

On the Arsenides and Antimonides of Tantalum

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The phase relationships in the systems tantalum-arsenic and tantalum-antimony have been studied by X-ray method. Density determinations and magnetic susceptibility measurements have been carried out. Five intermediate phases have been identified:

1. TaAs, with NbAs-type structure, $a = 3.4348 \text{ \AA}$,
 $c = 11.641 \text{ \AA}$, density = 12.25 g cm^{-3} .
2. TaAs₂, with NbAs₂-type structure, $a = 9.3385 \text{ \AA}$,
 $b = 3.3851 \text{ \AA}$, $c = 7.7568 \text{ \AA}$, $\beta = 119.70^\circ$, density = 10.26 g cm^{-3} .
3. Ta₃Sb, with β W-type structure, $a = 5.2646 \text{ \AA}$.
4. Ta₃Sb₄, with Ti₃Te₄-type structure, $a = 10.248 \text{ \AA}$,
 $c = 3.5460 \text{ \AA}$, density = 12.22 g cm^{-3} .
5. TaSb₂, with NbAs₂-type structure, $a = 10.2218 \text{ \AA}$,
 $b = 3.6447 \text{ \AA}$, $c = 8.2915 \text{ \AA}$, $\beta = 120.39^\circ$, density = 10.53 g cm^{-3} .

The TaAs, TaAs₂, and TaSb₂ phases have diamagnetic susceptibilities, whereas the Ta₃Sb₄ phase shows weak temperature independent paramagnetism.

In the course of continued studies on transition metal chalcogenides and pnictides at this Institute an investigation of structural and magnetic properties of tantalum arsenides and antimonides has been carried out. A study of these systems has been prompted by interesting structural findings in the corresponding niobium-arsenic and niobium-antimony systems.¹⁻⁴

The present communication forms a supplement to recent publications on the tantalum arsenides by Boller and Parthé⁵ and Saini *et al.*⁶, where phases with composition TaAs and TaAs₂ have been described. The older literature⁷ claims the existence of a phase with composition TaAs_{1.4}. Ta₃Sb is the only phase previously reported⁸ in the tantalum-antimony system.

EXPERIMENTAL

Materials. The tantalum metal used in this study was "Spectrographically standardized tantalum" from Johnson, Matthey & Co., Ltd.; with reported impurities (in ppm): Nb (<200), Fe (300), Si (100), Al (20), Cr (20), Sn (20), Mn (5), and Mg (1). The "Spectrographically standardized" arsenic and antimony from Johnson, Matthey & Co., Ltd. contained (in ppm): Na (3), Si (2), Cu (<1), Mg (<1), and Ag (<1) for the arsenic and Cu (<1), Mg (<1), Si (<1), and Ag (<1) for the antimony.

Preparation. Samples were prepared by heating accurately weighed quantities of tantalum and arsenic or antimony, respectively, in evacuated and sealed silica tubes. Samples with composition 33.33, 50.00, 66.67, and 75.00 atomic % As and samples with 20.00, 25.00, 33.33, 44.44, 50.00, 60.00, 66.67, and 75.00 atomic % Sb were heated at 850°C for 10 days and quenched in ice water.

Samples of TaAs, Ta₃Sb, and Ta₅Sb₄ were also prepared by thermal decomposition of TaAs₂ and TaSb₂, respectively.

X-Ray diffraction. All samples were crushed and X-ray photographs were taken in a Guinier focusing camera of 80 mm diameter using strictly monochromatized CuK α ₁-radiation. For the calculation of lattice constants potassium chloride (Analar, The British Drug Houses Ltd., $a = 6.2919 \text{ \AA}$) was added to the specimen as an internal standard. Lattice constants are expressed in Ångström units on the basis of $\lambda(\text{CuK}\alpha_1) = 1.54050 \text{ \AA}$.

Density measurements. The density measurements were carried out pycnometrically at 25°C with kerosene as displacement liquid. To remove gases adsorbed by the sample the pycnometer was filled under vacuum with kerosene. The samples weighed approximately 2 g.

Magnetic measurements. The magnetic susceptibilities were measured by the Gouy method at three different maximum field strengths ($H_{\text{max}} = 4015, 4700, \text{ and } 5110 \text{ O}$). The samples were enclosed in evacuated and sealed Pyrex tubes of 3 mm internal diameter to a height of about 85 mm.

RESULTS

In the tantalum-arsenic system only the two intermediate phases TaAs and TaAs₂, previously described,^{5,6} were found. In the tantalum-antimony system the existence of two new, intermediate phases was ascertained, *i.e.* the Ta₅Sb₄ phase and the TaSb₂ phase. Furthermore, the existence of the Ta₃Sb phase (known from the earlier study of Nevitt⁸) was confirmed.

