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The Crystal Structure of $NaMe_2^{IV}(PO_4)_3$; Me^{IV} = Ge, Ti, Zr

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The crystal structure of $NaZr_2(PO_4)_3$, a representative of an extensive group of isomorphous mixed phosphates containing alkali metals and germanium, titanium, zirconium or hafnium, has been determined from three-dimensional X-ray data. The space group is $R\bar{3}/c$ and the dimensions of the hexagonal unit cell for the three members of the series studied by the present authors are

$NaZr_2(PO_4)_3$	$a = 8.8043 \pm 2$ Å	$c = 22.7585 \pm 9$ Å
$NaTi_2(PO_4)_3$	$a = 8.4924 \pm 5$ Å	$c = 21.7788 \pm 15$ Å
$NaGe_2(PO_4)_3$	$a = 8.1123 \pm 4$ Å	$c = 21.5133 \pm 11$ Å

The crystals are built up of MeO_6 octahedra and PO_4 tetrahedra which are linked by corners to form a three-dimensional network. The sodium atoms are octahedrally surrounded by oxygen atoms. A discussion of the structure is given.

Studies on metal phosphates and in particular on transition metal phosphates have been conducted at this Institute for several years.[1] In connection with an investigation now in progress of the detailed superstructure of ZrP_2O_7 [2] it was found of interest to analyze the atomic arrangement of zirconium phosphates less complex in structure. The mixed phosphate $NaZr_2(PO_4)_3$ was selected for such an investigation.

Within the present study the compounds $NaZr_2(PO_4)_3$, $NaTi_2(PO_4)_3$, and $NaGe_2(PO_4)_3$ have been synthesized and found to be isomorphous. Sljukić *et al.* have prepared mixed zirconium and hafnium phosphates of all the alkali metals $AMe_2^{IV}(PO_4)_3$.[3] The X-ray data reported by these authors suggest that all these compounds are isostructural.

EXPERIMENTAL

Preparations of the crystals. A mixture of sodium metaphosphate (12.5 g, British Drug Houses, *p.a.*) and metal dioxide (1.2 g ZrO_2, Schering-Kahlbaum, *p.a.*, 1.0 g GeO_2, Fairmont, *p.a.* or 0.75 g TiO_2, Merck, *p.a.*) was heated in a platinum crucible for 24 h at 1200°C.[4] The products thus obtained were crystalline and gave good X-ray powder patterns but did not contain single crystals well suited for collecting extensive X-ray data. Good crystals could, however, be obtained after tempering in platinum crucible for several weeks at 1100°C, or according to a method given by Matković *et al.*[5] by crystal-

Table 1. X-Ray powder data of $NaGe_2(PO_4)_3$. Cu$K\alpha_1$ radiation. (λCu$K\alpha = 1.54056$).

h k l	Obs.	Calc.	Delta	D_{obs}	I_o
0 1 2	1697	1715	−18	5.91	s
1 0 4	3237	3253	−16	4.28	vs
1 1 0	3601	3606	−5	4.06	vs
1 1 3	4752	4760	−8	3.53	vs
0 2 4	6835	6860	−25	2.95	vs
1 1 6	8201	8221	−20	2.69	vs
2 1 1	8537	8543	−6	2.64	s
0 1 8	9391	9407	−16	2.51	m
2 1 4	10450	10466	−16	2.38	s
3 0 0	10801	10819	−18	2.34	vs
2 0 8	13009	13013	−4	2.14	m
1 1 9	13971	13990	−19	2.06	m
2 2 0	14434	14425	9	2.03	m
2 1 7	14694	14696	−2	2.01	w
3 0 6	15429	15434	−5	1.96	m
2 2 3	15569	15579	−10	1.95	w
3 1 2	16145	16140	5	1.92	m
1 2 8	16613	16619	−6	1.89	s
0 2 10	17617	17628	−11	1.84	s
0 0 12	18469	18461	8	1.79	m
2 2 6	19041	19040	1	1.77	s
0 4 2	19744	19747	−3	1.73	s
2 1 10	21229	21235	−6	1.67	vs
1 3 7	21883	21909	−26	1.65	m
3 2 1	22969	22968	1	1.61	w
3 1 8	23828	23832	−4	1.58	s
3 2 4	24892	24891	1	1.54	s
4 1 0	25250	25244	6	1.53	s
2 3 5	26059	26045	14	1.51	vw
0 1 14	26323	26329	−6	1.50	m
0 4 8	27416	27438	−22	1.47	m
1 3 10	28450	28447	3	1.44	s
3 0 12	29272	29280	−8	1.42	w
2 3 8	30989	31040	−51	1.38	w
3 1 11	31134	31139	−5	1.38	vw
4 0 10 0 5 4	32065	32054	11	1.36	s
1 1 15 3 3 0	32446	32451	−5	1.35	s
1 2 14	33558	33542	16	1.33	m
3 2 10 2 4 4	35684	35660	24	1.29	m
5 1 4	39350	39317	33	1.23	m
3 1 14	40767	40754	13	1.21	w
2 1 16	41235	41234	1	1.20	vw
0 0 18	41550	41536	14	1.19	w
6 0 0	43270	43270	0	1.17	m

lization from a melt of boric acid. The crystals thus obtained were found to consist of colourless, rectangular prisms.

