The Crystal Structure of Mo_3Sb_7

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Mo_3Sb_7 has a cubic Ir_3Ge_7 type structure with unit cell dimension $a = 9.5713 \pm 0.0008$ Å. The space group is $Im3m$ with 12 Mo in (e) with $x_1 = 0.3425 \pm 0.0013$, $B_1 = 0.46 \pm 0.12$ Å², 12 Sb_I in (d) with $B = 0.50 \pm 0.11$ Å², and 16 Sb_{II} in (f) $x_2 = 0.1624 \pm 0.0004$, $B_2 = 0.56 \pm 0.09$ Å².

In the course of studying the transition metal chalcogenides and pnictides, the existence of intermediate phases with peculiar and unexpected compositions has often been observed. A rather recent and striking example is provided by the occurrence of the Mo_3Sb_7 phase established independently by Brown [1] and Jensen *et al.*[2] In view of the apparently anomalous composition of this phase it was considered of great interest to acquire experimental data which might yield information about the nature of its chemical bonding. The present paper gives an account of the determination of the crystal structure. (The brief description of the Mo_3Sb_7 structure given by Brown [1] came to hand when the structure solution reported here was almost completed.)

RESULTS

(i) *Unit cell and space group.* According to Jensen *et al.*[2] no extended range of homogeneity of the Mo_3Sb_7 phase exists and the composition is unequivocally determined to be Mo_3Sb_7. The Mo_3Sb_7 phase crystallizes cubically with the unit cell dimension (calculated from Guinier photograph data):

$$a = 9.5713 \pm 0.0008 \text{ Å}$$

The lattice constant, $a = 9.5688 \pm 0.0001$ Å, independently reported by Brown [1] is essentially in agreement with this value although the two values fall beyond the limits of error stated. It should in this connection be emphasized that the accuracy of about 10 ppm claimed by Brown is exceptionally good. Brown and Jensen *et al.* have also independently examined the $MoAs_2$ phase. For the latter phase, however, the two studies concur both with respect to cell dimensions and the associated error limits. Judging from this agreement, it might seem that a misprint has crept into the error limit stated by Brown.

Further consideration must await the publication of Brown's primary diffraction data. It should nevertheless be mentioned finally that the lattice dimension reported by Jensen *et al.* is found to be invariant, within the indicated error limit, for several specimens with different initial proportions of the components.

On the basis of the observed density 8.55 g cm^{-3}, the unit cell contains 4 ($Z_c = 3.96$) Mo_3Sb_7-groups.

Single crystals of approximately spherical shape were obtained by means of chemical transport reactions using traces of one of the elements chlorine, bromine, or iodine as transport agent.

The only systematically missing reflections in the X-ray photographs were of the type *(hkl)* absent when $h+k+l = 2n+1$. The possible space groups are accordingly $I23$, $I2_13$, $Im3$, $I432$, $I\overline{4}3m$, and $Im3m$.

(ii) *Determination of the structure.* Three-dimensional X-ray data were collected using an integrating Weissenberg camera of 57.3 mm diameter with Mo-radiation. Intensity measurements were carried out microphotometrically using the multiple-film technique. An approximately spherical crystal of radius 0.059 mm was used to collect the intensity data. The intensities were corrected for the combined Lorentz and polarization factor and for absorption ($\mu R = 1.5$). For the calculation of F_c-values the atomic scattering factors were taken from *International Tables*.[3] The agreement between F_o and F_c is expressed by the reliability index $R = \sum || F_o| - |F_c || / \sum |F_o|$. (Undetected reflections are not included in these calculations.)