These phases are all completely analogous to the phases in the niobium-arsenic and niobium-antimony systems, as described by Furusetth and Kjekshus.¹⁻⁴

The Ta₃Sb phase. Guinier photographs of the samples with < 44.44 atomic % Sb showed the presence of a phase with cubic symmetry. The indexed reflections are no doubt due to the Ta₃Sb phase, described by Nevitt.⁸

The purest samples of the Ta₃Sb phase were obtained by thermal decomposition of the TaSb₂ phase at 1150°C. After degradation the residuum was found to contain Ta₃Sb as the only phase from the tantalum-antimony system. However, a parallel, interfering reaction with silica gave the samples an unavoidable contamination. (A similar observation is made in a study of tantalum chalcogenides with high tantalum content.¹⁰)

The lattice constant of the Ta₃Sb phase (the purest sample judging from the Guinier photograph (Table 1)) is $a = 5.2646 \text{ \AA}$ in close agreement with the value $a = 5.2595 \pm 0.0010 \text{ \AA}$ reported by Nevitt.⁸ According to the approximately constant a -axis for samples of different composition, the homogeneity range of the Ta₃Sb phase is not noticeable.

The observed density is approximately 10 % lower than the calculated density, 15.12 g cm⁻³, from the X-ray measurements assuming 2 Ta₃Sb-groups per unit cell. This discrepancy is readily explained by the contamination of the sample and gives no reason to reject the stoichiometric formula Ta₃Sb.

According to Nevitt⁸ Ta₃Sb should be listed among substances having βW -type structure. A comparison of observed and calculated intensities of the

Table 1. Guinier photograph data of Ta₃Sb taken with strictly monochromatized CuK α_1 radiation.

I_{obs}	$\sin^2\theta \times 10^5$		hkl	I_{obs}	$\sin^2\theta \times 10^5$		hkl
	obs	calc			obs	calc	
vw	4 286	4 281	110	st	27 839	27 828	320
m	8 563	8 562	200	m	34 255	34 250	400
vst	10 699	10 703	210	m	42 821	42 812	420
st	12 843	12 844	211	st	44 969	44 953	421
m	25 679	25 687	222	st	47 144	47 093	332

reflections on the Guinier photographs confirmed the proposed structure. The shortest interatomic distances in Ta₃Sb are (in Å):

$$\begin{aligned} \text{Ta} - 10 \text{ Ta: } & 2.632 (2); 3.224(8) \\ & - 4 \text{ Sb: } 2.943 \\ \text{Sb} - 12 \text{ Ta: } & 2.943 \\ & - 8 \text{ Sb: } 4.559 \end{aligned}$$

The shortest Ta-Ta distance is some 8 % shorter than in metallic tantalum (2.863 Å¹¹). Similar short metal-metal distances observed in all phases with β W-type structure, are one of the most interesting features of this class of phases (see the discussion by Geller¹² and Pauling;¹³ see also Nevitt⁸).

The Ta₅Sb₄ phase. The disappearing phase method applied to the Guinier photographs indicated the existence of a phase with composition 44.44

Table 2. Guinier photograph data of Ta₅Sb₄ taken with strictly monochromatized CuK α_1 radiation.

I_{obs}	$\sin^2\theta \times 10^5$		hkl	I_{obs}	$\sin^2\theta \times 10^5$		hkl
	obs	calc			obs	calc	
st	1 131	1 130	110	w	20 315	20 335	006
w	2 259	2 259	200	w	21 100	{ 21 099	521
w	4 524	4 519	220			{ 21 132	202
vw	5 643	5 649	310	m	22 585	22 595	620
st	7 542	7 542	211	vw	23 397	23 392	222
vst	9 789	9 802	301	w	25 637	25 618	611
st	10 168	10 168	330	st	27 929	{ 27 878	541
st	11 302	11 297	420			{ 27 911	402
m	12 056	12 061	321	m	28 238	28 244	{ 710
vst	14 313	14 321	411				{ 550
m	14 685	14 687	510	m	29 055	29 041	332
vw	18 065	18 076	440	st	30 183	30 170	422
		{ 18 840	{ 431	w	33 573	33 560	512
m	18 867	{ 18 873	{ 501	st	34 670	34 656	721
w	19 193	19 206	530	vw	36 134	36 152	800
vw	20 010	20 003	112	vw	36 979	36 949	442

Table 3. Interatomic distances in Ta₅Sb₄ (Å).

