Fig. 8. Axes of the rigid body vibration.

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The Crystal Structure of Nb₂₁S₈*

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The crystal structure of $Nb_{21}S_8$ has been determined from single-crystal X-ray diffraction data. The compound crystallizes in the tetragonal system, space group $I4/m$ with unit-cell parameters $a = 16.794$ Å, $c = 3.359$ Å. The unit cell contains two 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. Pauling bond orders indicate that the coordination of sulfur in this compound is seven. This result is consistent with sulfur atoms utilizing d orbitals to form electron deficient bonds to the metal atoms.

Introduction

The high temperature (ca. 1350°C) preparation of a new subsulfide in the niobium–sulfur system, characterized as Nb_2S, and some crystallographic data for the compound were recently reported (Franzen, De-Jong & Conard, 1966). The compositions reported were obtained by combustion techniques on samples which have since been identified as containing two phases. A more recent composition analysis is reported below.

Previous studies of the niobium–sulfur system in the range $0 \leq S/Nb \leq 1.0$ resulted in the identification of two phases, neither of which was the same as the phase reported here. Biltz & Köcher (1938) reported a phase with the homogeneity range $0.5 \leq S/Nb \leq 1.0$; Jellinek

(1962) observed a NbS_{1-x} ($x = 0.1$ to ?) phase with an ordered NiAs-type structure.

Investigations of the lower sulfides of Hf and Ti, namely Hf_2S (Franzen & Graham, 1966) and Ti_2S (Owens, Conard & Franzen, 1966), have resulted in a new interpretation of the bonding of sulfur in the mono-sulfides and lower sulfides of transition metals (Franzen, 1966). The interest in the crystal structure of $Nb_{21}S_8$ stemmed from a desire to describe more completely the chemistry of sulfur in the lower sulfides of transition metals.

Experimental

The previously reported crystallographic data for $Nb_{21}S_8$ are summarized as follows. The space group was reported to be $I4/m$, the lattice parameters reported were $a = 16.794 \pm 0.005$, $c = 3.359 \pm 0.002$ Å, and the number of 'Nb_2S' formula units per unit cell was estimated to be between 21 and 24, based on a measured

density of 8·8 g.cm⁻³ (which corresponded to 2·3 $Nb_{21}S_8$ formula units per cell).

The density has been redetermined for a single phase sample of $Nb_{21}S_8$ to be $7·8 \pm 0·1$ g.cm⁻³, which corresponds to 2·0 $Nb_{21}S_8$ formula units per unit cell. More recent combustion analyses have been performed on single-phase samples under more carefully controlled conditions than before and yielded S/Nb = 0·34.

Intensity data were collected with Mo $K\alpha$ radiation using a General Electric spectrogoniometer with a scintillation counter detector. A total of 557 independent reflections of $hk0$ and $hk1$ types were measured. Lorentz and polarization corrections were applied. Absorption corrections, based on the crystal's trapezoidal shape (average side length of about 40 μ and thickness of about 30 μ) were made with use of a program by Busing & Levy (1957) adapted to the IBM 360/50 computer. A total linear absorption coefficient of 136·5 cm⁻¹ was used in the absorption correction calculation. No extinction corrections were made.

Structure determination

Unitary structure factors were obtained from the observed structure factors by a graphical method (Woolfson, 1961). Except for attenuation normally expected for the increase in scattering angle, the intensity data were observed to depend on l only so far as l was even or odd, indicating a layered structure with all atoms in the mirror planes of the centrosymmetric space group (Franzen, DeJong & Conard, 1966). It follows that $U_{hkl+2} = U_{hkl} = U_{\bar{k}hl} = U_{k\bar{h}l}$. Thus, by the Harker-Kasper inequalities (Harker & Kasper, 1948) if U_{hkl} and $U_{h-k,h+k,0}$ are sufficiently large, then $U_{h-k,h+k,0}$ is positive, and a similar remark holds for $U_{h+k,k-h,0}$.