Chemical analysis. A sample of the zirconium compound was fused with sodium potassium carbonate in a platinum crucible. After leaching with boiling water the amount of *phosphorus* in the solution was determined gravimetrically as $Mg_2P_2O_7$.[6] The residue, insoluble in water, was in turn fused with sodium hydrogen sulphate in a platinum

crucible. After dissolving in hot water the amount of *zirconium* was determined gravimetrically as ZrO_2.[6] The following data were obtained:

	Calc. for $NaZr_2(PO_4)_3$	Obs.
ZrO_2	50.26	48.5 weight %
P_2O_5	43.43	45.1
Na_2O	6.31	6.4 (residue)

X-Ray data collecting and treatment. The powder patterns of the three mixed sodium-transition metal phosphates prepared within this study could all be interpreted assuming a hexagonal (rhombohedral) unit cell. Accurate values of the cell dimensions were cal-

Table 2. X-Ray powder data of $NaTi_2(PO_4)_3$. Cu$K\alpha_1$ radiation. (λCu$K\alpha_1$=1.54056).

h k l	Obs.	Calc.	Delta	D_{obs}	I_o
0 1 2	1606	1597	9	6.08	s
1 0 4	3099	3098	1	4.38	vs
1 1 0	3295	3291	4	4.24	vs
1 1 3	4420	4417	3	3.66	vs
2 0 2	4895	4888	7	3.48	vw
0 2 4	6388	6389	−1	3.05	vs
1 1 6 2 1 1	7803	7804	−1	2.76	vs
2 1 4	9700	9680	20	2.47	s
3 0 0	9883	9872	11	2.45	m
2 0 8	12383	12394	−11	2.19	m
1 1 9	13403	13423	−20	2.10	w
2 1 7	13810	13808	2	2.07	vw
2 2 3	14276	14289	−13	2.04	w
3 0 6 1 3 1	14364	14376	−12	2.03	m
1 2 8	15665	15684	−19	1.95	s
1 3 4	16256	16262	−6	1.91	s
0 2 10	16908	16897	11	1.87	s
2 2 6	17684	17666	18	1.83	m
2 1 10	20184	20188	−4	1.71	s
1 3 7	20401	20390	11	1.71	m
3 1 8	22278	22266	12	1.63	s
3 2 4	22838	22843	−5	1.61	s
4 1 0	23027	23035	−8	1.61	m
4 1 3	24175	24161	14	1.57	m
0 4 8 0 1 14	25582	25557	25	1.52	s
1 3 10	26793	26769	24	1.49	s
4 1 6	27587	27539	48	1.47	m
3 0 12	27898	27886	12	1.46	w
5 0 12 2 0 14	28914	28906	8	1.43	s
3 1 11 0 5 4	29443	29425	18	1.42	m
1 2 14	32188	32196	−8	1.36	m
3 3 6 5 1 1	34163	34130	33	1.32	w
1 5 5	37106	37132	−26	1.26	w
4 2 8 3 1 14	38764	38778	−14	1.24	w
6 0 0	39497	39489	8	1.23	m

Table 3. X-Ray powder data of $NaZr_2(PO_4)_3$. Cu$K\alpha_1$ radiation. (λCu$K\alpha$=1.54056).