Ta _I	— 2 Ta _I	: 3.546 (2)
	— 8 Ta _{II}	: 2.91 (8)
	— 4 Sb	: 2.93 (4)
Ta _{II}	— 2 Ta _I	: 2.91 (2)
	— 6 Ta _{II}	: 3.26 (2); 3.43 (2); 3.546 (2)
	— 5 Sb	: 2.72 (2); 2.76 (3)
Sb	— 1 Ta _I	: 2.93
	— 6 Ta _{II}	: 2.72 (2); 2.76 (4)
	— 10 Sb	: 3.546 (2); 3.75 (4); 4.15 (2); 4.32 (2)

atomic % Sb. Thermal decomposition of the TaSb₂ phase at 1000°C confirmed this composition and the phase was accordingly designated Ta₅Sb₄. Density measurements and structure determination proved the composition.

The Guinier photographs (Table 2) were indexed on tetragonal axes:

$$a = 10.248 \text{ \AA}, c = 3.5460 \text{ \AA}, c/a = 0.3460$$

The lattice constants of the stoichiometric Ta₅Sb₄ sample vary only slightly from the lattice constants of Ta₅Sb₄ in samples where the Ta₅Sb₄ phase is in equilibrium with the Ta₃Sb and TaSb₂ phases. This indicates that the homogeneity range of the Ta₅Sb₄ phase is rather narrow.

According to the pycnometric density 12.25 g cm⁻³ the unit cell contains 2 ($Z_c = 1.97$) Ta₅Sb₄-groups. The calculated density from the X-ray data is 12.41 g cm⁻³.

The tetragonal structure of a phase Ti₅Te₄ has been described by Grønvold *et al.*¹⁴ As it has been shown^{1,2} that the compounds Nb₅Sb₄ and Ti₅Te₄ are isostructural, and as the Guinier photograph of Ta₅Sb₄ resembles that of Nb₅Sb₄ both with regard to line pattern and intensities, the possibility of Ta₅Sb₄ also being isostructural with Ti₅Te₄ was investigated.

In terms of the space group $I4/m$ the atomic arrangement in Ti₅Te₄ is as follows (the parameters have been rounded off):

$$\begin{aligned}
 &2 \text{ Ti}_I \text{ in } (a) \ 0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \\
 &8 \text{ Ti}_{II} \text{ in } (h) \ \pm(x, y, 0; \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2}; \bar{y}, x, 0; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2}) \\
 &\quad \text{with } x_1 = 0.31 \text{ and } y_1 = 0.38 \\
 &8 \text{ Te in } (h) \ \text{with } x_2 = 0.06 \text{ and } y_2 = 0.28
 \end{aligned}$$

Table 4. Guinier photograph data of TaAs taken with strictly monochromatized CuK α_1 -radiation.

I_{obs}	$\sin^2\theta \times 10^6$		hkl	I_{obs}	$\sin^2\theta \times 10^6$		hkl
	obs	calc			obs	calc	
m	5 462	5 466	101	w	25 582	25 580	211
m	6 995	7 004	004	w	25 819	25 817	116
m	8 965	8 969	103	w	26 487	26 480	107
vst	11 806	11 808	112	m	27 118	27 118	204
w	15 968	15 973	105	vw	28 027	28 018	008
m	20 107	20 114	200	w	29 083	29 083	213

Table 5. Lattice constants of TaAs.

a (Å)	c (Å)	c/a	Reference
3.4348	11.641	3.3891	Present
3.43 ₇	11.65 ₄	3.39 ₁	Boller and Parthé ⁵
3.436 ± 0.002	11.644 ± 0.005	3.389	Saini <i>et al.</i> ⁶

These parameters were used in the calculation of intensities of the Guinier photographs. A reasonable agreement between observed and calculated intensities was obtained, indicating that the proposed structure is correct. Further refinement of the parameters was not attempted.

The shortest interatomic distances, based on the above parameters, are listed in Table 3. A discussion of this structure type is given by Grønvold *et al.*¹⁴

Seven phases are known with the Ti_5Te_4 -type structure, *i.e.* Ti_5Te_4 ,¹⁴ V_5S_4 ,¹⁵ V_5Se_4 ,¹⁶ Nb_5Se_4 ,¹⁷ Nb_5Te_4 ,¹⁷ Nb_5Sb_4 ,^{1,2} and Ta_5Sb_4 while V_5Te_4 ¹⁸ has a monoclinic structure of similar dimensions. The existence of Nb_5Sb_4 and Ta_5Sb_4 emphasizes the metallic character of these phases as already pointed out by Furuseth and Kjekshus.²

The TaAs phase. The purest samples of the TaAs phase were made by thermal decomposition of the $TaAs_2$ phase. Complete degradation of $TaAs_2$ at 900°C gave TaAs as residual crystalline phase.

