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The Crystal Structure of Roussin's Red Ethyl Ester

BY J. T. THOMAS, J. H. ROBERTSON AND E. G. COX

Department of Inorganic & Structural Chemistry, The University, Leeds 2, England

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Roussin's red ethyl ester, $(NO)_4Fe_2S_2(C_2H_5)_2$, is monoclinic with $a = 7{\cdot}81$, $b = 12{\cdot}67$, $c = 7{\cdot}01$ Å and $\beta = 111° 24'$; space group $P2_1/a$; $Z = 2$. The structure has been determined by three-dimensional Patterson methods followed by differential refinement. The two iron and two sulphur atoms are co-planar, forming a rhombus with Fe–S = 2·27 Å and Fe · · · Fe = 2·72 Å. The NO groups are attached in pairs to the iron atoms in planes at right angles to that of the rhombus, so that the bonds about the iron atoms are roughly tetrahedral. The Fe–N and N–O bonds are 1·67 and 1·17 Å respectively, and are not quite collinear: the angle Fe–N–O is about 167°. The S–C distance is 1·84 Å.

Introduction

Compounds of the kind originally described by Roussin (1858) fall into two series, the black and the red, typified by the salts $K[Fe_4S_3(NO)_7]$ and $K_2[Fe_2S_2(NO)_4]$ respectively. The molecular formulae were found by Hofmann & Wiede (1895) and Reihlen & Friedolsheim (1927) and established beyond doubt by Lee (1952), who showed, by the formation of compounds of the type $(NO)_4Fe_2S_2R'R''$ (R', R'' alkyl or aryl) and by other methods, that alkyl and aryl derivatives of the red series are dimeric. The structures of Roussin's salts, which have been the subject of much speculation, are of considerable interest, both in themselves and in relation to the metallic nitrosyls and carbonyls generally. Several of Roussin's salts and esters have been examined in this laboratory and this paper describes the crystal structure of the ethyl ester of the red series $(NO)_4Fe_2S_2(C_2H_5)_2$.

Experimental

The ethyl ester, which is much more stable than the alkali metal salts $X_2[Fe_2S_2(NO)_4]$, was prepared by the method of Hofmann & Wiede (1895), which consists in passing nitric oxide gas into a suspension of ferrous hydroxide to which ethyl mercaptan has been added. Well-formed reddish-black crystals were obtained by recrystallization from alcohol. They were generally tabular on (001) and showed a marked cleavage parallel to (010).

All X-ray photographs were taken with Co K radiation. The unit-cell dimensions were obtained from oscillation and Weissenberg photographs:

$$a = 7{\cdot}81 \pm 0{\cdot}02,\ b = 12{\cdot}67 \pm 0{\cdot}04,\ c = 7{\cdot}01 \pm 0{\cdot}02 \text{ Å},$$
$$\beta = 111° 24'.$$

These are in good agreement with previous measurements (Jennings, 1939), and the axial ratios ($a:b:c$ = 0·616:1:0·553) are in agreement with those of Pawel (1882). The density observed was 1·79 g.cm.$^{-3}$; that calculated for two molecules per unit cell is 1·819 g.cm.$^{-3}$. The systematic absences ($h0l$ absent for h odd, $0k0$ absent for k odd) determine the space group uniquely as $P2_1/a$.

The hkl intensities were collected on equi-inclination Weissenberg photographs about the three principal axes. Absorption errors were reduced to a minimum by the use of crystals of equant cross-section about each axis. The multiple-film technique was used and 833 intensities were estimated visually. They were corrected for Lorentz and polarization factors with the aid of a Cochran chart. The corrected intensities were then scaled graphically by Wilson's method (1949); the value of the average temperature factor, B = 2·86 Å^2, obtained from the gradient of the curve was used for all atoms in the preliminary Fourier syntheses.

Determination of the structure

Since the unit cell contains only two molecules $(NO)_4Fe_2S_2(C_2H_5)_2$ in the space group $P2_1/a$, each must lie on a centre of symmetry.

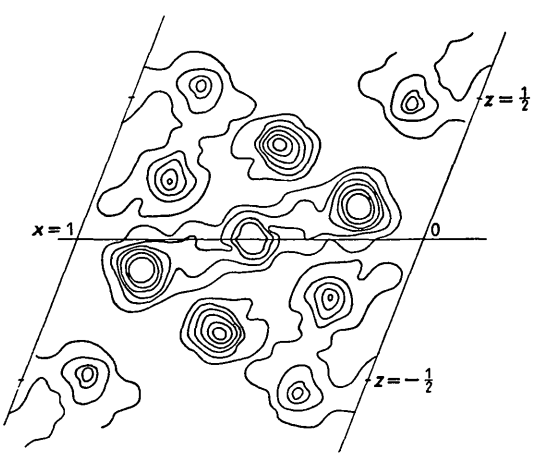

Fig. 1. Harker section, $y = \frac{1}{2}$.

The approximate co-ordinates of the iron and sulphur atoms were found from the three-dimensional Patterson function to be (0·144, 0·037, −0·055) and (0·155, 0, 0·267) respectively. The Fe_2S_2 plane is thus nearly parallel to the (010) plane, the angle between the Fe · · · Fe axis and (010) being 18°. The pattern in the Harker section at $y = \frac{1}{2}$ (Fig. 1) therefore shows additional peaks of weight 2 FeS midway between the Fe^2 and S^2 vectors.

The *h*0*l* and 0*kl* Fourier projections were then calculated with phases determined by the Fe and S contributions. The 0*kl* projection was well resolved and was refined until the disagreement index R, given by $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ was reduced to 0·176. Fig. 2

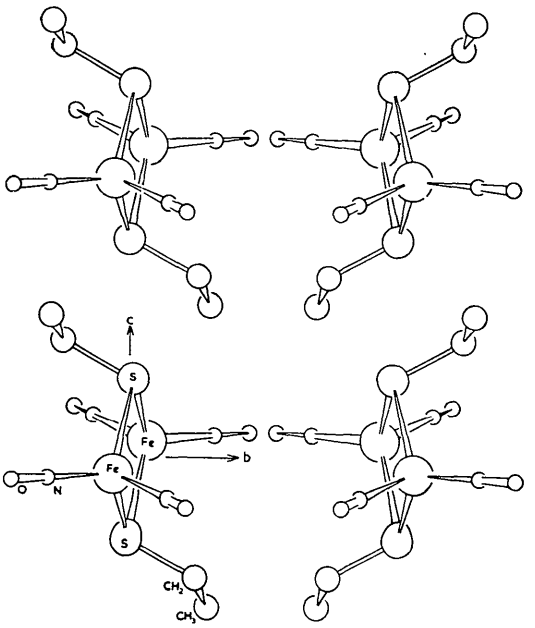

Fig. 2. Molecular arrangement.

