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The Crystal Structure of α-$Sr_2P_2O_7$

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The structure of the high-temperature modification of strontium diphosphate, α-$Sr_2P_2O_7$, has been derived on the basis of three-dimensional X-ray data and refined with least-squares methods. The orthorhombic unit cell, space group *Pnma*, which contains four formula units, has the dimensions

$$a = 8.9104 \pm 6 \text{ Å}$$
$$b = 5.4035 \pm 4 \text{ Å}$$
$$c = 13.1054 \pm 14 \text{ Å}$$
$$V = 631.0 \text{ Å}^3$$

The structure contains ecliptic diphosphate groups (*m* symmetry) with a $P-O_{bridge}-P$ angle of 130.7°. The average bond distances are $P-O_{bridge}=1.60$ Å and $P-O_{terminal}=1.50$ Å. The strontium atoms have nine oxygen neighbours. A discussion of the structure is given.

Studies on phosphates of different degrees of condensation have for several years been conducted at this Institute.[1–4] One of the main interests in this research has been the detailed structure of the diphosphate group. Several observations are reported in the literature on the polymorphism of the diphosphates of the alkaline earth metals. The so called α-modification has been found with calcium, strontium as well as barium,[5] while the β-modification has been observed to form at lower temperatures with calcium and strontium only.[6–8] The crystal structure of β-$Ca_2P_2O_7$ was recently reported by Webb.[9] This article will describe the results of an X-ray crystallographic investigation of α-$Sr_2P_2O_7$.

PREPARATION OF THE CRYSTALS

Single crystals of α-strontium diphosphate were prepared according to a method described by Klement [10] by slow cooling of a melt of strontium carbonate and sodium trimetaphosphate both of reagent grade. In this way the compound could be obtained as long transparent needles.

Table 1. X-Ray powder data of α-$Sr_2P_2O_7$. Cu$K\alpha_1$-radiation.

$h\ k\ l$	$\sin^2\theta 10^5$ obs	$\sin^2\theta 10^5$ calc	(obs−calc)10^5	d_{obs}	I_{obs}
1 0 1	1087	1092	− 5	7.39	vs
0 0 2	1379	1379	0	6.56	w
2 0 0	2992	2989	3	4.45	vw
1 0 3	3846	3851	− 5	3.93	w
2 0 2	4368	4368	0	3.68	vvw
2 1 0	5006	5021	−15	3.44	vs
0 1 3	5121	5136	−15	3.40	vs
2 1 1	5355	5366	−11	3.33	s
0 0 4	5519	5518	1	3.28	vvw
1 1 3	5872	5883	−11	3.18	w
2 0 3	6079	6093	−14	3.12	w
2 1 2	6411	6401	10	3.04	w
3 0 1	7068	7070	− 2	2.90	m
3 0 2 2 1 3 0 2 0	8105	8105 8125 8128	0 −20 −23	2.71	vs
1 1 4	8283	8292	− 9	2.68	m
2 0 4	8508	8508	0	2.64	vvw
3 1 1	9099	9102	− 3	2.55	m
1 0 5	9370	9370	0	2.52	w
3 1 2	10140	10137	3	2.42	vw
1 2 2	10245	10255	−10	2.41	w
2 1 4	10546	10540	6	2.37	vvw
0 1 5	10642	10655	−13	2.36	vvw
2 2 0	11109	11116	− 7	2.31	vw
2 2 1	11472	11462	10	2.27	vw
4 0 1	12300	12301	− 1	2.20	m
0 0 6	12427	12417	10	2.18	m
1 0 6	13178	13164	14	2.12	vw
2 2 3	14212	14222	−10	2.04	vs
1 2 4	14391	14394	− 3	2.03	w
4 0 3	15068	15061	7	1.98	vvw
1 1 6 3 2 1	15206	15197 15199	9 7	1.98	vvw
4 1 2	15368	15368	0	1.96	vw
3 2 2	16261	16234	27	1.91	vvw
2 2 4	16654	16636	18	1.89	w
4 1 3	17098	17093	5	1.86	m
2 1 6	17452	17438	14	1.84	m
0 1 7	18969	18933	36	1.77	vvw
4 1 4	19515	19508	7	1.74	vvw
5 0 2	20067	20062	5	1.72	vvw
3 2 4 4 2 1 1 3 2	20418	20373 20430 20416	45 −12 2	1.70	vw
0 2 6 4 0 5	20554	20546 20580	8 −26	1.70	vw
5 1 1	21066	21059	7	1.68	vvw
1 2 6	21264	21293	−29	1.67	w
0 3 3	21382	21393	−11	1.67	vw
2 3 1	21633	21623	10	1.66	vvw
5 1 2	22123	22094	29	1.64	vvw
4 2 3	23189	23189	0	1.60	vvw
2 2 6	23532	23535	− 3	1.59	vvw
2 3 3	24390	24382	8	1.56	vvw

Table 1. Continued.