Tentative atomic positions for a trial structure were deduced from a three-dimensional Patterson synthesis. (On more careful examination, it turned out that this was in fact the only possible solution of the Patterson synthesis.) As the observed intensities showed that $F(hkl) = F(khl)$ it was decided to start the calculations in the highest symmetric space group $Im3m$. (This
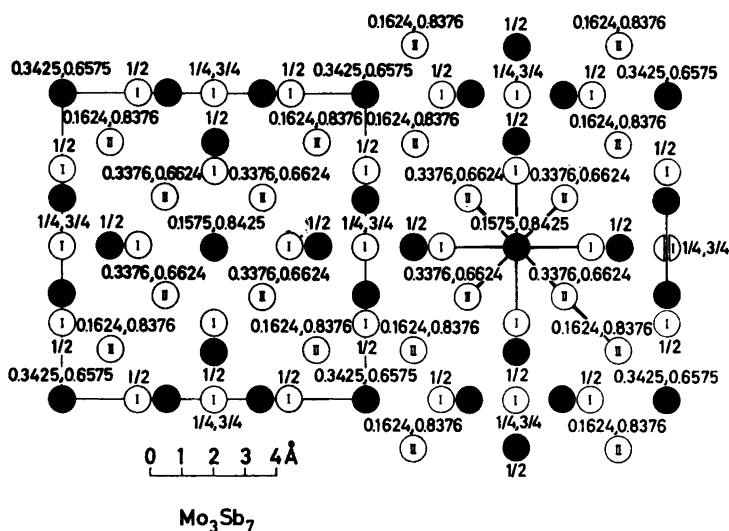

Mo_3Sb_7

Fig. 1. The structure of Mo_3Sb_7. Filled circles represent metal atoms and open circles represent metalloid atoms. The numbers indicate fractions of the projection axis.

Table 1. Observed and calculated structure factors for Mo₃Sb₇.

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
4 0 0	302.1	271.8	11 11 0	0	9.0	12 4 2	129.1	124.4
6 0 0	845.0	968.9	13 11 0	0	− 10.6	14 4 2	102.6	−107.4
8 0 0	426.8	371.3	15 11 0	0	− 16.0	5 5 2	0	5.8
10 0 0	81.8	− 84.4	17 11 0	0	10.0	7 5 2	82.2	− 60.1
12 0 0	650.0	686.1	12 12 0	420.2	407.8	9 5 2	180.8	163.4
14 0 0	144.3	143.3	14 12 0	0*	88.1	11 5 2	0	32.7
16 0 0	0	36.7	16 12 0	0	26.9	13 5 2	0	− 48.7
18 0 0	327.4	277.0	18 12 0	178.2	179.6	6 6 2	346.8	−369.9
20 0 0	220.3	183.3	13 13 0	0	20.3	8 6 2	0	− 7.7
22 0 0	0	− 43.0	15 13 0	105.6	−112.0	10 6 2	150.4	−159.5
24 0 0	187.3	181.6	17 13 0	0	− 13.3	12 6 2	96.7	−106.6
3 1 0	348.3	−326.2	14 14 0	0	11.6	14 6 2	0*	−118.2
5 1 0	0	− 4.9	16 14 0	0	52.9	7 7 2	144.8	−123.6
7 1 0	0	8.9	15 15 0	187.1	125.4	9 7 2	157.2	149.2
9 1 0	213.2	−196.6	16 16 0	164.6	127.4	11 7 2	0	− 8.4
11 1 0	0	− 7.7	2 1 1	150.0	−129.6	13 7 2	83.2	− 92.8
13 1 0	0	10.7	4 1 1	498.2	−479.1	8 8 2	0	34.0
15 1 0	125.8	−114.8	6 1 1	263.3	255.0	10 8 2	201.9	−173.1
17 1 0	0	− 7.7	8 1 1	215.7	−247.7	12 8 2	0*	106.4
19 1 0	0	9.7	10 1 1	138.1	−123.7	14 8 2	0	− 63.4
4 2 0	377.0	304.2	12 1 1	0	− 19.1	9 9 2	0	28.9
6 2 0	234.1	−198.2	14 1 1	0	12.4	11 9 2	141.5	114.4
8 2 0	234.0	214.4	16 1 1	185.6	−185.0	13 9 2	0*	101.5
10 2 0	0	3.2	3 2 1	374.2	320.1	10 10 2	288.9	−350.2
12 2 0	0	31.8	5 2 1	0	− 42.9	12 10 2	0	− 13.2
14 2 0	0	− 2.8	7 2 1	98.3	−118.9	14 10 2	165.0	−186.2
16 2 0	105.9	110.1	9 2 1	171.4	182.5	4 3 3	331.0	−309.9
18 2 0	0	− 70.5	11 2 1	0	10.4	6 3 3	740.9	849.1
20 2 0	0	68.4	13 2 1	90.3	− 83.7	8 3 3	81.6	− 67.6
3 3 0	815.7	833.0	15 2 1	95.3	91.9	10 3 3	0	− 77.8
5 3 0	170.3	−148.0	4 3 1	0	3.5	12 3 3	358.0	348.7
7 3 0	296.8	−301.7	6 3 1	0	7.9	14 3 3	190.4	134.0
9 3 0	490.8	493.3	8 3 1	0	− 8.1	16 3 3	176.8	−166.3
11 3 0	0	− 17.9	10 3 1	178.5	185.4	5 4 3	0	− 7.4
13 3 0	210.5	−213.9	12 3 1	142.1	−146.0	7 4 3	0	12.2
15 3 0	269.6	261.1	14 3 1	137.0	115.5	9 4 3	198.8	−208.2
17 3 0	0	31.3	16 3 1	0	9.1	11 4 3	0	− 11.9
19 3 0	102.9	−132.5	5 4 1	327.6	−336.5	13 4 3	0	14.1
4 4 0	627.1	560.4	7 4 1	365.8	−375.3	15 4 3	120.1	−124.9
6 4 0	0	− 35.7	9 4 1	0	− 10.6	6 5 3	94.9	94.1
8 4 0	389.5	398.4	11 4 1	138.4	−171.0	8 5 3	0	0.0
10 4 0	183.9	188.7	13 4 1	225.0	−241.9	10 5 3	158.9	155.6
12 4 0	138.5	122.8	15 4 1	0	− 20.8	12 5 3	0	− 80.6
14 4 0	95.5	109.8	6 5 1	233.3	213.5	14 5 3	170.3	116.6
16 4 0	234.9	217.4	8 5 1	186.9	−185.6	7 6 3	83.7	− 59.7
18 4 0	0	− 12.9	10 5 1	0	− 73.0	9 6 3	550.7	575.9
20 4 0	0*	127.4	12 5 1	0	− 19.6	11 6 3	149.6	124.4
5 5 0	0	− 0.2	14 5 1	0	28.7	13 6 3	0	− 68.1
7 5 0	0	− 5.1	16 5 1	154.4	−148.7	8 7 3	0	− 10.8
9 5 0	165.1	−103.3	7 6 1	212.2	198.1	10 7 3	207.0	163.9
11 5 0	0	2.3	9 6 1	0	3.5	12 7 3	185.3	−164.6
13 5 0	0	− 1.8	11 6 1	112.4	135.6	14 7 3	93.2	92.6
15 5 0	0	− 65.5	13 6 1	121.4	128.7	9 8 3	0	− 53.8
17 5 0	0	2.4	15 6 1	0	0.8	11 8 3	0	5.3

