is probably possible as a result of the motion, thus re-establishing the relative equilibrium configuration.

A study which is based solely on intensities of diffraction maxima, gives only restricted information about the average equilibrium properties, and it is clear that much additional information is latent in the diffuse part of the scattering. It may be concluded at the present, however, that the molecule spends considerably more time at points close to the indicated equilibrium positions than elsewhere. A similar conclusion applies to the integrated time spent in these regions. Although the energy spectrum of the lattice is complex, the above conclusion indicates that the majority of the system is in quantum states lying between the extreme cases approximated by the harmonic oscillator and the free rotator (Eyring, Walter & Kimball, 1949) respectively, at temperatures a little below the melting point. This situation pertains also in a number of other cases which will be discussed elsewhere.

Consideration of the configurational entropies implied by the distinctly different statistical models discussed above; and comparison with the experimental values of the entropy changes at the low temperature phase transformations, may further illuminate the structural problems considered here.

The full-matrix least-squares refinement program is a somewhat revised version of the original form written by Gantzel, Sparks & Trueblood (I.U.C. World List No 384). The Fourier program was written by Gantzel & Hope (Department of Chemistry, University of California, Los Angeles 24, California).

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Preparation, Structure and Properties of Triniobium Tetrasulphide, Nb_3S_4

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In the system niobium–sulphur a new phase, Nb_3S_4, has been prepared from the elements at 1000–1300°C. Fairly large needle-shaped crystals could be obtained by vapour transport with iodine. Nb_3S_4 is hexagonal ($a = 9{\cdot}5806$ Å; $c = 3{\cdot}3747$ Å; $c/a = 0{\cdot}35224$; space group $P6_3/m$) and isotypic with Nb_3Te_4 and Nb_3Se_4. The structure was refined from single-crystal diffractometer data obtained with Mo radiation. The structure is built up from NbS_6 octahedra which are linked together by shared faces and edges. Each metal atom is displaced by 0·306 Å from the octahedron centre towards one of the faces, In this way infinite zigzag metal chains are formed with Nb–Nb distances similar to those in Nb metal. Furthermore, the structure contains wide empty channels in the **c** direction. Nb_3S_4 is a metallic conductor with temperature-independent paramagnetism.

Introduction

The system Nb–S has been studied by Jellinek, Brauer & Müller (1960). The phases NbS_3, 2*s*-NbS_2, 3*s*-NbS_2, 2*s*-$Nb_{1+x}S_2$ and 3*s*-$Nb_{1+x}S_2$ were characterized, but the phase relationships in the more metal-rich range could not be disentangled. An investigation of this range has, therefore, been undertaken. The new phases found are Nb_3S_4 and NbS_{1-x}, the latter existing in an orthorhombic high-temperature form and a hexagonal low-temperature form which have superstructures of the MnP and NiAs types respectively; the transition temperature is 730°C (Kadijk & Jellinek, 1968). The phase $Nb_{21}S_8$ recently described by Franzen, Beineke & Conard (1968) was also observed in some of our samples. The present communication describes the preparation, physical properties and crystal structure of Nb_3S_4.

Preparation and properties

Mixtures of niobium and sulphur in atomic proportions of about 1:1 were heated at 1000–1300°C in evacuated quartz tubes and cooled by quenching. Small needle-shaped crystals of a new phase were obtained, together with polycrystalline material. The crystals were hexagonal with $a \simeq 9{\cdot}6$ Å, $c \simeq 3{\cdot}4$ Å; the powder contained the same phase, together with several contaminants.

The shape of the hexagonal crystals and the unit-cell dimensions are similar to those reported for Nb_3Te_4 and Nb_3Se_4 (Selte & Kjekshus, 1964). Assuming the composition of the new phase to be Nb_3S_4 and adopting the atomic parameters reported for Nb_3Te_4, qualitative agreement of observed and calculated powder intensities was obtained (Huisman, Kadijk & Jellinek, 1967). The composition Nb_3S_4 was confirmed by a refinement of the crystal structure from single-crystal data.

Single crystals suitable for the X-ray intensity measurements were prepared by transport reactions using iodine as a carrier; various starting compositions and temperature gradients (about 900°→1000°C) were tried. In all cases two kinds of crystals grew in the high-temperature region of the quartz tube, namely hexagonal needles of Nb_3S_4 and hard plates of orthorhombic NbS_{1-x}.