1 3 4	24562	24555	7	1.55	vvw
3 3 1	25356	25359	− 3	1.53	vvw
4 1 6	26422	26406	16	1.50	vw
0 3 5	26908	26912	− 4	1.48	vvw
5 2 2	28218	28191	27	1.45	vvw
1 0 9	28663	28686	−23	1.44	vw
6 1 1	29269	29280	−11	1.42	vvw
6 1 2	30307	30315	− 8	14.0	vw
1 2 8	30946	30951	− 5	1.38	vw
4 3 2	31640	31625	15	1.37	vw
0 4 0 }	32514	32514	0 }	1.35	w
4 2 6 }		32503	11 }		
5 1 6	33106	33132	−26	1.34	vw
4 3 3	33329	33350	−21	1.33	vw
2 3 6	33677	33695	−18	1.33	w

X-RAY DATA COLLECTING AND TREATMENT

The powder pattern was found to be in fair accordance with the data given by Ranby, Mash and Henderson.[5] The photographs were taken with strictly monochromatized Cu$K\alpha_1$ (λ=1.54056 Å) radiation in a Guinier-Hägg type focusing camera. Potassium chloride (a=6.29228 Å)[11] was used as an internal standard (see Table 1). The dimensions of the orthorhombic unit cell thus obtained are (25°C)

$$\begin{aligned} a &= 8.9104 \pm 6 \text{ Å} \\ b &= 5.4035 \pm 4 \text{ Å} \\ c &= 13.1054 \pm 14 \text{ Å} \\ V &= 631.0 \text{ Å}^3 \end{aligned}$$

The value of 3.60 g/cm³ for the density, found from the apparent loss of weight in benzene, gives 4 formula units in the unit cell (δ_{calc}=3.68).

Weissenberg photographs of the layer lines $h0l$—$h3l$ and $0kl$ were registered with CuK radiation using multiple film technique. The crystal used had the dimensions 0.08 mm (in the direction of the a axis) ×0.13 mm (b axis) ×0.03 mm (c axis). The relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times. Correction was made for the absorption in the crystal (μ=292.7 cm^{-1}).[12]

STRUCTURE DETERMINATION

The reflections systematically absent in the single-crystal data are $0kl$ with $k+l=2n+1$ and $hk0$ with $h=2n+1$ which is characteristic of the space groups *Pnma* (No. 62) and $Pn2_1a$ (No. 33). As a test for piezoelectricity was negative the structure determination was started assuming the symmetry to be the higher of the two alternatives, *viz. Pnma.* In this space group the following point positions exist

4 (a): $0,0,0;\ 0,\frac{1}{2},0;\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},\frac{1}{2}$
4 (b): $0,0,\frac{1}{2};\ 0,\frac{1}{2}\,\frac{1}{2};\ \frac{1}{2},0,0;\ \frac{1}{2},\frac{1}{2},0$
4 (c): $\pm(x,\frac{1}{4},z);\ \pm(\frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z)$
8 (d): $\pm(x,y,z);\ \pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z);\ \pm(x,\frac{1}{2}-y,z);\ \pm(\frac{1}{2}+x,y,\frac{1}{2}-z)$

The eight strontium atoms in the unit cell have to be situated in positions 4 (*c*), *i.e.* in the mirror planes because of the short *b* axis. By comparing the interatomic vectors required by the strontium atoms thus situated with the highest peaks found in the Patterson sections $P(uv\frac{1}{2})$, $P(u\frac{1}{2}w)$, $P(u0w)$ and $P(\frac{1}{2}vw)$ the following atomic positions were obtained:

$$4\ \mathrm{Sr}(1)\ \text{in}\ 4(c):\quad x \approx 0.12,\quad y = 1/4,\quad z \approx 0.08$$
$$4\ \mathrm{Sr}(2)\ \text{in}\ 4(c):\quad x \approx 0.17,\quad y = 1/4,\quad z \approx 0.76$$

The electron density function was then calculated using the signs of $F(hkl)$ obtained from the strontium contributions only. (In this and all subsequent calculations the atomic scattering curves for un-ionized atoms were used. The real part of the anomalous dispersion correction according to Dauben and Templeton [13] was also applied.) The electron density section $\varrho(x,\frac{1}{4},z)$ thus obtained, clearly showed maxima corresponding to the strontium and also the phosphorus atoms which were found to occupy two fourfold positions 4(*c*). In addition to these maxima there were also minor peaks which could be interpreted as due to oxygen atoms. By calculations of the three-dimensional Patterson and electron density functions using all the observed reflections, all the oxygen atoms of the unit cell could be located with a moderate accuracy. They were found to occupy three sets of 4(*c*) and two sets of 8(*d*) positions.

A refinement of the coordinates so obtained was then performed by means of the method of least-squares. Starting values of the individual isotropic temperature factors were zero for all the atoms. Initially all 479 independent reflections measured were included in the calculations. After a few cycles, when the discrepancy factor

$$R = \sum||F_{\mathrm{obs}}(hkl)|-|F_{\mathrm{calc}}(hkl)||:\ \sum|F_{\mathrm{obs}})|,$$

was 0.115, nineteen strong, low-angle reflections were omitted as suffering from extinction. The refinement was considered to be complete when the parameter shifts in one cycle were less than 5 % of the standard deviations, at which stage the discrepancy factor was 0.088. Hughes' weighting function

Table 2. Weight analyses obtained in the final cycle of the least-squares refinement of α-$Sr_2P_2O_7$.