The 51 unitary structure factors with magnitudes greater than or equal to 0·39, about 9% of the total number of the observed reflections, were examined. Application of the reasoning described above yielded the sign of 19 of these as positive. One of the two degrees of freedom with respect to sign determination for the tetragonal case is removed by the body-center (Hauptmann & Karle, 1953), and thus only one unitary structure factor sign could be arbitrarily determined. $U_{3,4,1}$ was arbitrarily taken to be positive. This sign, together with the 19 positive unitary structure factors discussed above and the Harker-Kasper inequalities, yielded 15 more positive structure factors. The sign of $U_{2,5,1}$ was designated a, and combination of this structure factor and those known to be positive with those of the original 51 whose signs were as yet undetermined yielded 13 structure factors with the sign a.

Two electron density maps were computed utilizing the 47 unitary structure factors, one map with a positive, the other with a negative. These maps contained more peaks than could be explained on the basis of the cell content given by the density and lattice parameters by about a factor of two. Of several attempts to solve the

structure utilizing these electron density maps and the Patterson map, the following scheme resulted in a structure which refined to an acceptable reliability index.

The strongest peak on the electron density map obtained with a negative was taken to be an atom position $x',y',0$. A corresponding Patterson peak occurred at $2x',2y',0$ in the zero section of the Patterson map. A superposition of zero section Patterson maps was performed with the origin of the superimposed map placed at $x',y',0$ on the primary map. A trial structure in the $x,y,0$ plane was obtained. This trial structure was superimposed on the electron density map discussed above and a second trial structure was obtained from the coincident peaks. The second trial structure contained an atom at the origin and six other independent atom positions.

At this point in the structure determination, use was made of the known structural chemistry of lower transition metal sulfides (Owens, Conard & Franzen, 1967), and the niobium and sulfur atoms were distributed among the six independent positions and the position at the origin in an attempt to obtain a structure in which there were six niobium atoms about each sulfur atom in a trigonal prism. There was an obvious hole in the structure which resulted from this distribution, and the placement of a niobium atom at this position completed the trigonal prism of niobium atoms about one of the independent sulfur positions. This resulted in a final trial structure with a niobium in the twofold position at the origin, and five independent niobium atoms and two independent sulfur atoms in the eightfold positions, $x,y,0$. This final structure was refined by least-squares computation (Busing, Martin & Levy, 1962) using atomic scattering factor tables given by Hansen, Herman, Lea & Skillman (1964), and after three cycles of refinement, a reliability index, defined by $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, of 0·12 was obtained.

The structure was further refined by least-squares computation of the 14 positional parameters and eight isotropic temperature factor coefficients, using a weighting scheme based on statistical counting errors. The weights were assigned by calculating a relative error in the observed structure factor for each reflection, namely,

$$\sigma F = \frac{\sigma I}{2F(\text{Lp})},$$

where σI is the estimated error in the intensity corrected for absorption, F is the observed structure factor and Lp is the Lorentz and polarization correction factor. The square of the error in intensity, σ_I^2, was taken to be the total counts plus the background counts plus the square of 5% of the total counts plus the square of 5% of the background counts plus an estimated error in the absorption correction. The goodness of fit, defined by

$$\frac{\sum_i w^2(F_o-F_c)^2}{n-s},$$

was equal to 1·35, where w is the weight ($1/\sigma_F$) of the ith reflection, n is the number of reflections and s is the number of variables. A final unweighted $R=0\cdot063$ was obtained. Table 1 lists the values obtained. Table 2 lists the observed and calculated structure factors for all 557 observed reflections, and in addition, lists 60 unobserved reflections using parentheses to indicate $F_{\min}$ calculated using the background intensity. The unweighted R including the unobserved reflections was 0·086. Only the observed reflections were used in the least-squares refinement.

All 47 signs assigned by the direct method agreed with those obtained for the refined structure. For the purpose of checking the correctness of the refinement, a difference Fourier synthesis was performed using all 557 reflections. The synthesis showed the highest peaks, corresponding to about 0·8 electron, in the $z=0$ section. Specifically, the atomic position for Nb(2) had a positive $\varrho_o-\varrho_c$ corresponding to 0·8 electron, while those of Nb(3) and Nb(5) had negative peaks corresponding to about 0·7 electron. All other atomic positions in the difference Fourier map had negligible peaks. Interatomic distances obtained from the positional parameters of Table 1 are listed in Table 3. The Thermal Ellipsoid Plot computer program written by Johnson (1965) was used with Slater's (1964) radii to draw the stereoscopic view of the structure along the c axis. The illustration is presented in Fig. 1.

