Acta Cryst. (1965). **18**, 815

Verfeinerung der Struktur von Heptaschwefelimid, S_7NH.

Von JOHANNES WEISS und HANS-STEPHAN NEUBERT, *Anorg. Chem. Institut der Universität Heidelberg, Deutschland*

(*Eingegangen am* 31. *Oktober* 1964 *und wiedereingereicht am* 7. *Dezember* 1964)

In einer früheren Arbeit konnten wir zeigen (Weiss, 1960) dass S_7NH und $S_6(NH)_2$ dieselbe Struktur besitzen wie rhombischer Schwefel (Warren & Burwell, 1935; Abrahams, 1955) und $S_4(NH)_4$ (Lund & Svendson, 1957; Sass & Donohue, 1958). Die Strukturbestimmung war jedoch, da damals noch kein Elektronenrechner zur Verfügung stand, relativ ungenau. Insbesondere waren die S–S-Abstände im S_7NH sehr unterschiedlich gefunden worden, und es war fraglich, ob dem eine reale Bedeutung zukommt. Es schien deshalb notwendig, die Struktur des S_7NH weiter zu verfeinern.

Die am Einkristall mit dem Zählrohr neu bestimmten Gitterkonstanten sind: $a=7,608$, $b=8,006$, $c=13,086$ Å. [Raumgruppe *Pbnm* (D_{2h}^{16}) mit 4 Molekülen S_7NH in der Elementarzelle].

Es wurden zunächst 3-dim. Fouriersynthesen durchgeführt, bis die anschliessende F_c-Berechnung keine Vorzeichenänderung mehr ergab. Anschliessend wurde eine 'back-shift'-Korrektur gemacht (Booth, 1946). Tabelle 1 enthält in Spalte I die früher gefundenen Parameter, in Spalte II die sich aus der letzten F_o-Synthese ergebenden Werte, Spalte III die korrigierten Werte und Spalte IV die Standard-Abweichung.

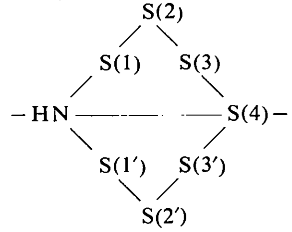
Tabelle 1. *Parameter*

		I	II	III	IV
S(1)	x	0,247	0,2440	0,2439	0,0035
	y	0,161	0,1673	0,1665	0,0029
	z	0,142	0,1446	0,1407	0,0010
S(2)	x	0,485	0,4880	0,4863	0,0037
	y	0,228	0,2288	0,2285	0,0031
	z	0,080	0,0794	0,0803	0,0009
S(3)	x	0,660	0,6582	0,6581	0,0043
	y	0,045	0,0425	0,0426	0,0032
	z	0,136	0,1321	0,1270	0,0013
S(4)	x	0,790	0,7891	0,7899	0,0028
	y	0,127	0,1288	0,1285	0,0035
	z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	—
N	x	0,214	0,2131	0,2108	0,0088
	y	0,272	0,2781	0,2762	0,0071
	z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	—
$R=\frac{\Sigma\lvert F_o-F_c\rvert}{\Sigma\lvert F_o\rvert}$		0,18	0,15	0,12	

Tabelle 2 zeigt, dass im Gegensatz zur früheren Bestimmung [S(1)–S(2) 2,05 Å, S(2)–S(3) 2,11 Å, S(3)–S(4) 1,90 Å] die Unterschiede in den S–S-Bindungsabständen wesentlich geringer geworden sind und nur wenig von den im rhombischen Schwefel gefundenen Abständen (2,04 Å) abweichen. Auch die Bindungswinkel sind mit denen im rhombischen Schwefel praktisch identisch.

Tabelle 2. *Abstände und Winkel im* S_7NH

S(1)–S(2)	2,05 Å	N S(1) S(2)	108,6°
S(2)–S(3)	2,07	S(1) S(2) S(3)	107,0
S(3)–S(4)	2,02	S(2) S(3) S(4)	107,5
S(1)–N	1,73	S(3) S(4) S(3′)	106,4
		S(1) N S(1′)	115,8
S(1)–S(1′)	2,94		
S(1)–S(3)	3,31	S(1′) S(1) S(3)	92,6
S(3)–S(3′)	3,22	S(1) S(3) S′(3)	87,4
S(1)–S(3′)	4,52		
S(2)–S(2′)	4,42		
S(4)–N	4,57		



Die Verfeinerung wurde mit einem eigenen Programm, das die oben angegebenen Schritte selbstständig nacheinander durchführt, auf dem Siemens Digitalrechner 2002 gerechnet.