h k l	Obs.	Calc.	Delta	D_{obs}	I_o
0 1 2	1488	1479	9	6.31	s
1 0 4	2862	2853	9	4.55	vs
1 1 0	3073	3062	11	4.39	vs
1 1 3	4104	4093	11	3.80	vs
0 2 4	5921	5915	6	3.17	vs
1 1 6	7194	7186	8	2.87	vs
2 1 1	7262	7259	3	2.86	s
0 1 8	8353	8352	1	2.67	m
2 1 4	8983	8977	6	2.57	s
3 0 0	9188	9185	3	2.54	vs
2 0 8	11411	11414	−3	2.28	m
2 2 0	12260	12247	13	2.20	m
1 1 9	12338	12341	−3	2.19	m
1 0 10	12478	12476	2	2.18	m
2 1 7	12753	12757	−4	2.16	w
3 0 6	13305	13309	−4	2.11	s
3 1 2	13711	13726	−15	2.08	w
1 2 8	14487	14476	11	2.02	s
1 3 4	15118	15100	18	1.98	s
0 2 10	15528	15538	−10	1.95	s
3 1 5	16122	16131	−9	1.92	w
2 2 6	16372	16371	1	1.90	vs
0 0 12	16497	16496	1	1.90	w
0 4 2	16772	16787	−15	1.88	m
4 0 4	18160	18162	−2	1.81	w
2 1 10	18615	18599	16	1.79	vs
1 3 7	18889	18881	8	1.77	m
3 2 1	19491	19506	−15	1.74	vvw
3 1 8	20603	20599	4	1.70	s
3 2 4	21229	21224	5	1.67	s
4 1 0	21470	21432	38	1.66	vs
2 2 9	21522	21526	−4	1.66	vw
2 3 5	22287	22255	32	1.63	m
4 1 3	22425	22463	−38	1.63	m
0 1 14	23492	23473	19	1.59	m
0 4 8	23657	23661	−4	1.58	m
1 3 10	24724	24723	1	1.55	s
3 2 7	25000	25004	−4	1.54	vw
4 1 6	25560	25556	4	1.52	s
3 0 12	25686	25681	5	1.52	w
2 0 14	26538	26535	3	1.50	s
2 3 8	26726	26722	4	1.49	w
3 1 11	27132	27129	3	1.48	vw
0 5 4	27344	27347	−3	1.47	m
3 3 0	27550	27556	−6	1.47	m
4 0 10	27791	27785	6	1.46	m
3 3 3	28580	28587	−7	1.44	vw
1 1 15	28846	28836	10	1.43	m
1 2 14	29603	29597	6	1.42	s
1 0 16	30300	30346	−46	1.40	m
4 1 9	30706	30711	−5	1.39	vw
3 2 10	30851	30846	5	1 39	m
3 3 6	31675	31680	−5	1.37	m
5 1 1	31744	31752	−8	1.37	w
1 3 13	32603	32627	−24	1.35	vw
5 1 4	33481	33471	10	1.33	s

Table 3. Continued.

2 4 7	34186	34189	−3	1.32	vvw
1 5 5	34506	34502	4	1.31	vw
3 1 14	35726	35720	6	1.29	m
2 1 16	36463	36470	−7	1.28	w
6 0 0	36731	36741	−10	1.27	m
0 0 18	37104	37116	−12	1.26	w
5 1 7	37245	37251	−6	1.26	w
2 5 2	38216	38220	−4	1.25	w
4 3 4	39613	39594	19	1.22	w
5 2 0	39797	39803	−6	1.22	m
2 4 10	40042	40032	10	1.22	m
6 0 6	40872	40865	7	1.20	w
2 3 14	41858	41844	14	1.19	m
5 1 10	43102	43093	9	1.17	vw
5 2 6	43925	43927	−2	1.16	m
2 5 8	45103	45093	10	1.15	m
1 5 11	45502	45499	3	1.14	w
1 6 4	45710	45718	−8	1.14	w
3 0 18	46319	46301	18	1.13	w
4 1 15	47213	47207	6	1.12	w
3 2 16	48707	48717	−10	1.10	w
4 4 0	48970	48988	−18	1.10	w

culated from Guinier-Hägg powder photographs taken with strictly monochromatic Cu$K\alpha_1$ radiation ($\lambda = 1.54056$ Å) with potassium chloride ($a = 6.29228$ Å) [7] added to the specimens as an internal standard. The hexagonal unit cell dimensions refined by the method of least-squares are (25°C):

$NaZr_2(PO_4)_2$	$a_H =$	8.8043 ± 2 Å
	$c_H =$	22.7585 ± 9 Å
$NaTi_2(PO_4)_2$	$a_H =$	8.4924 ± 5 Å
	$c_H =$	21.7788 ± 15 Å
$NaGe_2(PO_4)_3$	$a_H =$	8.1123 ± 4 Å
	$c_H =$	21.5133 ± 11 Å

The value of 3.20 g/cm³ for the density of $NaZr_2(PO_4)_3$, found from the apparent loss of weight in benzene, corresponds to six formula units in the unit cell ($\varrho_{calc} = 3.18$ g/cm³).

Crystals of all the three compounds were studied by taking rotation and Weissenberg photographs which confirmed the presence of strict isomorphism. Complete three-dimensional data were collected for $NaZr_2(PO_4)_3$ using CuK radiation. The crystal used was a rectangular prism measuring 1.07×10^{-4} mm³. Multiple film technique was used for the Weissenberg photographs. The relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times. A correction for absorption was included in the computation of the F^2 values. (The linear absorption coefficient $\mu = 234.1$ cm^{-1}).[8]

In the first stages of this structural study the computational work was performed using the computers Facit EDB and TRASK. The limited capacity of these machines made it necessary to conduct the structural refinement with the unit cell described as monoclinic ($C2/c$). All the final calculations, however, made use of the computer CD 3600. This allowed the final structural refinement to be performed with the hexagonal description of the structure.