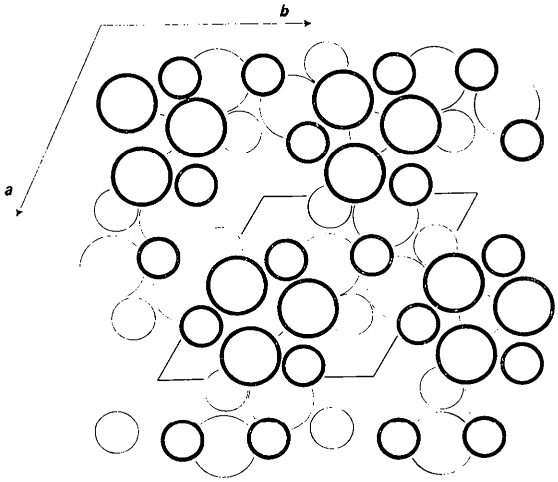

Fig. 1. The structure of Nb_3S_4 projected along the c axis. Nb atoms are indicated by large circles, sulphur by small circles. Atoms at $z=\frac{1}{4}$ are drawn with heavy lines, atoms at $z=\frac{3}{4}$ with thin lines.

Some of the Nb_3S_4 crystals were large enough to allow an investigation of the electrical properties by a four-point-contact method. Metallic behaviour was found with $\varrho \simeq 10^{-4}$ ohm. cm at room temperature and $\frac{1}{\varrho} \times \frac{d\varrho}{dT} = 0{\cdot}004$ deg^{-1}; the Seebeck coefficient is of negative sign. From 100–370°K Nb_3S_4 shows nearly temperature-independent paramagnetism with $\chi_{\text{mol}} = +147 \times 10^{-6}$ c.g.s. units per mole of Nb_3S_4 (not corrected for diamagnetism).

Structure determination

Accurate unit cell dimensions of Nb_3S_4 were determined from powder diffractograms taken with Cu $K\alpha$ radiation (20°C); silicon powder was used as an internal standard [$\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54051$ Å; $\lambda(\text{Cu } K\alpha_2) = 1{\cdot}54433$ Å; $a(\text{Si}) = 5{\cdot}4306$ Å]. Calculations by least squares gave the values:

$$a = 9{\cdot}5806 \text{ Å (e.s.d. } 0{\cdot}0004 \text{ Å)};$$
$$c = 3{\cdot}3747 \text{ Å (e.s.d. } 0{\cdot}0003 \text{ Å)};$$
$$c/a = 0{\cdot}35224\,.$$

With a unit-cell content of Nb_6S_8 the density is calculated as 5·038 g.cm^{-3}, which is a reasonable value.

The intensities of the X-ray reflexions were measured with a Nonius automatic single-crystal diffractometer by the θ–2θ scan method; Zr-filtered Mo K radiation was used. The dimensions of the crystal were $0{\cdot}43 \times 0{\cdot}16 \times 0{\cdot}16$ mm^3. Reliable intensities of 1384 independent reflexions with $\sin\theta/\lambda < 1{\cdot}20$ Å^{-1} were measured; the intensities were corrected for Lorentz and polarization factors and for absorption [$\mu(\text{Mo}) = 74$ cm^{-1}].

The Laue group is $6/m$ and reflexions $00l$ are systematically absent for $l = 2n+1$; the space group, therefore, is $P6_3$ or $P6_3/m$. The intensity sequence of reflexions hkl' was found to be the same as that of $hk(l' \pm 2)$, showing that all the atoms lie in planes with $z = \pm\frac{1}{4}$. Therefore, the centrosymmetric space group $P6_3/m$ (no. 176) was adopted; the Nb atoms and the six S(2) atoms were placed in positions $6(h)$: $\pm(x, y, \frac{1}{4}; \bar{y}, x-y, \frac{1}{4}; y-x, \bar{x}, \frac{1}{4})$, the two S(1) atoms in position $2(c)$: $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$. The same arrangement had been chosen for Nb_3Te_4 (Selte & Kjekshus, 1964).

Starting from the atomic parameters of Nb_3Te_4, the structure of Nb_3S_4 was refined by least squares (with a program based on the block diagonal approximation). The atomic scattering factors were taken from Moore (1963) and corrected for anomalous dispersion (*International Tables*, 1962).

Extinction effects appeared to be appreciable, so to account for them the seven strongest reflexions (which also showed the greatest difference between F_o and F_c) were excluded in the last cycles of the refinement. The remaining 1377 reflexions were divided into twenty groups of increasing F_o. To the reflexions of each group a weight was assigned which was inversely proportional to $\langle(\Delta F)^2\rangle$, where the average was taken over all the reflexions of each group. At the end of the re-

Table 1. *Observed and calculated structure factors of* Nb_3S_4 *on* 10 *times absolute scale*

Reflexions marked by an asterisk were not included in the refinement.