Die Deutsche Forschungsgemeinschaft unterstützte diese Arbeit durch eine Sachbeihilfe.

References

ABRAHAMS, S. C. (1955). *Acta Cryst.* **8**, 661.
BOOTH, A. D. (1946). *Proc. Roy. Soc.* A, **188**, 77.
LUND, E. W. & SVENDSON, S. R. (1957). *Acta Chem. Scand.* **11**, 940.
SASS, R. L. & DONOHUE, J. (1958). *Acta Cryst.* **11**, 497.
WARREN, B. E. & BURWELL, J. T. (1935) *J. Chem. Phys.* **3**, 6.
WEISS, J. (1960). *Z. anorg. Chem.* **305**, 190.

Acta Cryst. (1965). **18**, 815

On the thermal expansion of protactinium metal.

BY J. A. C. MARPLES, *Atomic Energy Research Establishment, Harwell, Didcot, Berks., England*

(*Received* 4 *September* 1964)

A small quantity of protactinium metal was prepared by reducing the tetrafluoride with calcium and arc melting the resulting fine dispersion of metal in calcium fluoride to form a bead weighing about 80 mg. This bead was malleable and readily flattened (a phenomenon previously reported by Zachariasen, 1952) to form a disc about 7 mm in diameter.

This disc was mounted in a high temperature diffractometer and the X-ray pattern recorded at various temperatures. The lines obtained agreed with the body-centred tetragonal indexing proposed by Zachariasen (1952) and the lattice parameters obtained at room temperature also agreed fairly well with his revised values (Zachariasen, 1959) (see Table 2). The lines could not be satisfactorily indexed on the basis of the orthorhombic cell with $a/c=\sqrt{3}$ proposed by Donohue (1959). A typical pattern (obtained at 638 °C when the lines were at their sharpest, see below) is shown in Table 1.

Table 1. *Protactinium X-ray pattern obtained at* 638 °C

Observed values			Indexing on tetragonal cell (Zachariasen, 1952)		
d	Intensity	$1/d^2 \times 10^4$	Index	Calc. $1/d^2 \times 10^4$	$\Delta(1/d^2) \times 10^4$
2·7788	*m*	1295	110	1294	+1
2·5210	*m*	1574	101	1572	+2
1·5507	*m*	4158	211	4159	−1
1·4149	*w*	4994	112	4994	0
1·3902	*w*	5174	220	5174	0
1·2611	*w*−	6288	202	6287	+1
1·2433	*w*−	6468	310	6468	0
1·2177	*w*	6744	301	6746	−2
1·0615	*vw*	8876	222	8874	+2
1·0555	*m*	8978	103	8972	+6
1·0350	*w*	9335	321	9333	+2
0·9915	*w*	10172	312	10168	+4
0·9301	*w*	11559	213	11559	0
0·9159	*w*+	11921	411	11920	+1
0·8439	*w*−	14041	402	14048	−7
0·8410	*w*−	14139	303	14146	−7

$a = 3{\cdot}9321 \pm 0{\cdot}0003$ Å
$c = 3{\cdot}2879 \pm 0{\cdot}0004$ Å

The lattice parameters measured at various temperatures are given in Table 2 and in Fig. 1: Fig. 2 shows the variation with temperature of the axial ratio and the cell volume: from the latter the mean linear expansion coefficient between room temperature and 700 °C is $9{\cdot}9 \times 10^{-6}$/°C. An interesting feature of the lattice parameter *versus* temperature curves is the negative expansion coefficient in the *a* direction above 500 °C and the increase in the expansion coefficient in the *c* direction. As a consequence of these changes the axial ratio, about 0·825 at room temperature, increases more and more rapidly towards unity as the temperature is raised, *i.e.* the structure tends towards b.c.c. at high temperatures: extrapolating the axial ratio *versus* temperature curve suggests a transition point in the neighbourhood of 1200 °C.

