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The Crystal Structure of Ti_2S*

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The crystal structure of dititanium sulfide, Ti_2S, has been determined from single-crystal X-ray diffraction data. The compound crystallizes in the orthorhombic system, space group *Pnnm*, with unit-cell dimensions $a=11{\cdot}35$, $b=14{\cdot}06$, $c=3{\cdot}32$ Å. The unit cell contains 12 formula units. All atoms are located in layers separated by $c/2$. Refinement of the structure was performed by least-squares treatment of x and y positional parameters and isotropic temperature factor coefficients. The sulfur bonding is interpreted with bond order calculations and is shown to be consistent with sulfur atoms utilizing d orbitals to form either electron deficient bonds to at least seven metal atoms or directional electron deficient bonds to six metals with trigonal prismatic symmetry.

Introduction

The titanium–sulfur system has received much attention since a systematic study by Biltz, Ehrlich & Meisel (1937). The stoichiometries of the condensed phases in this system are still not thoroughly understood. In the lower sulfide region ($M/S \geq 1$) especially, the situation is unclear owing to a lack of information on the stability and homogeneity ranges of the reported phases.

Filonenko & Kydryavtsev (1953) described a hexagonal 'τ-Ti_2S' phase which later was shown by Kudielka & Rohde (1960) to be a phase with the ideal composition Ti_2CS. Hägg & Schönberg (1954) suggested the existence of a stable Ti_2S to explain powder diffraction data which were obtained from their subsulfide preparations. Abendroth & Schlechten (1959) reported some of the same diffraction lines as did Hägg & Schönberg, although they ascribed the other lines present in their subsulfide pattern to the 'Ti_5S_4' phase.

In a review of transition metal sulfides, Jellinek (1963) suggested that the additional lines in Hägg & Schönberg's and Abendroth & Schlechten's patterns were due to impurities formed by reaction of the metal with the quartz preparative tubes. Work on the extent of impurities in lower titanium sulfides was also performed by Bartrum (1958) and by Hahn & Ness (1959).

Franzen & Gilles (1965), while studying the vaporization behavior of TiS, prepared a subsulfide, the further characterization of which was undertaken by Stone (1963).

Stone obtained accurate lattice parameters by a least-squares fit of Guinier powder diffraction lines. His values were $a=11{\cdot}35$, $b=14{\cdot}06$, $c=3{\cdot}32$ Å. The parameters obtained from single-crystal diffraction patterns in the work reported here are in complete agreement with these values. Stone also determined the space group symmetry and concluded that two space groups were possible, namely *Pnn*2 and *Pnnm*, in agreement with our findings as discussed below. Density determinations performed by Stone, employing a buoyancy method with two liquids and a pycnometer method with the same liquids, yielded an average density of $4{\cdot}80$ g.cm^{-3}, corresponding to $11{\cdot}97$ Ti_2S units per unit cell. It was reported by Stone that combustion analysis yielded $S/Ti=0{\cdot}498$.

The work reported here was conducted for the purpose of establishing the existence and structure of the Ti_2S phase.

Experimental

The dititanium sulfide samples were prepared by annealing pellets composed of equimolar quantities of titanium monosulfide and titanium filings. The titanium monosulfide samples were prepared by heating mixtures of titanium filings and sulfur in sealed Vycor tubes

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evacuated to 10^{-2} Torr. The 99·93% titanium metal was obtained from the Chicago Development Corporation. The 99·999% sulfur was obtained from the Galland Schlesinger Chemical Mfg. Corp. The elementary mixtures in the sealed Vycor tubes were heated at 400–500 °C for 9 days. Then the products were mixed with equimolar amounts of titanium filings, compressed into pellet form and annealed at *ca.* 1375 °C for $2\frac{1}{2}$ hr in an inductively heated tungsten crucible under high vacuum (residual pressure less than 10^{-6} Torr). The crucible and samples were quenched by radiative heat loss.

X-ray examination of the samples was performed with powder and Weissenberg single-crystal techniques. A single crystal was selected from the annealed sample and data were collected from zero, first, second, and third layer Weissenberg photographs around the *c* axis using a Chas. G. Supper Co. Weissenberg camera and molybdenum $K\alpha$ radiation with a zirconium filter.