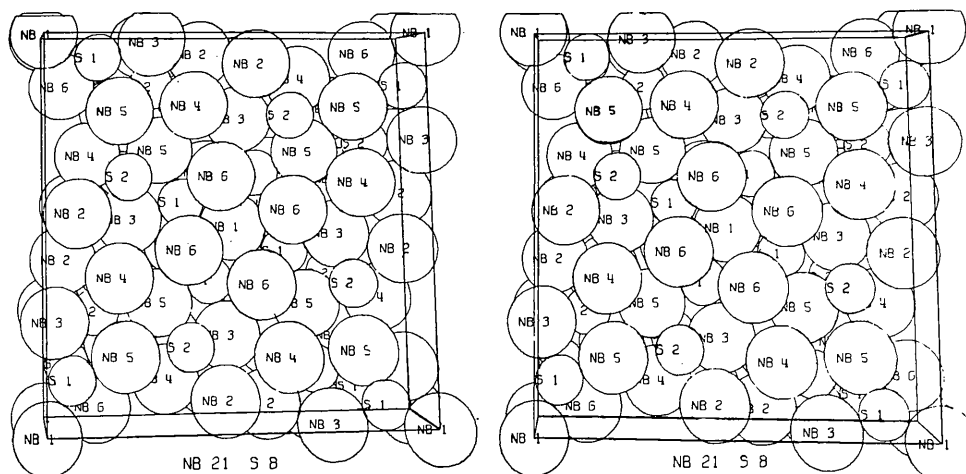

Discussion

The apparent coordination of both independent sulfur atoms in $Nb_{21}S_8$ is similar to that of the sulfur atoms in Ti_2S (Owens, Conard & Franzen, 1967), to that of phosphorus and silicon in compounds with the cementite structure as discussed by Aronsson, Lundstrom & Rundqvist (1965) and to that of Ta and Nb in K_2TaF_7 and K_2NbF_7, respectively (Hoard, 1939). Each sulfur atom is surrounded by a slightly distorted trigonal prism of niobium atoms with additional close metal atoms around the waist of the trigonal prism, *i.e.* ideally, on lines perpendicular to the centers of the rectangular faces of the prism, as shown for S(1) in Fig. 2.

Table 1. *Refined atomic positions for* $Nb_{21}S_8$

	Wyckoff notation	x	y	$\sigma(x)$	$\sigma(y)$	B	$\sigma(B)$
Nb(1)	2(*a*)	0·0	0·0			0·36 Å^2	0·05 Å^2
Nb(2)	8(*h*)	0·0813	0·4502	0·0001	0·0001	0·26	0·02
Nb(3)	8(*h*)	0·2777	0·0202	0·0001	0·0001	0·58	0·03
Nb(4)	8(*h*)	0·3843	0·1851	0·0001	0·0001	0·47	0·03
Nb(5)	8(*h*)	0·1919	0·1986	0·0001	0·0001	0·54	0·03
Nb(6)	8(*h*)	0·4509	0·3643	0·0001	0·0001	0·53	0·03
S(1)	8(*h*)	0·1377	0·0637	0·0003	0·0003	0·30	0·07
S(2)	8(*h*)	0·2126	0·3644	0·0003	0·0003	0·35	0·07