STRUCTURE DETERMINATION

The Weissenberg data, which confirmed the hexagonal (rhombohedral) symmetry of the crystal, showed the Laue symmetry to be $\bar{3}m$. The reflections systematically absent are $hkil$ with $-h+k+l \neq 3n$ and $h\bar{h}0l$ with $l \neq 2n$.

This is characteristic of the space groups $R\bar{3}c$ (No. 167) and $R3c$ (No. 161). A test for piezoelectricity gave no effect. The structural investigation was thus undertaken assuming the atomic arrangement to be in accordance with the higher symmetry $R\bar{3}c$.

In the space group $R\bar{3}c$ (hexagonal axes) the following point positions exist:

(000; $\frac{1}{3},\frac{2}{3},\frac{2}{3}$; $\frac{2}{3},\frac{1}{3},\frac{1}{3}$)+
6(a) (0,0,$\frac{1}{4}$; 0,0,$\frac{3}{4}$)
6(b) (0,0,0; 0,0,$\frac{1}{2}$)
12(c)±(0,0,z; 0,0,$\frac{1}{2}+z$)
18(d) ($\frac{1}{2}$,0,0; 0,$\frac{1}{2}$,0; $\frac{1}{2},\frac{1}{2}$,0; $\frac{1}{2}$,0,$\frac{1}{2}$; 0,$\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$)
18(e)±(x,0,$\frac{1}{4}$; 0,x,$\frac{1}{4}$; $\bar{x},\bar{x},\frac{1}{4}$)
36(f)±(x,y,z; $\bar{y},x-y,z$; $y-x,\bar{x},z$; $\bar{y},\bar{x},\frac{1}{2}+z$; $x,x-y,\frac{1}{2}+z$; $y-x,y,\frac{1}{2}+z$)

From calculations of the Patterson projection $P(pvw)$ and section $P(0vw)$ and subsequent calculations of the electron density distributions in $\varrho(pyz)$ and $\varrho(0yz)$ the positions of the twelve zirconium, the eighteen phosphorus, and the six sodium atoms — found to be situated in 12(c), 18(e), and 6(b) — in the unit cell could easily be determined with moderate accuracy. Starting from these data it was possible to make three-dimensional electron density calculations and find the positions of the 72 oxygen atoms situated in 2×36 (f) point positions. At the electron density calculations and subsequent refinement atomic scattering curves for unionized atoms were used. The real part of the anomalous dispersion correction [9] was applied to the scattering curves.

A refinement of the coordinates so obtained was then performed by means of the least-squares method. The starting values of the individual isotropic temperature factors used in the program, were zero for all of the atoms. Initially all 296 of the independent reflections measured were included in the calculations, but after a few cycles, eight strong, low-angle reflections were omitted as suffering from extinction. The refinement was considered as

Table 4. Weight analyses obtained in the final cycle of the least-squares refinement of $NaZr_2(PO_4)_3$.

Interval sin θ	Number of independent reflections	$\overline{w\,\Delta^2}$	Interval F_{obs}	Number of independent reflections	$\overline{w\,\Delta^2}$
0.0000—0.4642	30	1.36	0.0— 23.1	28	0.14
0.4642—0.5848	36	0.98	23.1— 31.3	29	0.47
0.5848—0.6694	30	0.58	31.3— 52.2	29	1.22
0.6694—0.7368	35	0.80	52.2— 63.4	29	1.06
0.7368—0.7937	27	1.02	63.4— 82.5	29	1.61
0.7937—0.8434	22	0.47	82.5— 99.6	29	1.28
0.8434—0.8879	36	0.85	99.6—115.5	28	1.14
0.8879—0.9283	23	1.13	115.5—143.3	30	1.18
0.9283—0.9655	30	0.97	143.3—192.1	28	0.61
0.9655—1.0000	19	1.84	192.1—345.3	29	1.29

Table 5. 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.

