₅ ratio is slightly higher than 2.0 and the MgO/As₂O₅ ratio fluctuates significantly around 0.5. On the basis of (1) the results obtained by Guérin *et al.* (1967) on synthetic picropharmacolite, (2) the criticism of the available chemical analyses, and (3) a close similarity with the layered structure of guerinite, Abbona and Ferraris favored the hypothesis that there was no solid solution between Ca and Mg in picropharmacolite; a limited substitution involving Ca²⁺, Mg²⁺, and H⁺ was, however, not completely excluded. A structural study of picropharmacolite was undertaken to clarify its crystallochemical features and to throw light on its relationships with other members of the family.

Experimental

A sample of picropharmacolite from Sainte-Marie-aux-Mines (Alsace) was kindly supplied by H. Bari (BRGM, Orléans). After a difficult search (which followed several unsuccessful attempts made previously at our institute on other samples), a tiny needle-like

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PICROPHARMACOLITE Ca4AgH2(ASO4)4.11H2O

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	0	0	66	-61	-12	3	0	65	-65	-1	5	0	68	-45	-1	8	0	64	-68	1	12	0	75	80
6	0	0	45	43	-11	3	0	115	120	5	5	0	130	126	2	8	0	82	79	4	12	0	115	-110
9	0	0	41	-50	-7	3	0	52	-56	5	5	0	51	-57	3	8	0	196	-193	5	12	0	116	121
10	0	0	106	104	-3	3	0	66	70	7	5	0	41	53	4	8	0	116	121	5	12	0	68	-63
-16	1	0	49	33	-2	3	0	220	-223	-13	6	0	48	-57	9	8	0	51	-45	-7	13	0	48	-59
-13	1	0	54	55	-1	3	0	73	66	-8	6	0	65	63	12	8	0	56	59	-4	13	0	81	91
-12	1	0	91	-92	6	3	0	130	123	-7	6	0	100	-98	13	8	0	53	-56	-3	13	0	58	-38
-11	1	0	49	52	1	3	0	68	-64	-6	6	0	95	99	-9	9	0	81	83	8	13	0	69	-79
-8	1	0	131	-129	2	3	0	75	-70	-4	6	0	77	80	-8	9	0	60	-63	-5	14	0	66	-44
-7	1	0	38	29	6	3	0	54	68	-3	6	0	49	-56	-5	9	0	136	137	-4	14	0	62	64
-5	1	0	48	40	7	3	0	39	29	-2	6	0	103	-94	-4	9	0	42	-44	-1	14	0	73	-91
-2	1	0	43	-44	8	3	0	91	-94	0	6	0	59	59	2	9	0	52	-43	0	14	0	45	47
-1	1	0	60	-69	9	3	0	116	-116	1	6	0	104	101	3	9	0	91	-85	-3	15	0	51	42
1	1	0	129	132	10	3	0	110	110	4	6	0	49	-34	7	9	0	121	120	-1	15	0	47	-49
2	1	0	28	-35	-12	4	0	48	-36	5	6	0	78	82	9	9	0	49	-48	3	15	0	71	-75
3	1	0	159	-161	-10	4	0	55	61	8	6	0	93	-82	-6	10	0	57	-52	-2	15	0	49	52
4	1	0	58	53	-9	4	0	62	64	11	6	0	62	62	-5	10	0	70	80	-4	14	0	61	-62
5	1	0	54	-58	-8	4	0	113	-107	12	6	0	85	-76	-1	10	0	65	49	0	14	0	91	-87
8	1	0	87	63	-7	4	0	59	52	-10	7	0	82	103	-2	10	0	134	-130	-1	14	0	65	58
12	1	0	65	63	-5	4	0	50	-50	-9	7	0	46	-39	5	10	0	62	66	-7	13	0	63	56
13	1	0	46	48	-2	4	0	44	-50	-8	7	0	46	-39	5	10	0	46	46	-6	13	0	46	-43
-15	2	0	44	-53	3	4	0	68	-68	-4	7	0	92	89	7	10	0	46	72	-2	13	0	81	-61
-14	2	0	39	35	1	4	0	327	293	-2	7	0	94	-85	7	10	0	70	70	-2	13	0	97	97
-9	2	0	77	73	2	4	0	281	-265	-1	7	0	151	-147	8	10	0	47	-53	-1	13	0	97	97
-8	2	0	93	-97	3	4	0	145	133	0	7	0	53	64	-9	11	0	54	58	0	13	0	74	-66
-4	2	0	37	-35	7	4	0	85	82	2	7	0	57	59	-8	11	0	70	-83	-2	13	0	60	-68
-3	2	0	105	-115	9	4	0	51	-41	7	7	0	48	-54	-2	11	0	48	-45	3	13	0	78	77
-1	2	0	31	-32	10	4	0	57	-52	7	7	0	72	79	1	11	0	93	106	5	13	0	56	-48
0	2	0	53	53	11	4	0	71	84	9	7	0	88	-94	3	11	0	59	-61	-10	12	0	60	61
4	2	0	44	-40	-11	5	0	90	-86	11	7	0	48	57	4	11	0	71	70	-9	12	0	58	-55
5	2	0	67	76	-10	5	0	88	80	-10	8	0	49	50	-9	12	0	50	40	-8	12	0	68	52
7	2	0	91	-107	6	5	0	53	52	-7	8	0	112	-114	-5	12	0	97	98	-4	12	0	74	-65
8	2	0	46	-50	-7	5	0	53	-56	-6	8	0	153	162	-4	12	0	94	98	-3	12	0	90	95
9	2	0	38	-33	-6	5	0	82	84	-5	8	0	80	-79	-3	12	0	60	55	-1	12	0	52	-34
10	2	0	135	139	-4	5	0	49	-52	-2	8	0	44	-54	-1	12	0	70	-71	0	12	0	47	43