H	K	L	FO	FC	AC	BC	
1	0	0	449	810	-810	-15	*
2	0	0	391	475	474	12	
3	0	0	253	248	248	1	
4	0	0	542	675	-674	-17	
5	0	0	677	900	-900	-24	
6	0	0	416	438	438	13	
7	0	0	597	692	-691	-23	
8	0	0	626	708	707	30	
9	0	0	88	84	-84	-3	
10	0	0	134	133	132	8	
11	0	0	52	45	45	3	
12	0	0	259	261	-261	-14	
13	0	0	316	315	-315	-16	
15	0	0	136	128	-127	-11	
16	0	0	170	161	160	13	
17	0	0	161	157	156	11	
18	0	0	178	173	173	12	
19	0	0	123	134	133	13	
0	1	0	498	810	-810	-15	*
1	1	0	258	273	-273	-5	
2	1	0	516	692	692	18	
3	1	0	585	766	-765	-17	
4	1	0	926	1533	1533	43	*
5	1	0	592	703	-703	-21	
6	1	0	140	138	-138	-2	
7	1	0	183	163	-162	-8	
8	1	0	220	221	-221	-10	
9	1	0	500	524	-524	-20	
10	1	0	575	626	625	26	
11	1	0	92	87	-87	-7	
12	1	0	538	562	561	33	
13	1	0	52	14	14	-1	
14	1	0	278	220	220	12	
15	1	0	139	128	-127	-8	
16	1	0	159	156	-155	-12	
17	1	0	171	172	-171	-14	
18	1	0	41	21	21	3	
19	1	0	122	132	-132	-12	
0	2	0	395	475	474	12	
1	2	0	540	754	-753	-19	
2	2	0	411	477	-477	-12	
3	2	0	297	314	-313	-8	
4	2	0	54	50	50	-2	
5	2	0	343	354	354	10	
6	2	0	554	606	606	23	
7	2	0	43	38	38	-2	
8	2	0	751	893	892	35	
9	2	0	552	596	-595	-25	
10	2	0	69	54	-54	-3	
11	2	0	166	157	-157	-10	
12	2	0	296	296	-295	-14	
13	2	0	231	232	-231	-13	
14	2	0	364	365	364	25	
15	2	0	197	201	-201	-14	
16	2	0	311	307	306	26	
17	2	0	103	105	-105	-9	
0	3	0	252	248	248	1	
1	3	0	853	1419	1419	34	*
2	3	0	48	49	49	4	
3	3	0	100	63	63	0	
4	3	0	149	148	148	4	
5	3	0	652	762	-761	-24	
6	3	0	435	458	-457	-18	
7	3	0	31	23	23	3	
8	3	0	289	298	-298	-11	
9	3	0	277	268	268	13	
10	3	0	270	276	275	17	
11	3	0	200	201	-200	-11	
12	3	0	378	384	384	21	
13	3	0	371	374	-374	-23	
14	3	0	136	133	-132	-10	
15	3	0	78	75	75	2	
16	3	0	79	85	-84	-6	
17	3	0	48	26	-26	-2	
18	3	0	357	375	373	32	
0	4	0	549	675	-674	-17	
1	4	0	67	69	-69	-2	
2	4	0	699	900	-900	-25	
3	4	0	654	785	785	28	
4	4	0	260	260	-260	-9	
5	4	0	618	702	702	27	
6	4	0	145	140	-140	-4	
7	4	0	167	167	-167	-8	
8	4	0	44	15	15	-2	
9	4	0	223	226	-226	-11	
10	4	0	292	296	-296	-17	
11	4	0	439	445	445	24	
13	4	0	220	214	213	15	
14	4	0	262	258	258	18	
15	4	0	116	119	-118	-10	
17	4	0	168	172	-171	-15	
0	5	0	684	900	-900	-24	
1	5	0	592	702	702	21	
2	5	0	205	199	-199	-9	
3	5	0	548	617	-616	-20	
4	5	0	189	160	-160	-8	
5	5	0	535	577	577	19	
6	5	0	478	515	-515	-20	
7	5	0	758	887	886	40	
8	5	0	47	52	52	-1	
9	5	0	224	222	221	14	
10	5	0	177	176	-175	-9	
11	5	0	105	97	-97	-8	
12	5	0	284	278	-278	-17	
13	5	0	81	93	-93	-5	
14	5	0	205	199	-198	-16	
15	5	0	226	233	232	21	
16	5	0	51	42	-41	-3	
0	6	0	419	438	438	13	
1	6	0	634	732	731	22	
2	6	0	168	167	-167	-5	
3	6	0	740	884	884	34	
4	6	0	403	425	-424	-18	
5	6	0	43	26	-26	1	
6	6	0	351	366	-365	-17	
7	6	0	387	401	-401	-18	
8	6	0	260	265	-265	-12	
9	6	0	318	318	317	17	
10	6	0	273	271	-271	-15	
11	6	0	442	444	442	31	
13	6	0	103	99	99	8	
14	6	0	164	167	-166	-13	
16	6	0	111	114	-114	-11	
0	7	0	605	692	-691	-23	
1	7	0	376	384	-384	-15	
2	7	0	148	149	-149	-4	
3	7	0	491	522	-522	-20	
4	7	0	342	359	359	16	
5	7	0	325	332	332	15	
6	7	0	46	23	-23	-1	
7	7	0	368	378	378	21	
8	7	0	240	237	-236	-15	
10	7	0	143	141	-140	-9	
11	7	0	113	106	-106	-8	
12	7	0	79	80	80	4	
13	7	0	232	227	226	18	
14	7	0	96	96	-95	-8	
15	7	0	285	300	299	27	
0	8	0	631	708	707	30	
1	8	0	110	105	-105	-4	
2	8	0	391	413	412	12	
3	8	0	216	219	-219	-8	
4	8	0	328	339	-339	-15	
6	8	0	186	187	187	11	
7	8	0	281	287	-287	-15	
8	8	0	517	544	543	30	
9	8	0	123	120	120	9	