Table 2. *Observed and calculated structure factors for* $Nb_{21}S_8$

H	F(O)	F(C)
K= 0,L= 0		
2	50	38
4	27	31
6	100	116
8	230	-229
10	139	140
12	349	-351
14	100	105
16	235	241
18	82	-89
20	(52)	36
22	189	182
24	(52)	-37
26	(52)	43
28	104	-87
30	103	-129
32	87	-71
K= 1,L= 0		
7	608	631
9	50	48
15	309	321
17	141	142
21	171	164
23	(52)	31
25	(52)	33
27	185	-180
29	(57)	77
31	109	136
K= 2,L= 0		
0	52	38
2	69	53
4	93	-83
6	520	-542
8	303	-274
10	93	-86
12	44	58
14	396	394
16	100	97
18	108	126
20	86	86
22	113	104
K= 3,L= 0		
1	97	90
5	364	-376
7	681	696
9	182	168
13	85	-83
15	341	-335
17	80	86
23	141	136
25	102	-98
27	(52)	25
29	111	123
31	81	-68
33	145	146
K= 4,L= 0		
0	20	21
2	32	27
4	89	96
6	87	84
8	412	406
10	165	178
12	41	56
14	443	432
16	107	114
20	294	-296
22	104	-108
24	86	75
K= 5,L= 0		
3	37	17
5	415	397
7	92	-91
9	171	163
11	462	451
13	318	-311
17	69	-61
21	379	369
23	48	46
25	237	236
27	(52)	0
29	(57)	-16
31	66	75
K= 6,L= 0		
0	100	116
2	100	113
4	91	85
8	108	-105
10	193	194
12	122	-122
18	121	123
20	88	-84
22	148	-151
24	81	51
26	182	183
28	172	170
30	99	92
32	75	56
K= 7,L= 0		
1	202	190
3	513	508
5	341	-317
7	58	67
11	111	-119
13	86	-90
17	126	122
21	88	81
23	(52)	32
25	160	158
27	168	-167
29	187	-181
K= 8,L= 0		
0	236	-229
2	475	454
4	402	371
6	265	230
8	51	-51
10	61	52
12	130	131
18	361	359
20	86	-78
22	61	68
24	65	49
26	127	-112
28	132	136
30	(57)	-70
32	101	107
K= 9,L= 0		
1	143	-136
3	263	243
5	604	-598
7	361	-330
11	217	203
13	282	272
15	111	-106
17	311	295
19	236	232
21	(52)	-12
23	(52)	-12
25	67	73
K=10,L= 0		
0	143	140
2	320	-315
4	207	199
6	322	293
8	197	-205
10	303	298
12	404	-390
14	118	-114
16	107	105
20	127	126
22	119	-110
24	(52)	10
26	128	111
K=11,L= 0		
1	79	-79
3	71	70
5	173	172
9	127	118
11	420	408
13	263	261
19	203	-209
21	78	-76
23	97	-97
25	(52)	66
27	(57)	-30
29	(57)	6
31	82	68
K=12,L= 0		
0	356	-351
2	229	209
4	197	178
8	157	156
10	241	237
16	145	-142
18	215	215
20	260	238
22	(52)	-5
24	52	68
K=13,L= 0		
1	82	-85
3	66	66
5	54	-48
7	194	199
9	105	-105
13	127	131
15	134	-159
17	98	100
19	198	-187
21	64	-59
23	(52)	62
25	117	114
27	279	277
29	47	83
K=14,L= 0		
0	124	105
2	122	118
6	157	156
8	39	-38
10	225	-213
16	164	-160
18	75	83
22	107	105
24	(52)	63
26	218	-225
30	47	-54
K=15,L= 0		
1	110	109
3	366	343
5	376	357
7	136	-131
9	52	42
15	129	114
21	186	189
23	141	-149
25	(57)	60
27	46	89
K=16,L= 0		
0	216	241
2	298	-275
4	363	-355
6	111	123
8	193	-199
10	196	192
14	140	139
16	180	183
20	231	240
K=17,L= 0		
1	182	-178
3	104	97
5	82	72
7	128	126
9	161	-154
11	414	-395
13	190	185
21	80	87
K=18,L= 0		
0	85	-89
2	93	95
4	178	-196
6	155	152
8	139	131
10	166	166
12	325	318
18	178	-184
20	80	-66
22	(57)	39
24	85	-81
26	99	-76
28	125	109
K=19,L= 0		
7	286	267
9	99	101
13	141	148
15	48	-57
17	208	201
19	112	102
21	(57)	-14
23	96	76
25	74	-76
27	100	80
K=20,L= 0		
2	201	-187
6	121	133
10	82	91
12	38	-48
14	142	157
18	287	-288
22	(57)	26
24	147	165
26	191	143
K=21,L= 0		
1	113	115
3	112	-92
5	165	179
7	73	-86
11	47	-54
13	93	-96
21	115	150
K=22,L= 0		
0	183	182
2	432	436
8	107	88
20	(57)	32
22	73	-52
24	202	144
K=23,L= 0		
1	132	-126
3	66	-81
5	85	-84
7	77	76
9	88	85
13	117	107
17	220	219
21	(57)	55
23	110	83
K=24,L= 0		
2	258	268
4	111	-86
8	153	-144
10	191	-189
16	70	100
18	72	61
20	(57)	-12
22	57	76
K=25,L= 0		
3	40	-24
5	395	410
K=26,L= 0		
4	51	78
10	149	150
16	268	270
18	(57)	-11
K=27,L= 0		
9	135	138
K=28,L= 0		
0	69	-87
2	168	175
6	116	-98
10	45	-30
12	(57)	0
14	108	-91
K=29,L= 0		
1	272	270
K=30,L= 0		
0	147	-129
4	120	117
14	119	77
K=31,L= 0		
1	97	78
7	307	-261
K=32,L= 0		
6	81	92
8	109	134
K= 0,L= 1		
1	52	51
3	94	-78
5	475	507