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PICROPHARMACOLITE Ca4MgH2(ASO4)4.11H2O

	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	
2-12	1			40	-46	4	-8		113	113	4	-8		52	45	-5	-2		57	-68	9	0		1	57	55
3-12	1			40	58	7	-8		56	-53	15	-5		56	40	0	-2		42	110	10	0		1	75	80
6-12	1			70	-73	8	-8		68	64	-15	-4		67	-45	1	-2		113	-121	-10	1		1	44	-49
-6-11	1			45	44	-14	-7		52	-51	-11	-4		51	-50	2	-2		59	-67	-5	1		1	65	60
-2-11	1			48	38	-10	-7		71	-60	-7	-4		116	-132	3	-2		102	-114	-4	1		1	65	55
0-11	1			93	-63	-9	-7		57	65	-6	-4		241	240	4	-2		206	205	-3	1		1	37	-52
1-11	1			69	75	-4	-7		94	-101	-5	-4		112	-114	5	-2		73	-82	-2	1		1	55	-54
9-11	1			102	106	-2	-7		65	69	-4	-4		81	-82	7	-2		45	43	-1	1		1	137	135
10-11	1			70	-82	1	-7		138	-134	-3	-4		51	55	9	-2		34	-24	0	1		1	61	-57
-12-10	1			83	77	2	-7		91	85	0	-4		170	-171	14	-2		42	33	1	1		1	49	-41
-11-10	1			56	-58	3	-7		60	-59	3	-4		87	79	15	-2		49	37	2	1		1	44	-50
-8-10	1			46	47	8	-7		61	68	4	-4		89	93	-11	-1		43	-51	4	1		1	74	82
-6-10	1			42	30	10	-7		81	65	5	-4		60	66	-8	-1		59	-65	5	1		1	68	-79
-3-10	1			51	-44	11	-7		103	-101	6	-4		77	-82	-7	-1		40	32	10	1		1	66	71
-1-10	1			55	-60	-11	-6		71	61	9	-4		59	50	-6	-1		150	153	13	1		1	49	-54
0-10	1			60	44	-10	-6		84	-96	-14	-3		49	-45	-5	-1		93	-99	14	1		1	93	89
1-10	1			126	-119	-7	-6		155	151	-12	-3		58	52	-4	-1		48	-48	15	1		1	53	-56
2-10	1			68	71	-1	-6		43	33	-9	-3		64	-69	-3	-1		43	-51	-8	1		1	84	-90
3-10	1			60	57	1	-6		43	31	-8	-3		63	70	-2	-1		102	121	-7	2		1	70	77
10-10	1			43	38	2	-6		169	-171	-7	-3		58	-64	0	-1		49	49	-5	2		1	118	117
12-10	1			47	-37	3	-6		195	189	-3	-3		147	-155	1	-1		39	43	-4	2		1	201	-191
-9-9	1			52	-52	4	-6		55	-44	-2	-3		108	115	2	-1		34	-25	-3	2		1	102	109
-6-9	1			48	45	5	-6		67	-60	1	-3		86	-84	3	-1		121	-120	2	2		1	223	-201
-5-9	1			69	-58	9	-6		54	56	2	-3		129	-140	4	-1		208	208	3	3		1	92	81
-3-9	1			47	48	14	-6		50	61	7	-1		166	169	7	-1		98	-100	5	2		1	154	160
0-9	1			63	64	-13	-5		47	43	4	-3		124	-120	8	-1		101	98	6	2		1	137	-140
1-9	1			118	-113	-9	-5		35	-60	7	-3		48	-52	12	-1		43	-55	9	2		1	63	-62
4-9	1			124	135	-7	-5		145	147	9	-3		53	40	-14	0		87	-87	10	2		1	54	41
5-9	1			116	-119	-4	-5		63	-74	11	-3		50	36	-13	0		48	49	-15	3		1	52	-50
-8-8	1			109	-114	-2	-5		166	151	12	-3		107	-105	-5	0		188	187	-7	3		1	66	-60
-7-8	1			102	102	1	-5		77	63	13	-3		86	92	-4	0		240	-251	-6	3		1	60	54
-5-8	1			60	-39	1	-5		84	-92	-10	-2		38	38	1	0		95	-93	-5	3		1	44	52
-2-8	1			122	120	3	-5		66	67	-9	-2		99	-100	2	0		70	65	-4	3		1	205	-210
-1-8	1			55	-53	5	-5		82	76	-8	-2		71	73	3	0		33	-39	-3	3		1	52	42
0-8	1			64	-61	6	-5		162	-172	-7	-2		48	-47	5	0		86	94	-1	3		1	135	125
2-8	1			68	-63	7	-5		53	55	-6	-2		89	89	7	0		89	-87	0	3		1	64	-53