10	8	0	136	137	-137	-8	
11	8	0	143	147	147	10	
12	8	0	241	241	-240	-18	
13	8	0	182	184	-184	-15	
0	9	0	97	84	-84	-3	
1	9	0	179	179	-179	-9	
2	9	0	694	792	791	35	
3	9	0	302	311	-311	-14	
4	9	0	501	532	531	28	
5	9	0	220	215	-218	-11	
6	9	0	98	97	-97	-5	
7	9	0	288	285	-284	-16	
8	9	0	223	215	-214	-12	
9	9	0	182	179	-179	-14	
10	9	0	244	243	242	19	
11	9	0	182	181	-180	-13	
12	9	0	319	333	332	27	
13	9	0	91	86	86	7	
0	10	0	135	133	132	8	
1	10	0	372	385	-384	-18	
2	10	0	379	390	-398	-18	
3	10	0	192	195	-194	-9	
4	10	0	75	46	46	3	
5	10	0	168	171	-171	-9	
6	10	0	594	631	630	38	
7	10	0	164	158	-158	-11	
8	10	0	261	258	257	19	
9	10	0	54	45	-45	-6	
10	10	0	57	50	-50	-5	
11	10	0	177	177	-177	-14	
12	10	0	55	58	57	4	
0	11	0	49	45	45	3	
1	11	0	36	29	29	4	
2	11	0	631	686	685	32	
3	11	0	214	207	-207	-13	
4	11	0	90	93	-93	-3	
5	11	0	51	19	-18	-5	
6	11	0	150	149	-147	-11	
7	11	0	95	88	-88	-4	
8	11	0	178	176	175	12	
10	11	0	256	260	259	24	
11	11	0	131	131	-131	-12	
0	12	0	260	261	-261	-14	
1	12	0	32	23	23	2	
2	12	0	221	216	-216	-14	
3	12	0	431	439	438	27	
4	12	0	56	58	-58	-2	
5	12	0	71	55	54	5	
6	12	0	154	153	153	11	
7	12	0	244	249	-249	-18	
8	12	0	173	171	-171	-12	
9	12	0	42	45	-44	-4	
10	12	0	114	118	-117	-11	
0	13	0	311	315	-315	-16	
1	13	0	83	79	79	5	
2	13	0	279	276	-276	-15	
3	13	0	180	175	-174	-11	
4	13	0	178	177	-177	-13	
5	13	0	104	108	107	10	
6	13	0	104	102	-102	-9	
7	13	0	418	427	426	33	
8	13	0	61	59	-58	-4	
9	13	0	93	88	57	7	
0	14	0	55	35	35	1	
1	14	0	316	315	314	22	
2	14	0	55	50	-50	-6	
3	14	0	495	511	510	34	
4	14	0	234	234	-234	-16	
6	14	0	72	74	-74	-8	
7	14	0	108	105	-105	-8	
8	14	0	123	127	-127	-12	
0	15	0	139	128	-127	-11	
1	15	0	301	298	-297	-19	
4	15	0	50	46	-46	-2	
5	15	0	224	234	233	21	
6	15	0	96	101	-100	-9	
7	15	0	148	154	153	15	
0	16	0	159	161	160	13	
1	16	0	136	136	136	10	
2	16	0	215	212	-212	-15	
3	16	0	61	59	-59	-4	
5	16	0	207	216	-215	-18	
6	16	0	78	81	80	8	
0	17	0	168	157	156	11	
1	17	0	163	172	-172	-14	
2	17	0	337	342	341	29	
4	17	0	159	162	161	14	
0	18	0	170	173	173	12	
1	18	0	190	195	-194	-16	
2	18	0	143	145	-144	-12	
3	18	0	74	70	-70	-7	
0	19	0	130	134	133	13	
1	0	1	609	750	750	18	
2	0	1	494	565	565	10	
3	0	1	578	674	674	18	
4	0	1	393	415	415	12	
5	0	1	242	236	-236	-12	
6	0	1	165	163	163	6	
7	0	1	784	926	-925	-33	
8	0	1	367	375	375	10	
9	0	1	79	60	-59	-1	
10	0	1	102	80	-80	0	
11	0	1	350	361	361	15	
12	0	1	335	336	335	20	
13	0	1	548	581	-580	-30	
14	0	1	314	312	311	19	
15	0	1	436	442	-441	-30	
16	0	1	141	139	-138	-8	
0	1	1	600	750	-750	-18	
1	1	1	202	213	-213	-9	
2	1	1	294	301	-301	-7	
3	1	1	357	389	-389	-9	
4	1	1	157	154	154	3	
5	1	1	635	736	736	26	
6	1	1	321	325	-325	-9	
7	1	1	323	330	330	13	
8	1	1	127	122	-122	-3	
9	1	1	581	623	-623	-27	
10	1	1	39	6	-6	0	
11	1	1	415	429	-429	-21	
12	1	1	111	108	103	4	
13	1	1	264	261	261	15	
14	1	1	56	55	55	5	
15	1	1	247	245	244	14	
16	1	1	277	277	277	20	
17	1	1	332	338	-337	-26	
18	1	1	167	165	165	13	
19	1	1	160	172	-171	-17	
0	2	1	495	565	-565	-10	
1	2	1	1051	1745	1744	42	*
2	2	1	940	1310	-1310	-33	*
3	2	1	105	66	66	5	
4	2	1	533	569	-568	-19	
5	2	1	404	412	-412	-14	
6	2	1	153	142	-142	-5	
7	2	1	322	324	324	12	
8	2	1	75	68	68	2	
9	2	1	736	824	823	37	
10	2	1	137	135	-135	-8	
11	2	1	200	201	200	10	
13	2	1	314	307	-307	-20	
14	2	1	79	77	-76	-4	
17	2	1	138	137	136	14	
18	2	1	36	15	15	2	
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6	7	2	75	[illegible]	21	1	