7	157	-147
11	678	709
15	203	193
17	203	-212
19	231	-248
23	212	-206
25	76	71
27	(52)	35
29	(57)	20
31	72	71
33	65	66
K= 1,L= 1		
0	60	51
4	298	316
6	165	161
8	122	126
10	141	147
12	80	80
16	61	-63
18	307	311
20	238	245
24	116	-113
26	59	50
28	(57)	10
K= 2,L= 1		
1	162	-167
3	323	323
7	281	280
9	68	-73
11	20	-30
13	79	-65
17	80	-93
19	63	-55
21	72	60
23	47	53
25	301	317
27	164	169
29	70	70
K= 3,L= 1		
0	100	-78
2	94	-72
4	169	169
6	163	169
10	294	-299
12	113	116
16	325	-323
18	265	266
20	43	-42
22	208	205
24	56	-31
26	200	-198
28	82	95
30	128	-120
32	92	106
K= 4,L= 1		
1	146	147
3	727	738
5	212	201
7	121	119
11	59	68
13	179	184
15	108	-108
17	50	-33
19	189	199
21	141	131
23	102	-101
25	105	93
27	61	77
29	(57)	42
31	199	-193
K= 5,L= 1		
0	481	507
2	887	-911
4	281	-262
6	219	213
8	200	-197
10	468	500
14	262	258
16	171	177
18	47	-31
20	215	218
26	94	88
28	(57)	-12
30	(57)	-43
32	149	94
K= 6,L= 1		
5	47	35
7	50	-44
9	480	-476
11	141	-125
13	130	139
15	172	178
17	79	80
21	107	107
23	73	-74
25	(52)	44
27	(52)	-12
29	90	91
K= 7,L= 1		
0	159	-147
4	73	75
8	155	151
10	287	317
12	244	256
14	139	152
16	290	-313
18	128	-136
20	(52)	-6
22	85	-96
24	81	-96
26	(52)	14
28	77	80
K= 8,L= 1		
1	49	50
3	110	104
7	484	492
9	66	-63
13	174	198
17	314	351
19	25	42
21	(52)	-8
23	(52)	-17
25	135	-144
K= 9,L= 1		
2	69	59
6	150	193
8	244	234
10	83	-84
12	87	-78
14	168	172
16	191	-199
18	42	-55
20	69	-66
22	218	232
24	349	317
26	(52)	18
28	122	122
K=10,L= 1		
1	40	-59
3	40	48
5	219	224
7	112	-118
13	291	-293
15	64	80
21	240	247
23	156	-166
25	(52)	10
27	(57)	-46
29	(57)	45
31	139	160
K=11,L= 1		
0	671	709
2	355	360
6	177	183
8	68	-79
10	172	170
12	198	-205
16	58	53
18	25	-3
20	53	51
24	147	162
30	65	-121
K=12,L= 1		
1	321	-316
5	243	-251
7	341	348
9	258	260
11	134	-135
13	178	181
15	180	176
17	157	167
21	100	105
23	(52)	72
25	(57)	21
27	95	-113
K=13,L= 1		
0	26	34
2	327	329
4	92	-294
6	210	-206
8	262	-264
10	99	-91
12	54	61
14	119	123
16	198	197
18	94	93
22	108	120
24	(52)	69
26	108	-106
28	107	119
K=14,L= 1		
1	51	47
3	61	75
5	240	-269
7	212	218
9	342	347
13	52	58
15	238	-237
21	148	-156
23	(52)	38
25	(57)	-47
27	(57)	3
29	65	70
K=15,L= 1		
0	197	153
4	81	87
6	142	142
10	224	235
12	114	-119
14	286	293
16	342	348
18	108	-96
20	(52)	1
22	132	-139
K=16,L= 1		
1	86	88
5	187	150
9	147	152
11	105	109
13	104	-105
21	220	222
23	168	164
25	118	129
K=17,L= 1		
0	213	-212
2	278	285
6	97	-83
12	119	-118
18	116	114
20	(52)	18
22	161	-163
K=18,L= 1		
1	164	168
3	202	203
7	104	107
15	178	-182
17	131	129
21	(52)	81
23	143	146
K=19,L= 1		
0	246	-248
2	119	118
6	227	232
12	180	168
14	60	63
18	132	134
20	(52)	32
22	(57)	13
24	95	56
26	79	-98
K=20,L= 1		
1	54	-50
5	126	-132
7	443	-465
9	62	77
11	69	74
13	101	103
17	77	70
19	128	137
21	(57)	59
23	(57)	-59
25	85	86
K=21,L= 1		
2	130	-126
6	214	228
8	107	-106
10	166	176
14	129	-144
16	65	70
20	69	78
22	171	-154
K=22,L= 1		
1	62	-74
3	103	99
5	73	87
11	66	80
13	368	371
15	72	73
21	(57)	-106
23	112	-58
K=23,L= 1		
0	202	-206
2	136	144
4	71	76
6	97	111
8	62	80
12	111	113
14	153	-165
18	88	82
20	138	154
22	85	98
K=24,L= 1		
1	39	45
7	39	53
9	49	-47
13	73	72
15	129	-121
17	103	91
21	120	-128
K=25,L= 1		
0	49	71
4	183	181
6	81	89
8	29	-27
12	73	-73
16	88	-83
18	45	-58
20	203	185
K=26,L= 1		
1	50	57
9	60	57
11	86	66
15	113	89
17	32	-22
K=27,L= 1		
0	30	35
4	254	-260
6	116	-117
12	62	70
14	(57)	54
16	64	91
18	72	61
K=28,L= 1		
1	30	-41
5	68	78
11	133	-147
K=29,L= 1		
2	53	81
4	131	-144
6	62	39
8	63	54
12	281	274
14	45	55
K=30,L= 1		
1	77	80
5	70	80
7	71	64
9	149	157
11	78	-111
K=31,L= 1		
0	71	71
2	110	-104
K=32,L= 1		
1	124	112
K=33,L= 1		
0	72	66
2	209	168