Interval $\sin\theta$	Number of independent reflections	$\overline{w\Delta^2}$	Interval F_{obs}	Number of independent reflections	$\overline{w\Delta^2}$
0.0000–0.4595	71	1.41	0.0– 18.2	45	0.52
0.4595–0.5790	62	1.04	18.2– 25.2	46	0.94
0.5790–0.6627	56	1.10	25.2– 32.6	45	0.87
0.6627–0.7294	47	1.14	32.6– 41.3	48	1.23
0.7294–0.7858	46	0.84	41.3– 50.9	46	0.97
0.7858–0.8350	44	0.87	50.9– 60.2	45	0.86
0.8350–0.8790	38	0.47	60.2– 68.9	46	1.25
0.8790–0.9190	40	0.61	68.9– 79.2	46	1.05
0.9190–0.9558	29	0.63	79.2– 98.9	47	0.78
0.9558–0.9900	27	1.88	98.9–131.4	46	1.52

Table 3. Observed and calculated structure factors. The five columns within each group contain the values h,k,l,F_c, and $k|F_o|$. The reflections deleted from the final cycles in the least-squares refinement are marked with an asterisk.

	h	k	l	F_c	$k\|F_o\|$
	0	0	2	-62	69
	0	0	4	75	80
*	0	0	6	-258	159
	0	0	8	-19	21
	0	0	10	-37	39
*	0	0	12	158	136
	0	0	14	-60	56
	0	0	16	-12	13
	1	0	1	72	-
	1	0	2	-24	25
	1	0	3	64	64
	1	0	4	-36	38
	1	0	5	-125	103
	1	0	6	112	106
	1	0	7	-70	69
	1	0	8	29	-
	1	0	9	51	47
	1	0	10	110	98
	1	0	11	16	14
	1	0	12	-61	59
	1	0	13	61	57
	1	0	14	3	-
	1	0	15	-26	25
	1	0	16	-79	70
	2	0	0	-86	94
	2	0	1	11	17
	2	0	2	-43	45
	2	0	3	-152	119
	2	0	4	-62	61
	2	0	5	20	22
	2	0	6	81	88
	2	0	7	15	17
	2	0	8	-47	54
	2	0	9	143	131
	2	0	10	55	55
	2	0	11	-26	25
	2	0	12	-3	-
	2	0	13	-13	13
	2	0	14	15	15
	2	0	15	-70	63
	2	0	16	21	21
	3	0	1	-147	113
	3	0	2	-33	29
	3	0	3	25	25
	3	0	4	-66	63
	3	0	5	34	33
	3	0	6	18	21
	3	0	7	130	120
	3	0	8	0	-
	3	0	9	-40	41
	3	0	10	-5	-
	3	0	11	-23	25
	3	0	12	-34	35
	3	0	13	-69	72
	3	0	14	-43	41
	3	0	15	70	62
	3	0	16	16	12
*	4	0	0	-167	166
*	4	0	1	-182	154
	4	0	2	8	-
	4	0	3	101	97
	4	0	4	36	35
	4	0	5	-129	113
*	4	0	6	173	180
	4	0	7	50	50
	4	0	8	-11	-
	4	0	9	-68	64
	4	0	10	-19	17
	4	0	11	61	64
	4	0	12	-112	109
	4	0	13	-62	61
	4	0	14	-39	38
	4	0	15	47	40
	5	0	1	-11	11
	5	0	2	61	60
	5	0	3	21	24
	5	0	4	7	-
	5	0	5	75	70
	5	0	6	-3	-
	5	0	7	-1	-
	5	0	8	26	27
	5	0	9	18	18
	5	0	10	-52	55
	5	0	11	-113	110
	5	0	12	78	79
	5	0	13	15	15
	5	0	14	5	-
	5	0	15	-34	24
	6	0	0	62	63
	6	0	1	27	27
	6	0	2	-90	82
	6	0	3	77	80
	6	0	4	45	43
	6	0	5	91	100
	6	0	6	-48	47
	6	0	7	-70	74
	6	0	8	44	46
	6	0	9	-8	-
	6	0	10	-34	40
	6	0	11	-2	-
	6	0	12	58	58
	6	0	13	34	32
	7	0	1	29	30
	7	0	2	83	87
	7	0	3	-16	16
	7	0	4	-12	18
	7	0	5	-63	67
	7	0	6	15	16
	7	0	7	-70	78
	7	0	8	-81	82
	7	0	9	43	39
	7	0	10	-33	32
	7	0	11	31	-
	7	0	12	6	-
	8	0	0	43	46
	8	0	1	57	62
	8	0	2	111	105
	8	0	3	-40	48
	8	0	4	-106	103
	8	0	5	71	69
	8	0	6	-17	15
	8	0	7	-105	105
	8	0	8	-83	88
	8	0	9	19	17
	8	0	10	74	68
	8	0	11	70	62
	8	0	12	27	21
	9	0	1	57	61
	9	0	2	-27	32
	9	0	3	24	26
	9	0	4	-37	40
	9	0	5	-47	49
	9	0	6	8	-
	9	0	7	-1	-
	9	0	8	-57	54
	9	0	9	-27	24
	9	0	10	8	-
	10	0	0	-19	-
	10	0	1	-101	93
	10	0	2	10	-
	10	0	3	3	-
	10	0	4	1	-
	10	0	5	-50	49
	10	0	6	3	-
	10	0	7	88	98
	10	0	8	8	-
	0	1	1	-30	28
*	0	1	3	-266	166
	0	1	5	55	71
	0	1	7	-116	112
	0	1	9	153	127
	0	1	11	-43	49
	0	1	13	-32	31
	0	1	15	-63	65
	1	1	1	2	-
	1	1	2	-7	-
	1	1	3	80	78
	1	1	4	-128	123
	1	1	5	33	33
	1	1	6	53	58
	1	1	7	57	66
	1	1	8	49	54
	1	1	9	-73	83
	1	1	10	23	26
	1	1	11	-18	17
	1	1	12	-26	29
	1	1	13	-97	103
	1	1	14	-22	22