	0	0	6	0	-		1	6	10	-157	160		3	2	7	-70	80		5	1	10	-71	64
*	0	0	12	235	198		1	6	13	11	-		3	2	10	-192	180		5	1	13	-68	56
*	0	0	18	-378	298		1	6	16	-50	69		3	2	13	68	73		5	1	16	-99	98
	0	0	24	-54	56		1	6	19	-3	-		3	2	16	-105	102		5	1	19	55	65
	0	1	2	-137	150		1	7	0	151	137		3	2	19	-37	29		5	1	22	71	83
	0	1	8	119	119		1	7	3	30	-		3	2	22	62	70		5	2	0	192	201
	0	1	14	269	251		1	7	6	123	125		3	2	25	28	31		5	2	3	-28	28
	0	1	20	212	204		1	7	9	4	-		3	3	0	270	303		5	2	6	186	182
	0	1	26	40	39		1	7	12	13	-		3	3	3	-72	87		5	2	9	18	-
*	0	2	4	-377	329		1	7	15	20	21		3	3	6	140	152		5	2	12	-2	-
	0	2	10	-253	256		1	7	18	-60	50		3	3	9	-6	-		5	2	15	-25	37
	0	2	16	-122	113		1	8	2	-9	-		3	3	12	52	56		5	2	18	-66	67
	0	2	22	79	87		1	8	5	-38	32		3	3	15	-38	52		5	2	21	8	8
	0	2	28	92	144		1	8	8	62	65		3	3	18	-108	106		5	3	2	-20	29
*	0	3	0	426	363		1	8	11	33	32		3	3	21	26	25		5	3	5	35	28
	0	3	6	206	204		1	9	1	-2	-		3	3	24	-84	91		5	3	8	105	89
	0	3	12	107	125		1	9	4	-92	80		3	4	2	-90	107		5	3	11	-25	28
	0	3	18	-153	157		2	0	2	39	47		3	4	5	-28	30		5	3	14	130	121
	0	3	24	-95	123		2	0	8	187	193		3	4	8	198	205		5	3	17	25	28
	0	4	2	-193	270		2	0	14	325	338		3	4	11	47	65		5	3	20	85	63
	0	4	8	218	246		2	0	20	134	129		3	4	14	124	103		5	4	1	-36	27
	0	4	14	132	124		2	0	26	46	65		3	4	17	12	-		5	4	4	-158	167
	0	4	20	208	191		2	1	1	-146	209		3	4	20	134	153		5	4	7	32	26
	0	4	26	2	-		2	1	4	-224	242		3	5	1	35	31		5	4	10	-88	87
	0	5	4	-255	265		2	1	7	-73	68		3	5	4	121	121		5	4	13	-35	-
	0	5	10	-53	64		2	1	10	-327	344		3	5	7	-22	30		5	4	16	-61	61
	0	5	16	-92	109		2	1	13	13	-		3	5	10	-152	156		5	5	0	152	147
	0	5	22	69	95		2	1	16	-98	87		3	5	13	23	-		5	5	3	25	25
	0	6	0	368	367		2	1	19	43	-		3	5	16	-64	78		5	5	6	112	117
	0	6	6	104	128		2	1	22	47	55		3	5	19	-17	17		5	5	9	-21	23
	0	6	12	57	54		2	1	25	7	-		3	6	0	146	134		5	5	12	-15	30
	0	6	18	-152	145		2	2	0	163	152		3	6	3	7	-		5	6	2	-15	13
	0	7	2	-109	121		2	2	3	90	95		3	6	6	105	97		5	6	5	27	20
	0	7	8	177	179		2	2	6	345	278		3	6	9	23	21		6	0	6	94	108
	0	7	14	62	71		2	2	9	74	79		3	6	12	-5	-		6	0	12	51	58
	0	7	20	136	108		2	2	12	-45	37		3	6	15	-9	-		6	0	18	-151	169
	0	8	4	-147	153		2	2	15	18	-		3	7	2	-63	76		6	1	2	-53	57
	0	8	10	-126	115		2	2	18	-37	35		3	7	5	9	-		6	1	5	17	-
	0	8	16	-48	54		2	2	21	-5	-		3	7	8	98	95		6	1	8	115	102
	0	9	0	115	115		2	2	24	-151	182		3	7	11	-20	20		6	1	11	-32	-
	0	9	6	112	115		2	2	27	-27	-		4	0	4	-94	109		6	1	14	139	143
*	1	0	4	-322	226		2	3	2	12	-		4	0	10	-258	261		6	1	17	8	-
	1	0	10	-155	147		2	3	5	78	74		4	0	16	-4	-		6	1	20	113	101
	1	0	16	-80	74		2	3	8	134	139		4	0	22	-2	-		6	2	1	35	29
	1	0	22	61	65		2	3	11	-49	55		4	1	3	105	105		6	2	4	-188	181
	1	0	28	83	104		2	3	14	244	245		4	1	6	225	252		6	2	7	-73	57