Fig. 1. Stereoscopic illustration of the $Nb_{21}S_8$ unit cell viewed along the c axis.

Table 3. *Interatomic distances in* $Nb_{21}S_8$ (± 0.003 Å)

Reference atom	Neighbor	Number of neighbors	Distance
Nb(1)	S(1)	4	2·547 Å
	Nb(6)	8	2·949
Nb(2)	S(2)	1	2·634
	Nb(2)	4	2·819
	Nb(4)	2	2·884
	Nb(3)	2	2·946
	Nb(2)	1	3·202
Nb(3)	S(1)	1	2·462
	S(2)	2	2·570
	Nb(4)	2	2·902
	Nb(2)	2	2·946
	Nb(6)	2	3·140
Nb(4)	S(2)	2	2·482
	Nb(5)	2	2·877
	Nb(2)	2	2·884
	Nb(3)	2	2·902
	Nb(6)	1	3·210
	Nb(5)	1	3·238
Nb(5)	S(1)	1	2·440
	S(2)	2	2·551
	S(2)	1	2·806
	Nb(4)	2	2·877
	Nb(5)	2	3·100
	Nb(6)	2	3·112
	Nb(4)	1	3·238
Nb(6)	S(1)	2	2·533
	S(1)	2	2·548
	Nb(1)	2	2·949
	Nb(5)	2	3·112
	Nb(3)	2	3·140
	Nb(4)	1	3·210
S(1)	Nb(5)	1	2·440
	Nb(3)	1	2·462
	Nb(6)	2	2·533
	Nb(1)	1	2·547
	Nb(6)	2	2·548
S(2)	Nb(4)	2	2·482
	Nb(5)	2	2·551
	Nb(3)	2	2·570
	Nb(2)	1	2·634
	Nb(5)	1	2·806

