Acta Cryst. (1957). **10**, 715

Partial order in the non-stoichiometric phase $Ti_{2+x}S_4 (0{\cdot}2 < x < 1)$.

By A. D. Wadsley, *Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia*

(*Received* 25 *June* 1957)

The crystal structures of a number of phases in the range TiS–TiS_3 were recently published by Hahn & Harder (1956). They confirmed the existence of the non-stoichiometric 'sesquisulphide' first noted by Biltz, Ehrlich & Meisel (1937), and proposed a structure for Ti_3S_4 in the space group $P6_3/mmc$ similar to that of titanium phosphide (Schönberg, 1954) but with the metal atoms randomly occupying only three-quarters of the octahedral sites available to them. A parallel examination of this particular phase had already been made in this laboratory as part of a more general study of the chalcogenides of the Group IV metals (McTaggart & Wadsley, 1957). Whilst the structure found for $Ti_{2{\cdot}67}S_4$ (i.e. Ti_2S_3) and for Ti_3S_4 by the present writer was substantially similar to that reported by Hahn & Harder, differences were noted which call for some comment.

The hexagonal lattice parameters of a series of compositions defining the phase limits, and given in Table 1, were determined from exposures in a Guinier-type focusing camera. The structure of $Ti_{2{\cdot}67}S_4$ was found by powder diffraction techniques, the intensities being estimated visually from multiple films simultaneously exposed with copper radiation in a camera 14·4 cm. in diameter. The absent reflexions were for $h,h,\overline{2h},l$ with l odd, and for $hk\bar{i}l$ with l odd when $h-k = 3n$, and these were characteristic of several hexagonal space groups provided the atoms were in one-, two-, or fourfold point positions. Satisfactory agreement between observed and calculated F values (Table 3) was reached by trial and error, the discrepancy factor being 0·16. The structure is based upon the atomic coordinates in Table 2 for the space group $P6_3mc$.

Table 1. *Crystallographic data*

Compound	a (Å)	c (Å)	Density (g.cm.$^{-3}$) Obs.	Density (g.cm.$^{-3}$) Calc.
TiS_2	3·90	5·70	3·15	3·28*
$Ti_{2{\cdot}22}S_4$	$3{\cdot}41_3$	11·46	3·35	3·37
$Ti_{2{\cdot}67}S_4$	$3{\cdot}42_6$	11·41	3·64	3·71
Ti_3S_4	$3{\cdot}44_5$	11·45	3·74	3·84

* Values for TiS_2 taken from Hägg & Schönberg (1954).

Table 2. *Fractional atomic parameters for* $Ti_{2+x}S_4$
Space group $P6_3mc$

Atom	No. of atoms occupying equivalent positions	Coordinates	z parameter
Ti_1	2	$\frac{1}{3}, \frac{2}{3}, z_1;\ \frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z_1$	$z_1 = \frac{3}{4}$
Ti_2	x	$\frac{1}{3}, \frac{2}{3}, z_2;\ \frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z_2$	$z_2 = 0$
S_1	2	$\frac{1}{3}, \frac{2}{3}, z_3;\ \frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z_3$	$z_3 = \frac{3}{8}$
S_2	2	$0, 0, z_4;\ 0, 0, \frac{1}{2}+z_4$	$z_4 = \frac{1}{8}$

Table 3. *Calculated and observed X-ray data*

$hkil$	$\sin^2\theta$ Calc.	$\sin^2\theta$ Obs.	$\|F\|_o$	$\|F\|_c$
0002	0·0182	0·0186	42	33
$10\bar{1}0$	0·0674	0·0682	22	21
$10\bar{1}1$	0·0720	0·0730	48	41
0004	0·0729			7
$10\bar{1}2$	0·0856	0·0863	91	112
$10\bar{1}3$	0·1084	0·1093	119	145
$10\bar{1}4$	0·1403	0·1409	73	91
0006	0·1640	0·1649	51	23
$10\bar{1}5$	0·1813	0·1823	110	129
$11\bar{2}0$	0·2021	0·2032	178	157
$11\bar{2}2$	0·2203	0·2214	68	52
$10\bar{1}6$	0·2314	0·2324	87	88
$20\bar{2}1$	0·2741	0·2753	55	69
$11\bar{2}4$	0·2750			14
$20\bar{2}2$	0·2877	0·2890	80	82
$10\bar{1}7$	0·2906	0·2928	126	26
0008	0·2916			80
$20\bar{2}3$	0·3105	0·3119	107	94
$20\bar{2}4$	0·3424	0·3439	72	67
$11\bar{2}6$	0·3661	0·3679	74	41
$20\bar{2}5$	0·3834	0·3853	91	82
$20\bar{2}6$	0·4335	0·4353	69	71
$10\bar{1}9$	0·4364			22
$21\bar{3}1$	0·4762	0·4760	43	30
$21\bar{3}2$	0·4898	0·4906	77	95
$20\bar{2}7$	0·4927	0·4948	203	54
$11\bar{2}8$	0·4937			157
$21\bar{3}3$	0·5126	0·5143	126	122
$1,0,\bar{1},10$	0·5230	0·5225	63	65
$21\bar{3}4$	0·5445	0·5455	69	77
$21\bar{3}5$	0·5855	0·5868	113	112
$30\bar{3}0$	0·6063	0·6078	137	99
$1,0,\bar{1},11$	0·6187	0·6187	63	78
$21\bar{3}6$	0·6356	0·6368	75	81
0,0,0,12	0·6561	0·6574	38	4
$1,1,\bar{2},10$	0·6577			31
$1,0,\bar{1},12$	0·7235	0·7228	44	46
$22\bar{4}0$	0·8084	0·8091	105	85
$30\bar{3}8$	0·8979	0·8979	127	116
$31\bar{4}3$	0·9168	0·9167	73	88

The atomic arrangement is shown in Fig. 1 viewed down the a axis. It differs from that of Hahn & Harder (1956) by the choice of space group, and a different origin results from the loss of the centre of symmetry. Better agreement was reached in the present instance, however, by postulating alternate filled and partly occupied sheets of metal atoms, rather than by assuming that the metals were statistically distributed over both sites with a small adjustment of the z parameter.