The intensities were estimated by visual multiple film techniques using an intensity scale obtained from timed oscillations of the crystal under study. Corrections were applied to obtain unresolved $K\alpha$ intensities. Lorentz-polarization corrections were made graphically. From several rather poorly focused microphotographs (× 500) of the irregular crystal, it was estimated that the bulk of the crystal was contained approximately in a parallelepiped $50\mu \times 30\mu \times 20\mu$ and thus that absorption corrections were negligible. This assumption was approximately valid, as can be seen from the reasonable thermal parameters obtained. The thermal parameters may, however, be somewhat in error owing to the fact that no absorption corrections were made. Also, no extinction corrections were made.

Structure determination

From Weissenberg and precession patterns the conditions for reflection were observed to be:

hkl	no conditions
$0kl$	$k+l=2n$
$h0l$	$h+l=2n$
$hk0$	no conditions
$h00$	$h=2n$
$0k0$	$k=2n$
$00l$	$l=2n$.

The reflection conditions indicate two possible space groups *Pnn*2 (C_{2v}^{10}) and *Pnnm* (D_{2h}^{12}), differing by a center of symmetry. The Laue group is *mmm* (D_{2h}).

A Patterson synthesis was performed using $hk0$, $hk1$, $hk2$, and $hk3$ data and was solved by superposition techniques for possible titanium atom positions. In the centrosymmetric space group, *Pnnm*, the fourfold positions (*g*) $x,y,0$ were chosen as the positions of lowest symmetry for both the Ti and S atoms, since the *c* lattice parameter of 3·32 Å would not allow atoms at both x,y,z and $x,y,\bar{z}$. The Patterson map, in agreement with this choice, showed all maxima to occur at $z=0$ and $z=\frac{1}{2}$. Accordingly, the Patterson section at $z=0$ was solved to yield seven atomic positions. *Pnnm* Fourier syntheses were employed to locate all positions and, after several computations, the agreement between F_o and F_c, expressed by the reliability index $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$, was 0·22, with all nine independent atoms located.

The atomic positions were refined further by four cycles of least-squares computation (Busing, Martin & Levy, 1962) using atomic scattering factor tables given by Hansen, Herman, Lea & Skillman (1964) and isotropic temperature factor coefficients. The weighting scheme due to Hughes (1941) was initially employed; the weights were checked by a plot of $|F_o-F_c|^2/\sigma^2$ *versus* F_o, where σ is the estimated relative error in F_o. A straight line of slope 0·14 was drawn through the points representing groups of 75 reflections, and revised weights were assigned such that the line would have zero slope. A cycle of least-squares computation with the revised weights yielded an unweighted $R=0·10$. All atoms are fourfold $x,y,0$ positions. Table 1 contains a listing of the positional parameters and temperature factor coefficients obtained. Table 2 lists the observed and calculated structure factors for all 535 observed reflections.

Refinement of the structure utilizing two-dimensional anisotropic temperature factors resulted in no significant change in the positional parameters or the

Table 1. *Final atomic parameters for* Ti_2S

All atoms occupy fourfold positions (*g*) $x,y,0$ of space group *Pnnm*.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	B	$\sigma(B)$
Ti(1)	0·1543	0·0004	0·0206	0·0003	0·51 Å^2	0·06 Å^2
Ti(2)	0·0867	0·0004	0·2553	0·0003	0·55	0·06
Ti(3)	0·5881	0·0004	0·0797	0·0003	0·44	0·06
Ti(4)	0·4696	0·0004	0·3904	0·0003	0·55	0·06
Ti(5)	0·8073	0·0004	0·2078	0·0003	0·46	0·06
Ti(6)	0·8797	0·0004	0·4221	0·0003	0·57	0·06
S(1)	0·4320	0·0005	0·2068	0·0004	0·56	0·08
S(2)	0·2451	0·0006	0·4124	0·0005	0·68	0·08
S(3)	0·6841	0·0005	0·3498	0·0004	0·34	0·07

Zero layer scale factor = 0·0221, σ = 0·0003
First layer scale factor = 0·0204, σ = 0·0003
Second layer scale factor = 0·0216, σ = 0·0003
Third layer scale factor = 0·0219, σ = 0·0004