The two bonding interpretations proposed for S in Ti_2S can be discussed with regard to $Nb_{21}S_8$. The first interpretation was based on the assumption that all bond orders are given approximately by the empirical relationship due to Pauling (1960):

$$D(n) = D(1) - 0.6 \log n .\tag{1}$$

This interpretation yields, in this case, the approximate niobium and sulfur valences listed in column two of Table 4. These valences are reasonable if it is assumed that niobium has a maximum valence of five and that sulfur has a valence of about four, in accordance with
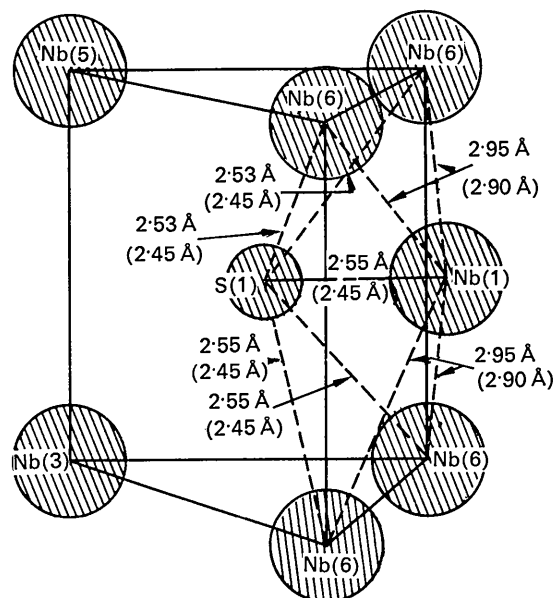

Fig. 2. A sulfur atom is surrounded by a slightly distorted trigonal prism of Nb atoms with an additional close metal atom just removed from one of the rectangular faces of the prism. The values in parentheses are summations of Slater's radii.

the bonding scheme utilizing sulfur d orbitals previously proposed (Franzen, 1966).

Table 4. Valences for $Nb_{21}S_8$

	Valence based on 7-fold coordination	Valence based on trigonal prismatic coordination only
Nb(1)	4·97	2·86
Nb(2)	4·50	4·12
Nb(3)	3·62	3·62
Nb(4)	4·31	4·31
Nb(5)	3·86	3·67
Nb(6)	3·74	3·74
S(1)	4·22	3·69
S(2)	3·93	3·36

Interatomic distances less than 3·25 Å are used.

The second proposal was based on the hypothesis that sulfur bonding in compounds of this type is directional in nature, with the bonding orbitals directed toward the corners of a trigonal prism. The basis for this hypothesis was the marked tendency of sulfur, selenium and tellurium to form compounds in which the coordination of the chalcogen is trigonal prismatic and the lack of structures in which the chalcogens expanded their coordination beyond six. According to this interpretation, the short S(1)–Nb(1) distance would be primarily determined by the bonding of both S(1) and Nb(1) to four Nb(6), as shown in Fig. 2. The valences calculated assuming that the only niobium atoms to which the sulfur atoms are bonded are those at the corners of trigonal prisms but that equation (1) otherwise applies, are given in column three of Table 4 and are again in accord with the scheme in which sulfur d orbitals are utilized in the formation of sulfur–niobium bonds.

Evidence favoring the proposal that sulfur is bonded to 7 metals is provided by a comparison of the valences of Nb(1) in columns two and three of Table 4. The valence of 2·9 calculated on the assumption that the waist niobium atoms are not bonded to the sulfur is unreasonably low, while the value 5·0, obtained by the assumption of equation (1) only, is entirely reasonable for a compound of this kind.

It is concluded that the nature of the bonding of sulfur in compounds of the types discussed here (Ti_2S and $Nb_{21}S_8$) is metallic, i.e. that the bonding is of the delocalized, electron deficient type characteristic of metals. It is furthermore concluded that there is a significant contribution of the sulfur d orbitals to the valence (conduction) band.

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