	1	1	15	49	49
	1	1	16	-62	57
*	2	1	0	-226	141
	2	1	1	-116	104
	2	1	2	55	56
	2	1	3	78	76
	2	1	4	-32	39
	2	1	5	-25	30
*	2	1	6	198	184
	2	1	7	58	66
	2	1	8	-27	33
	2	1	9	20	25
	2	1	10	-11	15
	2	1	11	61	69
	2	1	12	-117	116
	2	1	13	-38	44
	2	1	14	17	15
	2	1	15	32	31
	2	1	16	2	-
	3	1	1	-101	95
	3	1	2	66	65
	3	1	3	-31	38
	3	1	4	74	75
	3	1	5	73	75
	3	1	6	-19	22
	3	1	7	34	40
	3	1	8	3	-
	3	1	9	-6	-
	3	1	10	-88	103
	3	1	11	-32	38
	3	1	12	94	85
	3	1	13	-15	17
	3	1	14	-17	19
	3	1	15	33	32
	3	1	16	61	51
	4	1	0	19	22
	4	1	1	20	24
	4	1	2	-110	103
*	4	1	3	162	138
	4	1	4	86	84
	4	1	5	4	-
	4	1	6	-89	86
	4	1	7	-68	73
	4	1	8	103	117
	4	1	9	-124	126
	4	1	10	-53	66
	4	1	11	-34	45
	4	1	12	42	45
	4	1	13	14	15
	4	1	14	-12	-
	4	1	15	90	76
	5	1	1	110	100
	5	1	2	64	65
	5	1	3	-41	46
	5	1	4	2	-
	5	1	5	-1	-
	5	1	6	-6	-
	5	1	7	-74	81
	5	1	8	-100	110
	5	1	9	14	16
	5	1	10	-34	39
	5	1	11	24	29
	5	1	12	-6	-
	5	1	13	44	48
	5	1	14	68	70
	6	1	0	72	68
	6	1	1	80	85
	6	1	2	119	124
	6	1	3	-74	77
	6	1	4	-45	55
	6	1	5	107	111
	6	1	6	-102	110
	6	1	7	-66	77
	6	1	8	-24	29
	6	1	9	84	89
	6	1	10	40	48
	6	1	11	-40	44
	6	1	12	23	26
	6	1	13	33	33
	7	1	1	32	40
	7	1	2	-34	41
	7	1	3	-34	37
	7	1	4	-53	57
	7	1	5	-47	53
	7	1	6	38	41
	7	1	7	3	-
	7	1	8	74	84
	7	1	9	-36	45
	7	1	10	58	62
	7	1	11	113	100
	7	1	12	6	-
	7	1	13	-26	21
	8	1	0	-98	99
	8	1	1	-103	107
	8	1	2	46	47
	8	1	3	-27	31
	8	1	4	-61	68
	8	1	5	-79	82
	8	1	6	15	16
	8	1	7	72	78
	8	1	8	-16	18
	8	1	9	16	22
	8	1	10	33	35
	8	1	11	49	52
	9	1	1	-27	33
	9	1	2	-52	58
	9	1	3	-16	19
	9	1	4	-24	26
	9	1	5	64	76
	9	1	6	-37	43
	9	1	7	17	19
	9	1	8	42	43
	9	1	9	9	-
	10	1	0	14	14
	10	1	1	-5	-
	10	1	2	-57	62
	10	1	3	0	-
	10	1	4	109	98
	10	1	5	-24	27
	10	1	6	10	-
	10	1	7	19	21
*	0	2	0	-306	161
	0	2	2	18	22
	0	2	4	-18	25
	0	2	6	110	103
	0	2	8	13	18
	0	2	10	12	16
	0	2	12	-108	102
	0	2	14	73	69
	0	2	16	18	18
	1	2	1	-24	17
	1	2	2	88	64
	1	2	3	-24	24
	1	2	4	80	75
	1	2	5	51	51
	1	2	6	-69	67
	1	2	7	60	58
	1	2	8	-70	65
	1	2	9	-85	96
	1	2	10	-119	120
	1	2	11	22	26
	1	2	12	30	32
	1	2	13	-64	68
	1	2	14	16	18
	1	2	15	52	50
	1	2	16	81	66
	2	2	0	90	79
	2	2	1	-47	46
	2	2	2	-24	28
*	2	2	3	271	183
	2	2	4	97	82
	2	2	5	-30	33
	2	2	6	-82	81
	2	2	7	15	22
	2	2	8	74	69
*	2	2	9	-193	173
	2	2	10	-65	75
	2	2	11	13	19
	2	2	12	2	-
	2	2	13	1	-
	2	2	14	-25	25
	2	2	15	86	74
	3	2	1	64	57
	3	2	2	65	56
	3	2	3	-33	33
	3	2	4	60	53
	3	2	5	12	19
	3	2	6	19	25
	3	2	7	-72	77
	3	2	8	-41	45
	3	2	9	52	57
	3	2	10	21	29
	3	2	11	6	-
	3	2	12	1	-
	3	2	13	42	45
	3	2	14	66	67
	3	2	15	-79	67
	4	2	0	59	56
	4	2	1	88	74
	4	2	2	-5	-
	4	2	3	-74	68
	4	2	4	-43	45
	4	2	5	55	54
	4	2	6	-101	89
	4	2	7	-10	12
	4	2	8	22	29
	4	2	9	60	70
	4	2	10	27	33
	4	2	11	-29	31
	4	2	12	81	79
	4	2	13	52	51
	4	2	14	24	25
	5	2	1	14	18
	5	2	2	-95	83
	5	2	3	-33	36
	5	2	4	-64	58
	5	2	5	-51	53
	5	2	6	2	-
	5	2	7	-19	17
	5	2	8	-14	12
	5	2	9	4	-
	5	2	10	91	95
	5	2	11	87	85
	5	2	12	-74	78
	5	2	13	5	-
	5	2	14	2	-
	6	2	0	-69	63
	6	2	1	-39	44
	6	2	2	147	107
	6	2	3	-99	97
	6	2	4	-92	82
	6	2	5	-101	96
	6	2	6	51	60
	6	2	7	70	77
	6	2	8	-84	90
	6	2	9	24	29
	6	2	10	50	54
	6	2	11	15	19
	6	2	12	-51	52
	6	2	13	-31	28
	7	2	1	8	16
	7	2	2	-74	71
	7	2	3	12	-
	7	2	4	26	34
	7	2	5	49	57
	7	2	6	-21	20
	7	2	7	23	28
	7	2	8	82	83

