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The Crystal Structure of Zr_9S_2*

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The crystal structure of body-centered tetragonal Zr_9S_2 has been determined. It belongs to space group $I4_1/amd$ (No. 141), and its lattice parameters are $a=9{\cdot}752 \pm 0{\cdot}001$ and $c=19{\cdot}216 \pm 0{\cdot}003$ Å. The structure is interpreted as consisting of interpenetrating distorted C.N.14 Kasper polyhedra coordinating central Zr atoms, and square antiprisms coordinating sulfur atoms. Two S atoms replace two Zr atoms at the 1 and 3 positions of one of the hexagonal rings of the Kasper polyhedra. It is shown that these structure features are also found in several structure types common to a number of metal-rich compounds with group V*b* and VI*b* elements. The significance of the occurrence of the Kasper polyhedra and square antiprisms in Zr_9S_2 is discussed from the viewpoint of chemical bonding in solids.

Introduction

The zirconium–sulfur compounds that are stable at high temperatures have been examined in the composition range S/Zr < 1.5 by Conard & Franzen (1971). In the metal-rich region three phases, namely Zr_2S, $Zr_{21}S_2$ and Zr_9S_2 were reported. The Zr_2S phase, isostructural with Ti_2S (Owens, Conard & Franzen, 1967), has the Ta_2P-type structure, and $Zr_{21}S_8$ is isostructural with $Nb_{21}S_8$ (Franzen, Beineke & Conard, 1968). In both Zr_2S and $Zr_{21}S_8$, the sulfur atoms have capped trigonal-prismatic coordination while the metal atoms have capped cubic coordination, as in the b.c.c. structure of pure metals. The tendency for the sulfur atoms to have capped trigonal-prismatic coordination, and for the metal atoms to have capped cubic coordination is common to many metal-rich chalcogenides, (Franzen, Smeggil & Conard, 1967). The purposes of the investigation reported here were to determine the crystal structure of the Zr_9S_2 phase and to examine and discuss the various coordinations of both metal and chalcogen atoms in metal-rich compounds.

The preliminary crystallographic data reported for Zr_9S_2 by Conard (1969)† and later by Conard & Franzen (1971) can be summarized as follows. Compound Zr_9S_2, body-centered tetragonal, $a=9{\cdot}752 \pm 0{\cdot}001$ and $c=19{\cdot}216 \pm 0{\cdot}003$ Å, $V=1827{\cdot}5$ Å^3, $D_m=6{\cdot}4 \pm 0{\cdot}1$, $D_x=6{\cdot}422$ g.cm^{-3}, $Z=8$. Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å), $\mu=102$ cm^{-1}. Nonextinction conditions: hkl when $h+k+l=2n$; $hk0$ when $h=2n$; and hhl when $2h+l=4n$. Space group $I4_1/amd$ (No. 141).

Experimental

Single-crystal X-ray diffraction data were collected with a Hilger–Watts four-circle automatic diffractometer, coupled with an SDS 910 computer as described elsewhere (Dahm, Bensen, Nimrod, Fitzwater & Jacobsen, 1967). The data were recorded with Mo $K\alpha$ radiation filtered by zirconium. Peak-height intensities were measured for all the nonextinguished reflections in the first octant with $\theta \le 30°$. In addition, integrated intensity data were obtained for some selected strong reflections covering the whole θ range. The peak-height data were converted into integrated intensities with the factors obtained, as a function of the θ angle, from the ratio of the 102 integrated data to the corresponding peak-height data. Lorentz and polarization corrections were applied. The irregularly shaped single crystal used in the data collection could be approximated to a sphere with a radius of 20 microns. For this small crystal, $\mu R=0{\cdot}02$ cm^{-1}, no absorption correction was made.

Determination and refinement of structure

Based on the assumption that the fluctuation level of the counter was proportional to the square root of the total counts, the uncertainties of the intensity data were calculated as $(A+B)^{1/2}/(A-B)$, where A and B are respectively the peak height and the background counts. Of the 1536 intensity data obtained, 607 had less than 25% uncertainty. These 607 data were used in the structure determination and refinement.

The crystal structure was determined by superposition of the three-dimensional Patterson maps. If the possibility of a homometric vector set is ignored, the application of the superposition technique in two successive steps in principle yields an unambiguous crystal structure, provided that the Patterson vector set is determined accurately. To obtain the Patterson vector set the value of the Patterson function was calculated at approximately 0·15 Å intervals. The Patterson map was analyzed graphically for peak locations with the following assumptions: (1) every variation of Patterson function values is significant; (2) only Zr–Zr peaks are important; and finally (3) a single Zr–Zr peak is

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† The phase was then designated as Zr_5S instead of Zr_9S_2.