ORSEVERO AND CALCULATED STRUCTURE FACTORS FOR PICROPHARMACOLITE Ca4MgH2(ASO4)4.11H2O

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	3	3	109	-85	-6	0	1	142	153	2	9	1	113	-104	-3-15	2	53	43	-7	-9	2	78	-78	
3	3	1	134	-121	-5	6	1	93	-91	7	9	1	105	-101	-2-15	2	45	-38	-6	-9	2	68	-64	
5	3	1	157	152	-3	6	1	131	-126	8	9	1	96	98	3-15	2	67	83	-3	-9	2	45	48	
6	3	1	139	-140	-2	6	1	155	151	9	9	1	66	-70	4-15	2	53	-57	0	-9	2	115	-109	
7	3	1	52	48	-1	6	1	79	-72	7	10	1	57	-50	-5-14	2	64	-59	2	-9	2	88	92	
8	3	1	78	-73	0	6	1	88	85	-6	10	1	47	48	-3-14	2	49	73	3	-9	2	42	-43	
9	3	1	104	112	1	6	1	42	33	-5	10	1	93	88	6-14	2	57	-49	5	-9	2	67	-71	
-13	4	1	91	-88	3	6	1	59	-58	-4	10	1	104	-113	7-14	2	65	69	8	-9	2	42	43	
-12	4	1	108	114	4	6	1	109	101	-2	10	1	54	-53	-9-13	2	54	56	-12	-8	2	51	46	
-4	4	1	51	54	6	6	1	44	56	-1	10	1	81	76	-2-13	2	54	46	-7	-8	2	64	73	
-3	4	1	114	-117	7	6	1	99	-114	0	10	1	49	-61	0-13	2	43	-32	-6	-8	2	121	-126	
-2	4	1	85	89	-14	7	1	57	-62	1	10	1	97	105	1-13	2	79	86	-1	-8	2	43	-45	
-1	4	1	63	59	-5	7	1	102	106	3	10	1	65	-65	2-13	2	55	-43	3	-8	2	44	44	
1	4	1	89	-97	-3	7	1	156	-149	5	10	1	77	81	8-13	2	43	32	5	-8	2	96	-97	
3	4	1	43	-29	-2	7	1	133	130	8	10	1	60	-53	-8-12	2	89	72	8	-8	2	48	33	
4	4	1	47	-41	1	7	1	55	-52	9	10	1	72	69	-7-12	2	44	-49	9	-8	2	47	-34	
4	4	1	44	38	3	7	1	53	-58	-5	11	1	43	41	-1-12	2	47	-30	13	-8	2	43	32	
6	4	1	48	38	3	7	1	53	-58	-5	11	1	43	41	-1-12	2	47	-30	13	-8	2	43	32	
7	4	1	50	-47	5	7	1	55	46	-3	11	1	92	-93	2-12	2	57	45	-7	-7	2	63	68	
8	4	1	38	-37	6	7	1	48	44	-1	11	1	95	103	3-12	2	42	24	-4	-7	2	130	-140	
9	4	1	65	66	7	7	1	113	-111	0	11	1	77	-74	4-12	2	70	-67	-3	-7	2	209	217	
12	4	1	43	-41	9	7	1	53	-53	5	11	1	45	51	-5-11	2	129	-129	-2	-7	2	101	-106	
-11	5	1	63	50	10	7	1	69	79	8	11	1	70	-79	-4-11	2	119	126	-1	-7	2	44	38	
-9	5	1	76	-89	11	7	1	67	-56	-10	12	1	58	59	-3-11	2	52	-49	0	-7	2	39	-36	
-8	5	1	58	45	12	7	1	55	57	-9	12	1	61	-75	-2-11	2	48	57	1	-7	2	50	53	
-6	5	1	95	95	-11	8	1	98	105	-8	12	1	46	41	4-11	2	91	92	2	-7	2	58	49	
-3	5	1	54	35	-10	8	1	82	-81	0	12	1	123	124	-11-10	2	120	-120	6	-7	2	141	-146	
0	5	1	71	73	-2	8	1	92	-93	1	12	1	96	-82	-4-10	2	48	-41	7	-7	2	122	121	
5	5	1	43	52	-1	8	1	170	165	3	13	1	80	-83	-3-10	2	41	103	-14	-6	2	65	51	
5	5	1	176	-169	4	8	1	85	68	4	13	1	54	58	-1-10	2	99	-106	-11	-6	2	91	-93	
6	5	1	64	81	10	8	1	45	46	-3	14	1	86	-94	0-10	2	42	36	-2	-6	2	101	106	
7	5	1	46	-44	-8	9	1	47	-50	-2	14	1	54	50	7-10	2	43	-35	5	-6	2	113	-113	
8	5	1	65	66	-7	9	1	48	41	2	14	1	48	52	8-10	2	65	77	-1	-6	2	108	-113	
10	5	1	45	-55	-4	9	1	70	-69	5	14	1	61	51	9-10	2	75	-73	0	-6	2	145	145	
12	5	1	42	43	-2	9	1	41	-29	-2	15	1	47	-34	9-10	2	57	45	1	-6	2	75	78	
-11	6	1	43	-31	0	9	1	93	90	0	15	1	54	64	-13-9	2	57	45	2	-6	2	75	78	
-10	6	1	43	-31	0	9	1	93	90	0	15	1	54	64	-13-9	2	57	45	2	-6	2	75	78	
-8	6	1	85	-97	1	9	1	65	62	-5	15	2	56	64	-8-9	2	46	56	3	-6	2	86	97	