Table 2. *Observed and calculated structure factors for* Ti_2S

H	K	L	F_o	F_c
0	4	0	162	-175
0	10	0	83	87
0	12	0	54	62
0	14	0	59	55
0	16	0	51	-49
0	18	0	105	-83
0	22	0	93	-78
1	5	0	17	24
1	7	0	164	152
1	8	0	155	-143
1	9	0	49	49
1	10	0	18	-72
1	13	0	73	-85
1	14	0	32	-71
1	15	0	39	-40
1	19	0	58	57
1	25	0	37	-48
2	5	0	38	-42
2	6	0	82	-84
2	8	0	33	41
2	9	0	155	-145
2	11	0	70	71
2	13	0	97	-93
2	14	0	54	-51
2	16	0	43	49
2	17	0	44	-42
3	1	0	21	-21
3	2	0	17	-17
3	4	0	29	30
3	5	0	183	-197
3	6	0	87	-89
3	7	0	44	-45
3	8	0	30	37
3	11	0	51	49
3	16	0	62	-65
3	17	0	66	67
3	18	0	30	38
4	0	0	107	-100
4	1	0	19	-19
4	2	0	41	-37
4	3	0	110	95
4	4	0	106	-95
4	5	0	104	-100
4	6	0	23	26
4	7	0	51	51
4	9	0	44	51
4	10	0	44	47
4	11	0	56	64
4	12	0	59	-59
4	14	0	30	-37
4	17	0	30	-34
4	18	0	53	59
4	20	0	52	39
5	1	0	167	168
5	2	0	155	143
5	3	0	116	-94
5	4	0	167	150
5	6	0	42	-42
5	7	0	114	-110
5	9	0	35	40
5	12	0	36	35
5	13	0	69	55
5	14	0	92	90
5	25	0	38	43
6	0	0	54	-54
6	1	0	60	63
6	2	0	43	46
6	3	0	58	-55
6	6	0	194	170
6	8	0	43	41
6	11	0	113	121
6	12	0	77	-83
6	18	0	49	50
6	21	0	50	46
6	24	0	77	-61
7	1	0	61	65
7	3	0	37	34
7	8	0	61	-63
7	9	0	33	38
7	14	0	74	-69
7	20	0	53	47
8	0	0	57	-54
8	1	0	63	61
8	2	0	127	124
8	3	0	34	33
8	4	0	55	-48
8	6	0	60	-63
8	7	0	107	-123
8	9	0	23	-26
8	11	0	55	-55
8	12	0	78	70
8	15	0	51	-51
8	20	0	54	-53
9	1	0	84	-87
9	3	0	20	-25
9	5	0	33	38
9	6	0	92	-98
9	13	0	49	-45
9	16	0	54	-49
9	18	0	41	-46
9	19	0	34	38
10	0	0	33	27
10	1	0	52	55
10	2	0	76	-74
10	3	0	101	93
10	6	0	37	-37
10	7	0	65	-62
10	10	0	27	-37
10	11	0	75	-65
10	13	0	59	58
10	14	0	31	37
11	3	0	40	-42
11	4	0	71	-61
11	6	0	38	41
11	10	0	100	94
11	12	0	51	56
11	20	0	68	62
12	0	0	55	54
12	3	0	36	31
12	4	0	40	42
12	11	0	57	62
12	12	0	48	48
12	18	0	51	-47
13	2	0	67	56
13	3	0	107	89
13	4	0	43	45
13	7	0	45	40
13	8	0	73	-76
13	9	0	30	-35
13	19	0	58	-49
14	0	0	41	-36
14	1	0	78	-69
14	4	0	79	70
14	5	0	105	-88
14	15	0	36	-50
14	17	0	69	-57
15	2	0	31	36
15	10	0	47	-44
15	12	0	59	-51
16	2	0	32	-36
16	5	0	33	-28
16	8	0	57	-55
16	14	0	62	66
18	0	0	94	-75
18	5	0	55	51
19	2	0	67	-57
19	8	0	59	68
20	11	0	55	-60
0	5	1	203	227
0	7	1	48	-52
0	9	1	19	27
0	13	1	42	-48
0	15	1	61	67
0	17	1	60	-56
0	21	1	63	-60
1	3	1	17	19
1	4	1	190	151
1	5	1	56	-54
1	7	1	25	25
1	8	1	18	26
1	9	1	72	-75
1	10	1	61	-63
1	11	1	42	-46
1	12	1	44	45
1	13	1	73	-86
1	15	1	42	42
1	18	1	39	-39
2	2	1	73	-64
2	4	1	206	-227
2	5	1	44	-40
2	6	1	23	21
2	9	1	67	-71
2	10	1	64	62