shows the orientation of the molecules in this projection. The light atoms were less well resolved in the *h*0*l* projection, but approximate co-ordinates were obtained with the help of a model, and these gave $R = 0{\cdot}21$. These final values of R for the two projections were obtained with temperature factors of $B = 1{\cdot}95$ Å^2 for Fe and S and $B = 3{\cdot}76$ Å^2 for all light atoms, in place of the initial average value $B = 2{\cdot}86$ Å^2. Structure factors for C, N, and O were calculated from the f curves of Berghuis *et al.* (1955) and for Fe and S from those of Viervoll & Ögrim (1949). Allowance was made for the nearness of the iron absorption edge to the Co K wavelength; the real part of $\Delta f(-3{\cdot}8$, according to the tables given by James, 1954) due to K electrons alone was included, and the small imaginary term, due to L and M electrons, was ignored.

More accurate co-ordinates for all atoms were found from a three-dimensional Fourier synthesis computed on the Ferranti Mark I electronic computer at Manchester University. All atomic peaks were well shaped, and the background varied by not more than $\pm\frac{1}{2}$ e.Å^{-3}. After three cycles of differential refinement, with corrections for elimination of series-termination errors (Booth, 1946, 1947; Ahmed & Cruickshank, 1953), the final value of R (for observed reflections only) was 0·129. Table 1 lists the observed and final calculated structure factors.

Table 2 shows, for each atom, the ratio of observed to calculated peak electron-density, ϱ_o/ϱ_c, and the ratios of observed to calculated curvatures

$$\frac{\partial^2\varrho_o}{\partial x_i^2}\Big/\frac{\partial^2\varrho_c}{\partial x_i^2}.$$

The final isotropic temperature factors are shown in the last column. Although it can be seen from the curvature ratios that the thermal vibrations of some atoms, particularly O_1, O_2 and C_2, are certainly not isotropic, it was not considered worth while to pursue the refinement with anisotropic temperature factors.

Table 3 gives the atomic co-ordinates and their standard deviations calculated from the formulae of Cruickshank (1949) and Table 4 lists the bond lengths, interatomic distances and principal bond angles in the molecule, together with their standard deviations calculated from those of the co-ordinates.

Discussion of the structure

The structure now established for the molecule of $(Fe(NO)_2SC_2H_5)_2$ (Fig. 3) is one which has been suggested by various workers (e.g., Seel, 1942; Ewens,

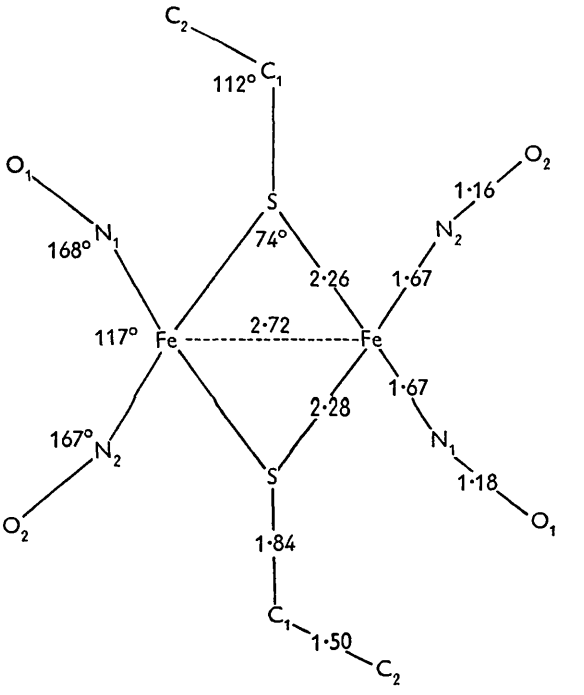

Fig. 3. Molecular dimensions.