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PICOPHARMACOLITE Ca4Mg2(AsO4)4.11H2O

PAGE 2

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	-5	2	44	-41	-3	-3	2	43	-54	8	-1	2	113	112	-11	2	2	54	-71	3	4	2	53	-41
8	-6	2	40	33	-2	-3	2	211	224	9	-1	2	50	-56	-9	2	2	61	-60	4	4	2	108	97
9	-6	2	42	50	-1	-3	2	147	-204	10	-1	2	75	67	-8	2	2	120	123	4	4	2	39	51
10	-6	2	114	-122	0	-3	2	113	121	14	-1	2	45	39	-7	2	2	44	-48	10	4	2	45	-52
11	-6	2	61	55	1	-3	2	45	-57	-13	0	2	66	70	-4	2	2	46	-52	-14	5	2	44	-31
-12	-5	2	82	77	6	-3	2	39	-45	-12	0	2	71	-66	-3	2	2	75	67	-12	5	2	51	41
-8	-5	2	79	84	7	-3	2	66	-70	-9	0	2	61	-54	-2	2	2	37	-30	-10	5	2	53	-44
-7	-5	2	51	-44	8	-3	2	173	174	-8	0	2	64	59	0	2	2	94	-90	-8	5	2	47	50
-6	-5	2	77	-83	9	-3	2	75	-75	-7	0	2	46	38	1	2	2	146	-120	-6	5	2	81	82
-3	-5	2	57	-46	-14	-2	2	50	-37	-3	0	2	174	174	3	2	2	60	59	-4	5	2	36	-41
-2	-5	2	99	94	-13	-2	2	79	51	-2	0	2	43	-43	4	2	2	98	-95	-3	5	2	74	-64
0	-5	2	50	-80	-10	-2	2	107	-111	3	0	2	119	115	5	2	2	70	70	-2	5	2	81	82
1	-5	2	49	-53	-9	-2	2	56	55	0	0	2	78	-81	11	2	2	42	-34	-1	5	2	43	38
2	-5	2	78	75	-8	-2	2	63	64	8	0	2	86	86	12	2	2	45	-45	0	5	2	44	34
3	-5	2	102	109	-4	-2	2	124	-138	11	0	2	59	-42	13	2	2	77	82	1	5	2	253	-222
4	-5	2	53	-64	-2	-2	2	74	78	13	0	2	50	-45	-9	2	2	102	-96	2	5	2	293	266
5	-5	2	41	44	0	-2	2	166	-178	-10	1	2	99	-100	-8	2	2	124	134	3	5	2	140	-122
6	-5	2	65	-64	1	-2	2	105	-104	-9	1	2	91	90	-5	2	2	96	-106	4	5	2	56	59
7	-5	2	70	73	2	-2	2	118	132	-6	1	2	66	-60	-3	2	2	45	42	5	5	2	56	59
-10	-4	2	41	-44	3	-2	2	55	-54	-5	1	2	49	-46	0	2	2	39	33	6	5	2	59	-51
-6	-4	2	64	61	4	-2	2	59	67	-4	1	2	48	-44	2	2	2	79	66	9	5	2	44	44
-5	-4	2	90	-91	8	-2	2	60	54	-3	1	2	48	53	3	2	2	66	-52	10	5	2	45	34
-4	-4	2	67	80	9	-2	2	62	66	-2	1	2	120	118	5	2	2	131	-133	11	5	2	54	-56
-3	-4	2	47	-51	11	-2	2	105	-111	-1	1	2	187	169	9	2	2	84	91	12	5	2	44	51
-1	-4	2	44	-44	12	-2	2	48	45	0	1	2	371	-341	10	2	2	91	-94	-11	6	2	75	80
0	-4	2	42	-39	-11	-1	2	59	58	1	1	2	170	144	11	2	2	45	49	-10	6	2	91	-103
2	-4	2	76	-87	-10	-1	2	104	-97	2	1	2	57	-53	-12	2	2	41	39	-7	6	2	65	69
3	-4	2	54	61	-9	-1	2	37	35	3	1	2	39	-23	-11	2	2	54	-70	-6	6	2	54	-72
4	-4	2	48	63	-7	-1	2	102	104	4	1	2	73	74	-9	2	2	46	-42	-2	6	2	54	57
6	-4	2	65	-60	-6	-1	2	38	-37	5	1	2	57	50	-7	2	2	88	88	1	6	2	139	-127
7	-4	2	86	86	-5	-1	2	49	51	6	1	2	78	-79	-4	2	2	43	-42	3	6	2	86	86
9	-4	2	43	-35	-1	-1	2	50	57	8	1	2	53	51	2	2	2	185	173	5	6	2	68	-69
-11	-3	2	66	-69	0	-1	2	85	-88	9	1	2	93	91	-1	2	2	86	-78	6	6	2	48	59
-10	-3	2	74	69	1	-1	2	71	84	10	1	2	99	-100	0	2	2	60	60	7	7	2	52	-50
-5	-3	2	40	-90	3	-1	2	91	-90	-13	2	2	52	-40	1	2	2	49	49	-9	7	2	67	-59
-4	-3	2	45	-50	7	-1	2	61	-66	-12	2	2	81	88	2	2	2	44	26	-7	7	2	112	108