Table 3. Continued.

	7	2	9	-34	34
	7	2	10	16	20
	7	2	11	-36	35
	7	2	12	13	12
	8	2	0	-43	45
	8	2	1	-11	-
	8	2	2	-82	79
	8	2	3	41	47
	8	2	4	82	83
	8	2	5	-27	27
	8	2	6	18	19
	8	2	7	78	75
	8	2	8	62	59
	8	2	9	-25	24
	8	2	10	-64	58
	9	2	1	-67	64
	9	2	2	38	43
	9	2	3	-25	26
	9	2	4	65	69
	9	2	5	53	57
	9	2	6	-15	13
	9	2	7	13	12
	9	2	8	-52	50
	9	2	9	30	24
	10	2	0	11	-
	10	2	1	117	104
	10	2	2	-34	37
	10	2	3	-21	23
	10	2	4	16	17
	10	2	5	65	64
	10	2	6	12	17
	0	3	1	-14	19
	0	3	3	205	155
	0	3	5	-66	69
	0	3	7	108	101
	0	3	9	-130	119
	0	3	11	52	60
	0	3	13	27	23
	0	3	15	54	45
	1	3	1	22	17
	1	3	2	7	-
	1	3	3	-58	51
	1	3	4	87	76
	1	3	5	-37	38
	1	3	6	-39	39
	1	3	7	-66	67
	1	3	8	-43	38
	1	3	9	64	73
	1	3	10	-8	-
	1	3	11	16	-
	1	3	12	19	-
	1	3	13	96	91
	1	3	14	24	23
	1	3	15	-44	35
	2	3	1	81	71
*	2	3	0	178	115
	2	3	2	-23	26
	2	3	3	-54	53
	2	3	4	7	-
	2	3	5	14	-
*	2	3	6	-163	134
	2	3	7	-45	47
	2	3	8	8	-
	2	3	9	-22	-
	2	3	10	14	-
	2	3	11	-54	56
	2	3	12	109	107
	2	3	13	33	32
	2	3	14	-11	-
	3	3	1	85	75
	3	3	2	-45	47
	3	3	3	25	31
	3	3	4	-48	48
	3	3	5	-59	54
	3	3	6	18	-
	3	3	7	-40	37
	3	3	8	-10	-
	3	3	9	11	-
	3	3	10	72	74
	3	3	11	23	29
	3	3	12	-89	83
	3	3	13	21	-
	3	3	14	18	21
	4	3	0	-39	42
	4	3	1	1	-
	4	3	2	96	84
	4	3	3	-126	104
	4	2	4	-79	73
	4	3	5	9	-
	4	3	6	93	93
	4	3	7	56	66
	4	3	8	-92	99
	4	3	9	105	120
	4	3	10	52	63
	4	3	11	22	-
	4	3	12	-44	46
	4	3	13	-13	-
	5	3	1	-103	94
	5	3	2	-57	55
	5	3	3	30	30
	5	3	4	3	-
	5	3	5	9	-
	5	3	6	1	-
	5	3	7	72	81
	5	3	8	93	100
	5	3	9	-7	-
	5	3	10	26	27
	5	3	11	-27	29
	5	3	12	11	-
	5	3	13	-42	38
	6	3	0	-68	68
	6	3	1	-65	60
	6	3	2	-106	103
	6	3	3	47	51
	6	3	4	41	43
	6	3	5	-92	99
	6	3	6	94	100
	6	3	7	54	54
	6	3	8	25	30
	6	3	9	-66	70
	6	3	10	-36	33
	6	3	11	37	35
	6	3	12	-24	25
	7	3	1	-28	34
	7	3	2	21	17
	7	3	3	31	28
	7	3	4	40	43
	7	3	5	40	43
	7	3	6	-40	41
	7	3	7	-2	-
	7	3	8	-58	62
	7	3	9	30	33
	7	3	10	-50	47
	7	3	11	-100	87
	8	3	0	102	102
	8	3	1	94	97
	8	3	2	-43	50
	8	3	3	18	17
	8	3	4	59	67
	8	3	5	73	77
	8	3	6	-24	24
	8	3	7	-68	73
	8	3	8	14	12
	8	3	9	-10	-
	9	3	1	29	24
	9	3	2	51	60
	9	3	3	17	14
	9	3	4	25	26
	9	3	5	-65	69
	9	3	6	35	37
	9	3	7	-17	17
*	0	4	0	313	197
	0	4	2	-38	43
	0	4	4	46	56
*	0	4	6	-155	138
	0	4	8	-8	-
	0	4	10	-25	-
	0	4	12	121	107
	0	5	1	-17	-
*	0	5	3	-153	128
	0	5	5	21	30
	0	5	7	-68	67
	0	5	9	106	94
*	0	6	0	-178	148
	0	6	2	20	-
	0	6	4	-24	30

Table 4. The structure of α-$Sr_2P_2O_7$.