*	1	1	0	380	301		2	3	17	26	-		4	1	9	-71	84		6	2	10	-117	120
*	1	1	3	299	236		2	3	20	107	103		4	1	12	-2	-		6	2	13	51	46
*	1	1	6	378	309		2	3	23	-26	-		4	1	15	47	52		6	2	16	-82	84
	1	1	9	-118	123		2	4	1	9	-		4	1	18	-124	121		6	2	19	-24	21
	1	1	12	-25	30		2	4	4	-178	188		4	1	21	-45	60		6	3	3	-13	-
	1	1	15	138	165		2	4	7	46	51		4	1	24	-118	143		6	3	6	126	126
	1	1	18	-90	85		2	4	10	-170	186		4	2	2	-24	27		6	3	9	27	22
	1	1	21	-90	99		2	4	13	-51	56		4	2	5	-54	57		6	3	12	1	-
	1	1	24	-161	176		2	4	16	81	79		4	2	8	122	130		6	3	15	0	-
	1	1	27	37	51		2	4	19	12	-		4	2	11	34	44		6	4	2	-66	66
	1	2	2	-5	-		2	4	22	41	44		4	2	14	181	185		6	4	5	-5	-
	1	2	5	-5	-		2	5	3	-51	52		4	2	17	1	-		6	4	8	81	89
	1	2	8	274	300		2	5	6	156	161		4	2	20	115	120		6	4	11	19	20
	1	2	11	-29	21		2	5	9	27	42		4	2	23	18	20		6	5	1	36	28
	1	2	14	248	286		2	5	12	-12	-		4	3	1	12	-		6	5	4	-101	96
	1	2	17	-74	70		2	5	15	-23	28		4	3	4	-107	116		7	0	4	-37	-
	1	2	20	138	147		2	5	18	-72	87		4	3	7	67	61		7	0	10	-215	182
	1	2	23	23	-		2	5	21	23	27		4	3	10	-249	221		7	0	16	-8	-
	1	2	26	27	37		2	6	2	20	-		4	3	13	-29	33		7	1	3	36	-
	1	3	1	27	45		2	6	5	59	60		4	3	16	-18	-		7	1	6	104	95
	1	3	4	-214	251		2	6	8	65	65		4	3	19	-2	-		7	1	9	2	-
	1	3	7	-135	150		2	6	11	-63	61		4	3	22	4	-		7	1	12	5	-
	1	3	10	-280	291		2	6	14	174	185		4	4	0	177	204		7	1	15	19	15
	1	3	13	61	59		2	6	17	24	17		4	4	3	-20	22		7	1	18	-64	42
	1	3	16	-49	42		2	7	1	-25	23		4	4	6	133	116		7	2	2	-12	-
	1	3	19	-19	-		2	7	4	-118	117		4	4	9	-16	-		7	2	5	2	-
	1	3	22	29	30		2	7	7	-17	18		4	4	12	9	-		7	2	8	78	74
	1	3	25	34	-		2	7	10	-122	114		4	4	15	-7	-		7	2	11	-10	-
	1	4	0	368	362		2	7	13	8	-		4	4	18	-73	64		7	2	14	117	98
	1	4	3	62	61		2	8	0	106	108		4	5	2	-9	-		7	3	1	14	-
	1	4	6	224	285		2	8	3	26	26		4	5	5	-43	26		7	3	4	-68	55
	1	4	9	-60	57		2	8	6	91	83		4	5	8	40	37		7	3	7	-25	25
	1	4	12	-6	-		2	8	9	-19	22		4	5	11	27	23		7	3	10	-136	129
	1	4	15	58	55		3	0	6	149	163		4	5	14	149	153		7	4	3	-6	-
	1	4	18	-122	131		3	0	12	93	109		4	5	17	-22	19		8	0	2	-16	-
	1	4	21	-26	26		3	0	18	-164	158		4	6	1	-23	23		8	0	8	77	88
	1	4	24	-119	132		3	0	24	-77	80		4	6	4	-70	62		8	0	14	140	113
	1	5	2	-2	-		3	1	2	-81	100		4	6	7	18	15		8	1	1	-60	51
	1	5	5	-92	92		3	1	5	71	88		4	6	10	-115	134		8	1	4	-109	119
	1	5	8	25	-		3	1	8	221	273		4	7	0	145	132		8	1	7	34	-
	1	5	11	100	102		3	1	11	-93	101		4	7	3	9	-		8	1	10	-103	106
	1	5	14	223	240		3	1	14	217	241		5	0	2	-37	42		8	1	13	-27	-
	1	5	17	-66	69		3	1	17	9	-		5	0	8	8	-		8	2	3	33	-
	1	5	20	103	104		3	1	20	161	179		5	0	14	225	213		8	2	6	95	100
	1	5	23	38	-		3	1	23	-15	-		5	0	20	129	127		8	2	9	-20	20
	1	6	1	10	-		3	1	26	17	19		5	1	1	-114	88		9	0	6	97	101
	1	6	4	-141	149		3	2	1	53	54		5	1	4	-253	268		9	1	2	-22	27
	1	6	7	-34	29		3	2	4	-250	272		5	1	7	115	120		9	1	5	-12	14