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PICHOPIPHARMACOLITE Ca4MgH2(AsO4)4.11H2O

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	7	2	65	-72	-9	10	2	68	-77	0-13	3	3	90	89	-2	-8	3	62	49
-4	7	2	77	-74	-6	10	2	42	39	-1-12	3	3	79	-76	0	-4	3	94	-94
-2	7	2	43	49	-5	10	2	53	-48	2-12	3	3	47	43	1	-6	3	115	114
-1	7	2	50	45	-4	10	2	61	68	3-12	3	3	69	-73	4	-8	3	117	-123
1	7	2	41	-39	-1	10	2	67	62	-10-11	3	3	54	-50	8	-8	3	44	51
2	7	2	41	-44	1	10	2	72	-66	-9-11	3	3	70	77	-8	-7	3	107	108
5	7	2	43	49	4	10	2	48	48	-4-11	3	3	74	87	-7	-7	3	98	-108
6	7	2	103	-99	6	10	2	48	-54	-3-11	3	3	81	-81	-4	-7	3	63	57
11	7	2	59	-63	8	10	2	44	-40	0-11	3	3	79	-82	-2	-7	3	108	-103
-10	8	2	59	-75	-9	11	2	69	62	1-11	3	3	78	76	0	-7	3	61	-59
-8	8	2	40	-38	-5	11	2	60	-62	3-11	3	3	42	-26	2	-7	3	124	133
-6	8	2	46	94	-3	11	2	49	-52	6-11	3	3	56	51	4	-7	3	76	-73
-5	8	2	70	-59	-2	11	2	63	64	7-11	3	3	50	-45	8	-7	3	60	-52
-4	8	2	59	-62	2	11	2	44	-39	-11-10	3	3	55	51	-14	-6	3	48	38
-2	8	2	37	23	-8	12	2	48	48	-10-10	3	3	43	-35	-13	-6	3	45	-39
-1	8	2	107	106	-7	12	2	49	-44	-7-10	3	3	44	-28	-9	-6	3	39	-33
0	8	2	135	-132	-2	12	2	44	38	-6-10	3	3	65	-72	-6	-6	3	86	-91
1	8	2	39	27	1	12	2	72	-78	1-10	3	3	47	-47	-4	-6	3	128	136
5	8	2	55	60	6	12	2	48	36	4-10	3	3	54	-62	-2	-6	3	43	-50
7	8	2	54	-54	-7	13	2	45	32	6-10	3	3	69	73	1	-6	3	59	66
8	8	2	47	35	-5	13	2	62	-56	9-10	3	3	82	-85	2	-6	3	44	-45
8	8	2	57	65	-4	13	2	54	65	10-10	3	3	84	76	3	-6	3	74	72
9	8	2	46	-45	-3	13	2	79	-82	-12-9	3	3	64	-64	4	-6	3	91	-95
11	8	2	55	54	-1	13	2	64	89	-9-9	3	3	54	40	5	-6	3	54	-64
-7	9	2	41	-48	4	13	2	70	66	-	3	3	41	31	6	-6	3	70	72
-6	9	2	42	47	5	13	2	85	-90	-6-9	3	3	42	-45	10	-6	3	58	-60
-5	9	2	42	-54	-4	14	2	49	-58	-3-9	3	3	48	45	11	-6	3	90	85
-4	9	2	52	-64	0	14	2	50	51	-2-9	3	3	102	-95	-10	-5	3	73	79
-3	9	2	70	53	-1	15	3	52	-44	0-9	3	3	78	-79	-9	-5	3	51	-46
-2	9	2	52	70	3	15	3	51	-33	1-9	3	3	126	128	-8	-5	3	63	69
-1	9	2	53	-50	4	15	3	53	-35	2-9	3	3	62	-64	-7	-5	3	64	-63
0	9	2	73	-76	3	14	3	69	-46	4-9	3	3	46	-49	-5	-5	3	42	-34
2	9	2	169	173	4	14	3	54	-43	10-9	3	3	46	-42	-4	-5	3	51	61
3	9	2	147	-149	-3	13	3	67	71	-11-8	3	3	60	-62	-3	-5	3	52	55
4	9	2	57	62	-4	13	3	78	-87	-6-8	3	3	76	-76	-2	-5	3	53	55
5	9	2	80	72	-1	13	3	75	-64	-5-8	3	3	51	62	-1	-5	3	86	-89