Table 1 (*cont.*)

H	K	L	FO	FC	AC	BC
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8	8	2	474	492	-491	-29
9	8	2	109	110	-110	-9
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13	9	2	82	80	-80	-7
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8	7	3	371	370	-369	-27
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6	9	3	242	241	-240	-14
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8	9	3	98	79	-79	-7
9	9	3	306	310	309	26
11	9	3	167	167	166	14
0	10	3	88	63	-63	0
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3	10	3	60	57	-57	-1
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7	10	3	91	88	-88	-8
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9	10	3	272	275	-274	-22
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6	11	3	300	298	297	22
7	11	3	68	58	-58	-2
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9	11	3	114	112	111	9
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2	16	3	89	101	-100	-12
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7	0	4	410	418	-417	-21
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12	0	4	182	175	-174	-13
13	0	4	219	213	-212	-14
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12	2	4	199	199	-198	-13
13	2	4	166	160	-159	-11
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13	3	4	261	263	-262	-20
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14	4	4	185	189	189	16
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7	10	4	123	114	-113	-10
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6	11	4	116	110	-109	-10
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5	12	4	45	42	42	4
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3	0	5	267	267	266	15
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12	0	5	191	197	196	17
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11	1	5	241	240	-239	-18
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13	1	5	155	155	154	13
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6	2	5	77	73	-73	-4
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6	3	5	370	370	-369	-25
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9	3	5	66	56	-56	-5
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8	4	5	179	178	-177	-12
9	4	5	232	235	235	18
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3	5	5	199	205	-205	-10
4	5	5	139	137	-136	-10
5	5	5	41	6	6	0
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8	5	5	95	93	92	7
9	5	5	87	92	92	6
10	5	5	235	238	237	18
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12	5	5	114	116	-115	-11
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3	6	5	118	127	127	6
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7	9	5	82	79	-78	-6
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4	10	5	185	183	-183	-13
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3	11	5	246	246	245	21
4	11	5	87	85	-84	-8
5	11	5	220	227	227	20
6	11	5	214	222	-221	-20
0	12	5	196	197	-196	-17
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4	13	5	243	251	-250	-23
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2	0	6	137	122	-122	-10
4	0	6	219	202	202	13
5	0	6	302	294	294	19
6	0	6	171	155	-155	-10
7	0	6	260	255	254	18
8	0	6	288	278	-277	-23
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10	0	6	49	62	-62	-7
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13	0	6	143	144	143	12
0	1	6	203	188	188	12
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Table 1 (*cont.*)