Table 1. Continued.

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
19	5	0	0	1.1	8	7	1	209.0	−220.3	13	8	3	0	− 7.7
6	6	0	592.6	546.8	10	7	1	149.0	−129.9	10	9	3	0	− 58.6
8	6	0	175.0	121.9	12	7	1	0	− 13.4	12	9	3	278.5	260.8
10	6	0	214.4	−231.2	14	7	1	0	− 2.3	14	9	3	95.5	104.5
12	6	0	455.9	458.5	16	7	1	184.0	−179.7	11	10	3	91.1	102.1
14	6	0	0	11.4	9	8	1	0	− 14.9	13	10	3	116.3	118.5
16	6	0	0	− 62.0	11	8	1	90.7	−102.0	4	4	4	62.4	66.1
18	6	0	176.4	167.7	13	8	1	125.3	−153.7	6	4	4	216.3	218.7
20	6	0	0*	100.5	15	8	1	0	− 20.0	8	4	4	196.9	136.2
7	7	0	0	18.4	10	9	1	139.3	130.8	10	4	4	126.2	−142.3
9	7	0	218.1	−213.9	12	9	1	136.4	−115.4	12	4	4	236.0	261.1
11	7	0	0	− 12.7	14	9	1	82.5	87.6	14	4	4	0	− 3.6
13	7	0	0	19.2	16	9	1	0	0.9	16	4	4	0	2.6
15	7	0	106.8	−131.4	11	10	1	0	− 22.3	5	5	4	239.5	−247.7
17	7	0	0	− 13.8	13	10	1	82.2	−101.0	7	5	4	274.2	−285.7
19	7	0	0	15.6	2	2	2	656.7	−720.9	9	5	4	0	− 15.9
8	8	0	438.1	333.1	4	2	2	458.0	−392.2	11	5	4	134.6	−132.7
10	8	0	143.6	134.4	6	2	2	254.0	−261.1	13	5	4	157.6	−192.5
12	8	0	198.3	199.8	8	2	2	222.1	−205.2	15	5	4	0	− 22.0
14	8	0	105.8	112.0	10	2	2	386.3	−439.1	6	6	4	219.0	−226.1
16	8	0	177.8	172.3	12	2	2	0	− 19.6	8	6	4	139.9	159.5
18	8	0	0	42.4	14	2	2	191.6	−220.1	10	6	4	0	8.1
20	8	0	138.2	129.1	16	2	2	143.5	−158.3	12	6	4	0	− 20.2
9	9	0	378.8	348.6	3	3	2	82.7	71.4	14	6	4	0	− 13.5
11	9	0	0	− 17.6	5	3	2	282.4	257.5	16	6	4	111.9	101.1
13	9	0	148.6	−168.3	7	3	2	231.2	224.0	7	7	4	309.7	−330.9
15	9	0	218.1	201.2	9	3	2	0	41.7	9	7	4	0	− 2.5
17	9	0	0	22.6	11	3	2	161.4	156.6	11	7	4	187.2	−160.9
19	9	0	100.6	−109.7	13	3	2	152.8	137.5	13	7	4	218.4	−230.5
10	10	0	0	21.0	15	3	2	0	21.9	8	8	4	140.4	165.4
12	10	0	0	− 48.6	4	4	2	128.7	−139.1	10	8	4	0	− 53.7
14	10	0	0	− 14.0	6	4	2	0	− 8.0	12	8	4	230.5	214.9
16	10	0	107.9	99.4	8	4	2	0	− 23.3	9	9	4	138.9	−157.9
18	10	0	83.8	− 96.2	10	4	2	262.4	−281.1	10	10	4	222.1	−246.3