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PICROPHARMACOLITE Ca4MgH2(AsO4)4·11H2O

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-2	-2	3	42	-42	-14	1	3	70	67	0	3	3	96	-85	6	6	3	45	80	0	10	3	62	-66
0	-2	3	50	39	-10	1	3	40	37	2	3	3	163	149	7	6	3	48	-34	2	10	3	62	67
1	-2	3	42	-33	-8	1	3	46	57	4	3	3	122	-118	8	6	3	59	45	4	10	3	62	38
2	-2	3	83	85	-4	1	3	69	-68	4	3	3	133	129	10	6	3	44	-56	-4	11	3	78	68
3	-2	3	44	-91	-5	1	3	205	-204	7	3	3	45	-39	-7	7	3	39	35	-2	11	3	60	64
4	-2	3	64	97	-4	1	3	231	232	10	3	3	54	-52	-6	7	3	70	-78	-1	11	3	53	-42
5	-2	3	133	-132	0	1	3	72	-68	-8	3	3	48	54	-4	7	3	69	-65	0	11	3	52	58
6	-2	3	44	-45	2	1	3	40	30	-7	4	3	53	54	-3	7	3	56	75	-3	11	3	87	-97
7	-2	3	67	67	3	1	3	65	55	-6	4	3	112	-122	-2	7	3	54	-53	3	11	3	56	64
-15	-1	3	48	-30	5	1	3	91	-88	-5	4	3	37	-35	-1	7	3	79	88	-1	12	3	79	-70
-9	-1	3	83	82	7	1	3	84	78	-4	4	3	149	146	0	7	3	111	-110	0	12	3	67	74
-8	-1	3	78	-83	10	1	3	43	-40	-1	4	3	60	-54	1	7	3	81	-74	1	13	3	87	-93
-7	-1	3	73	80	-13	2	3	53	43	1	4	3	99	-92	2	7	3	60	58	2	13	3	75	74
-6	-1	3	84	-86	-12	2	3	44	-48	2	4	3	75	73	3	7	3	66	60	-5	14	4	57	-55
-5	-1	3	78	77	-11	2	3	45	-39	3	4	3	89	88	4	7	3	84	-73	3	14	4	72	-74
-3	-1	3	55	62	-6	2	3	57	66	5	4	3	127	-128	7	7	3	73	78	4	14	4	89	80
3	-1	3	152	152	-6	2	3	58	60	6	4	3	97	89	9	7	3	49	38	-7	13	4	63	60
4	-1	3	120	-119	-5	2	3	106	-109	8	4	3	55	54	-7	8	3	62	57	-5	13	4	64	-31
5	-1	3	149	150	-3	2	3	78	83	10	4	3	45	46	-5	8	3	65	-69	-2	12	4	61	-52
6	-1	3	49	-47	-2	2	3	37	-41	11	4	3	43	-39	-3	8	3	78	76	-1	12	4	52	36
7	-1	3	66	-67	-1	2	3	64	-69	-13	5	3	50	43	-2	8	3	93	-83	4	12	4	52	-47
8	-1	3	39	35	0	2	3	38	42	-12	5	3	68	-67	2	8	3	73	-63	6	12	4	49	43
10	-1	3	40	-39	1	2	3	44	33	-11	5	3	49	59	3	8	3	121	123	3	12	4	52	35
-8	0	3	129	128	2	2	3	43	36	-7	5	3	67	66	5	8	3	80	-85	-8	11	4	72	-79
-7	0	3	89	-88	3	2	3	47	41	-3	5	3	201	200	7	8	3	62	82	-7	11	4	71	78
-6	0	3	139	-143	4	2	3	115	-106	-2	5	3	147	-148	9	8	3	49	53	9	11	4	44	-37
-5	0	3	37	37	5	2	3	39	40	4	5	3	81	78	9	8	3	75	-77	-2	11	4	71	78
2	0	3	66	66	6	2	3	65	-70	5	5	3	48	-46	-11	9	3	68	81	-11	9	4	43	-69
3	0	3	132	126	7	2	3	43	51	5	5	3	54	-46	-10	9	3	72	81	-10	9	4	44	-34
4	0	3	172	-172	-13	3	3	44	35	7	6	3	56	-53	-9	9	3	83	-62	-9	10	4	44	-44
5	0	3	62	59	-8	3	3	101	88	-7	6	3	51	47	-1	9	3	124	-133	-2	10	4	89	90
7	0	3	109	116	-7	3	3	98	-93	-5	6	3	42	-34	0	9	3	67	60	-3	10	4	59	71
8	0	3	106	-104	-6	3	3	38	44	-3	6	3	52	37	6	9	3	46	-53	-2	10	4	63	-54
9	0	3	81	80	-5	3	3	91	-94	0	6	3	75	-67	6	9	3	44	-48	6	10	4	41	-27
11	0	3	50	-60	-4	3	3	91	112	0	6	3	81	78	-9	10	3	44	44	-9	10	4	75	-77
12	0	3	49	54	-3	3	3	96	-84	1	6	3	42	-49	-5	10	3	43	-50	10	10	4	97	97