Guinier photographs (Table 4) of the TaAs phase were indexed on the basis of a tetragonal unit cell. The lattice dimensions of TaAs being essentially constant for samples with lower and higher arsenic content than stoichiometric TaAs, show that the homogeneity range must be rather narrow.

For comparison with the values previously determined by Boller and Parthé⁵ and Saini *et al.*⁶ the lattice constants have been listed in Table 5. The three sets of values are in good agreement.

The pycnometric density of TaAs prepared by thermal decomposition of $TaAs_2$, 12.25 g cm⁻³, is in close accordance with the calculated density, 12.37 g cm⁻³, from the X-ray data (assuming 4 ($Z_c = 3.96$) TaAs-groups per unit cell).

The crystal structure of TaAs has been determined by Boller and Parthé.⁵ (A tentative confirmation is also given by Saini *et al.*⁶) TaAs is isostructural with NbAs, a structure independently determined by Boller and Parthé⁵ and Furuseth and Kjekshus.³ In terms of space group $I4_1md$ 4 Ta and 4 As are in (a):

$$0, 0, z; 0, \frac{1}{2}, \frac{1}{4} + z; \frac{1}{2}, 0, \frac{3}{4} + z; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$$

with $z_{Ta} = 0$ and $z_{As} \approx 5/12$

This structure was also verified in the present study by comparing observed and calculated intensities of the Guinier photographs, though minor deviations from $z_{As} = 5/12$ were not tested.

Table 6. Guinier photograph data of TaAs₃ taken with strictly monochromatized CuK α ₁ radiation.

I_{obs}	$\sin^2\theta \times 10^5$		hkl	I_{obs}	$\sin^2\theta \times 10^5$		hkl
	obs	calc			obs	calc	
m	1 300	1 307	001	w	27 702	27 717	510
st	2 758	2 762	20 $\bar{1}$	w	27 768	27 774	221
w	3 598	3 606	200	w	28 238	28 255	40 $\bar{2}$
m	4 525	4 532	20 $\bar{2}$	w	29 619	29 624	22 $\bar{3}$
vw	5 220	5 227	00 $\bar{2}$	m	29 811	29 828	31 $\bar{5}$
m	6 072	6 079	110	m	31 282	31 282	114
m	6 305	6 310	11 $\bar{1}$	w	31 764	31 758	42 $\bar{2}$
w	7 054	7 064	201	w	32 147	32 140	42 $\bar{1}$
vst	8 458	8 461	111	m	32 473	{32 457	600
m	8 905	8 914	20 $\bar{3}$			{32 470	023
st	9 143	9 155	11 $\bar{2}$	w	32 854	32 862	60 $\bar{5}$
w	11 041	11 049	40 $\bar{2}$	vw	33 108	33 117	204
w	11 369	11 372	31 $\bar{1}$	vw	33 380	33 370	11 $\bar{5}$
m	11 422	11 430	40 $\bar{1}$	vw	33 487	33 499	51 $\bar{5}$
st	11 751	11 761	00 $\bar{3}$	m	33 986	33 990	42 $\bar{3}$
st	12 059	12 066	31 $\bar{2}$	m	34 396	34 401	511
vst	13 272	{13 281	40 $\bar{3}$	w	34 740	34 731	313
		{13 292	310	m	35 148	35 135	420
st	13 444	13 457	11 $\bar{2}$	vw	35 653	35 657	40 $\bar{6}$
m	14 420	14 425	400	w	36 638	36 620	224
m	14 605	14 613	11 $\bar{3}$	w	37 747	37 743	20 $\bar{6}$
st	15 361	15 373	31 $\bar{3}$	st	38 536	38 531	71 $\bar{3}$
m	15 897	15 911	204	vw	38 850	38 836	424
vw	17 811	17 825	311	vw	39 097	39 091	403
vw	18 125	18 126	404	vw	40 156	{40 150	714
w	20 028	20 034	401			{40 216	601
st	20 696	20 710	020	w	40 764	{40 743	421
vw	21 043	21 066	113	w	40 996	{40 784	60 $\bar{6}$
w	21 282	21 294	314	w	40 996	40 976	31 $\bar{6}$
m	21 802	21 819	203	st	42 532	{42 496	51 $\bar{6}$
vw	22 004	22 017	021			{42 529	223
m	22 171	22 189	51 $\bar{2}$	vw	43 136	43 133	71 $\bar{1}$
vw	22 666	22 685	114	vw	43 690	{43 651	80 $\bar{3}$
w	23 334	23 346	51 $\bar{3}$			{43 698	512
w	23 471	23 472	22 $\bar{1}$	m	44 149	{44 124	115
vw	23 634	23 646	51 $\bar{1}$			{44 195	804
vw	24 312	24 316	220	vw	44 401	44 383	71 $\bar{5}$
vw	24 766	24 778	60 $\bar{2}$	w	45 503	{45 488	62 $\bar{2}$
vw	24 962	24 971	312	w	45 503	{45 569	62 $\bar{3}$
w	25 238	25 241	22 $\bar{2}$	w	45 742	45 721	80 $\bar{2}$
w	25 497	25 520	20 $\bar{5}$	w	46 273	{46 230	22 $\bar{5}$
vw	25 935	25 937	022			{46 295	42 $\bar{5}$
vw	27 114	27 116	514	m	46 717	46 669	11 $\bar{6}$
vw	27 285	27 311	601	vw	47 131	47 104	314
w	27 538	27 554	604	vw	47 374	47 352	80 $\bar{5}$