Space group: *Pnma*

Unit-cell dimensions:

$a = 8.9104 \pm 6$ Å
$b = 5.4035 \pm 4$ Å
$c = 13.1054 \pm 14$ Å
$V = 631.0$ Å^3

Cell content: 4 $Sr_2P_2O_7$

4 Sr_1, 4 Sr_2, 4 P_1, 4 P_2, 4 $O_1 - 4\,O_3$ in 7 $\times$ 4(*c*): $\pm(x,\frac{1}{4},z)$; $\pm(\frac{1}{2}+x,\frac{1}{4},\frac{1}{2},-z)$

8 O_4, 8 O_5 in 2 $\times$ 8(*d*): $\pm(x,y,z)$; $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z)$; $\pm(x,\frac{1}{2}-y,z)$; $\pm(\frac{1}{2}+x,y,\frac{1}{2}-z)$

Atomic parameters and isotropic temperature factors with estimated standard deviations ($\pm\,\sigma$)

Atom	x	y	z	B Å^2
Sr_1	0.1244 ± 2	$\frac{1}{4}$	0.0871 ± 1	0.42 ± 5
Sr_2	0.1724 ± 2	$\frac{1}{4}$	0.7604 ± 1	0.29 ± 5
P_1	0.0310 ± 5	$\frac{1}{4}$	0.3186 ± 3	0.18 ± 9
P_2	0.2756 ± 5	$\frac{1}{4}$	0.4653 ± 3	0.25 ± 9
O_1	0.3666 ± 16	$\frac{1}{4}$	0.1652 ± 11	0.98 ± 26
O_2	0.1047 ± 15	$\frac{1}{4}$	0.4317 ± 10	0.51 ± 23
O_3	0.2725 ± 16	$\frac{1}{4}$	0.5790 ± 10	0.78 ± 25
O_4	0.4167 ± 11	-0.0203 ± 26	0.7645 ± 7	0.98 ± 18
O_5	0.1486 ± 11	-0.0225 ± 29	0.9241 ± 6	1.02 ± 19

$w=1/h^2|F_{obs}, \min|^2$ for $|F_{obs}| \leq h|F_{obs}, \min|$ and $w=1/|F_{obs}|^2$ for $|F_{obs}| > |F_{obs}, \min|$ with $h=4.0$ was used in the refinement. A weight analysis obtained in the final cycle is given in Table 2. The values of $\overline{w\Delta^2}$

Table 5. Interatomic distances and bond angles in α-$Sr_2P_2O_7$.

A. P_2O_7-group. Distances and standard deviations ($\pm\sigma$) in Å. Angles in degrees. (Standard deviations ($\pm\sigma$) of angles $\sim\pm 0.5°$)

P(1)− P(2)	[P(2)−P(1)] = 2.907 ± 6
P(1)− O(2)	[O(2)−P(1)] = 1.614 ± 13
P(2)− O(2)	[O(2)−P(2)] = 1.585 ± 14
P(1)− O(1)	[O(1)−P(1)] = 1.482 ± 15
P(1)−2O(4)	[O(4)−P(1)] = 1.500 ± 14
P(2)− O(3)	[O(3)−P(2)] = 1.489 ± 13
P(2)−2O(5)	[O(5)−P(2)] = 1.508 ± 15
O(1)−2O(4)	[O(4)−O(1)] = 2.473 ± 17
O(1)− O(2)	[O(2)−O(1)] = 2.472 ± 19
O(4)− O(4)	[O(4)−O(4)] = 2.470 ± 31
O(3)−2O(5)	[O(5)−O(3)] = 2.478 ± 16
O(3)− O(2)	[O(2)−O(3)] = 2.445 ± 18
O(5)− O(5)	[O(5)−O(5)] = 2.470 ± 34

P(1)−O(2)−P(2) = 130.7	
O(1)−P(1)−O(2) = 105.9	O(3)−P(2)−O(2) = 105.3
O(1)−P(1)−O(4) = 2 × 112.1	O(3)−P(2)−O(5) = 2 × 111.6
O(4)−P(1)−O(4) = 110.9	O(5)−P(2)−O(5) = 110.0
O(4)−P(1)−O(2) = 2 × 107.8	O(5)−P(2)−O(2) = 2 × 109.1