Table 1. *Refined atomic parameters for* Zr_9S_2

	Wyckoff notation	Point symmetry	x	y	z	β(Å²)
Zr(1)	16(*f*)	2	0·1788 (2)	0	0	0·51 (4)
Zr(2)	16(*h*)	*m*	0	0·3981 (3)	0·3014 (1)	0·39 (5)
Zr(3)	16(*h*)	*m*	0	0·0789 (3)	−0·4309 (1)	0·53 (5)
Zr(4)	16(*h*)	*m*	0	−0·0289 (3)	0·1422 (1)	0·51 (5)
Zr(5)	8(*e*)	*mm*	0	0·25	0·0106 (2)	0·63 (7)
S	16(*g*)	2	0·2723 (4)	0·25+x	$\frac{1}{8}$	0·37 (10)

symmetrical with a base no more than 1·0 Å in diameter. The validity of the last assumption was concluded rather arbitrarily from the analysis of some of the simplest peaks in the map. On the basis of these assumptions, 705 Patterson vectors were located in half of the Patterson space covering z from $-\frac{1}{4}$ to $\frac{1}{4}$. These vectors were used in the superposition operation, which was simply to numerically match the vector coordinates from two maps after the origin of one of the maps was moved to a vector position on the other. The shift vector chosen corresponded to a peak on the Patterson map with low intensity and whose location was determined with the highest certainty. Two vectors were considered superimposed if their three positional coordinates were within 0·15 Å of each other. The number of vectors was reduced to 82 at the end of the first step and further reduced to 36 after the second-step superposition. The relative positions of these vectors were taken as the locations of 36 Zr atoms, or 72 in a full-unit cell. An inversion center in the distribution of these atoms positions was chosen for the origin. It was found that the 72 atomic positions could be represented by five independent positions. Sixteen sulfur atoms, all equivalent, were later located from Fourier synthesis. The structure was refined using least-squares computation (Busing, Martin & Levy, 1962), with atomic scattering factors by Hansen, Herman, Lea & Skillman (1964), corrected for anomalous dispersion according to Cromer & Liberman (1970). Isotropic temperature factors were assumed in the refinement. Every Zr atom was located by the superposition technique to within 0·1 Å and none of the 36 peaks was rejected.