As pointed out by Furusetth and Kjekshus³ there are slight mistakes in the interatomic distances listed by Boller and Parthé.⁵ With the present lattice dimensions the shortest interatomic distances are (in Å):

Table 7. Guinier photograph data of TaSb₃ taken with strictly monochromatized CuK α_1 -radiation.

I_{obs}	$\sin^2\theta \times 10^5$		hkl	I_{obs}	$\sin^2\theta \times 10^5$		hkl
	obs	calc			obs	calc	
w	1 160	1 160	001	w	25 641	25 643	223
m	2 312	2 309	20 $\bar{1}$	w	26 054	26 051	315
vw	3 056	3 053	200	w	27 099	27 098	42 $\bar{2}$
vw	3 885	3 884	20 $\bar{2}$	w	27 417	{27 426	42 $\bar{1}$
w	5 228	5 229	110	vw		{27 473	600
vw	5 434	5 437	11 $\bar{1}$	w	27 596	27 594	114
vw	6 132	6 116	201	w	27 905	27 911	60 $\bar{5}$
vst	7 341	7 341	111	m	28 301	28 302	023
m	7 774	7 779	20 $\bar{3}$	w	29 087	29 089	42 $\bar{3}$
st	7 965	7 965	11 $\bar{2}$	w	29 464	{29 464	511
w	9 228	9 234	40 $\bar{2}$	w		{29 465	11 $\bar{5}$
w	9 567	9 562	40 $\bar{1}$	m	30 075	30 074	420
m	9 631	9 638	31 $\bar{1}$	vw	30 335	30 340	313
m	10 253	10 262	31 $\bar{2}$	vw	31 112	31 118	40 $\bar{6}$
m	10 436	10 438	003	vw	31 850	31 858	224
m	11 222	11 225	40 $\bar{3}$	m	32 310	32 308	71 $\bar{3}$
st	11 330	11 334	310	w	33 375	{33 383	20 $\bar{6}$
m	11 771	11 772	112	w		{33 400	424
m	12 204	12 210	400	vw	34 073	34 072	403
w	12 808	12 812	11 $\bar{3}$	vw	35 035	35 042	421
m	13 201	13 205	31 $\bar{3}$	vw	36 432	{36 421	024
w	13 997	13 994	204	vw		{36 433	803
vw	15 339	15 350	311	m	36 743	36 740	51 $\bar{6}$
vw	17 171	17 178	401	m	37 072	37 067	223
m	17 857	17 864	020	vw	37 722	37 703	512
w	18 446	18 468	314	vw	38 239	38 249	80 $\bar{2}$
w	18 663	18 664	51 $\bar{2}$	w	38 991	38 985	115
w	19 203	19 203	203	vw	39 771	39 759	80 $\bar{5}$
vw	19 704	19 704	51 $\bar{3}$	vw	40 019	40 031	42 $\bar{5}$
vw	19 972	{19 945	51 $\bar{1}$	vw	40 408	40 393	22 $\bar{5}$
vw		{19 979	114	vw	40 807	40 785	62 $\bar{1}$
vw	20 164	20 172	22 $\bar{1}$	vw	41 051	41 048	624
vw	20 681	20 689	60 $\bar{2}$	w	41 275	{41 272	116
w	21 676	21 685	31 $\bar{2}$	w		{41 315	314
vw	22 167	22 167	40 $\bar{5}$	w	41 864	41 860	710
vw	22 534	{22 503	022	w		{42 329	422
vw		{22 529	22 $\bar{5}$	vw	42 364	{42 385	80 $\bar{1}$
vw	23 187	23 184	604	vw		{42 388	407
vw	23 548	23 544	510	w	43 076	43 069	131
vw	24 002	23 978	514	w		{43 632	716
vw	24 443	24 465	402	w	43 655	{43 692	13 $\bar{2}$