H	K	L	FO	FC	AC	BC
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12	1	6	256	269	-268	-26
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1	2	6	212	202	202	15
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3	2	6	113	98	98	6
4	2	6	56	15	-15	2
5	2	6	137	127	-127	-8
6	2	6	230	227	-227	-18
8	2	6	353	359	-358	-27
9	2	6	242	245	244	19
11	2	6	79	75	75	8
12	2	6	125	133	132	11
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6	3	6	177	175	174	14
8	3	6	122	119	119	8
9	3	6	122	118	-117	-10
10	3	6	120	134	-133	-14
11	3	6	86	93	93	8
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6	4	6	60	52	52	3
7	4	6	77	69	69	6
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6	5	6	209	207	206	15
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7	6	6	171	172	171	14
8	6	6	118	116	115	9
9	6	6	141	151	-150	-14
0	7	6	255	255	254	18
1	7	6	148	144	143	11
2	7	6	67	55	55	3
3	7	6	214	206	205	15
4	7	6	158	152	-152	-13
5	7	6	146	141	-140	-12
7	7	6	162	177	-176	-16
8	7	6	102	120	120	12
0	8	6	284	278	-277	-23
1	8	6	46	42	42	3
2	8	6	156	156	-156	-9
3	8	6	91	88	88	6
4	8	6	139	145	145	12
6	8	6	77	88	-87	-8
7	8	6	127	132	131	11
0	9	6	43	31	31	2
1	9	6	82	79	79	7
2	9	6	321	331	-330	-27
3	9	6	131	131	131	11
4	9	6	229	241	-240	-22
5	9	6	104	98	98	8
6	9	6	52	44	44	4
0	10	6	45	62	-62	-7
1	10	6	164	163	163	14
2	10	6	167	170	170	14
3	10	6	81	86	86	7
4	10	6	46	25	-25	-2
2	11	6	297	300	-299	-24
3	11	6	104	104	103	10
0	12	6	115	119	119	11
2	12	6	105	110	109	11
0	13	6	145	144	143	12
1	0	7	151	152	-151	-13
2	0	7	119	116	-115	-7
3	0	7	144	155	-154	-13
4	0	7	88	100	-99	-8
5	0	7	70	69	69	9
6	0	7	42	49	-48	-5
7	0	7	272	278	277	24
8	0	7	113	105	-105	-7
9	0	7	37	13	13	0
0	1	7	149	152	151	13
1	1	7	60	55	54	7
2	1	7	52	68	68	5
3	1	7	81	88	88	6
5	1	7	200	205	-204	-18
6	1	7	85	87	86	6
7	1	7	104	104	-104	-10
9	1	7	194	207	206	19
0	2	7	118	116	115	7
1	2	7	362	389	-387	-30
2	2	7	302	308	307	24
4	2	7	151	155	155	14
5	2	7	117	119	118	10
6	2	7	49	43	43	3
7	2	7	99	101	-101	-8
0	3	7	150	155	154	13
2	3	7	195	197	-196	-14
3	3	7	206	213	-212	-17
4	3	7	96	101	101	8
5	3	7	363	378	-377	-30
6	3	7	214	233	232	22
7	3	7	35	35	35	1
0	4	7	97	100	99	8
1	4	7	99	99	-99	-8
2	4	7	248	258	257	23
4	4	7	63	77	76	6
6	4	7	80	85	-85	-9
7	4	7	97	102	-101	-11
0	5	7	66	69	-69	-9
2	5	7	188	198	-198	-18
3	5	7	112	118	117	8
4	5	7	86	87	86	8
5	5	7	46	4	-4	0
6	5	7	178	193	192	18
0	6	7	49	49	48	5
1	6	7	105	105	105	8
2	6	7	79	86	-86	-6
3	6	7	71	71	-71	-5
4	6	7	177	194	-193	-19
0	7	7	265	278	-277	-24
1	7	7	265	280	279	24
2	7	7	137	140	-140	12
3	7	7	199	208	207	19
4	7	7	119	123	122	10
0	8	7	105	105	105	7
1	8	7	118	125	-124	-11
2	8	7	100	104	-104	-10
0	9	7	51	13	-13	0
1	9	7	213	221	220	20
0	0	8	409	442	441	38
1	0	8	139	109	-109	-10
2	0	8	96	76	76	8
0	1	8	131	109	-109	-10
1	1	8	56	33	-33	-3
0	2	8	86	76	74	8