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PICROPHARMACOLITE Ca4MgH2(AsO4)4·11H2O

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-4	-9	4	56	55	0	-6	4	111	111	-9	-2	4	48	55	8	0	4	55	-65	-1	3	4	48	-46
-3	-9	4	105	-104	7	-6	4	89	-97	-7	-2	4	59	-71	10	0	4	49	-49	1	3	4	106	94
-1	-9	4	45	58	-14	-5	4	54	-54	-5	-2	4	44	55	-11	1	4	63	-73	2	3	4	42	-41
1	-9	4	53	44	-12	-5	4	58	-52	-3	-2	4	52	56	-9	1	4	75	-76	3	3	4	48	-47
6	-9	4	55	49	-4	-5	4	72	31	-2	-2	4	116	-129	-8	1	4	47	-36	4	3	4	56	45
8	-9	4	47	-58	-2	-5	4	79	-88	-1	-2	4	117	121	-7	1	4	52	-65	5	3	4	65	-67
9	-9	4	56	56	-1	-5	4	72	25	0	-2	4	82	-85	-6	1	4	37	35	-9	4	4	97	93
-10	-6	4	44	39	0	-5	4	63	72	1	-2	4	71	74	-4	1	4	49	50	-8	4	4	83	-86
-9	-9	4	52	-47	1	-5	4	75	-77	7	-2	4	57	59	-3	1	4	95	-99	-4	4	4	51	-41
-4	-8	4	72	71	2	-5	4	47	53	8	-2	4	129	-132	-1	1	4	42	-47	-3	4	4	86	85
-2	-8	4	66	-73	3	-5	4	62	-49	9	-2	4	70	72	1	1	4	84	77	-2	4	4	41	45
0	-8	4	68	101	4	-5	4	54	39	-14	-1	4	45	49	3	1	4	65	-57	-1	4	4	69	-73
2	-8	4	63	-77	10	-5	4	59	74	-13	-1	4	54	-59	4	1	4	60	-47	1	4	4	87	78
3	-8	4	44	45	11	-5	4	43	-35	-10	-1	4	102	105	6	1	4	61	56	3	3	4	61	-56
4	-8	4	49	-60	-12	-4	4	58	-64	-9	-1	4	40	-45	-8	2	4	42	34	9	4	4	67	-80
5	-8	4	48	49	-4	-4	4	60	-65	-4	-1	4	70	80	-6	2	4	43	-40	-12	5	4	49	-38
9	-8	4	46	-38	-2	-4	4	111	-115	-2	-1	4	80	-81	-4	2	4	42	46	-9	5	4	54	58
10	-8	4	58	48	0	-4	4	57	61	-1	-1	4	85	-85	-2	2	4	62	-55	-7	5	4	64	-67
-12	-7	4	65	-64	1	-4	4	53	50	0	-1	4	119	113	-1	0	4	126	-119	-3	5	4	64	49
-11	-7	4	43	47	2	-4	4	75	-82	3	-1	4	63	-58	0	2	4	179	174	-2	5	4	77	-74
-7	-7	4	46	-31	5	-4	4	95	-96	3	-1	4	43	47	1	2	4	133	-122	-1	5	4	78	78
-6	-7	4	98	106	6	-4	4	69	78	4	-1	4	68	-57	2	2	4	99	95	0	5	4	81	-77
-5	-7	4	53	-42	9	-4	4	55	-64	7	-1	4	53	61	3	2	4	40	-27	1	5	4	45	42
-4	-7	4	62	67	11	-4	4	55	46	8	-1	4	52	-48	5	2	4	49	-47	4	5	4	68	68
-1	-7	4	65	-73	-14	-3	4	43	-26	11	-1	4	59	54	6	2	4	54	51	6	5	4	65	64
0	-7	4	67	69	-13	-3	4	46	57	12	-1	4	47	-46	9	2	4	66	-74	-9	6	4	45	45
2	-7	4	42	-29	-12	-3	4	41	-41	-10	0	4	115	113	10	2	4	103	108	-6	6	4	72	-67
5	-7	4	45	51	-11	-3	4	59	-59	-7	0	4	65	-66	11	2	4	47	-44	-4	6	4	46	46
8	-7	4	48	-33	-10	-3	4	64	73	-6	0	4	66	59	12	2	4	43	37	1	6	4	153	147
-7	-6	4	45	50	-5	-3	4	88	93	-3	0	4	60	56	-9	3	4	56	-52	2	6	4	139	-137
-4	-6	4	65	-25	-4	-3	4	75	-74	-2	0	4	50	-45	-8	3	4	55	51	3	6	4	134	131
-3	-6	4	107	71	-3	-3	4	38	43	0	0	4	89	94	-7	3	4	78	-83	4	6	4	91	-100
-2	-6	4	153	163	-2	-3	4	52	-55	1	0	4	59	56	-7	3	4	54	62	5	6	4	53	-55
-1	-6	4	67	-73	4	-3	4	59	64	3	0	4	116	-113	-4	3	4	74	76	7	7	4	65	58
0	-6	4	42	44	5	-3	4	42	-42	5	0	4	44	37	-3	3	4	44	46	-11	7	4	54	-60
0	-6	4	42	44	5	-3	4	43	45	7	0	4	80	87	-2	3	4	97	-95	-10	7	4	64	58