Ta(As) — 4 Ta(As): 3.379
 — 4 Ta(As): 3.435
 — 2 As(Ta): 2.591
 — 4 As(Ta): 2.615

Table 8. Lattice constants of TaAs₂ and TaSb₂.

Phase	a (Å)	b (Å)	c (Å)	β (°)
TaAs ₂ ^a	9.3385	3.3851	7.7568	119.70
TaAs ₂ ^b	9.350 ± 0.002	3.388 ± 0.002	7.760 ± 0.002	119.75 ± 0.08
TaSb ₂ ^a	10.2218	3.6447	8.2915	120.39

^a This study. ^b Quoted from Saini *et al.*⁶

Four phases are known with the NbAs-type structure, *i.e.* NbAs,^{3,5,6} NbP,^{5,19} TaP,^{5,19} and TaAs.^{5,6}

The TaAs₂ and TaSb₂ phases. The phases TaAs₂ and TaSb₂ were easily achieved by heating mixtures of the elements. Guinier photographs (Tables 6 and 7) of the stoichiometric TaAs₂ and TaSb₂ samples were indexed monocrinally. The unit cell dimensions will be seen from Table 8, where also the values previously determined for TaAs₂ by Saini *et al.*⁶ are listed. Although the present values do not fall within the error limits given by them, the accordance is considered satisfactory.

On the basis of the observed densities 10.26 g cm⁻³ (TaAs₂) and 10.53 g cm⁻³ (TaSb₂) the unit cells contain 4 TaX₂-groups ($Z_c = 3.97$ for TaAs₂ and $Z_c = 3.98$ for TaSb₂). The calculated densities from the X-ray data are 10.33 g cm⁻³ (TaAs₂) and 10.58 g cm⁻³ (TaSb₂).

Guinier photographs of TaAs₂ and TaSb₂ in samples where these phases are in equilibrium with phases of higher and lower metal content, give no significant variation of the lattice constants. The ranges of homogeneity are thus rather narrow.

The systematic extinctions are of the type

$$hkl \text{ absent when } h + k = 2n + 1$$

Characteristic space groups are accordingly *C2*, *Cm*, and *C2/m*.

Obvious relationships in lattice dimensions and possible space groups indicated that the structure of both phases might be of the NbAs₂-type.^{1,4} To confirm this suggestion, a set of calculated structure factors (based on the parameter values (rounded off) from NbAs₂ and NbSb₂) were compared with those observed. All possible reflections in the Guinier photographs were included in the calculation. The obtained agreements were surprisingly good and the proposed NbAs₂-type structure must be considered proved.

In terms of space group *C2* all atoms are in

$$(c) \ x, y, z; \bar{x}, y, \bar{z}; \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$$

with:

$$\begin{array}{l} \text{TaAs}_2: \quad x_{\text{Ta}} = 0.34, \quad y_{\text{Ta}} = \frac{1}{2}, \quad z_{\text{Ta}} = 0.30 \\ \quad \quad x_{\text{AsI}} = 0.09, \quad y_{\text{AsI}} = 0.49, \quad z_{\text{AsI}} = 0.39 \\ \quad \quad x_{\text{AsII}} = 0.14, \quad y_{\text{AsII}} = 0.07, \quad z_{\text{AsII}} = 0.03 \end{array}$$

$$\begin{aligned} \text{TaSb}_2: \quad x_{\text{Ta}} &= 0.34, \quad y_{\text{Ta}} = \frac{1}{2}, \quad z_{\text{Ta}} = 0.30 \\ x_{\text{SbI}} &= 0.10, \quad y_{\text{SbI}} = 0.5, \quad z_{\text{SbI}} = 0.39 \\ x_{\text{SbII}} &= 0.14, \quad y_{\text{SbII}} = 0.0, \quad z_{\text{SbII}} = 0.03 \end{aligned}$$

The parameter values are considered to be quite good.