finement the discrepancy factor $R=\dfrac{\Sigma\,|F_o-F_c|}{\Sigma\,|F_o|}$ was 0·06. Observed and calculated structure factors are listed in Table 1.

The final positional and thermal parameters with the standard deviations calculated by the least-squares program are given in Table 2. The structure was checked by a difference Fourier synthesis, which showed no unusual features. In particular, no evidence of scattering was found in the large channels parallel to the *c* axis around the origin (Fig. 1); this shows that the adopted composition Nb_3S_4 is correct.

Table 2. *Positional and thermal parameters of* Nb_3S_4 (Å²)

Standard deviations in units of the last decimal are given in brackets.

	Nb	S(1)	S(2)
x	0·48538 (2)	$\frac{1}{3}$	0·34495 (7)
y	0·11392 (2)	$\frac{2}{3}$	0·28723 (7)
z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
U_{11}	0·00400 (5)	0·00449 (12)	0·00711 (15)
U_{22}	0·00340 (5)	0·00449 (12)	0·00544 (15)
U_{33}	0·00399 (5)	0·00418 (24)	0·00500 (16)
$2U_{12}$	0·00355 (8)	0·00449 (12)	0·00719 (26)
$2U_{13}=2U_{23}$	0	0	0

Discussion

The structure of Nb_3S_4 is shown in Fig. 1; interatomic distances and their standard deviations are listed in Table 3.

The structure is built up by distorted NbS_6 octahedra joined together to form a three-dimensional network; each octahedron is linked to two other octahedra by common faces and to four octahedra by common edges. The Nb atoms are not at the centres of the octahedra but are shifted by 0·306 Å in the direction of a face sharing two edges with other octahedra; thus zigzag Nb–Nb–Nb chains are formed running in the **c** direction (which is the needle axis). The metal–metal distances (and also the next-nearest-neighbour distances) in the chains are comparable to those in metallic Nb (*cf.* Table 4). Similar zigzag metal–metal chains have been found in Mo_2S_3 (Jellinek, 1961) and the isotypic compounds Nb_2Se_3 and Ta_2Se_3 (Kadijk, Huisman & Jellinek, 1968), in Nb_3Se_4 and Nb_3Te_4 (Selte & Kjekshus, 1964) and in the MnP-type substructure of $TiSe_{1-x}$ (Grønvold & Langmyhr, 1961) and probably also of orthorhombic NbS_{1-x} (Kadijk & Jellinek, 1968). Some Nb–Nb distances are compared in Table 4.

Table 3. *Interatomic distances in* Nb_3S_4 (Å)

Standard deviations in units of the last decimal are given in brackets.