Table 1. *Observed and calculated structure factors*

hkl	F_c	F_o
000	356	
001	106.4	65.0
002	34.6	37.7
003	10.4	17.5
004	17.3	23.2
005	- 22.4	22.6
006	- 31.1	29.5
007	- 7.8	5.9
200	-106.5	58.8
400	- 62.3	60.3
600	37.3	36.6
800	13.3	5.5
201	- 87.1	63.9
202	25.5	32.7
203	56.6	50.9
204	34.1	31.0
205	22.6	18.4
206	32.3	24.9
401	8.5	7.0
402	- 18.0	21.5
403	- 36.0	36.4
404	- 28.2	24.2
405	1.2	4.1
601	6.5	7.9
602	- 15.9	15.7
603	- 6.3	4.9
$20\bar{1}$	- 0.1	3.4
$20\bar{2}$	- 66.7	59.7
$20\bar{3}$	- 79.6	70.2
$20\bar{4}$	- 45.5	47.6
$20\bar{5}$	- 2.9	6.4
$20\bar{6}$	- 12.6	16.1
$20\bar{7}$	- 23.5	21.4
$40\bar{1}$	- 33.1	36.3
$40\bar{2}$	22.7	19.9
$40\bar{3}$	18.1	19.3
$40\bar{4}$	- 17.6	17.8
$40\bar{5}$	3.2	6.9
$40\bar{6}$	32.3	31.0
$40\bar{7}$	25.6	22.6
$60\bar{1}$	- 3.3	5.7
$60\bar{2}$	8.8	14.6
$60\bar{3}$	45.2	42.6
$60\bar{4}$	45.3	41.7
$60\bar{5}$	5.6	9.7
$60\bar{6}$	- 6.3	5.7
$60\bar{7}$	8.3	5.6
$80\bar{1}$	24.1	18.2
$80\bar{2}$	- 8.4	9.1
$80\bar{3}$	- 25.6	23.7
$80\bar{4}$	- 7.4	9.5
$80\bar{5}$	- 0.9	1.6
011	- 0.9	3.8
012	33.3	35.2
013	26.6	28.6
014	32.3	31.4
015	18.1	17.7
016	4.0	3.3
017	3.1	2.9
110	65.1	48.4
111	37.1	37.3
112	84.6	67.1
113	93.3	76.8
114	34.2	36.3
115	- 5.8	6.2
210	- 34.3	33.3
211	- 36.5	37.4
212	- 19.2	18.4
213	- 18.5	19.6
214	- 4.7	3.4
215	- 11.7	10.1
310	- 78.5	61.5
311	- 36.3	37.2
312	2.1	4.4
313	- 22.3	21.3
314	- 14.2	13.8
315	14.8	12.6
410	14.8	16.7
411	16.8	16.7
412	6.1	3.3
413	5.3	5.2
414	- 6.5	7.3
510	1.8	2.6
511	8.0	7.8
512	- 28.7	28.3
513	- 29.8	26.7
514	- 6.6	4.9
611	1.8	3.7
612	1.8	3.0
710	34.3	31.3
810	- 1.6	2.9
$11\bar{1}$	33.0	40.8
$11\bar{2}$	- 72.8	69.2
$11\bar{3}$	- 34.2	41.1
$11\bar{4}$	- 7.1	8.3
$11\bar{5}$	- 12.8	16.8
$11\bar{6}$	- 42.7	39.0
$11\bar{7}$	- 23.1	20.1
$21\bar{1}$	- 24.3	30.4
$21\bar{2}$	27.3	27.8
$21\bar{3}$	10.5	12.6
$21\bar{4}$	30.6	32.1
$21\bar{5}$	2.7	7.0
$21\bar{6}$	9.2	9.6
$21\bar{7}$	4.7	4.4
$31\bar{1}$	- 36.8	37.8
$31\bar{2}$	- 15.9	22.7
$31\bar{3}$	- 60.7	58.2
$31\bar{4}$	- 34.9	37.7
$31\bar{5}$	3.0	3.8
$31\bar{6}$	18.8	17.8
$31\bar{7}$	- 8.5	7.7
$41\bar{1}$	2.1	5.3
$41\bar{2}$	1.1	2.9
$41\bar{3}$	2.5	5.9
$41\bar{4}$	- 2.2	3.8
$41\bar{5}$	5.7	9.2
$41\bar{6}$	- 6.4	7.4
$41\bar{7}$	- 0.4	1.3
$51\bar{1}$	- 25.5	27.4
$51\bar{2}$	18.4	20.4
$51\bar{3}$	41.6	40.3
$51\bar{4}$	22.4	25.8
$51\bar{5}$	11.0	16.5
$51\bar{6}$	30.1	28.6
$51\bar{7}$	30.5	27.1
$61\bar{1}$	5.3	4.4
$61\bar{2}$	- 6.6	8.7
$61\bar{4}$	- 4.8	7.2
$61\bar{5}$	2.0	2.6
$61\bar{6}$	0	2.2
$71\bar{1}$	33.5	31.7
$71\bar{2}$	0.7	6.3
$71\bar{3}$	10.9	14.3
$71\bar{4}$	14.3	11.8
$71\bar{5}$	- 4.2	6.1
$71\bar{6}$	- 25.9	22.1
$81\bar{2}$	- 0.5	1.8
$81\bar{3}$	- 5.9	5.4
$81\bar{4}$	- 0.2	1.8
$81\bar{5}$	- 5.5	6.0
020	105.3	61.6
021	47.9	48.3
022	- 24.0	26.9
023	23.5	27.1
024	26.8	29.9
025	- 9.5	11.4
026	- 21.7	21.3
027	2.5	3.3
120	- 38.3	40.2
121	21.1	21.6
122	- 15.8	17.6
123	- 14.5	15.4
124	3.6	6.1
125	9.3	10.1
126	10.5	8.7
220	- 13.7	19.0
221	- 24.5	29.2
222	42.7	43.2
223	50.5	47.3
224	11.1	12.4
225	6.7	5.8
226	24.3	20.8
320	- 4.5	14.9
321	- 16.6	15.2
322	- 37.1	36.8
323	- 8.7	9.2
324	- 10.5	11.3
325	- 6.1	7.3
420	- 62.4	54.7
421	- 17.0	18.4
422	- 10.9	11.6
423	- 37.1	37.3
424	- 15.9	16.2
425	9.7	8.4
520	19.7	22.1
521	2.9	3.8
522	17.7	17.5
523	5.0	2.2
620	33.2	30.6
621	11.7	9.9
622	- 19.9	18.6
623	- 8.0	6.9
720	- 6.9	6.8
$12\bar{1}$	- 18.1	17.1
$12\bar{2}$	- 86.5	74.8
$12\bar{3}$	- 31.0	34.7
$12\bar{4}$	- 14.2	17.4
$12\bar{5}$	- 4.9	7.5
$12\bar{6}$	3.0	4.0
$12\bar{7}$	4.0	4.6
$22\bar{1}$	34.9	34.0
$22\bar{2}$	- 9.8	14.3
$22\bar{3}$	- 67.9	64.5
$22\bar{4}$	- 35.7	40.1
$22\bar{5}$	- 6.7	8.9
$22\bar{6}$	- 24.3	24.3
$22\bar{7}$	- 28.0	22.5
$32\bar{1}$	21.3	27.5
$32\bar{2}$	29.9	30.5
$32\bar{3}$	8.9	11.0
$32\bar{4}$	19.5	22.0
$32\bar{5}$	20.9	24.7
$32\bar{6}$	8.3	9.3
$32\bar{7}$	8.8	7.7
$42\bar{1}$	- 64.6	57.1
$42\bar{2}$	0.7	3.7
$42\bar{4}$	- 17.9	22.6
$42\bar{5}$	6.6	8.6
$42\bar{6}$	40.7	36.0
$42\bar{7}$	21.2	18.4
$52\bar{1}$	6.3	7.8
$52\bar{2}$	19.2	24.2
$52\bar{3}$	3.5	7.9
$52\bar{4}$	- 9.8	10.1
$52\bar{5}$	- 7.3	9.7
$52\bar{7}$	- 4.7	4.1