The interatomic distances are listed in Table 9. For a detailed description of the NbAs_2 -type structure reference is made to Furuseth and Kjekshus.⁴ Six phases are known at present with the NbAs_2 -type structure, *i.e.* NbAs_2 ,^{1,4} NbSb_2 ,^{1,4} TaAs_2 , TaSb_2 , MoAs_2 ,²⁰ and WAs_2 .²¹

Table 9. Interatomic distances in TaAs_2 and TaSb_2 (Å).

TaAs_2 :	Ta	— 3 Ta	: 3.06; 3.385 (2)
		— 5 As_I	: 2.66; 2.70; 2.72; 2.75; 2.76
		— 3 As_II	: 2.47; 2.67; 2.78
As_I		— 5 Ta	: 2.66; 2.70; 2.72; 2.75; 2.76
		— 5 As_I	: 2.93; 3.11 (2); 3.385 (2)
		— 6 As_II	: 3.21; 3.37; 3.49; 3.63; 3.73; 3.93
As_II		— 3 Ta	: 2.47; 2.67; 2.78
		— 6 As_I	: 3.21; 3.37; 3.49; 3.63; 3.73; 3.93
		— 5 As_II	: 2.42; 2.87 (2); 3.385 (2)
TaSb_2 :	Ta	— 3 Ta	: 3.28; 3.645 (2)
		— 5 Sb_I	: 2.90; 2.95 (2); 2.99 (2)
		— 3 Sb_II	: 2.81 (2); 2.85
Sb_I		— 5 Ta	: 2.90; 2.95 (2); 2.99 (2)
		— 5 Sb_I	: 3.22 (2); 3.36; 3.645 (2)
		— 6 Sb_II	: 3.58 (2); 3.69 (2); 4.10; 4.15
Sb_II		— 3 Ta	: 2.81 (2); 2.85
		— 6 Sb_I	: 3.58 (2); 3.69 (2); 4.10; 4.15
		— 5 Sb_II	: 2.65; 3.12 (2); 3.645 (2)

Magnetic properties. The magnetic susceptibilities of Ta_5Sb_4 , TaAs , TaAs_2 , and TaSb_2 were measured at temperatures between 90 and 725°K. (The Ta_3Sb

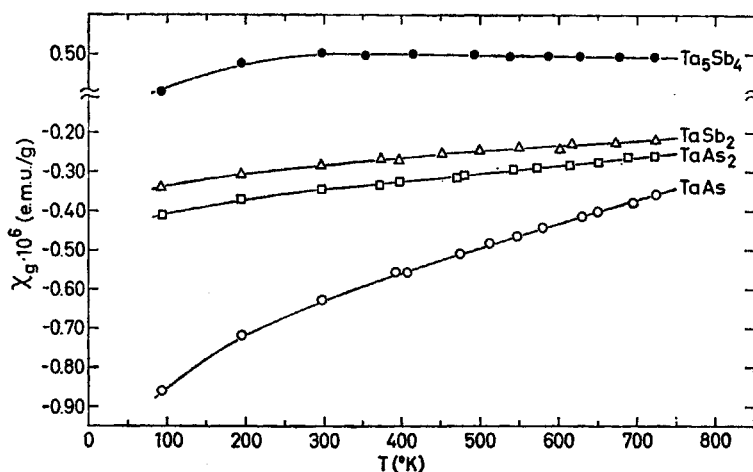


Fig. 1. The magnetic susceptibilities of TaAs , TaAs_2 , Ta_5Sb_4 , and TaSb_2 , as a function of temperature.

phase was considered too impure to be included among the results of magnetic susceptibility measurements in this communication.) The results, *cf.* Fig. 1, show either diamagnetic or weak almost temperature independent susceptibilities.

The expected diamagnetism resulting from the atomic cores in the three diamagnetic substances TaAs, TaAs₂, and TaSb₂ is of the same size as observed. The core contributions are -0.31×10^{-6} , -0.43×10^{-6} , and -0.48×10^{-6} e.m.u. per gram TaAs, TaAs₂, and TaSb₂, respectively. (These values were calculated from the diamagnetic corrections -14×10^{-6} e.m.u. per mole Ta⁵⁺ according to Klemm²² and -64.6×10^{-6} e.m.u. per mole As³⁻ and -94.4×10^{-6} e.m.u. per mole Sb³⁻ according to Angus.²³) By subtracting these values from the susceptibilities measured the total susceptibilities of localized, non-bonding electrons, valence electrons and conduction electrons are obtained. The measurements show that no unpaired *d*-electrons are present on the tantalum atoms, and suggest a covalent type of bonding in TaAs, TaAs₂, and TaSb₂.