Table 2. *Observed and calculated structure factors for* Zr_9S_2

H	K	FO	FC
L = 0			
4	0	546	553
6	0	441	428
8	0	343	322
10	0	142	128
12	0	292	310
2	2	66	65
4	2	247	247
6	2	72	-65
8	2	72	73
10	2	85	80
0	4	546	553
2	4	246	-247
6	4	202	199
0	6	441	-428
2	6	72	-65
4	6	202	-199
6	6	159	-154
8	6	215	-229
12	6	122	-141
0	8	343	322
2	8	72	-73
6	8	215	229
0	10	142	-128
2	10	85	80
0	12	292	310
6	12	122	141
L = 1			
3	0	82	-97
5	0	107	123
7	0	92	-103
11	0	95	96
4	1	173	186
6	1	132	-144
8	1	82	88
3	2	146	-148
5	2	95	-92
7	2	122	123
9	2	162	-175
0	3	82	97
2	3	146	-148
4	3	85	-86
10	3	130	-130
1	4	173	186
3	4	85	86
5	4	252	262
11	4	151	175
0	5	107	123
2	5	95	92
4	5	252	262
8	5	170	168
1	6	132	144
7	6	176	190
0	7	92	103
2	7	122	123
6	7	176	190
1	8	81	88
5	8	170	168
2	9	162	175
8	9	57	43
10	9	107	127
3	10	130	-130
9	10	107	-127
0	11	95	-96
4	11	151	-175
6	11	85	101
L = 2			
4	0	212	-202
6	0	138	127
8	0	126	-112
12	0	85	-71
1	1	35	31
5	1	47	37
7	1	61	-51
9	1	115	106
11	1	112	-108
6	2	144	137
8	2	189	-175
10	2	90	84
3	3	71	68
11	3	113	108
0	4	212	202
6	4	64	67
1	5	47	37
5	5	56	59
7	5	68	-62
9	5	123	123
11	5	90	-116
0	6	138	127
2	6	144	-137
4	6	64	67
1	7	61	51
5	7	68	62
0	8	126	112
2	8	189	-175
1	9	115	106
5	9	123	123
9	9	130	163
2	10	90	-84
1	11	112	108
5	11	90	116
0	12	85	71
L = 3			
3	0	87	91
5	0	53	48
4	1	111	113
10	1	115	107
3	2	449	-477
5	2	70	68
7	2	116	-106
9	2	161	-154
0	3	87	91
2	3	449	477
6	3	367	355
8	3	120	116
10	3	149	137
1	4	111	-113
7	4	116	-114
0	5	53	-48
2	5	70	68
3	6	367	-355
7	6	82	-83
9	6	143	-145
2	7	116	106
4	7	116	-114
6	7	82	83
3	8	120	116
2	9	161	-154
6	9	143	-145
1	10	115	107
3	10	149	-137
3	12	82	86
L = 4			
0	0	74	67
4	0	62	-60
6	0	95	92
12	0	108	113
3	1	368	-367
9	1	152	-143
2	2	367	-372
4	2	126	-123
6	2	128	-130
8	2	198	-182
10	2	101	-95
1	3	368	-367
5	3	276	-269
7	3	238	-228
9	3	76	-70
11	3	106	-95
13	3	128	-154
0	4	62	-60
2	4	126	123
4	4	157	-158
6	4	170	169
8	4	80	-82
3	5	276	-269
9	5	117	-113
0	6	95	-92
2	6	128	-130
4	6	170	-169
8	6	218	-217
3	7	238	228
9	7	104	103
2	8	198	182
4	8	80	-82
6	8	218	217
1	9	152	143
3	9	76	-70
5	9	117	113
7	9	104	103
2	10	101	-95
3	11	106	95
0	12	108	113
3	13	128	-154
L = 5			
1	0	47	48
3	0	225	-218
9	0	183	-159
11	0	92	77
0	1	47	48
4	1	156	152
3	2	145	-144
5	2	80	80
7	2	180	-171
9	2	70	67
11	2	92	-85
0	3	225	218
2	3	145	-144
4	3	75	75
6	3	77	-78
8	3	145	135
10	3	93	-103
1	4	156	152
3	4	75	-75
5	4	131	132
7	4	115	113
9	4	86	-81
11	4	125	138
2	5	80	-80
4	5	131	132
6	5	84	-81
3	6	77	-78
5	6	84	81
7	6	118	-113
2	7	180	-171
4	7	115	-113
6	7	118	-113
10	7	104	-121
3	8	145	-135
9	8	112	-141
0	9	183	-159
2	9	70	-67
4	9	86	-81
8	9	112	-141
3	10	93	-103
7	10	104	-121
0	11	92	-77
2	11	92	-85
4	11	125	-138
L = 6			
2	0	84	78
4	0	166	-162
6	0	262	243
8	0	207	-185
10	0	86	82
5	1	121	-118
7	1	118	110
9	1	71	-70
0	2	84	78
6	2	74	72
5	3	102	99
7	3	77	-66
0	4	166	162
6	4	164	154
8	4	70	-66
1	5	121	-118
3	5	102	-99
5	5	229	-210
9	5	154	-155
0	6	262	243
2	6	74	-72
4	6	164	154
8	6	108	97
1	7	118	-110
3	7	77	-66
7	7	138	-127
0	8	207	185
4	8	70	66
6	8	108	97
1	9	71	-70
5	9	154	-155
9	9	102	-126
0	10	86	82
L = 7			
1	0	489	473
3	0	234	227
5	0	360	343
7	0	367	341
9	0	133	122
11	0	255	238
13	0	125	132
0	1	489	-473
2	1	117	115
4	1	103	-104
6	1	150	-144
8	1	83	-81
1	2	117	115
3	2	86	80
5	2	147	137
11	2	161	167
0	3	234	227
2	3	86	-80
4	3	86	-85
6	3	169	162
8	3	76	-66
1	4	103	104
3	4	86	-85
5	4	57	61
7	4	97	91
0	5	360	-343
2	5	147	137
4	5	57	-61
6	5	89	-82
1	6	150	-144
3	6	169	-162
5	6	89	-82
7	6	141	-128
9	6	156	-148
0	7	367	341
4	7	97	91
6	7	141	128
1	8	83	81
3	8	76	-66
0	9	133	-122
6	9	156	-148
0	11	255	238
2	11	161	-167
0	13	125	-132
L = 8			
0	0	162	150
2	0	269	-267
4	0	267	257
6	0	237	-229
5	1	76	-75
7	1	77	83
0	2	269	267
2	2	317	-319
4	2	143	-141
8	2	87	-88
10	2	163	-157
5	3	93	86
0	4	267	257
2	4	143	141
4	4	346	345