complete when the parameter shifts were less than 5 % of the standard deviations, at which stage the discrepancy index R was 0.089. Hughes' weighting function $w=1/h^2|F_{obs},\min|^2$ for $|F_{obs}|\leq h|F_{obs},\min|$ and $w=1/|F_{obs}|^2$ for $|F_{obs}|>h|F_{obs},\min|$ with $h=4.0$ was used in the refinement. A weight analysis obtained in the final cycle is given in Table 4.

Table 6. Interatomic distances and estimated standard deviations ($\pm\sigma$) in Å.

Zr –O	Zr –3 O_1 = 2.048±13	
	Zr –3 O_2 = 2.084±12	
P –O	P –2 O_1 = 1.516±13	
	P –2 O_2 = 1.546±13	
Na–O	Na–6 O_2 = 2.538±12	
	Na–6 O_1 = 3.689±13	
O–O	O_1 –4 O_2 = 2.48±2;	2.52±2
	(O_2 –4 O_2) = 2.94±2;	3.01±2
	O_1 –4 O_1 = 2.50±2;	2×2.96±2
	3.21±2	
	O_2 –3 O_2 = 2.52±2;	2×2.761±2

Additional distances

Zr–Na(Na–2Zr) = 3.315±2
Zr–3 P(P–2Zr) = 3.444±3
Zr–3 P(P–2Zr) = 3.493±5
P –2 Na(Na–6P) = 3.667±3

Table 7. The structure of $NaZr_2(PO_4)_3$.

Space group: $R\bar{3}/c$
Unit cell dimensions: a = 8.8043±2 Å
c = 22.7585±9 Å
V = 1527.7 Å^3

Cell content: 6 $NaZr_2(PO_4)_3$

6 Na in 6(b): (0,0,0; 0,0,½)
12 Zr in 12(c): ±(0,0,z; 0,0,½,+z)
18 P in 18(e): ±(x,0,¼; 0,x,¼; $\bar{x}$,$\bar{x}$,¼)
36 O_1 and 36 O_2
in 2×36(f): ±(x,y,z; $\bar{y}$,$x-y$,z; $y-x$,$\bar{x}$,z; $\bar{y}$,$\bar{x}$,½+z; x,$x-y$,½+z; $y-x$,y,½+z)

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

Atom	x	y	z	B Å^2
Na	0	0	0	4.20±40
Zr	0	0	0.1456±1	1.80± 7
P	0.2909± 6	0	¼	2.40±10
O_1	0.1860±15	−0.0144±15	0.1949±5	3.20±20
O_2	0.1913±15	0.1683±15	0.0866±5	2.90±20

A list of the observed and calculated structure factors is given in Table 5. A three-dimensional difference synthesis calculated over the unique part of the unit cell at points 0.2 Å apart showed very small maxima and minima. The largest maximum in this synthesis has a magnitude of about 20 % of the heights of the oxygen peaks in the electron density functions. Thus, from this calculation as well as from a computation of the interatomic distances (*cf.* Table 6), which were found to be within the normal range, further evidence was obtained that the atomic parameters arrived at in the final cycle of refinement and listed in Table 7 should present an adequate description of the structure. Also an attempt to improve the structure by lowering the symmetry to *R*3*c* was unsuccessful.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of $NaZr_2(PO_4)_3$ thus derived may be described in terms of PO_4 tetrahedra and ZrO_6 octahedra which are linked by corners to a three-dimensional network (*cf.* Fig. 1). Every oxygen atom thus belongs simultaneously within a PO_4 group and a ZrO_6 group. The sites of the sodium atoms are in the strongly distorted octahedra formed by the triangular faces of two ZrO_6 octahedra stacked on top of each other as illustrated in Fig. 2. The groups $O_3ZrO_3NaO_3ZrO_3$ thus formed may be considered as major struc-