B. SrO_9 − groups

Sr(1)−O(1)	= 2.384 ± 14
Sr(1)−O(5)	[Sr(1)−O($\bar{5}$)] = 2.602 ± 12
Sr(1)−O(4)	[Sr(1)−O(4′)] = 2.656 ± 11
Sr(1)−O(5′)	[Sr(1)−O($\bar{5}$′)] = 2.732 ± 12
Sr(1)−O(3)	[Sr(1)−O(3′)] = 2.856 ± 14
Sr(1)−O(3)	= 3.817 ± 14
O(1) −Sr(1)−O(3)	[O(1) −Sr(1)−O($\underline{3}$′)] = 74.1
O(1) −Sr(1)−O(5)	[O(1) −Sr(1)−O($\bar{5}$)] = 106.1
O(1) −Sr(1)−O(5′)	[O(1) −Sr(1)−O($\bar{5}$′)] = 145.9
O(1) −Sr(1)−O(4)	[O(1) −Sr(1)−O(4′)] = 75.6
O(3) −Sr(1)−O(3′)	= 142.2
O(3) −Sr(1)−O(5)	[O(3′)−Sr(1)−O($\bar{5}$)] = 53.8
O(3) −Sr(1)−O(5′)	[O(3′)−Sr(1)−O($\bar{5}$′)] = 81.8
O(3) −Sr(1)−O(4)	[O(3′)−Sr(1)−O(4′)] = 68.8
O(4) −Sr(1)−O(4′)	= 55.4
O(4) −Sr(1)−O(5)	[O(4′)−Sr(1)−O($\bar{5}$)] = 117.9
O(4) −Sr(1)−O(5′)	[O(4′)−Sr(1)−O($\bar{5}$′)] = 97.7
O(5) −Sr(1)−O($\bar{5}$)	= 68.6
O(5′)−Sr(1)−O($\bar{5}$′)	= 53.8
O(5) −Sr(1)−O($\underline{5}$′)	[O($\bar{5}$) −Sr(1)−O($\bar{5}$′)] = 77.0
O(5) −Sr(1)−O($\bar{5}$′)	[O($\bar{5}$) −Sr(1)−O(5′)]= 106.5
O(4) −O(5′)−O(5)	[O(4′)−O($\bar{5}$′)−O($\bar{5}$)] = 90.0
Sr(2)−O(3)	= 2.539 ± 13
Sr(2)−O(5)	[Sr(2)−O($\underline{5}$′)] = 2.607 ± 12
Sr(2)−O(4)	[Sr(2)−O($\underline{\bar{4}}$)] = 2.627 ± 12
Sr(2)−O(4′)	[Sr(2)−O($\bar{4}$′)] = 2.727 ± 12
Sr(2)−O(1)	[Sr(2)−O(1′)] = 2.997 ± 6
Sr(2)−2O(2)	= 4.029 ± 10

Table 5. Continued.

O(3) –Sr(2)–O(1)	[O(3) –Sr(2)–O(1′)] =	69.5
O(3) –Sr(2)–O(4′)	[O(3) –Sr(2)–O($\bar{4}$′)] =	100.5
O(3) –Sr(2)–O(5)	[O(3) –Sr(2)–O(5′)] =	143.0
O(3) –Sr(2)–O(4)	[O(3) –Sr(2)–O($\bar{4}$)] =	74.2
O(1) –Sr(2)–O(1′)	=	128.7
O(1) –Sr(2)–O(4′)	[O(1′)–Sr(2)–O($\bar{4}$′)] =	51.0
O(1) –Sr(2)–O(5)	[O(1′)–Sr(2)–O(5′)] =	80.0
O(1) –Sr(2)–O(4)	[O(1′)–Sr(2)–O($\bar{4}$)] =	66.4
O(4) –Sr(2)–O($\bar{4}$)	=	67.9
O(4) –Sr(2)–O(4′)	[O($\bar{4}$) –Sr(2)–O($\bar{4}$′)] =	113.2
O(4) –Sr(2)–O(5)	[O($\bar{4}$) –Sr(2)–O(5′)] =	74.7
O(4′)–Sr(2)–O($\bar{4}$′)	=	65.1
O(5) –Sr(2)–O(5′)	=	68.5
O(4′)–Sr(2)–O(5)	[O($\bar{4}$′)–Sr(2)–O(5′)] =	74.2
O(4′)–Sr(2)–O(5′)	[O($\bar{4}$′)–Sr(2)–O(5)] =	109.4
O(4) –O(5)–O(4′)	[O($\bar{4}$)–O(5′)–O($\bar{4}$′)] =	88.8

deviate as much from unity as could be expected for the photographically registered set of data. A list of the observed and calculated structure factors is given in Table 3. The position parameters and isotropic temperature factors of all the atoms and the standard deviations are listed in Table 4. The calculated interatomic distances and bond angles are given in Table 5. All distances are within the normal range and thus support the correctness of the coordinates arrived at in the last cycle.

The result obtained from the refinement was further confirmed by a three-dimensional electron density difference which contained very small residual

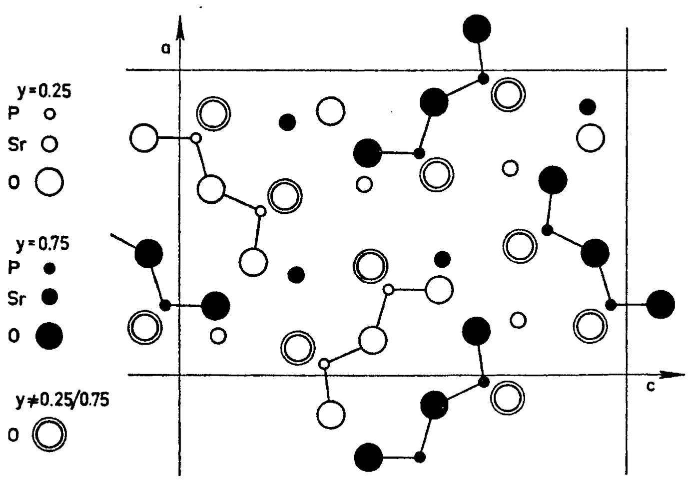


Fig. 1. Projection of the structure along the *b* axis. The concentric circles represent pairs of oxygens related by the mirror planes.

maxima and minima. The highest maximum had a magnitude of about 20 % of the height of the oxygen peaks in the F_{obs} syntheses.

Attempts to improve the structure by introducing anisotropic temperature factors for the strontium atoms or by lowering the symmetry to $Pn2_1a$ were unsuccessful. This is taken as further support of the adequacy of the description of the atomic arrangement derived in this study (*cf.* Table 4).