6	4	90	88
8	4	136	125
10	4	228	216
1	5	76	75
3	5	93	86
7	5	135	129
0	6	237	229
4	6	90	-88
6	6	304	288
1	7	77	83
5	7	135	129
9	7	95	95
2	8	87	88
4	8	136	125
10	8	128	156
7	9	95	95
2	10	163	-157
4	10	228	-216
8	10	128	-156
L = 9			
1	0	125	127
3	0	96	-102
5	0	90	97
0	1	125	127
4	1	62	63
9	2	148	-147
11	2	187	188
0	3	96	102
4	3	139	138
8	3	129	135
1	4	62	63
3	4	139	-138
5	4	57	51
0	5	90	97
4	5	57	51
9	6	160	-159
11	6	115	124
3	8	129	-135
2	9	148	147
6	9	160	159
2	11	187	188
6	11	115	124
L = 10			
8	0	172	-174
10	0	113	121
3	1	105	-117
5	1	70	72
4	2	228	-249
6	2	123	121
8	2	106	-109
1	3	105	117
3	3	220	229
5	3	64	73
7	3	104	111
2	4	228	-249
6	4	106	-106
8	4	165	-158
1	5	70	72
3	5	64	-73
5	5	118	115
2	6	123	-121
4	6	106	-106
10	6	107	-128
3	7	104	111
9	7	99	93
0	8	172	174
2	8	106	-109
4	8	165	158
3	9	138	-138
7	9	99	-93
0	10	113	121
6	10	117	128
L = 11			
1	0	84	86
3	0	333	-351
5	0	94	103
9	0	109	-116
0	1	84	-86
2	1	200	-211
4	1	149	-165
6	1	101	-100
8	1	120	-128
12	1	117	-117
1	2	200	-211
3	2	70	-72
5	2	95	-111
7	2	198	-204
0	3	333	-351
2	3	70	72
4	3	215	-226
8	3	168	-165
1	4	149	165
3	4	215	-226
5	4	166	167
0	5	94	-103
2	5	95	-111
4	5	166	-167
8	5	126	-128
1	6	101	-100
7	6	119	-112
2	7	198	204
6	7	119	112
1	8	120	128
3	8	168	-165
5	8	126	128
0	9	109	116
1	12	117	117
L = 12			
0	0	84	75
2	0	54	-46
3	1	132	140
7	1	77	-81
9	1	155	160
0	2	54	46
2	2	129	-140
4	2	94	-107
10	2	92	-89
1	3	132	140
7	3	174	184
11	3	99	96
2	4	94	107
6	4	157	164
10	4	98	103
7	5	122	-126
4	6	157	-164
6	6	80	87
8	6	114	-108
1	7	77	-81
3	7	174	-184
5	7	122	-126
9	7	183	-189
6	8	114	108
8	8	127	-124
1	9	155	-160
7	9	183	-189
2	10	92	-89
4	10	98	-103
3	11	99	-96
0	12	83	100
L = 13			
1	0	84	84
7	0	75	77
0	1	84	84
2	1	82	-88
6	1	72	-72
1	2	82	88
3	2	90	-104
5	2	174	185
2	3	90	-104
2	5	174	-185
6	5	138	-152
1	6	72	72
5	6	138	152
0	7	75	-77
8	7	88	-87
7	8	88	87
L = 14			
2	0	309	325
6	0	209	227
10	0	176	179
1	1	143	-148
5	1	79	-87
7	1	119	-128
6	2	221	240
10	2	125	108
2	4	59	63
1	5	79	-87
0	6	209	227
2	6	221	-240
1	7	119	128
7	7	159	157
0	10	176	179
2	10	125	-108
L = 15			
9	0	116	-129
4	1	164	-173
6	1	121	132
3	2	160	-170
9	2	93	-90
2	3	160	170
4	3	146	161
10	3	184	176
1	4	164	173
3	4	146	161
5	4	121	135
7	4	176	186
4	5	121	-135
6	5	143	150
1	6	121	132
5	6	143	150
4	7	176	186
0	9	116	129
2	9	93	-90
3	10	184	-176
L = 16			
0	0	409	404
2	0	92	-91
4	0	140	150
6	0	109	128
3	1	79	84
0	2	92	91
2	2	114	-116
4	2	117	122
1	3	79	84
9	3	100	92
0	4	140	150
2	4	117	-122
6	4	79	85
8	4	88	-77
3	5	73	69
0	6	109	-128
4	6	79	-85
6	6	89	-75
8	6	134	-133
4	8	88	-77
6	8	134	133
3	9	100	92
L = 17			
3	0	143	-137
7	0	79	-68
4	1	66	-56
9	2	95	-94
0	3	143	137
4	3	148	158
1	4	66	-56
3	4	148	-158
7	4	98	-94
9	4	129	-119
8	5	96	88
0	7	79	68
4	7	98	94
5	8	96	88
2	9	95	94
4	9	129	-119
L = 18			
2	0	168	-169
4	0	188	-193
8	0	161	-163
1	1	162	-168
5	1	141	-149
7	1	116	-120
0	2	168	-169
4	2	104	-116
8	2	169	-157
3	3	148	-152
0	4	188	193
2	4	104	-116
1	5	141	-149
5	5	109	-122
7	5	124	-129
1	7	116	120
5	7	124	129
0	8	161	163
2	8	169	-157
L = 19			
5	0	110	112
7	0	113	-113
9	0	104	123
3	2	191	-199
9	2	143	-146
2	3	191	199
6	3	197	186
7	4	117	-112
0	5	110	-112
3	6	197	-186
0	7	113	-113
4	7	117	-112
0	9	104	-123
2	9	143	-146
L = 20			
0	0	199	187
3	1	103	-108
1	3	103	-108
5	3	125	-123
3	5	125	-123
6	6	123	106
L = 21			
1	0	90	67
5	0	120	125
0	1	90	67
2	1	145	-150
1	2	145	150
5	2	150	139
0	5	120	125
2	5	150	-139
L = 22			
4	0	196	-193
6	0	135	131
8	0	144	-145
3	3	195	182
0	4	196	193
6	4	189	181
0	6	135	131
4	6	189	181
0	8	144	145
L = 23			
1	0	118	123
3	0	92	93
5	0	110	102
7	0	142	147
0	1	118	-123
0	3	92	93
6	3	156	146
0	5	110	-102
3	6	156	-146
0	7	142	147
L = 24			
2	0	142	-134
0	2	142	134
2	2	218	-201
L = 25			
1	0	116	-114
3	0	101	-99
5	0	129	-124
0	1	116	-114
3	2	107	-102
0	3	101	99
2	3	107	-102
0	5	129	-124