2	12	1	48	-49
2	13	1	56	69
2	14	1	58	-57
2	16	1	25	-33
2	17	1	42	-47
2	18	1	74	-69
3	0	1	250	-184
3	1	1	92	-91
3	2	1	43	-40
3	3	1	208	216
3	4	1	57	-53
3	6	1	47	49
3	9	1	116	-120
3	10	1	102	-107
3	11	1	74	-82
3	12	1	34	36
3	15	1	67	67
3	21	1	100	-91
4	1	1	94	-86
4	2	1	145	-122
4	3	1	26	-20
4	5	1	33	30
4	6	1	60	58
4	7	1	25	-23
4	8	1	50	54
4	9	1	53	-48
4	10	1	50	51
4	11	1	40	-38
4	18	1	28	42
5	0	1	26	-20
5	1	1	154	-125
5	4	1	37	38
5	6	1	28	27
5	7	1	95	93
5	8	1	99	-92
5	9	1	72	72
5	10	1	90	93
5	12	1	55	-62
5	14	1	67	57
5	19	1	46	37
6	2	1	66	65
6	3	1	67	67
6	5	1	45	58
6	6	1	105	97
6	9	1	32	34
6	16	1	96	100
7	0	1	64	60
7	1	1	31	38
7	2	1	112	96
7	3	1	124	-123
7	5	1	27	-24
7	8	1	52	-49
7	9	1	34	38
7	10	1	35	32
7	13	1	25	-26
7	14	1	53	53
7	19	1	54	-55
7	20	1	45	-43
8	1	1	75	-67
8	4	1	31	21
8	7	1	172	144
8	9	1	43	-43
8	10	1	91	-95
8	11	1	55	-51
8	12	1	68	-59
8	15	1	39	-43
8	17	1	50	51
9	1	1	55	-51
9	2	1	56	-37
9	3	1	106	-114
9	4	1	44	-38
9	5	1	34	30
9	6	1	41	-40
9	9	1	40	44
9	11	1	51	-54
9	15	1	69	-67
10	2	1	71	-72
10	3	1	31	-34
10	4	1	38	40
10	5	1	51	-53
10	7	1	69	-72
10	8	1	42	39
10	11	1	37	36
10	18	1	32	27
11	2	1	82	-78
11	4	1	64	60
11	5	1	71	61
11	8	1	43	42
11	9	1	26	-28
11	14	1	49	-53
11	15	1	80	75
11	17	1	45	40
12	4	1	39	-40
12	8	1	65	64
13	6	1	26	34
13	6	1	97	91
13	13	1	30	-38
13	14	1	76	-71
15	9	1	47	-51
16	9	1	53	51
16	13	1	68	-65
0	6	2	194	-122
0	10	2	68	68
0	12	2	52	51
0	14	2	52	48
0	16	2	47	-43
0	18	2	80	-74
0	22	2	75	-71
1	7	2	132	112
1	8	2	141	-109
1	9	2	39	36
1	13	2	60	-69
1	15	2	38	-34
1	19	2	47	52
1	23	2	45	-31
1	25	2	50	-44
2	2	2	19	-11
2	4	2	21	-12
2	5	2	36	-29
2	6	2	67	-60
2	8	2	36	30
2	9	2	110	-113
2	11	2	56	60
2	13	2	73	-78
2	14	2	33	-44
2	16	2	36	43
3	1	2	19	-13
3	3	2	20	8
3	4	2	24	22
3	5	2	189	-140
3	6	2	69	-66
3	7	2	39	-34
3	8	2	41	31
3	16	2	57	-56
3	17	2	59	60
4	0	2	72	-69
4	1	2	20	-13
4	2	2	27	-26
4	3	2	77	67
4	4	2	80	-67
4	5	2	76	-74
4	6	2	17	18
4	7	2	40	39
4	9	2	44	41
4	10	2	38	39
4	11	2	48	51
4	12	2	50	-48
4	14	2	34	-31
4	18	2	47	53
5	1	2	157	120
5	2	2	132	103
5	3	2	83	-69
5	4	2	159	111
5	6	2	31	-33
5	7	2	86	-83
5	9	2	32	32
5	13	2	44	47
5	14	2	78	78
5	17	2	46	-46
5	18	2	29	30
5	25	2	51	40
6	0	2	43	-39
6	1	2	47	46
6	2	2	38	33
6	3	2	45	-41
6	6	2	124	134
6	8	2	34	34
6	11	2	95	102
6	12	2	63	-70
6	18	2	44	44
6	21	2	48	42
6	24	2	55	-56
6	27	2	46	-22
7	1	2	53	50
7	3	2	29	25
7	8	2	47	-51
7	9	2	33	32
7	14	2	63	-60
7	20	2	50	43
8	0	2	47	-44
8	1	2	49	47
8	2	2	98	100