DESCRIPTION AND DISCUSSION

The crystal structure of α-$Sr_2P_2O_7$ contains diphosphate ions linked by strontium ions to form a three-dimensional network (Fig. 1). Each strontium atom coordinates nine terminal oxygens from five different diphosphate groups. The two crystallographically different SrO_9 polyhedra are very similar. They may be visualized as being derived from a cube. Six oxygen atoms are close to six corners of the cube, which define three edges in the y direction of the structure. The remaining three oxygens are very roughly arranged along the fourth parallel cube edge as illustrated in Fig. 2. The strontium-oxygen distances (*cf.* Table 5) average 2.70 Å which may be compared with the values found for SrO (2.55 Å, six-coordination),[14] $SrCl_2 \cdot 6H_2O$ (2.75 Å, nine-coordination)[15] and $Sr_3(PO_4)_2$ (2.67 Å and 2.87 Å for ten- and twelve-coordination, respectively).[16]

The configuration of the diphosphate group is of the eclipsed type. The distortion is less than was found by Webb[9] for the β-modification of $Ca_2P_2O_7$. While in the latter the P_2O_7 groups are asymmetric the anions of α-$Sr_2P_2O_7$ possess a mirror plane symmetry. The deviations from *mm* symmetry are

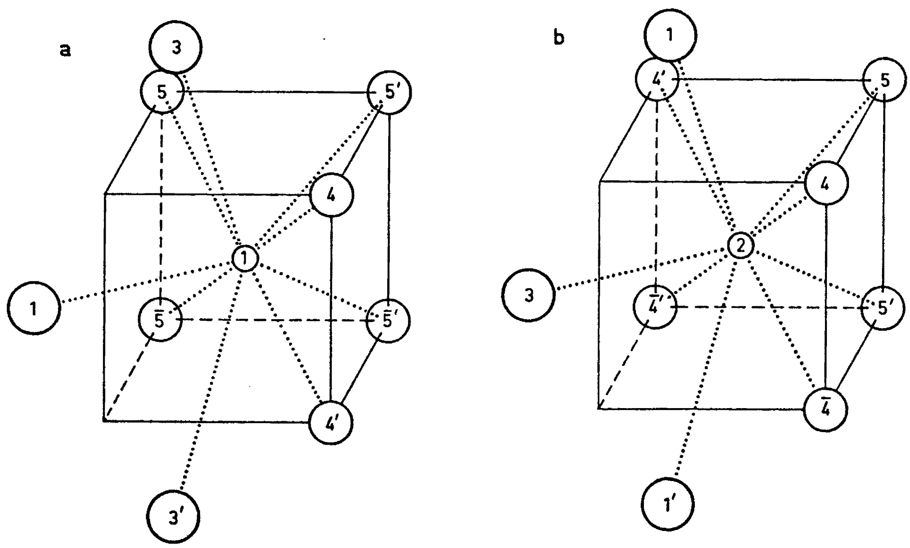
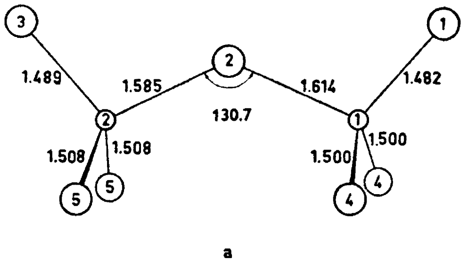


Fig. 2. Coordination figures around the strontium atoms.



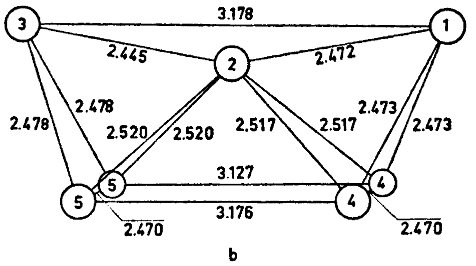


Fig. 3a. Interatomic distances and P—O—P angle in the diphosphate group.

Fig. 3b. Oxygen to oxygen distances in the diphosphate group.

illustrated in Fig. 3. The P—O and O—O distances and the interbond angles all have normal values, close to those found by Webb [9] for β-$Ca_2P_2O_7$ and also by McDonald and Cruickshank [17] for the staggered P_2O_7 ion of $Na_4P_2O_7 \cdot 10H_2O$.

The coordination of metal atoms around the diphosphate anions is markedly different in the α- and β-modifications. In β-$Ca_2P_2O_7$, the two different P_2O_7 groups coordinate eleven and ten calcium atoms, respectively, whereas both anions are surrounded by ten Sr atoms in α-$Sr_2P_2O_7$. This deviation is associated with the different roles of the bridge oxygens in the two structures. These oxygen atoms are in contact with the metal atom in the β structure but not in the α structure.

Addendum. After the termination of this study an article appeared describing an investigation of α-$Sr_2P_2O_7$ by Grenier and Masse,[18] who report structural parameters close to those found in the present work. The atomic arrangement given by Grenier and Masse, however, lacks a center of symmetry. The centrosymmetric structure derived by the present authors is in concordance with the EPR findings reported by Calvo [19] for Mn^{2+} doped α-$Sr_2P_2O_7$ crystals. The structure found by Calvo [19] for α-$Ca_2P_2O_7$ is essentially of the same type as α-$Sr_2P_2O_7$ but has monoclinic symmetry. The metal-oxygen coordination is also somewhat different.

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