The final refinement of the position parameters and the temperature factors resulted in the data shown in Table 1. The uncertainties in the atom positions were generally within 0·003 Å. The 607 calculated structure factors are compared with the observed structure factors in Table 2. The unweighted R value was 0·055, and the value decreased to 0·049 if the data were weighted with $w = 1/\sigma^2(F_o)$, where $\sigma^2(F_o)$ is the probable error of F_o, calculated from the uncertainties of the intensity data. The difference Fourier map obtained with these data was devoid of significant maxima. Overall, the highest value in the difference electron density map corresponded to about 0·5 e, and specifically at the atom positions, the residual peaks had values corresponding to less than 0·25e.

The nearest neighbors and their interatomic distances for the six independent atoms calculated from the position parameters in Table 1 are listed in Table 3, and the coordinations are shown in Fig. 1. For each independent atom, the next nearest neighbors, which are not included in the coordination polyhedra in Fig. 1, are listed in the last rows in Table 3. The overall structure viewed along the *b* axis, with some special emphasis to be discussed later, is shown in Fig. 2.

Results and discussion

As can be seen in Fig. 1, all the metal atoms in Zr_9S_2 have complex coordination polyhedra. Among them are slightly distorted C.N. 14 Kasper polyhedra for Zr(2) and Zr(3). The sulfur coordination is square-antiprismatic. The distortions in the coordination polyhedron of Zr(2), from an ideal Kasper polyhedron, are partly the result of substituting two sulfur atoms fo two zirconium atoms in the 1,3 positions of one of the six-membered rings. The Zr atoms in the other six-membered ring lie in a mirror plane which bisects the distance between the central Zr(2) and the apical Zr(2) atoms. Because of the mirror plane, the apical Zr(2) atom is also the central atom of a second Kasper polyhedron, which penetrates the first in such a way that the center of one is the apex of the other. The combined structure of the two interpenetrating Kasper polyhedra has the following sequence: Zr(5); a six-membered ring containing two sulfur atoms; Zr(2); a planar six-membered ring containing only zirconium atoms; Zr(2); a six-membered ring containing two sulfur atoms; and Zr(5). The outer apices of the two interpenetrating polyhedra are formed by two Zr(5) atoms. The coordination of Zr(5) is not simply related to a Kasper polyhedron, as can be seen in Fig. 1(*e*). There are six near neighbors of Zr(5): four Zr(1) atoms at 3·004 Å and two Zr(2) atoms at 3·135 Å. The remaining atoms shown in Fig. 1(*e*) are at distances between 3·520 and 3·713 Å.

A view of the structure, emphasizing the polyhedra around the Zr(2) atoms, is shown in Fig. 2. In the direction of the *b* axis, the pairs of interpenetrating polyhedra are joined by common apical Zr(5) atoms. These interpenetrating polyhedra form zigzag chains in the **a** direction by sharing triangular faces. In a unit cell, there are fragments of two such chains, each containing two units of the interpenetrating polyhedra. Finally, consideration of the operation of the 4_1 axis on the chains of these polyhedra completes the description of the structure. The regions of the structure where no solid lines are drawn in Fig. 2 contain the interpenetrating polyhedra, with the zigzag chains running in the **b** direction, and with the principal axes of the polyhedra parallel to the **a** direction. Polyhedra with principal axes at right angles interpenetrate, such that apical and central Zr(2) atoms in the **a** direction polyhedra are ring atoms in the **b** direction polyhedra.

The Zr_9S_2 structure has little similarity to the struc-

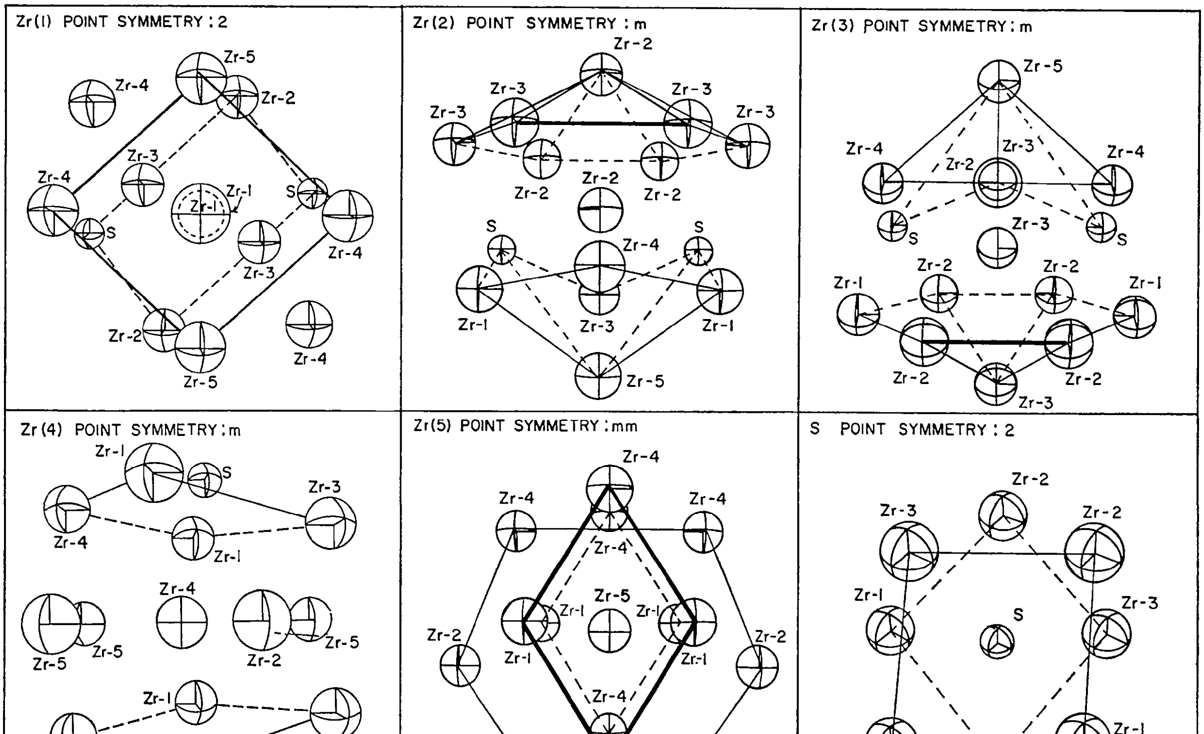
Table 3. *The nearest neighbors and their interatomic distances in* Zr_9S_2