The sulphur atoms for this structure are in alternate hexagonal and cubic close packing, so that the filled Ti–S layers are grouped together as in the $C27$ structure type. The supernumerary metal atoms find another set of octahedral sites between adjacent layers and increasing numbers may be admitted until half filled. This corresponds to Ti_3S_4, which is the limiting composition. No evidence was found for superlattice reflexions corresponding to a multiple a axis, and the metal atoms and vacancies in the defective sheets are not ordered as in Cr_2S_3 (Jellinek, 1955).

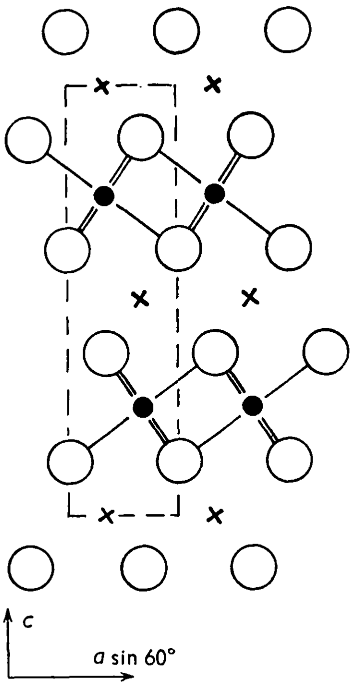

Fig. 1. The structure of $Ti_{2+x}S_4$ viewed down the a axis. Sulphur atoms are drawn as larger circles, completely filled Ti_1 sites as small black circles, and partly occupied Ti sites as crosses. The unit cell is drawn in projection with broken lines.

The titanium atoms are each distant 2·45 Å from six sulphurs at the corners of a nearly regular octahedron, and have an additional metal 2·86 Å away as a seventh neighbour through the centre of an octahedral face. In each octahedron there are six S–S distances of 3·43 Å (the a axis length) and six of 3·48 Å. The Ti–Ti distance in metallic titanium is 2·90 Å, and it is possible that some form of metal-to-metal bonding exists between adjacent octahedra sharing a face parallel to (0001). The two sulphur atoms have different environments, S_1 is at the centre of a trigonal prism of titanium atoms, whilst S_2 is at the centre of an octahedron.

Many of the sesqui-selenides and -tellurides of the transition metals may perhaps be regarded as the 'averaged mean' of the closely related $C6$ and $B8$ structures. TiS_2 has the $C6$ arrangement, whilst in the high-temperature form of TiS the $B8$ grouping is modified by regular stacking disorders (Hahn & Harder, 1956). The non-stoichiometric titanium 'sesquisulphide' therefore represents a transitional or intermediate structure between the two.

The writer desires to thank Mr F. K. McTaggart for kindly placing the specimens at his disposal.

References

Biltz, W., Ehrlich, P. & Meisel, K. (1937). *Z. anorg. Chem.* **234**, 97.

Hägg, G. & Schönberg, N. (1954). *Ark. Kemi*, **7**, 40, 371.

Hahn, H. & Harder, B. (1956). *Z. anorg. Chem.* **288**, 241.

Jellinek, F. (1955). *Proc. K. Ned. Akad. Wet.* B, **58**, 213.

McTaggart, F. K. & Wadsley, A. D. (1957). To be published.

Schönberg, N. (1954). *Acta Chem. Scand.* **8**, 226.

Acta Cryst. (1957). **10**, 716

Lattice parameters of cold-worked Cu–Zn–Ga alloys.

By L. Castelliz, C. S. Barrett and T. B. Massalski,* *Institute for the Study of Metals, University of Chicago, Chicago, Illinois, U.S.A.*

(*Received* 5 *June* 1957)

Massalski & Barrett (1957) have recently shown that ternary Cu–Zn–Ga alloys with the body-centered cubic structure, in the region of the equilibrium diagram where this high-temperature structure can be retained by a rapid quench, can be subsequently transformed by cold working.

Three such alloys, falling along the line of constant valence-electron:atom ratio (e/a = 1·476), have been subjected to cold work after quenching from the b.c.c. region, and the lattice parameters of the transformation structure are reported in this note.

The alloys were obtained from materials of 99·98–99·99% purity, cast in 'Vycor' tubing, homogenized at 800° C. and quenched in brine. Their composition is given in Table 1. X-ray patterns were obtained with monochromatized Cu $K\alpha$ radiation in a G. E. X-ray diffraction unit. After filing at room temperature, and immediate X-ray exposure, lines of a transformation structure were

Table 1. *Lattice parameters*

	Composition (atomic %)			
Alloy*	Cu	Zn	Ga	Lattice parameter (Å)
1 Ga	54·9	42·5	2·6	3·730 ± 0·002
2 Ga	57·4	37·5	5·1	3·717 ± 0·002
*D*5	65·07	23·67	11·26	3·705 ± 0·002

* Alloy designations are the same as those used by Massalski & Barrett (1957).

---

* Presently at the Department of Physical Metallurgy, The University, Birmingham 15, England.