8	3	2	32	27
8	4	2	41	-38
8	6	2	54	-53
8	7	2	91	-100
8	11	2	40	-47
8	12	2	60	61
8	13	2	26	27
8	15	2	42	-45
8	20	2	48	-48
9	1	2	73	-70
9	5	2	33	32
9	6	2	77	-81
9	12	2	26	16
9	13	2	41	-39
9	16	2	44	-45
9	18	2	43	-41
9	19	2	43	34
10	1	2	40	45
10	2	2	64	-61
10	3	2	71	78
10	6	2	23	-31
10	7	2	44	-52
10	9	2	25	24
10	10	2	39	-32
10	11	2	52	-57
10	12	2	26	14
10	13	2	45	51
10	14	2	39	34
11	3	2	36	-36
11	4	2	57	-52
11	6	2	34	36
11	10	2	77	82
11	12	2	51	50
11	20	2	54	56
12	0	2	41	46
12	3	2	26	27
12	11	2	67	56
12	12	2	44	43
12	19	2	46	24
13	2	2	51	49
13	3	2	82	78
13	4	2	40	40
13	8	2	55	-67
14	1	2	65	-61
14	4	2	55	62
14	5	2	67	-79
14	15	2	45	-46
14	17	2	50	-53
15	12	2	48	-46
16	8	2	46	-50
16	14	2	50	60
18	0	2	76	-68
18	5	2	45	47
19	2	2	49	-52
19	8	2	55	62
0	3	3	32	35
0	5	3	175	132
0	7	3	35	-36
0	9	3	27	21
0	13	3	33	-36
0	15	3	47	51
0	17	3	42	-45
0	21	3	50	-49
1	4	3	87	84
1	5	3	37	-34
1	9	3	47	-44
1	10	3	45	-42
1	11	3	36	-33
1	12	3	35	32
1	13	3	67	-63
1	18	3	38	-31
2	2	3	32	-32
2	4	3	169	-130
2	5	3	29	-23
2	9	3	47	-46
2	10	3	44	43
2	12	3	49	-36
2	13	3	51	52
2	14	3	40	-43
2	17	3	37	-36
2	18	3	51	-55
3	0	3	100	-98
3	1	3	45	-51
3	2	3	26	-22
3	3	3	156	124
3	4	3	39	-33
3	5	3	26	13
3	6	3	38	32
3	9	3	83	-80
3	10	3	79	-76
3	11	3	57	-59
3	15	3	56	51
3	21	3	72	-74
3	27	3	31	37
4	1	3	49	-50
4	2	3	79	-72
4	3	3	16	-11
4	5	3	26	20
4	6	3	40	40
4	7	3	26	-12
4	8	3	33	31
4	9	3	31	-32
4	10	3	32	36
4	11	3	31	-28
5	1	3	91	-77
5	6	3	18	14
5	7	3	57	61
5	8	3	58	-63
5	9	3	50	50
5	10	3	54	68
5	12	3	37	-46
6	2	3	47	44
6	3	3	44	45
6	5	3	32	35
6	6	3	63	64
6	15	3	26	-23
6	16	3	71	80
7	0	3	42	41
7	1	3	29	28
7	2	3	61	60
7	3	3	89	-77
7	8	3	37	-34
7	9	3	31	29
7	14	3	40	41
7	19	3	47	-45
7	20	3	42	-37
8	1	3	44	-44
8	7	3	101	106
8	9	3	37	-32
8	10	3	69	-72
8	11	3	37	-39
8	12	3	42	-46
8	15	3	38	-34
8	17	3	44	40
8	21	3	31	31
9	0	3	35	35
9	1	3	36	-37
9	2	3	21	-27
9	3	3	99	-81
9	4	3	33	-27
9	5	3	31	22
9	6	3	27	-28
9	9	3	37	33
9	11	3	38	-42
9	15	3	51	-54
10	2	3	45	-53
10	4	3	35	31
10	5	3	37	-39
10	7	3	53	-55
10	8	3	34	29
11	1	3	52	49
1	2	3	57	-58
1	4	3	52	46
1	5	3	41	46
11	14	3	44	-43
11	15	3	49	61
12	1	3	45	46
12	4	3	39	-32
12	8	3	40	50
12	10	3	38	29
12	11	3	27	28
12	21	3	44	-34
13	7	3	45	36
13	8	3	66	74
13	13	3	29	-30
13	14	3	55	-59
14	1	3	45	55
15	1	3	47	-43
15	9	3	47	-41
16	1	3	44	-40
16	3	3	44	-33
16	9	3	46	42
16	13	3	52	-53
16	19	3	47	48
17	2	3	42	39
17	4	3	50	-54
17	6	3	51	-45
21	7	3	43	-23
22	2	3	43	37
22	5	3	47	-38