Central atom	Type of neighbors	No. of neighbors	Distances (±0·003 Å)
Zr(1)	S	2	2·578
	Zr(5)	2	3·004
	Zr(2)	2	3·126
	Zr(4)	2	3·226
		2	3·254
	Zr(1)	1	3·487
	Zr(3)	2	3·488
	Zr(3)	2	4·247*
Zr(2)	S	2	2·745
	Zr(2)	1	2·889
	Zr(3)	1	3·050
	Zr(1)	2	3·126
	Zr(3)	2	3·199
	Zr(4)	1	3·314
	Zr(2)	2	3·489
	Zr(5)	1	3·520
	Zr(3)	2	3·534
	S	2	4·375*
Zr(3)	S	2	2·657
	Zr(2)	1	3·050
	Zr(3)	1	3·069
	Zr(2)	2	3·199
	Zr(4)	2	3·276
	Zr(3)	1	3·337
	Zr(1)	2	3·488
	Zr(2)	2	3·534
	Zr(5)	1	3·673
	Zr(1)	2	4·247*
Zr(4)	S	2	2·722
	Zr(4)	2	3·122
	Zr(5)	1	3·135
	Zr(1)	2	3·226
		2	3·254
	Zr(3)	2	3·276
	Z(2)	1	3·314
	Zr(5)	1	3·643
		1	3·713
	Zr(4)	1	4·314*
Zr(5)	Zr(1)	4	3·004
	Zr(4)	2	3·135
	Zr(2)	2	3·520
	Zr(4)	2	3·642
	Zr(3)	2	3·673
	Zr(4)	2	3·713
	S	4	4·101*
S	Zr(1)	2	2·578
	Zr(3)	2	2·657
	Zr(4)	2	2·722
	Zr(2)	2	2·745
	Zr(5)	2	4·101*

* The last row for each central atom represents its next nearest neighbors.

tures of the other known zirconium-rich sulfides, Zr_2S and $Zr_{21}S_8$. As shown in Fig. 1, there is a variety of Zr coordination in Zr_9S_2. None of it is cubic, and the coordination of sulfur is square-antiprismatic. On the other hand, a close examination of the crystal structures of α-V_3S and β-V_3S, reported by Pedersen & Grønvold (1959), revealed their similarity to the structure of Zr_9S_2. In these vanadium sulfides, the basic structural units of two tnterpenetrating C.N. 14 Kasper polyhedra (whose axes lie in [110] direction) differ from that of Zr_9S_2 in that the terminating apical atoms in the former fall on the axes of the polyhedra, while those of the latter do not, apparently because the distortion caused by the substitution of two metal atoms by sulfur atoms in the Kasper polyhedra are greater in the case of Zr than they are in the case of V substitution. The sulfur atoms in both V_3S phases have square-antiprismatic coordinations. The principal structural difference between α- and β-V_3S is that in the former the two substituting sulfur atoms in the Kasper polyhedra occupy 1,3 positions, as in Zr_9S_2, while in the latter they occupy 1,4 positions. The structural unit formed by the interpenetration of two C.N. 14 Kasper polyhedra can also be found for zirconium in Zr_3Si, reportedly of Ti_3P-type structure (Schubert, Raman & Rossteutscher, 1964), with the axes also lying in the [110] direction. The Si coordination in Zr_3Si, however, is tricapped trigonal-prismatic, or tetrakaidecahedral, with a coordination number of 9.

An interesting feature of the Zr_9S_2 structure is the presence of a short Zr–Zr distance of 2·89 Å. This distance is considerably less than distances found in the h. c. p. form of zirconium metal (3·18 and 3·23 Å) and is comparable to that found in the high pressure ω-phase structure of the metal (2·91 Å) when quenched to one atmosphere (Jamieson, 1963). Short intermetallic distances have also been found in other zirconium-rich compounds, such as the σ-like Zr_4Al_3 (2·70 Å) and the D^8_m-type Zr_5Al_3 (2·70 Å) as discussed by Edshammar (1962), and other metal-rich sulfides, such as Ta_6S (Franzen & Smeggil, 1970), Ta_2S (Franzen & Smeggil, 1969), and the two V_3S phases mentioned earlier. In all these cases, the short distances always appear between the apical and the central atoms of Kasper polyhedra. The geometry of an ideal C.N. 14 Kasper polyhedron (Frank & Kasper, 1958) requires a short distance between the central and the apical atoms, but no theoretical explanation based on chemical bonding has been given for this tendency. The short Zr–Zr distance in Zr_9S_2 is almost 0·2 Å greater than that in Zr_4Al_3 or in Zr_5Al_3. This difference is structurally significant. As described earlier, the pairs of Zr(2) atoms serve as central-apical atoms of a Kasper polyhedron in the **a** direction as well as the


Zr(1) POINT SYMMETRY : 2

Zr(2) POINT SYMMETRY : m

Zr(3) POINT SYMMETRY : m

Zr(4) POINT SYMMETRY : m

Zr(5) POINT SYMMETRY : mm

S POINT SYMMETRY : 2

Fig. 1. Coordinations and nearest neighbors of Zr and S atoms in Zr_9S_2.