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PICROPHARMACOLITE Ca4MgH2(AS04)4.11H2O

H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC
1	5	5	64	54	-6	-6	6	45	-49	1	-2	6	50	-63	0	3	5	98	-88	-4	-4	7	53	56
5	5	5	56	55	-5	-6	6	65	66	-11	-1	6	52	36	1	3	6	100	89	-6	-4	7	68	-75
7	7	5	59	-66	-4	-6	6	64	-60	-9	-1	6	54	-57	2	3	6	105	-105	1	-4	7	44	-40
4	7	5	43	40	-2	-6	6	56	55	-3	-1	5	53	-57	-8	4	6	65	59	3	-4	7	42	51
3	7	5	62	-49	0	-6	6	62	-48	-2	-1	6	50	62	-6	4	6	59	57	-9	-3	7	43	-46
8	7	5	56	-47	8	-6	6	49	36	-1	-1	5	79	-84	-3	4	6	46	-37	-5	-3	7	64	-64
4	8	5	51	-49	-10	-5	5	50	-49	0	-1	6	129	128	-2	4	6	52	48	-4	-3	7	40	22
1	8	5	74	72	-4	-5	6	57	-57	1	-1	6	75	-79	1	4	6	46	-51	1	-3	7	44	-51
0	8	5	68	-71	-3	-5	6	69	72	7	-1	6	50	-58	5	4	6	74	77	2	-3	7	48	62
5	8	5	43	53	-2	-5	6	61	-79	8	-1	5	69	80	-9	5	6	60	-58	4	-3	7	65	56
6	8	5	61	-31	-1	-5	6	94	95	-10	0	6	44	-52	-3	5	6	79	-78	5	-3	7	57	-55
9	8	5	59	73	0	-5	6	69	-51	-6	0	6	48	39	-1	5	6	65	60	-7	-1	7	45	42
9	9	5	42	54	1	-5	6	41	-24	-4	0	5	55	-47	1	5	6	52	-63	-6	-1	7	65	-64
3	9	5	81	-84	6	-5	6	91	-91	-1	0	6	80	-91	2	5	6	44	29	2	-1	7	64	64
1	10	5	47	58	7	-5	6	49	51	0	0	6	55	-53	-4	7	6	51	-24	4	-1	7	55	52
1	10	5	89	69	-2	-5	6	96	-35	3	0	6	57	68	1	7	6	88	-89	-7	0	7	41	34
5	10	5	54	55	8	-5	6	44	96	4	0	6	74	82	2	7	6	59	59	-5	0	7	48	-42
1	11	6	52	-57	-1	-4	6	58	-70	-1	1	6	81	-74	3	7	6	104	-102	-4	0	7	46	34
7	11	6	73	57	2	-4	6	39	-52	0	1	6	50	-34	-3	8	6	59	55	-1	0	7	50	50
7	10	6	59	-61	4	-4	6	41	27	1	1	6	43	39	-1	8	6	43	38	3	3	7	41	47
6	10	6	51	40	9	-4	6	43	26	3	1	6	87	-93	-7	7	7	59	-49	5	0	7	61	-66
2	10	6	55	47	-6	-3	6	43	30	7	1	6	43	22	-6	-7	7	59	-49	-2	1	7	59	-63
0	10	6	47	-40	-4	-3	6	43	-48	8	1	6	43	22	0	-7	7	66	-58	3	1	7	90	86
2	10	6	44	45	-2	-3	6	97	91	-11	2	6	54	62	1	-7	7	63	53	4	4	7	59	-44
3	9	6	72	-60	0	-3	6	41	-51	-9	2	6	70	-66	3	-7	7	71	75	5	1	7	49	47
5	9	6	75	75	1	-3	6	52	-54	-8	2	6	53	58	4	-7	7	48	-45	4	4	7	45	-35
6	9	6	76	-73	2	-3	6	50	58	-3	2	6	43	30	-3	-6	7	58	41	-7	-3	7	50	38
4	8	6	51	43	-10	-2	6	73	-78	-2	2	6	72	-73	-8	-5	7	49	50	-5	3	7	63	-66
4	8	6	70	-67	-5	-2	6	59	-60	-1	2	6	93	97	-7	-5	7	80	-78	-4	3	7	68	71
3	8	6	73	67	-4	-2	6	43	52	1	2	6	56	-55	-6	-5	7	80	46	-3	3	7	57	-63
1	8	6	48	-60	-3	-2	6	83	-90	3	2	6	50	40	-5	-5	7	47	-37	-5	4	7	50	-63
4	7	6	80	-71	-2	-2	6	62	65	-7	3	6	46	55	0	-5	7	65	-53	-2	5	7	45	41
7	7	6	47	54	-1	-2	6	74	70	-1	3	6	72	73	2	-5	7	59	74	-1	5	7	45	-37