reliability index. A difference Fourier synthesis for the space group *Pnnm* was obtained and showed small residual peaks, corresponding to 0·7 to 1·0 electron, at thc metal positions.

The bond distances listed in column 3 of Table 3 were obtained from the Thermal-Ellipsoid Plot computer program written by Johnson (1965). The same program was used with Slater's (1964) radii to draw the stereoscopic view in Fig. 1. Slater's radii have been used to obtain Fig. 2, showing a layer of the unit cell perpendicular to the *c* axis. The bonding in this layer is less important than the bonding between layers, but that such bonding occurs in Ti_2S is a unique feature of this compound in comparison with other known mono- and di-transition metal chalconides.

Table 3. *Bond distances and bond orders for* Ti_2S

Reference atom	Coordinated atom	Distance
S(1)	Ti(2)	2·48 Å
	Ti(2)	2·48
	Ti(5)	2·49
	Ti(5)	2·49
	Ti(3)	2·52
	Ti(6)	2·53
	Ti(6)	2·53
	Ti(4)	2·62
S(2)	Ti(3)	2·44
	Ti(3)	2·44
	Ti(5)	2·48
	Ti(5)	2·48
	Ti(1)	2·53
	Ti(1)	2·53
	Ti(4)	2·58
	Ti(6)	2·71
	Ti(2)	2·85
S(3)	Ti(6)	2·44
	Ti(5)	2·44
	Ti(2)	2·49
	Ti(2)	2·49
	Ti(1)	2·49
	Ti(1)	2·49
	Ti(4)	2·51
Ti(1)	S(3)	2·49
	S(3)	2·49
	S(2)	2·53
	S(2)	2·53
	Ti(4)	2·84
	Ti(4)	2·84
	Ti(4)	2·95
	Ti(4)	2·95
	Ti(6)	3·16
	Ti(6)	3·16
Ti(2)	S(1)	2·48
	S(1)	2·48
	S(3)	2·49
	S(3)	2·49
	S(2)	2·85
	Ti(3)	2·86
	Ti(3)	2·86
	Ti(4)	2·95
	Ti(4)	2·95
	Ti(5)	3·06
	Ti(5)	3·06
Ti(3)	S(2)	2·44
	S(2)	2·44
	S(1)	2·52
	Ti(6)	2·79
	Ti(6)	2·79
	Ti(2)	2·86
	Ti(2)	2·86
	Ti(6)	2·89
	Ti(6)	2·89
	Ti(3)	3·00
	Ti(5)	3·08
Ti(4)	S(3)	2·51
	S(2)	2·58
	S(1)	2·62
	Ti(5)	2·83
	Ti(5)	2·83
	Ti(1)	2·84
	Ti(1)	2·84
	Ti(1)	2·95
	Ti(1)	2·95
	Ti(2)	2·95
	Ti(2)	2·95
	Ti(4)	3·16
Ti(5)	S(3)	2·44
	S(2)	2·48
	S(2)	2·48
	S(1)	2·49
	S(1)	2·49
	Ti(4)	2·83
	Ti(4)	2·83
	Ti(2)	3·06
	Ti(2)	3·06
	Ti(3)	3·08
	Ti(6)	3·12
Ti(6)	S(3)	2·44
	S(1)	2·53
	S(1)	2·53
	S(2)	2·71
	Ti(3)	2·79
	Ti(3)	2·79
	Ti(3)	2·89
	Ti(3)	2·89
	Ti(5)	3·12
	Ti(1)	3·16
	Ti(1)	3·16