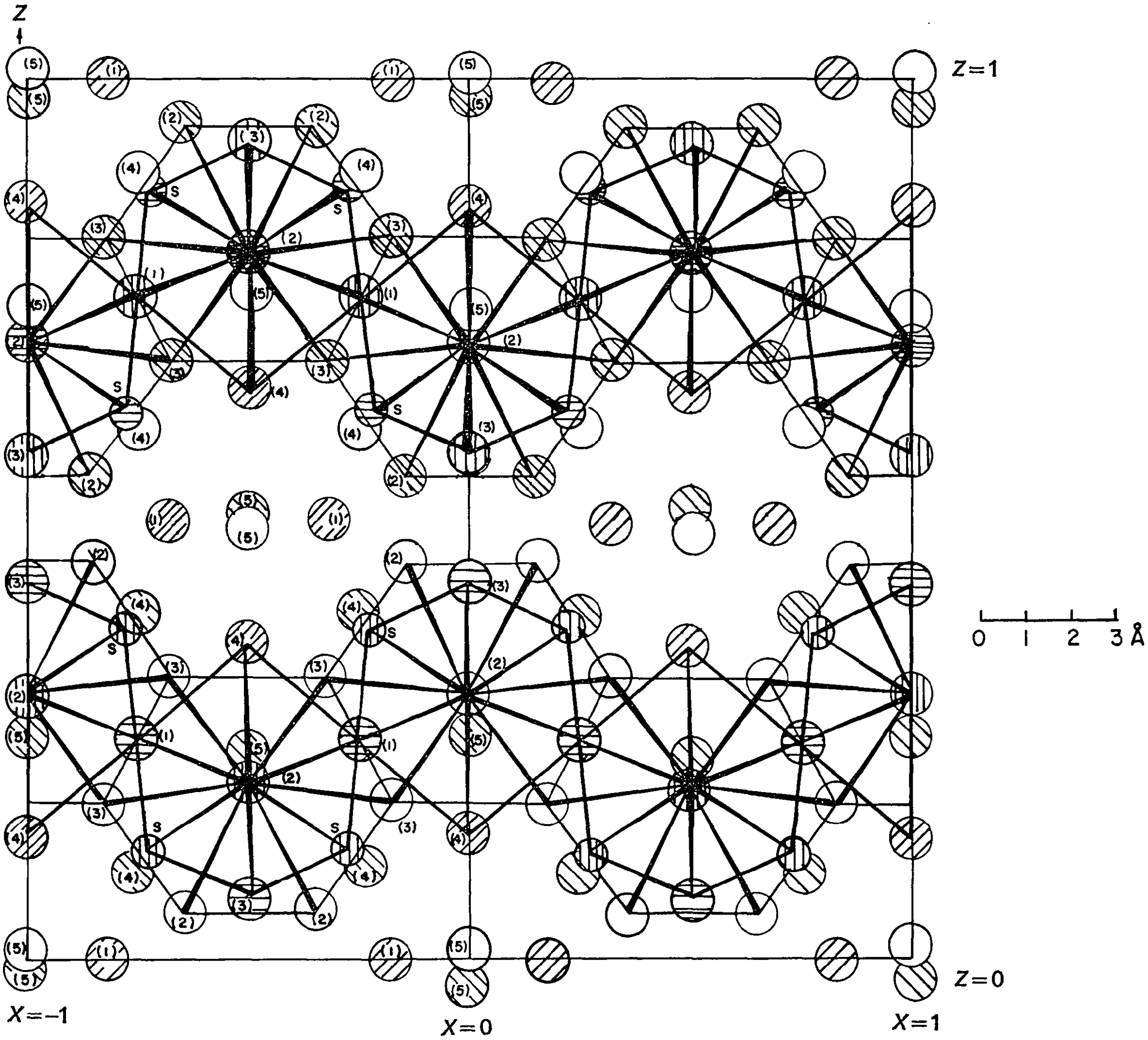


Fig. 2. Crystal structure of Zr_9S_2 with $0{\cdot}25 \leq y \leq 0{\cdot}75$ viewed along y axis.

○ $y=0{\cdot}25$, ▥ $0{\cdot}25<y<0{\cdot}5$, ▨ $y=0{\cdot}5$, ⊜ $0{\cdot}5<y<0{\cdot}75$, ▧ $y=0{\cdot}75$.

ring atoms in the **b** direction polyhedron. In the ring, a normal distance of about 3·2 Å would be expected. Thus, the pair of atoms satisfies this dual nature by assuming an intermediate distance. In Zr_4Al_3 or in Zr_5Al_3, the axes of the polyhedra are parallel to the fourfold axis, and the pair of the central apical zirconium atoms do not possess this dual nature. Another consequence of the dual nature in these two atoms is the presence of a short side on the hexagon, leading to a slight distortion of the ring which lies on the mirror plane.