* Unobserved reflection, possibly a result of indexing difficulties.

additional condition is not listed in *International Tables*,[4] but is easily verified by consideration of the geometrical structure factors given there.) A set of structure factors calculated on the basis of the atomic parameters obtained from the Patterson synthesis gave $R = 0.16$. The corresponding Fourier synthesis showed no significant shifts in the atomic coordinates and least-square refinement was accordingly started at once. This refinement was terminated with $R = 0.094$ after six cycles. (Three cycles were carried out before and three after correction for secondary extinction.[5])

The deduced atomic arrangement (Fig. 1) is in terms of space group $Im3m$ as follows:

    12 Mo   in (e) with $x_1 = 0.3425 \pm 0.0013$, $B_1 = 0.46 \pm 0.12$ Å^2
    12 Sb$_I$ in (d) with $B = 0.50 \pm 0.11$ Å^2
    16 Sb$_{II}$ in (f) with $x_2 = 0.1624 \pm 0.0004$, $B_2 = 0.56 \pm 0.09$ Å^2

The indicated error limits correspond to twice the standard deviation. The F_o and F_c values are listed in Table 1.

The Mo_3Sb_7 phase is accordingly isostructural with a class of other phases whose prototype is listed as Ir_3Ge_7 (Ir_3Sn_7)* in the complication of structures of metals and alloys by Pearson.[6] Owing to obvious relationships in composition, lattice dimension, space group, *etc.* a structure of this type might have been anticipated for the Mo_3Sb_7 phase. It must nevertheless be emphasized that considerations along these lines were not taken into account before after the structure was essentially solved. It also seems appropriate to recapitulate that the Mo_3Sb_7 structure has been verified on the basis of single crystal X-ray data as opposed to the previous determinations [7,8] of the isostructural phases which were based on X-ray powder data.

Brown[1] has independently arrived at the same type of structure for Mo_3Sb_7. His values for the variable parameters are $x_1 = 0.338$ and $x_2 = 0.163$. As these values were stated to be unrefined the agreement with the values obtained in this study must be said to be satisfactory.

(iii) *Interatomic distances and coordination.* The coordination around the molybdenum and antimony atoms can be seen in Fig. 1; and the shortest interatomic distances are listed in Table 2.

Each Mo atom is coordinated to eight Sb (four Sb_I and four Sb_{II}) atoms at the corners of a somewhat distorted square antiprism. Each Sb_I atom is surrounded by four Mo atoms tetrahedrally arranged, by four Sb_I atoms also in tetrahedral arrangement but at a greater distance, and by eight Sb_{II} atoms at a still greater distance forming a rectangular antiprism. The Sb_{II} atoms are coordinated to three Mo atoms and one Sb_{II} atom at the corners of a tetrahedron and to six, more distant, Sb_I atoms.