$62\bar{1}$	13.7	14.9
$62\bar{2}$	9.3	12.1
$62\bar{3}$	46.0	42.1
$62\bar{4}$	38.7	37.5
$62\bar{6}$	- 6.0	5.0
$62\bar{7}$	11.0	8.7
$72\bar{1}$	- 4.1	5.9
$72\bar{2}$	- 8.6	8.8
$72\bar{3}$	1.7	2.4
$72\bar{5}$	- 8.4	7.9
$72\bar{6}$	- 3.9	4.5
$82\bar{1}$	21.0	17.9
$82\bar{2}$	- 4.9	4.7
$82\bar{3}$	- 22.1	19.4
$82\bar{4}$	- 4.7	5.6
$82\bar{5}$	2.4	1.6
031	- 34.2	30.0
032	- 12.3	12.9
033	- 1.4	2.4
034	25.5	25.9
035	22.3	22.4
036	9.5	9.5
037	7.7	6.3
130	61.6	53.9
131	- 4.2	5.1
132	14.0	19.3
133	52.2	51.4
134	26.4	26.4
135	- 14.9	16.6
136	5.9	5.7
230	- 62.5	54.2
231	- 17.6	20.0
232	- 1.8	9.3
233	8.4	6.5
235	- 7.5	6.7
330	- 61.8	58.4
331	- 19.2	21.4
332	16.6	16.8
333	7.0	6.3
334	- 16.2	17.9
335	18.3	16.3
430	19.1	24.2
432	- 10.1	10.9
433	- 14.1	12.4
434	- 19.7	15.3
530	- 14.0	16.1
531	4.2	4.8
532	- 21.6	21.1
533	- 31.8	26.5
630	11.3	11.6
631	14.1	13.0
632	15.3	12.9
730	34.9	30.2
731	4.8	4.2
$13\bar{1}$	44.1	46.6
$13\bar{2}$	- 12.8	12.8
$13\bar{3}$	- 44.8	47.1
$13\bar{4}$	17.9	18.8
$13\bar{5}$	- 4.6	2.9
$13\bar{6}$	- 28.3	27.8
$13\bar{7}$	- 14.6	12.4
$23\bar{1}$	- 59.2	52.0
$23\bar{2}$	- 38.7	42.3
$23\bar{3}$	- 21.5	23.7
$23\bar{4}$	5.6	5.3
$23\bar{6}$	9.8	10.8
$23\bar{7}$	13.8	11.8
$33\bar{1}$	- 13.6	21.3
$33\bar{2}$	- 1.9	3.8
$33\bar{3}$	- 34.5	36.0
$33\bar{4}$	- 59.0	55.8
$33\bar{5}$	4.8	3.2
$33\bar{7}$	- 7.6	8.0
$43\bar{1}$	20.9	21.4
$43\bar{2}$	37.9	36.4
$43\bar{3}$	33.1	34.1
$43\bar{4}$	25.7	27.9
$43\bar{5}$	19.1	21.2
$43\bar{7}$	- 2.2	1.3
$53\bar{1}$	- 32.1	34.0
$53\bar{2}$	- 2.2	3.7
$53\bar{3}$	45.5	41.9
$53\bar{4}$	19.7	23.8
$53\bar{5}$	3.2	5.5
$53\bar{6}$	28.3	26.4
$53\bar{7}$	25.2	19.3
$63\bar{1}$	3.1	5.6
$63\bar{2}$	- 10.3	9.8
$63\bar{3}$	- 7.1	8.8
$63\bar{4}$	- 12.1	12.5
$63\bar{5}$	- 5.3	3.6
$73\bar{1}$	28.0	25.3
$73\bar{2}$	5.3	7.9
$73\bar{3}$	2.1	2.4
$73\bar{4}$	27.5	24.4
$73\bar{6}$	- 19.7	13.3
$83\bar{1}$	- 2.3	2.6
$83\bar{2}$	- 5.1	4.9
$83\bar{3}$	- 8.2	10.0
$83\bar{4}$	- 5.8	9.4
040	56.0	53.5
041	56.5	54.0
042	- 6.5	10.4
043	30.0	31.5
044	25.9	28.1
045	- 22.4	20.2
046	- 23.8	21.8
140	21.8	23.9
141	8.2	10.1
142	2.4	1.8
143	- 11.1	13.6
144	5.5	8.9
145	5.5	5.8
146	9.6	7.5
240	- 25.5	31.5
241	- 24.1	24.9
242	25.6	26.2
243	39.2	38.8
244	- 4.8	4.6
245	3.2	5.5
246	24.3	17.2
340	- 25.5	26.8
341	- 42.5	43.6
342	- 28.9	32.1
343	- 14.9	15.7
344	- 6.9	7.2
345	- 6.0	5.1
440	- 19.0	23.4
441	- 1.2	4.7
443	- 33.8	30.5
444	- 12.1	11.5
540	17.9	20.9
541	20.8	20.5
542	10.0	10.5
543	2.3	2.7
640	15.8	18.7
641	4.4	4.6
642	- 22.8	17.8
740	0.6	1.8
741	5.8	5.2
$14\bar{1}$	- 28.3	34.1
$14\bar{2}$	- 35.2	43.4
$14\bar{3}$	- 39.2	39.3
$14\bar{4}$	- 18.4	22.2
$14\bar{5}$	- 17.2	19.3
$14\bar{6}$	- 3.1	5.2
$24\bar{1}$	- 16.5	16.7
$24\bar{2}$	- 15.8	23.0
$24\bar{3}$	- 55.6	55.0
$24\bar{4}$	- 7.5	12.4
$24\bar{5}$	16.1	15.4
$24\bar{6}$	- 16.8	17.0
$24\bar{7}$	- 19.5	15.4
$34\bar{1}$	- 10.9	14.3
$34\bar{2}$	3.9	2.9
$34\bar{3}$	6.9	10.6
$34\bar{4}$	23.3	26.9
$34\bar{5}$	22.7	25.6
$34\bar{6}$	16.1	17.1
$34\bar{7}$	9.0	6.7
$44\bar{1}$	- 31.7	34.1
$44\bar{2}$	3.7	4.8
$44\bar{3}$	- 1.1	6.9
$44\bar{4}$	- 31.0	32.8
$44\bar{5}$	- 0.5	3.7
$44\bar{6}$	30.2	27.8
$44\bar{7}$	8.1	7.7
$54\bar{1}$	31.3	33.1
$54\bar{2}$	25.1	27.0
$54\bar{3}$	19.5	21.5
$54\bar{5}$	4.0	5.0
$54\bar{6}$	- 0.6	2.2
$54\bar{7}$	- 2.2	2.6
$64\bar{1}$	9.0	11.0
$64\bar{2}$	- 0.3	5.9
$64\bar{3}$	34.5	34.9
$64\bar{4}$	33.4	29.9
$64\bar{5}$	- 2.5	3.3
$74\bar{1}$	- 7.0	6.8
$74\bar{2}$	- 7.7	4.9
$74\bar{3}$	- 6.4	4.5
$74\bar{4}$	- 10.6	11.1
$74\bar{5}$	- 16.8	16.4
$74\bar{6}$	- 13.9	13.5
$84\bar{1}$	18.2	13.5
$84\bar{3}$	- 18.3	14.1
051	19.4	24.8
052	9.9	12.8
053	24.0	26.1
054	25.2	25.1
055	24.2	22.1
056	15.4	14.3
150	45.0	45.8
151	- 1.2	2.7
153	48.0	48.9
154	23.4	23.9
155	- 7.5	10.1
156	5.8	5.3
250	- 31.8	34.9
251	- 28.7	32.2
252	- 26.0	29.7
253	- 6.3	8.3
254	- 9.1	8.2
255	- 0.1	2.6
350	- 52.2	48.2
351	- 33.3	35.4
352	18.7	22.1
353	1.1	2.2
354	- 14.9	15.5
355	9.8	8.9
450	3.1	4.6
451	- 8.0	10.9
452	- 5.8	8.9
453	- 15.7	15.2
454	- 11.8	11.5
550	- 2.1	5.0
551	14.7	13.1
552	- 10.1	12.0
553	- 24.5	19.8