Square-antiprismatic coordination of sulfur has not been previously observed. Such a coordination, however, is known for Cu in the $CuAl_2$ structure, which is also the structure of a number of intermetallic compounds, for example, Zr_2X, X=Si, Ni, Co or Al (Pearson, 1967). Thus, square-antiprismatic coordination is well known for elements which are generally more metallic than sulfur, and in compounds that are generally more metallic than sulfides. Furthermore, the structures of many complex alloy compounds can be described with Kasper polyhedra, (Frank & Kasper, 1959). Hence, the fact that the structure of Zr_9S_2 can be viewed as consisting of Kasper polyhedra and square antiprisms emphasizes the similarity of this compound to intermetallic compounds, a similarity, which, if not anticipated, is at least not surprising in a compound with such a high metal content. However, the ability of sulfur to replace metal atoms in coordination polyhedra characteristic of metals, provides structural evidence in support of bonding models that include contributions of orbitals centered on the sulfur atoms to the conduction bands in conducting transition-metal sulfides (Franzen, 1966).

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Conard, B. R. (1969). Ph.D. thesis, Iowa State University.

Conard, B. R. & Franzen, H. F. (1971). *High Temp. Sci.* **3**, 49.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891.

Dahm, D. J., Bensen, J. E., Nimrod, D. M., Fitzwater, D. R. & Jacobson, R. A. (1967). USAEC Report IS-1701.

Edshammar, L. E. (1962). *Acta Chem. Scand.* **16**, 20.

Frank, H. F. & Kasper, J. C. (1958). *Acta Cryst.* **11**, 184.

Frank, H. F. & Kasper, J. C. (1959). *Acta Cryst.* **12**, 483.

Franzen, H. F. (1966). *J. Inorg. Nucl. Chem.* **28**, 1575.

Franzen, H. F., Beineke, T. A. & Conard, B. R. (1968). *Acta Cryst.* **B24**, 412.

Franzen, H. F. & Smeggil, J. (1969). *Acta Cryst.* **B25**, 1736.

Franzen, H. F. & Smeggil, J. (1970). *Acta Cryst.* **B26**, 125.

Franzen, H. F., Smeggil, J. & Conard, B. R. (1967). *Mat. Res. Bull.* **2**, 1087.

Hansen, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040.

Jamieson, J. C. (1963). *Science*, **140**, 72.

Owens, J. P., Conard, B. R. & Franzen, H. F. (1967). *Acta Cryst.* **23**, 77.

Pearson, W. B. (1967). *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2. International Series of Monographs in Metal Physics and Physical Metallurgy, Vol. 8. Oxford; Pergamon Press.

Pedersen, B. & Grønvold, F. (1959). *Acta Cryst.* **12**, 1022.

Schubert, K., Raman, A. & Rossteutscher, W. (1964). *Naturwiss.* **51**, 506.

Acta Cryst. (1972). **B28**, 1404

The Crystal Structure of V_4O_7

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Single crystals of V_4O_7 were synthesized by the chemical transport method. They are triclinic with space group $P\overline{1}$ and with $a=5{\cdot}504$, $b=7{\cdot}007$, $c=19{\cdot}243$ Å, $\alpha=41{\cdot}3$, $\beta=72{\cdot}5$, $\gamma=109{\cdot}4°$ and $Z=2$. 542 crystallographically independent reflexions were collected with a 4-circle single-crystal diffractometer. The structure was refined by full-matrix least-squares analysis to an R value of 0·084 for all the observed reflexions. The structure of V_4O_7 indicates considerable displacements of atoms from the ideal structure proposed by Andersson & Jahnberg [*Ark. Kem.* (1963), **21**, 413]. In particular, the distortions of the VO_6 octahedra in the crystallographic shear boundary are remarkable. The V–O distances are in the range $1{\cdot}78 \simeq 2{\cdot}12$ Å and the O–O distances in the range $2{\cdot}52 \simeq 3{\cdot}00$ Å. The shortest V–V distance is 2·778 Å in the crystallographic shear plane.

Introduction

In the composition range VO_x, $1{\cdot}750 < x < 1{\cdot}887$, the existence of the homologous series of $V_nO_{2n-1} (4 \leq n \leq 8)$, was revealed by X-ray powder diffraction (Andersson, Collen, Kuylenstierna & Magneli, 1957). The structure of Ti_5O_9, which is isostructural with V_5O_9, was then determined by the X-ray single-crystal method (Andersson, 1960). The structure model of Ti_5O_9 was extended and successfully used to interpret the X-ray powder patterns of the other members of the series of V_nO_{2n-1} and Ti_nO_{2n-1} by Andersson & Jahnberg (1963).

However, details of the crystal structures of the homologous series of V_nO_{2n-1} and Ti_nO_{2n-1} have been unknown because of the difficulty in obtaining single crystals suitable for X-ray single crystal work.

Single crystals of V_nO_{2n-1} $(3 \leq n \leq 8)$, of size 1 to 5 mm, were recently synthesized by the chemical transport method (Nagasawa, 1972), and the crystallography of V_nO_{2n-1} was studied, using these crystals, by the X-ray single-crystal method (Horiuchi, Tokonami, Morimoto, Nagasawa, Bando & Takada, 1972). According to this study, the lattices of the homologous series of V_nO_{2n-1} ($\mathbf{a}_n, \mathbf{b}_n$ and $\mathbf{c}_n$, $4 \leq n \leq 8$) can be systematically described on the basis of the parent rutile-type lattice ($\mathbf{a}_r$, $\mathbf{b}_r$ and $\mathbf{c}_r$) as follows:

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