The atomic arrangement in the Mo_3Sb_7 structure produces a distinct formation of Mo—Mo and Sb_{II}—Sb_{II} pairs. On the basis of the interatomic distances (Table 2), bonds (single electron pair bonds) are considered to exist between the paired atoms. (The Sb_{II}—Sb_{II} distance of 2.905 ± 0.014 Å is in good agreement with the expectation value of 2.86 ± 0.04 Å for the single bond Sb—Sb distance suggested by Furuseth *et al.*[10] The Mo—Mo

Table 2. Interatomic distances in Mo_3Sb_7 (Å). (The indicated error limits correspond to those stated for the parameters in the text.)

$$
\begin{array}{llll}
\text{Mo} & - & 4 \ Sb_I & : \ 2.828 \pm 0.007 \\
 & - & 4 \ Sb_{II} & : \ 2.793 \pm 0.010 \\
 & - & 1 \ Mo & : \ 3.015 \pm 0.025 \\[4pt]
Sb_I & - & 4 \ Mo & : \ 2.828 \pm 0.007 \\
 & - & 4 \ Sb_I & : \ 3.384 \\
 & - & 8 \ Sb_{II} & : \ 3.682 \pm 0.002 \\[4pt]
Sb_{II} & - & 3 \ Mo & : \ 2.793 \pm 0.010 \\
 & - & 6 \ Sb_I & : \ 3.682 \pm 0.002 \\
 & - & 1 \ Sb_{II} & : \ 2.905 \pm 0.014 \\
\end{array}
$$

* This structure type was first established for Ir_3Sn_7 and Ru_3Sn_7 by the late Swedish chemist Nial[7] and is described in a paper from 1947 written by his friends after his death. Schubert and Pfisterer[8] reported in 1950 that Ir_3Ge_7, Pd_3Ga_7, Pt_3Ga_7, and Pt_3In_7 crystallize with the same structure type. Schubert[9] uses the notation Ru_3Sn_7 type, whereas Brown[1] apparently quotes Pearson[6] by referring to the Ir_3Ge_7 type of structure. In an attempt to avoid confusion the latter notation has been adopted in the remainder of this paper.

distance of 3.015 ± 0.025 Å is somewhat longer than the corresponding distance of 2.726 Å in body centered molybdenum metal. [11]

The existence of Mo$-$Mo and $Sb_{II}-Sb_{II}$ bonds is of considerable interest in relation to the application of the general $(8-N)$ rule [12-16] on the Mo_3Sb_7 phase. It follows from the crystal structure that the number of electrons P and Q involved in forming antimony$-$antimony and molybdenum$-$molybdenum bonds per formula unit is, respectively, 4 and 3. The total number a of antimony atoms per formula unit is 7. The magnetic susceptibility measurements [2] were not entirely conclusive, but suggested 3 or 6 unpaired d-electrons (localized on the molybdenum atoms) per formula unit. Assuming that each antimony atom contributes 5 electrons to the total number n of valence electrons per formula unit, it appears to be impossible, with a reasonable valance for molybdenum, to satisfy the general $(8-N)$ rule:

$$n+P-Q = 8a$$

Allowing the Sb_I and Sb_{II} atoms to have different numbers N_I and N_{II} of electrons in the outer shell (*e.g.* $N_I = 6$ and $N_{II} = 8$) in an attempt to use the extended formulation of the general $(8-N)$ rule:[15]

$$n+P-Q = 3N_I + 4N_{II}$$

gives the same negative result. As a conclusion of this discussion we predict that the Mo_3Sb_7 phase will exhibit metallic conductivity. The same prediction is also forwarded for the isostructural phases Ir_3Sn_7,[7] Ru_3Sn_7,[7] Ir_3Ge_7,[8] Pd_3Ga_7,[8] Pt_3Ga_7,[8] Pt_3In_7,[8] $Co_3Al_3Si_4$,[17] $Ni_3(Al,Si)_7$,[18] Re_3As_7,[19] and $Nb_3(Sb,Te)_7$.[19]

For a discussion of the relationship between the Ir_3Ge_7 and other common structure types, reference is made to Schubert.[9]

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