Two attempts to verify this directly were thwarted by the rapid surface oxidation of the specimen above 1000 °C. On the second occasion however, after the b.c.t. 101 and 110 lines had disappeared (which may well have been due to oxidation) a very weak line was observed above 1170 °C with $d = 2{\cdot}696$ Å. If this is assumed to be line $N = 2$ of the b.c.c. then its lattice parameter would be about 3·81 Å and the transition temperature would be 1170 ± 20 °C. It must be stressed, however, that the evidence for this is very tenuous.

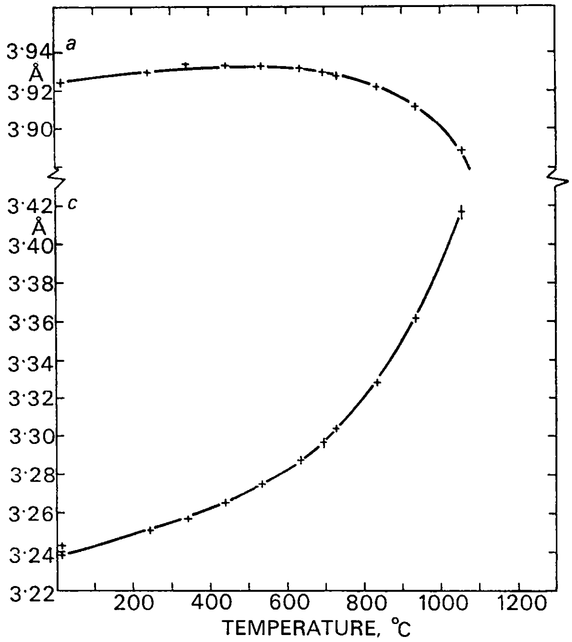


Fig. 1. Variation of lattice parameters with temperature.

An unfortunate consequence of the very anisotropic expansion coefficients is that, at any rate with massive specimens as distinct from powders, it seems impossible to obtain really sharp well resolved X-ray patterns at room temperature. Peaks that were sharp on the diffraction trace at 400 °C became diffuse on cooling — presumably because of the strain caused by the anisotropy.

A subsidiary experiment, using an optical pyrometer technique, gave the melting point of a small bead of the metal as 1575 ± 20 °C.

Table 2. *Lattice parameters and cell volume at different temperatures*

Temperature	a	c	c/a	Cell volume $=a^2c$
Room*	3·932 ± 0·003 Å	3·238 ± 0·003 Å	0·8235 ± 0·0013	50·06 ± 0·12 Å^3
18 °C	3·925 ± 0·002	3·242 ± 0·001	0·8260 ± 0·0007	49·95 ± 0·06
18	3·924$_1$ ± 0·0010	3·239$_1$ ± 0·0005	0·8254 ± 0·0002	49·88 ± 0·03
242	3·930$_1$ ± 0·0005	3·251$_3$ ± 0·0010	0·8273 ± 0·0002	50·22 ± 0·03
342	3·934$_6$ ± 0·0006	3·257$_6$ ± 0·0007	0·8279 ± 0·0002	50·43 ± 0·03
440	3·933$_2$ ± 0·0004	3·265$_5$ ± 0·0004	0·8302 ± 0·0001	50·52 ± 0·02
537	3·933$_0$ ± 0·0004	3·275$_5$ ± 0·0008	0·8328 ± 0·0002	50·67 ± 0·04
638	3·932$_1$ ± 0·0003	3·287$_9$ ± 0·0004	0·8362 ± 0·0001	50·84 ± 0·01
698	3·930 ± 0·001	3·297 ± 0·002	0·8389 ± 0·0008	50·92 ± 0·06
731	3·928$_0$ ± 0·0003	3·304$_2$ ± 0·0006	0·8412 ± 0·0002	50·98 ± 0·02
836	3·922$_6$ ± 0·0002	3·328$_4$ ± 0·0010	0·8485 ± 0·0002	51·21 ± 0·02
938	3·912$_1$ ± 0·0007	3·361$_7$ ± 0·0008	0·8593 ± 0·0004	51·45 ± 0·03
1055	3·889 ± 0·002	3·417 ± 0·003	0·8786 ± 0·0008	51·69 ± 0·06