The core contribution is -0.32×10^{-6} e.m.u. per gram Ta₅Sb₄. Ta₅Sb₄ is expected to have a metallic type of bonding and the observed paramagnetism should consequently be associated with the paramagnetism of the spin of the conduction electrons.

When it is added that magnetic measurements carried out on the impure Ta₃Sb sample indicate weak temperature independent paramagnetism, the almost complete identity in magnetic properties between corresponding niobium and tantalum arsenide and antimonide phases becomes evident.

DISCUSSION

A discussion of the bonding in the metallic like phases Ta₃Sb and Ta₅Sb₄ must await further experimental data.

The bonding in TaAs, TaAs₂, and TaSb₂ is conveniently discussed in terms of the general (8-N) rule:²⁴⁻²⁷

$$(n_v + b_a - b_c)/n_a = 8$$

where per formula unit n_v is the number of valence electrons, n_a the number of anions, b_a the number of valence electrons involved in anion-anion bond formation, and b_c is the number of valence electrons involved in cation-cation bond formation (together with any unshared electrons on the cations). (This rule is a mathematical formulation of the need for all the anions in a crystal to possess a complete octet.²⁷)

In the crystal structure of TaAs (similar for the isostructural phases NbAs, NbP, and TaP) there are no short As-As or Ta-Ta distances which can be associated with anion-anion or cation-cation bonds. According to its structure TaAs is therefore a normal valence compound. Furthermore, TaAs is diamagnetic (the same is found for NbAs²) and each tantalum atom must consequently contribute 5, 3, or 1 electron to n_v . Each arsenic atom provides 5 electrons. In order to comply with the rule three of the outer electrons from the tantalum atoms must therefore participate in the chemical bonding leaving an inert electron pair on each tantalum atom. Data for the electrical

Table 10. Application of the general (8-N) rule on some MX_2 -phases.

Phase	Structure type	n_c/n_a	b_a/n_a	b_c/n_a	Anion substructure	Reference
TlSb ₂ , HfAs ₂ ZrAs ₂ , ThSb ₂	CuAl ₂	7	1	$-\frac{1}{2}$	X-X pairs X-X pairs between I-I	Pearson ²⁸ Trzebiatowski <i>et al.</i> ²⁹ Jeitschko and Nowotny ³⁰ Pearson ²⁸
	PbCl ₂	7	$\frac{1}{2}$	-1		
	Cu ₂ Sb	7				
VSb ₂ , NbAs ₂ , NbSb ₂ , TaAs ₂ , TaSb ₂	CuAl ₂	$7\frac{1}{2}$	1	$\frac{1}{2}$	X-X pairs X-X pairs between II-II	Pearson ²⁸ Furuseth and Kjekshus ⁴
	NbAs ₂	$7\frac{1}{2}$	$\frac{1}{2}$			
CrSb ₂ , MoP ₂ , WP ₂ MoAs ₂ , WAs ₂ UP ₂ , UAs ₂ , USb ₂ , UBi ₂	Marcasite	8	1	1	X-X pairs X-X pairs between I-II X-X pairs between II-II	Pearson ²⁸ Rundqvist and Lundström ³¹ Jensen and Kjekshus ²⁰ Skansen and Kjekshus ²¹ Pearson ²⁸
	MoP ₂	8	1	1		
	NbAs ₂	8	$\frac{1}{2}$	$\frac{1}{2}$		
	Cu ₂ Sb	8		$\frac{1}{2}$		

conductivities or optical properties of these substances are needed before this suggestion can be fully accepted.

The general (8-N) rule has previously been applied to pnictogen phases with composition MX_2 , M being a transition metal from subgroup IV, V, or VI.⁴ Table 10 (which is quoted from Furusetth and Kjekshus⁴ with some additions) shows the partition of n_c/n_a (based on valences corresponding to the group numbers) b_a/n_a (according to the crystal structures) and b_c/n_a (assuming the general (8-N) rule satisfied) for the considered compounds.

The new phases included in Table 10 are $TaAs_2$, $TaSb_2$, $MoAs_2$, and WAs_2 , with the $NbAs_2$ -type structure. The rule appears to be fulfilled as far as $TaAs_2$ and $TaSb_2$ are concerned, whose $b_c/n_a = 0$ is consistent with the diamagnetism observed. For $MoAs_2$ and WAs_2 , however, the calculated $b_c/n_a = \frac{1}{2}$ suggests that one electron should be localized on each metal atom. This is in disagreement with the observed diamagnetism for $MoAs_2$ ²⁰ and WAs_2 .²¹ We are awaiting the gathering of more data on these substances before any conclusions can be drawn.

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