Table 1 (*cont.*)

hkl	F_c	F_o
650	17.3	16.7
651	20.8	17.8
652	15.6	15.1
750	21.3	17.9
$15\bar{1}$	54.5	55.7
$15\bar{2}$	- 21.7	29.2
$15\bar{3}$	- 44.1	45.5
$15\bar{4}$	2.9	3.7
$15\bar{5}$	- 4.0	5.7
$15\bar{6}$	- 26.6	25.2
$15\bar{7}$	- 9.7	7.7
$25\bar{1}$	- 27.9	32.2
$25\bar{2}$	- 40.5	40.1
$25\bar{3}$	- 1.2	5.0
$25\bar{5}$	15.7	15.3
$25\bar{6}$	6.4	5.8
$25\bar{7}$	11.9	8.0
$35\bar{1}$	- 20.6	22.9
$35\bar{2}$	21.4	23.5
$35\bar{3}$	- 22.8	25.7
$35\bar{4}$	- 34.3	35.7
$35\bar{5}$	9.4	10.1
$35\bar{6}$	13.2	11.9
$35\bar{7}$	- 5.9	4.7
$45\bar{1}$	23.1	27.3
$45\bar{2}$	25.1	28.8
$45\bar{3}$	17.4	23.8
$45\bar{4}$	20.6	22.6
$45\bar{5}$	13.3	13.8
$45\bar{6}$	14.2	14.2
$45\bar{7}$	2.3	2.9
$55\bar{1}$	- 23.1	24.7
$55\bar{3}$	40.1	37.5
$55\bar{4}$	11.2	14.7
$55\bar{5}$	- 9.7	7.1
$55\bar{6}$	14.7	13.5
$55\bar{7}$	15.3	6.3
$65\bar{1}$	7.9	7.4
$65\bar{2}$	16.5	15.4
$65\bar{3}$	2.9	3.2
$65\bar{4}$	- 0.1	5.2
$65\bar{6}$	- 10.0	10.3
$75\bar{1}$	17.1	15.7
$75\bar{2}$	- 10.3	8.9
$75\bar{3}$	- 3.1	4.6
$75\bar{4}$	21.0	16.5
$75\bar{5}$	2.6	1.8
$85\bar{2}$	- 19.2	13.9
$85\bar{3}$	- 14.1	10.9
060	39.5	41.9
061	- 5.6	4.9
062	- 3.7	8.4
063	20.1	23.6
064	33.2	31.4
065	- 12.9	13.6
066	- 15.5	13.2
160	- 15.6	22.2
161	- 23.5	26.1
162	- 12.7	17.7
163	8.1	6.7
164	10.1	9.8
165	14.2	14.9
166	9.3	7.7
260	- 6.9	7.9
261	- 5.0	7.9
262	27.5	28.2
263	25.4	28.4
264	- 11.1	10.8
360	- 24.2	23.7
361	- 35.9	37.2
362	- 17.1	19.6
363	- 19.7	20.6
$36\bar{4}$	- 14.7	9.8
$36\bar{5}$	- 12.2	8.6
460	- 34.0	34.8
461	2.7	3.7
462	- 7.9	7.7
463	- 24.2	21.2
464	- 10.8	9.7
560	19.5	23.1
561	27.6	25.7
562	11.5	12.0
660	27.9	24.3
661	9.7	8.5
662	- 9.7	8.5
$16\bar{1}$	- 47.5	52.3
$16\bar{2}$	- 29.9	34.3
$16\bar{3}$	- 2.0	35.2
$16\bar{4}$	- 27.9	27.8
$16\bar{5}$	- 15.5	15.9
$16\bar{6}$	- 6.6	7.1
$26\bar{1}$	17.2	19.4
$26\bar{2}$	- 19.5	21.1
$26\bar{3}$	- 46.9	44.9
$26\bar{4}$	- 17.3	18.9
$26\bar{5}$	9.1	6.5
$26\bar{6}$	- 12.1	11.7
$26\bar{7}$	- 15.5	7.9
$36\bar{1}$	- 5.4	11.5
$36\bar{2}$	- 0.4	2.7
$36\bar{3}$	26.4	26.5
$36\bar{4}$	28.1	19.9
$36\bar{5}$	24.3	24.9
$36\bar{6}$	15.3	15.2
$36\bar{7}$	6.0	4.2
$46\bar{1}$	- 20.1	23.1
$46\bar{2}$	12.5	12.1
$46\bar{3}$	19.1	17.8
$46\bar{4}$	- 11.6	9.7
$46\bar{5}$	11.1	14.8
$46\bar{6}$	25.1	20.4
$56\bar{1}$	28.5	31.1
$56\bar{2}$	22.9	25.1
$56\bar{3}$	10.1	11.6
$56\bar{4}$	9.3	11.0
$56\bar{5}$	3.4	5.3
$56\bar{6}$	2.3	3.7
$66\bar{1}$	1.5	2.2
$66\bar{2}$	- 5.2	4.1
$66\bar{3}$	12.1	12.2
$66\bar{4}$	12.0	10.6
$66\bar{5}$	- 16.6	14.5
$66\bar{6}$	- 7.3	5.2
$76\bar{1}$	- 8.1	6.8
$76\bar{2}$	- 6.2	4.9
$76\bar{3}$	- 11.0	9.1
$76\bar{4}$	- 16.6	15.6
$76\bar{5}$	- 16.3	13.9
071	27.4	26.5
072	15.1	18.6
073	18.8	20.5
074	20.7	22.6
075	24.9	25.2
076	18.0	16.3
170	25.9	28.6
171	- 24.0	23.9
172	- 8.1	9.6
173	24.5	26.6
174	7.9	8.3
175	- 8.8	9.3
270	- 18.7	24.1
271	- 42.7	41.5
272	- 25.6	25.6
273	- 16.9	19.7
274	- 3.3	2.6
275	- 1.0	3.0
370	- 38.7	39.2
371	- 9.1	13.1
372	23.1	23.4
373	- 2.4	3.3
374	- 10.9	10.2
470	8.4	11.0
471	- 3.4	4.8
472	- 8.0	9.1
473	- 13.1	10.0
474	- 14.5	11.2
570	9.1	10.9
571	17.9	16.3
572	- 10.4	9.1
573	- 14.9	10.0
670	6.4	4.6
671	21.7	17.4
$17\bar{1}$	38.5	39.4
$17\bar{2}$	- 18.7	21.1
$17\bar{3}$	- 11.6	13.8
$17\bar{4}$	7.2	8.9
$17\bar{5}$	3.3	2.7
$17\bar{6}$	- 20.9	18.3
$27\bar{1}$	- 45.7	43.6
$27\bar{2}$	- 43.9	42.1
$27\bar{3}$	- 24.6	28.6
$27\bar{5}$	15.1	16.7
$27\bar{6}$	15.5	14.1
$37\bar{1}$	- 7.5	10.3
$37\bar{2}$	13.5	11.6
$37\bar{3}$	- 21.5	25.5
$37\bar{4}$	- 14.0	16.4
$37\bar{5}$	10.8	11.0
$37\bar{6}$	18.9	17.1
$47\bar{1}$	46.3	43.6
$47\bar{2}$	41.1	40.5
$47\bar{3}$	31.5	33.4
$47\bar{4}$	19.9	20.7
$47\bar{5}$	15.4	15.0
$47\bar{6}$	9.8	10.8
$57\bar{1}$	- 15.7	13.7
$57\bar{2}$	12.1	16.1
$57\bar{3}$	25.2	23.4
$57\bar{5}$	- 15.2	16.5
$67\bar{2}$	3.1	4.9
$67\bar{3}$	- 2.3	2.4
$67\bar{4}$	- 11.2	9.6
$67\bar{5}$	- 13.8	14.3
$77\bar{2}$	- 19.3	16.9
774	11.4	11.5
080	33.3	35.4
081	- 6.7	4.9
082	- 24.7	23.6
083	10.2	9.9