Nb–2 S(2)	2·454 (1)	Nb–2 Nb	2·8813 (6)
–1 S(2)	2·492 (1)	–2 Nb	3·3695 (6)
–2 S(1)	2·5752 (3)	–2 Nb	3·3747 (3)
–1 S(2)	2·608 (1)		
		S(1)–6 S(2)	3·344 (1)
S(1)–6 Nb	2·5752 (3)	–2 S(1)	3·3747 (3)
		–3 S(2)	3·688 (1)
S(2)–2 Nb	2·454 (1)		
–1 Nb	2·492 (1)	S(2)–2 S(1)	3·344 (1)
–1 Nb	2·608 (1)	–2 S(2)	3·3747 (3)
		–4 S(2)	3·498 (2)
		–1 S(1)	3·688 (1)
		–2 S(2)	4·020 (2)

Another remarkable feature of the Nb_3S_4 structure is the number of large infinite channels in the **c** direction (Fig. 1). Although these channels are wide enough to accommodate additional atoms [distance S(2) to *c* axis 2·807 Å; Nb to *c* axis 3·722 Å], they appear to be empty. Thus, S(2) has very asymmetric surroundings formed by four Nb atoms, while S(1) has six Nb neighbours in a trigonal prism. The relation between this structure and those of $2s$–$Nb_{1+x}S_2$ and Nb_5Se_4 has been discussed by Selte & Kjekshus (1964).

The computer programs used in this investigation were written by Mrs R. Olthof-Hazekamp, Dr D. W. Smits, Dr J. H. Palm and Ir W. J. A. M. Peterse, and Mr. J. C. Eikelenboom.

Table 4. *Metal–metal distances* (Å) *in some* Nb *chalcogenides and in* Nb *metal*

	Nb_3S_4	Nb_2Se_3*		Nb_3Te_4†	Nb
		Nb(1)	Nb(2)		
Within zigzag chains					
Nb–2Nb	2·8813	2·972	3·127	2·973	2·8585 (8 ×)
Nb–2Nb	3·3747	3·434	3·434	3·647	3·3007 (6 ×)
∠ Nb–Nb–Nb	71·69°	70·57°	66·62°	75·66°	70·53°
Between chains					
Nb–Nb	3·3695 (2 ×)	3·329 (1 ×)	3·329 (1 ×)	3·854 (2 ×)	

* Kadijk, Huisman & Jellinek (1968).
† Selte & Kjekshus (1964).

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Zur Struktur des Wasserstoffperoxids

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Conflicting results of space group determinations of hydrogen peroxide in the literature have been checked by X-ray photographs of well formed hydrogen peroxide single crystals, using the Weissenberg camera. The observed reflexions 100, 001, 002, 003, 006 and 007, which are not allowed by the space group $P4_12_1$, originate from double reflexions of the pairs of planes $(\bar{2}21)$–$(3\bar{2}\bar{1})$, $(11\bar{3})$–$(\bar{1}\bar{1}4)$, (120)–$(\bar{1}\bar{2}2)$, (123)–$(\bar{1}\bar{2}0)$, $(\bar{1}22)$–$(1\bar{2}4)$, and (336)–$(\bar{3}\bar{3}\bar{1})$. The space group $P4_12_1$ is confirmed. This is a further interesting example of 'the double reflexion' effect as a possible source of error in structure determination.

Die Ergebnisse einer vollständigen röntgenographischen Feinstrukturuntersuchung an Wasserstoffperoxid wurden von Abrahams, Collin & Lipscomb (1951) mitgeteilt. Danach kristallisiert die Substanz im tetragonalen Kristallsystem mit den Gitterkonstanten $a = 4{,}06 \pm 0{,}02$ und $c = 8{,}00 \pm 0{,}02$ Å. Als Raumgruppe wird $P4_12_1$ genannt. Diese Angaben stehen teilweise im Widerspruch zu früheren Arbeiten von Fehér & Klötzer (1935, 1937), die zwar ebenfalls die Gitterkonstanten zu $a = 4{,}02$ und $c = 8{,}02$ Å bestimmten, aber auf Grund fehlender systematischer Auslöschungen und der Laue-Symmetrie D_4^1, D_{4h}^1, C_4^1, D_{2d}^1 und D_{2d}^5 als wahrscheinliche Raumgruppen anführten. Da die Ergebnisse von Fehér & Klötzer aus Untersuchungen an freien Wasserstoffperoxid-Einkristallen gewonnen wurden, während Abrahams *et al.* ihre Arbeiten an Wasserstoffperoxid ausgeführt hatten, das in Pyrexglaskapillaren kristallin erstarrt war, bestand die Möglichkeit, dass die abweichenden Angaben durch diese voneinander verschiedenen Arten der recht schwierigen Herstellung und Präparation der Einkristalle bedingt war.

Um die unterschiedlichen Angaben hinsichtlich der Raumgruppe zu überprüfen, haben wir die röntgenographischen Untersuchungen an freien Wasserstoffperoxid-Einkristallen erneut aufgegriffen.

Gut ausgebildete nadelförmige Einkristalle von Wasserstoffperoxid erhält man durch Animpfen von