Discussion

Two covalent interpretations of the bonding of sulfur in Ti_2S are presented. The first description is based on the empirical relationship due to Pauling (1960),

$$D(n)=D(1)-0{\cdot}6\log n\,, \qquad (1)$$

relating the bond distance, D, of a bond to its bond order n. From the distances in Table 3 it is accordingly concluded that each sulfur atom is coordinated to at least seven metal atoms, and one of the sulfur atoms is bonded possibly to nine metal atoms. The corresponding valence, obtained by the summation of bond orders, of the various atoms are listed in column two of Table 4. The geometry of the coordination of the sulfur is, in this case, slightly distorted trigonal prismatic with additional coplanar metals perpendicular to and slightly removed from the faces of the prisms.

In the cases of several transition metal lower chalconides, *e.g.* TiS and related compounds, it has been proposed (Franzen, 1966) that sulfur utilizes *d* orbitals in bonding. A sulfur atom that is seven-coordinated could accordingly involve from four to six electrons ($3s^2$, $2p^4$) in a variety of molecular orbitals with varying symmetries, since many different *s*, *p*, and *d* combinations would be possible. The valences of Table 4 and observed sulfur coordination symmetries suggest that such is the case in Ti_2S.

The coordination of the Ti atoms cannot be described by a simple symmetry. The metal atoms are bonded strongly to sulfur atoms, with significant metal–metal bonding also occurring; the stronger metal–sulfur bonds are expected from electronegativity differences between the elements.

The second interpretation is based on previous work (Geller, 1956; Rundle, 1948) which has suggested that in compounds with directional covalent bonds the Pauling bond order will result in valences which are too large. The bond order concept has been applied successfully in many intermetallic compounds, but Geller has pointed out its need for revision in the β-W-type structure. Rundle suggested that the bonding in some monoxides and mononitrides could be explained by directional covalent bonds, suggesting also that in these cases the criterion for bonding is not *merely* the distance between atoms. If this is the case, it is possible to provide a description of the coordination and valence of sulfur in Ti_2S which is more consistent with that given by Franzen (1966) for mono- and lower chalconides.

Table 4. *Atom valences for alternative bonding descriptions*

	Non-directional, covalent $V=\Sigma n$	Trigonal-prismatic covalent $V=\Sigma n$
S(1)	4·47	3·56
S(2)	4·69	3·84
S(3)	4·48	3·91
Ti(1)	4·10	4·10
Ti(2)	4·53	4·38
Ti(3)	5·24	4·70
Ti(4)	4·62	3·24
Ti(5)	4·95	4·95
Ti(6)	4·36	4·10

If, in Ti_2S, the Ti–S distances perpendicular to the faces of the prism are considered to be non-bonding [note that the equatorial titanium atoms are strongly bonded to the corner titanium atoms, *e.g.* Ti(3) to two Ti(6) and two Ti(2)], then the valences computed are as shown in Table 4, column 3. The coordination symmetry, the metal–sulfur distances, the brittleness and the metallic properties are consistent with the sulfur in Ti_2S utilizing approximately four electrons and six orbitals (including *d* orbitals) to form electron deficient,

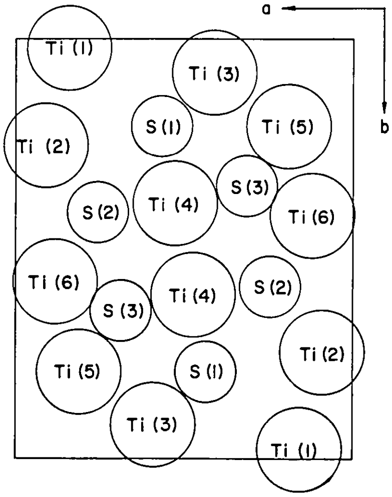

Fig. 2. *x*,*y* plane of Ti_2S structure. The atoms are drawn according to Slater's radii.