084	15.8	14.6
180	- 34.5	34.0
181	- 18.8	19.9
182	- 16.3	16.2
183	8.8	7.2
184	15.1	14.0
185	15.3	15.6
280	- 11.5	13.7
281	- 25.0	26.4
282	12.6	15.7
283	7.8	5.5
284	- 11.3	9.7
285	- 11.3	9.6
380	- 19.1	22.1
381	- 25.7	27.4
382	- 22.2	24.7
383	- 16.4	16.8
384	- 19.9	14.9
400	- 17.0	17.9
481	18.7	18.3
482	9.3	7.9
483	- 9.4	9.4
580	24.0	23.9
581	21.7	19.0
582	17.9	15.4
680	16.3	14.5
$18\bar{1}$	- 36.3	38.7
$18\bar{2}$	- 40.6	40.7
$18\bar{3}$	- 23.1	27.9
$18\bar{4}$	- 25.2	24.0
$18\bar{5}$	- 15.9	14.6
$18\bar{6}$	- 5.1	4.7
$28\bar{1}$	31.9	27.9
$28\bar{2}$	- 0.5	5.8
$28\bar{3}$	- 22.1	19.4
$28\bar{5}$	16.4	14.6
$38\bar{2}$	7.3	10.4
$38\bar{3}$	23.4	26.0
$38\bar{4}$	30.6	31.0
$38\bar{5}$	27.3	26.2
$38\bar{6}$	12.8	12.1
$48\bar{1}$	- 12.6	13.1
$48\bar{2}$	26.5	23.5
$48\bar{3}$	9.7	12.1
$48\bar{4}$	- 12.0	8.6
$48\bar{5}$	- 9.6	7.5
$48\bar{6}$	9.3	6.8
$58\bar{1}$	19.7	19.9
$58\bar{2}$	22.5	18.8
$68\bar{1}$	- 13.2	9.6
$68\bar{2}$	- 17.5	15.9
$78\bar{2}$	- 9.9	7.0
091	22.9	26.4
092	28.9	30.8
093	18.6	19.6
094	26.1	23.1
095	22.5	22.2
190	7.6	8.1
191	- 38.1	36.0
192	- 13.5	15.3
195	- 17.4	12.7
290	- 22.0	24.9
291	- 31.3	32.2
292	- 34.2	33.9
293	- 17.3	17.8
390	- 15.2	12.8
391	16.4	18.2
392	23.6	21.3
393	1.6	3.7
490	7.8	10.8
591	14.5	12.0
592	- 8.1	4.1
690	9.1	6.5
$19\bar{1}$	12.3	11.6
$19\bar{2}$	- 10.3	11.6
$19\bar{4}$	22.5	19.4
$19\bar{5}$	11.0	10.1
$29\bar{1}$	- 18.9	23.1
$29\bar{2}$	- 18.8	21.3
$29\bar{3}$	- 8.7	9.2
$29\bar{4}$	13.3	14.4
$29\bar{5}$	7.8	9.8
$29\bar{6}$	8.5	4.3
$39\bar{1}$	17.7	19.9
$39\bar{2}$	15.7	17.9
$39\bar{3}$	- 5.4	6.2
$39\bar{4}$	- 9.5	8.7
$39\bar{5}$	13.7	12.1
$49\bar{1}$	19.8	21.4
$49\bar{2}$	25.0	24.0
$49\bar{3}$	13.5	14.4
$49\bar{4}$	11.7	11.4
$49\bar{5}$	18.0	16.4
$59\bar{1}$	- 17.5	14.8
$69\bar{1}$	6.0	6.0
$69\bar{2}$	5.9	7.4
010,0	- 3.3	8.2
010,1	- 21.5	24.3
010,2	- 38.9	35.1
010,4	15.7	13.1
1,100	- 16.8	20.4
1,101	- 10.1	11.8
1,102	- 7.3	7.5
1,104	17.3	13.1
2,100	7.0	9.1
2,101	- 14.4	11.8
2,102	6.5	6.9
2,104	- 18.6	14.5
3,100	- 5.9	6.2
3,101	- 16.2	14.0
3,102	- 17.3	16.5
3,103	- 7.5	4.9
4,100	- 11.6	11.4
4,101	14.6	12.4
4,102	16.7	13.3
5,100	9.4	8.7
5,101	8.7	5.8
$1,10\bar{1}$	- 25.2	26.4
$1,10\bar{2}$	- 28.1	30.3
$1,10\bar{3}$	- 12.9	13.9
$1,10\bar{4}$	- 4.9	3.6
$1,10\bar{8}$	- 13.2	10.1
$2,10\bar{1}$	40.3	37.3
$2,10\bar{2}$	21.5	21.8
$2,10\bar{3}$	- 10.1	7.6
$2,10\bar{4}$	3.7	3.8
$2,10\bar{5}$	17.1	20.3
$3,10\bar{2}$	4.8	4.9
$3,10\bar{4}$	15.5	13.1
$3,10\bar{5}$	15.5	11.6
$4,10\bar{1}$	- 12.9	13.1
$4,10\bar{2}$	20.0	16.8
$4,10\bar{3}$	10.3	11.0
$4,10\bar{4}$	- 12.5	10.3
$4,10\bar{5}$	- 9.9	8.2
$5,10\bar{1}$	14.8	12.8
$5,10\bar{2}$	19.8	16.7
$6,10\bar{2}$	- 20.6	15.9
0.111	7.5	6.9
0,112	8.2	7.5
0,114	13.0	9.5
1,110	- 2.1	4.1
1,111	- 27.9	25.3
1,112	- 23.8	19.8
1,114	- 7.8	5.7
2,110	- 15.8	14.5
2,111	- 11.5	8.9
2,112	- 17.4	15.3
3,111	8.3	6.8
3,112	22.2	17.7
4,110	1.0	2.4
4,111	- 5.6	7.3
$1,11\bar{1}$	10.6	11.8
$1,11\bar{2}$	- 6.4	4.9
$1,11\bar{4}$	23.0	16.9
$2,11\bar{1}$	- 8.7	10.7
$2,11\bar{2}$	- 17.9	18.2
$2,11\bar{3}$	- 6.6	7.7
2,114	2.3	2.2
$3,11\bar{1}$	11.7	8.8
$3,11\bar{2}$	22.7	17.0
$3,11\bar{4}$	- 6.3	3.6
$4,11\bar{1}$	6.2	6.3
$4,11\bar{2}$	16.0	13.6
$4,11\bar{3}$	8.4	8.5
$4,11\bar{4}$	13.9	12.8
0,120	4.1	5.6
0,121	- 11.9	9.6
0,122	- 22.9	16.4
1,122	- 6.0	3.7
2,120	- 4.9	5.7
2,121	- 16.7	14.1
2,122	- 1.9	2.7
3,121	- 13.4	13.4
4,120	2.2	3.2
$1,12\bar{1}$	- 16.6	13.6
$1,12\bar{2}$	- 16.6	14.9
$1,12\bar{3}$	- 4.4	4.4
$2,12\bar{1}$	17.6	13.2
$2,12\bar{2}$	13.5	8.9
$2,12\bar{3}$	- 6.6	7.0
$2,12\bar{4}$	9.2	7.4
$3,12\bar{3}$	- 5.2	4.3
$4,12\bar{1}$	3.6	6.2
$4,12\bar{2}$	17.2	16.3
$4,12\bar{3}$	14.8	12.1
0,131	12.0	9.9
0,132	6.0	8.0
1,130	- 2.3	4.3
1,131	- 20.5	14.7
1,132	- 19.6	13.1
2,130	- 1.5	3.4
2,131	- 16.3	13.2
$1,13\bar{1}$	7.3	4.6
$1,13\bar{2}$	- 10.3	9.7
$2,13\bar{1}$	- 4.5	3.4
$2,13\bar{2}$	- 4.8	3.2
$3,13\bar{1}$	13.4	11.3
$3,13\bar{2}$	27.5	17.7
0,140	- 4.5	5.9