* Zachariasen (1959)

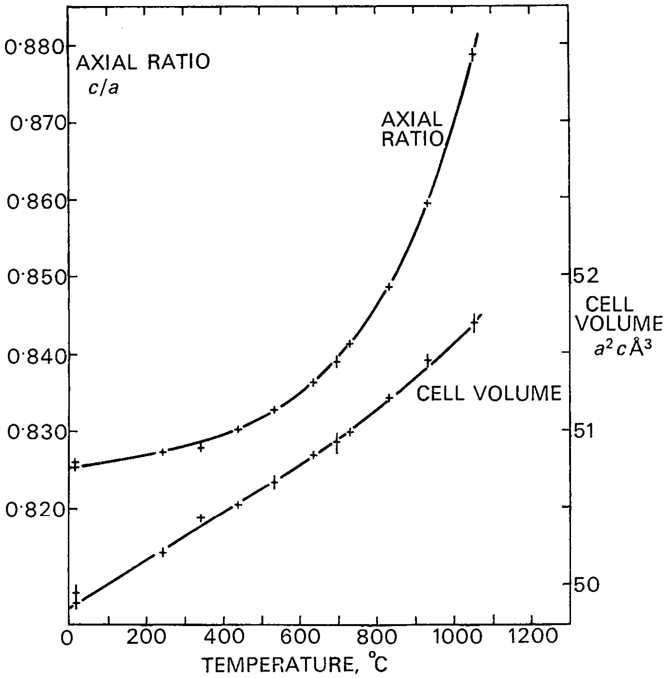


Fig. 2. Axial ratio and cell volume *versus* temperature.

The author's thanks are due to K. Bagnall, D. Brown and V. Emerson for producing the protactinium fluoride and to A. Hough for helping with the reduction.

References

Donohue, J. (1959). *Acta Cryst.* **12**, 697.
Zachariasen, W. H. (1952). *Acta Cryst.* **5**. 19.
Zachariasen, W. H. (1959). *Acta Cryst.* **12**, 698.

Acta Cryst. (1965). **18**, 817

$LiMg_2Tl$: preparation and structure*.

By William J. Ramsey, *Lawrence Radiation Laboratory, University of California, Livermore, California, U.S.A.*

(*Received* 29 *October* 1964)

A previously unreported compound, $LiMg_2Tl$, is interesting because of its ordered $L2_1$ structure type. We prepared the compound to compare its structure and properties with those of Li_2MgPb (Ramsey, 1961; Ramsey, Sands & Mead, 1963).

The compound was prepared in an Armco iron crucible in an argon atmosphere by melting together weighed amounts of the elements of greater than 99·5% purity. Slight excesses of lithium and magnesium were added to compensate for oxidation. Cooling curves showed that the compound melts congruently at approximately 594 °C. The solid has a grey metallic color, is brittle, and tarnishes in laboratory air in several minutes. The analysis of the material used in these studies was: Li, 26; Mg, 52; Tl, 22 at.%.

X-ray powder patterns of this material, taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), showed only a single, face-centered cubic phase with $a_0 = 6{\cdot}83_7$ Å. Neutron diffraction measurements on a powdered sample were necessary to establish the positions of the lighter elements within the unit cell. These measurements were carried out in a previously described (Mead & Sparks, 1960) apparatus. While X-ray patterns indicated a single f.c.c. phase, the neutron diffraction spectrum showed, in addition, two very weak lines from an impurity. From their positions, these impurity lines were tentatively ascribed to a trace of either magnesium metal or magnesium metal containing lithium in solid solution.

Taking the positions of the Tl atoms to be at (0,0,0) in the face-centered cubic lattice, the distributions of the lighter elements might occur as shown in Table 1.

Table 1. *Possible distributions of* Li *and* Mg *in* $LiMg_2Tl$

Position	Distribution		
	I	II	III
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	Li	Mg	$\frac{1}{3}$ Li, $\frac{2}{3}$ Mg
$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4}$	2 Mg	Mg, Li	$\frac{2}{3}$ Li, $\frac{4}{3}$ Mg

Distribution I corresponds to the $L2_1$ Heusler alloy type, while distributions II and III correspond to possible disordering.

---

* This work was performed under the auspices of the United States Atomic Energy Commission.