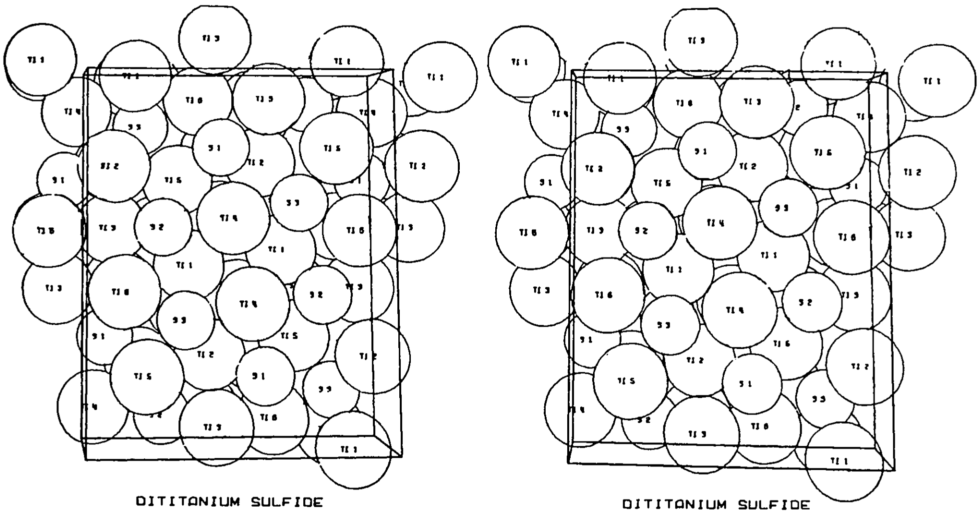

Fig. 1. Stereoscopic illustration of the Ti_2S structure viewed along the *c* axis. The box represents one unit cell.

directional bonds. A valence of four of Ti is expected since one would expect the $3d^24s^2$ electrons to be involved in bonding. The high Ti valences obtained using equation (1) could be due to short non-bonded Ti–Ti distances.

Summary

The bonding of each metal atom in Ti_2S is different and complex; bond order and valence calculations on all metal atoms yield fairly reasonable results. Two descriptions of the sulfur bonding have been presented:

(1) Sulfur coordination of from seven to nine metal atoms, six of which form a distorted trigonal prism with one or more metal atoms removed from the faces of the prism; this description is based on covalent, electron deficient interactions and Pauling bond orders.

(2) Sulfur coordination to six metal atoms in a slightly distorted trigonal prism based on covalent, directional, electron deficient interactions. The second description has been presented in an effort to correlate the sulfur bonding in Ti_2S with that in other lower chalconides.

A distinction between the two bonding alternatives will, it is hoped, be possible when more structural information is available for lower transition metal chalconides.

Note added in proof:- Ti_2S is isostructural with Ta_2P, the crystal structure of which was recently published by Nyland (1966).

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Double Oxides containing Niobium or Tantalum. II. Systems Involving Strontium or Barium

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The binary oxide systems $SrO–Nb_2O_5$, $BaO–Nb_2O_5$, and $SrO–Ta_2O_5$ have been studied. Unit-cell data for most of the previously reported compounds and for four new phases have been determined. Both 'ideal' and 'tripled' forms of the tetragonal bronze structure occur in these systems. $SrNb_2O_6$ is isostructural with the orthorhombic form of $CaTa_2O_6$.

Introduction

The procedure used in investigating these systems was that described earlier (Whiston & Smith, 1965). The relevant literature is reviewed under each section for convenience in presenting our results and comparing them with those of previous workers.

The system $SrO–Nb_2O_5$

Goldschmidt (1960) detected, by means of powder patterns, four phases of approximate compositions

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