Table 2. *Ratios of peak heights and curvatures; B factors*

Atom	ϱ_o/ϱ_c	$\frac{\partial^2\varrho_o}{\partial x^2}\Big/\frac{\partial^2\varrho_c}{\partial x^2}$	$\frac{\partial^2\varrho_o}{\partial y^2}\Big/\frac{\partial^2\varrho_c}{\partial y^2}$	$\frac{\partial^2\varrho_o}{\partial z^2}\Big/\frac{\partial^2\varrho_c}{\partial z^2}$	Mean curvature ratio	Value of B used
Fe	1·073	1·057	1·051	1·044	1·051	1·50 Å^2
S	1·017	0·968	0·984	0·984	0·979	2·00
N_1	1·048	1·009	1·237	1·085	1·110	3·30
N_2	1·046	1·132	1·063	1·063	1·086	3·30
O_1	1·000	0·844	1·187	0·943	0·991	5·10
O_2	0·972	1·130	0·936	0·952	1·006	5·10
C_1	1·015	1·038	0·990	1·088	1·039	3·00
C_2	1·012	1·010	0·901	0·947	0·953	4·75
Means	1·023	1·024	1·044	1·013	1·027	—

1948). The two iron and the two sulphur atoms are linked together in a plane rhombus; each iron atom is surrounded approximately tetrahedrally by two sulphur atoms and two nitrosyl groups and each sulphur is attached pyramidally to two iron atoms and an ethyl group.