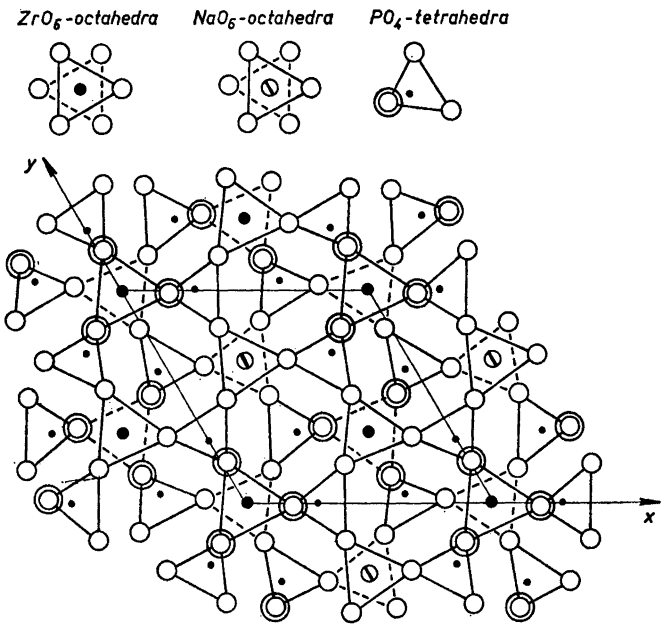

Fig. 1. Schematic drawing showing the structure of $NaZr_2(PO_4)_3$. The structure viewed along [001] showing the contacts between PO_4 tetrahedra, ZrO_6 octahedra and NaO_6 octahedra. Only one third of the structure has been indicated (*i.e.* atoms with z parameters within the limits $0.00 \leq z \leq 0.33$).

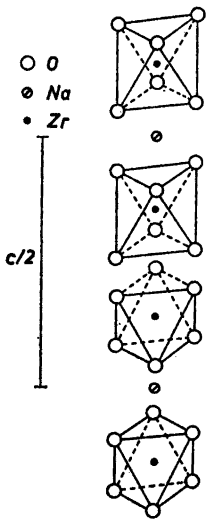

Fig. 2. Schematic drawing showing the sites of the sodium atoms between ZrO_6 octahedra in the structure of $NaZr_2(PO_4)_3$.

tural units of the atomic arrangement. Such groups are mutually linked in the *c* direction by PO_4 tetrahedra in such a way that empty trigonal prisms of oxygen atoms are formed. The endless columns resulting from this linking are also connected normal to the *c* direction by the PO_4 tetrahedra (*cf.* Fig. 1).

All the interatomic distances are of normal lengths (*cf.* Table 6). The PO_4 tetrahedra are nearly regular. The P—O distances are comparable to those found by Furberg [10] in H_3PO_4 and also by Cruickshank [11] and Kierkegaard [12] in several phosphate structures.

Rather few zirconium oxygen compounds have been found to contain ZrO_6 octahedra, more frequent coordination numbers of oxygen around this metal being seven (*e.g.* in ZrO_2, monoclinic,[12] and $Zr_4(OH)_6(CrO_4)_5 \cdot 2H_2O$ [14])

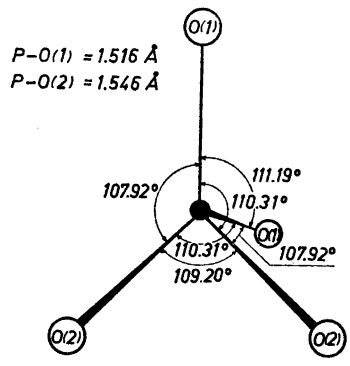

Fig. 3a. The PO_4 tetrahedron in the structure of $NaZr_2(PO_4)_3$.

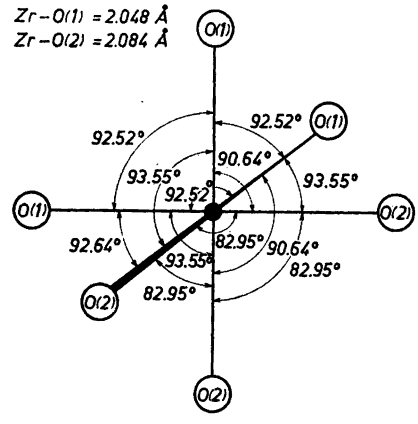

Fig. 3b. The ZrO_6 octahedron in the structure of $NaZr_2(PO_4)_3$.

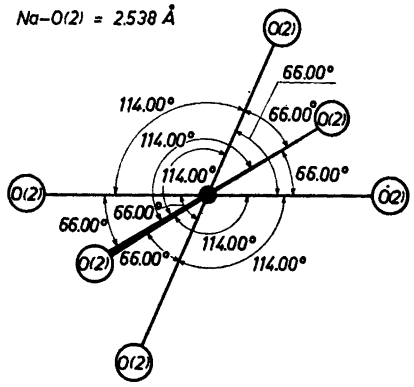

Fig. 3c. The NaO_6 octahedron in the structure of $NaZr_2(PO_4)_3$.

or eight (*e.g.* in ZrO_2, cubic,[15] $Zr(SO_4)_2 \cdot 4H_2O$,[16] $Zr(IO_3)_4$,[17] and $ZrOCl_2 \cdot 8H_2O$ [18]). The Zr—O distances of the somewhat distorted octahedra (Fig. 3b) of $NaZr_2(PO_4)_3$ (2.048 and 2.084 Å) are somewhat shorter than the value 2.097 Å reported for $BaZrO_3$ [18] of perovskite type structure.

The six-fold coordination of oxygen around sodium (Fig. 3c) represents a heavily distorted octahedron with O—Na—O angles of 66.0° and 114.0°.

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