Table 3. *Atomic co-ordinates and standard deviations*

Atom		Co-ordinates in Å	E.s.d. in Å
Fe	x	1·103	0·002
	y	0·411	0·002
	z	−0·389	0·002
S	x	1·220	0·003
	y	−0·065	0·003
	z	1·861	0·003
N_1	x	1·510	0·010
	y	2·023	0·014
	z	−0·448	0·011
N_2	x	2·088	0·011
	y	−0·707	0·014
	z	−0·873	0·012
O_1	x	1·988	0·012
	y	3·072	0·015
	z	−0·579	0·013
O_2	x	2·880	0·013
	y	−1·275	0·013
	z	−1·278	0·014
C_1	x	1·263	0·015
	y	1·546	0·017
	z	2·757	0·015
C_2	x	2·771	0·018
	y	2·047	0·017
	z	3·498	0·019

Table 4. *Bond lengths, angles and standard deviations*

Bond	Bond length Å	s.d. (Å)
Fe · · · Fe	2·72(0)	0·003
Fe–S	2·26(2)	0·004
Fe–S	2·27(7)	0·004
Fe–N_1	1·66(8)	0·01(4)
Fe–N_2	1·67(4)	0·01(5)
N_1–O_1	1·18(1)	0·02(0)
N_2–O_2	1·16(1)	0·02(2)
S–C_1	1·83(9)	0·01(7)
C_1–C_2	1·50(3)	0·02(1)
Bonds	**Angle**	**s.d.**
S–Fe–S	106·0°	0·1°
N_1–Fe–N_2	117·4	0·2
O_1–Fe–O_2	106·6	0·2
Fe–N_1–O_1	167·7	3·5
Fe–N_2–O_2	167·2	3·5
S–C_1–C_2	111·7	0·8

The Fe–S distances in the central ring are very close to previous values —2·26 Å for pyrites (Parker & Whitehouse, 1932) and 2·23 to 2·25 Å for marcasite (Buerger, 1937). The Fe · · · Fe distance (2·72 Å) is much longer than the 2·46 Å found in $Fe_2(CO)_9$ (Powell & Ewens, 1939) which corresponds to a single bond (twice metallic radius for C.N. 8). The interaction between the iron atoms must however be strong enough to account for the observed diamagnetism (Cambi & Szegö, 1931), and for the strong absorption of light.

The two crystallographically independent nitrosyl groups are both inclined at about 13° to the Fe–N bond. No such deviation from linearity has been observed in the carbonyls, but in the compound $[Co(S_2CNMe_2)_2NO]$ Alderman & Owston (1956) found a greater deviation (45°) for the Co–N–O angle.

The mean N–O distance of 1·17 Å lies in the range to be expected (cf. the spectroscopic values 1·15 Å in NO; 1·19 Å in N_2O; 1·20 Å for N=O in O=N−OH) but it is not very sensitive to changes in bond order. However, the non-linearity of the O–N–Fe bonds suggests that the hybridisation of the nitrogen is not pure *sp* but is intermediate between *sp* and sp^2, although nearer the former. It seems hardly necessary in this case to invoke unsymmetrical π-bonding, of the kind suggested by Alderman & Owston (1956) to account for the much larger deviation in their compound, although it should be noted that our Fe–N distance of 1·67 Å is substantially shorter than would be expected for a single bond (about 1·9 Å).

The S–C distance of 1·84 Å is in good agreement with accepted single-bond values (see review by Abrahams, 1956).

Our results for the interatomic distances in the red ester are very close to the corresponding ones found by Johansson & Lipscomb (1958) in the caesium black salt, $Cs[Fe_4S_3(NO)_7]H_2O$, the anion of which consists essentially of three molecules of the red ester (minus the ethyl groups and five NO groups) fused together so as to share Fe–S edges.

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Beta-Wolfram Structure of Compounds Between Transition Elements and Aluminum, Gallium and Antimony

BY E. A. WOOD, V. B. COMPTON, B. T. MATTHIAS AND E. CORENZWIT

Bell Telephone Laboratories, Murray Hill, N. J., U.S.A.

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The compounds Nb_3Al, Nb_3Ga and Cr_3Ga have the β-wolfram structure ($A15$) as determined by the powder method. The space group is O_h^3–$Pm3n$ with 2 formula weights in the unit cell. For Nb_3Al, $a_0 = 5{\cdot}187$ Å; for Nb_3Ga, $a_0 = 5{\cdot}171$ Å; for Cr_3Ga, $a_0 = 4{\cdot}645$ Å.

More complete data are given for Mo_3Ga, V_3Ga, V_3Sb and Nb_3Sb whose preliminary lattice constants were reported previously. For Mo_3Ga, $a_0 = 4{\cdot}943$ Å; for V_3Ga, $a_0 = 4{\cdot}816$ Å; for V_3Sb, $a_0 = 4{\cdot}932$ Å; for Nb_3Sb, $a_0 = 5{\cdot}262$ Å.

The superconducting transition temperature for Nb_3Al is 17·5 °K.; for Nb_3Ga, 14·5 °K. and for V_3Ga, 16·5 °K. The remaining compounds are not superconducting above 1·02 °K.

Three new beta-wolfram compounds have been made in the course of a continuing search for superconductivity in substances with the beta-wolfram structure (Matthias, Geballe, Geller & Corenzwit (1954); Geller, Matthias & Goldstein (1955); Wood & Matthias (1956); Matthias, Wood, Corenzwit & Bala (1956)). These are Nb_3Al, Nb_3Ga and Cr_3Ga. Full data are also given for Mo_3Ga, V_3Ga, V_3Sb and Nb_3Sb whose preliminary lattice constants were reported by Matthias, Wood, Corenzwit & Bala (1956). Our data for Mo_3Al which was assigned the beta-wolfram structure in a report of the Climax Molybdenum Co. of Michigan (1951) are also given.

The lattice constants, interatomic distances and superconductivity data are listed in Table 1. The observed intensities are listed in Table 2, together with the intensities calculated from the formula

$$I \propto p|F_{hkl}|^2\{(1+\cos^2 2\theta)/\sin^2\theta\cos\theta\}\times 10^{-5}\,,$$

where p is the multiplicity factor, F_{hkl} the structure amplitude, and the remaining term is twice the combined Lorentz and polarization factors. The scattering factors for Nb, Mo, Ga, and Sb were obtained from the paper by Thomas & Umeda (1957), for Cr and Al from the paper by Viervoll & Ögrim (1949) and for V from the *International Tables* (1935). Dispersion corrections from Dauben & Templeton (1955) were applied.

The agreement between observed and calculated intensities in Table 2 is satisfactory with the exception of the case of Nb_3Sb which is discussed in the last paragraph of the paper. Absorption most probably accounts for the low intensity of the low angle lines.

The β-wolfram structure belongs to space group