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, $a = 3.4348$ Å, $c = 11.641$ Å, density $= 12.25$ g cm^{-3}.
2. TaAs$_2$, with NbAs$_2$-type structure, $a = 9.3385$ Å, $b = 3.3851$ Å, $c = 7.7568$ Å, $\beta = 119.70°$, density $= 10.26$ g cm^{-3}.
3. Ta$_3$Sb, with βW-type structure, $a = 5.2646$ Å.
4. Ta$_5$Sb$_4$, with Ti$_5$Te$_4$-type structure, $a = 10.248$ Å, $c = 3.5460$ Å, density $= 12.22$ g cm^{-3}.
5. TaSb$_2$, with NbAs$_2$-type structure, $a = 10.2218$ Å, $b = 3.6447$ Å, $c = 8.2915$ Å, $\beta = 120.39°$, density $= 10.53$ g cm^{-3}.

The TaAs, TaAs$_2$, and TaSb$_2$ phases have diamagnetic susceptibilities, whereas the Ta$_5$Sb$_4$ 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 Parthé [5] and Saini *et al.*[6], where phases with composition TaAs and TaAs$_2$ have been described. The older literature [7] claims the existence of a phase with composition TaAs$_{1.4}$. Ta$_3$Sb is the only phase previously reported [8] 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, Ta_3Sb, and Ta_5Sb_4 were also prepared by thermal decomposition of $TaAs_2$ and $TaSb_2$, 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 $CuK\alpha_1$-radiation. For the calculation of lattice constants potassium chloride (Analar, The British Drug Houses Ltd., $a = 6.2919$ Å [9]) was added to the specimen as an internal standard. Lattice constants are expressed in Ångström units on the basis of $\lambda(CuK\alpha_1) = 1.54050$ Å.

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 ($H_{max} = 4015$, 4700, and 5110 Ø). 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 $TaAs_2$, previously described,[5,6] were found. In the tantalum-antimony system the existence of two new, intermediate phases was ascertained, *i.e.* the Ta_5Sb_4 phase and the $TaSb_2$ phase. Furthermore, the existence of the Ta_3Sb phase (known from the earlier study of Nevitt [8]) was confirmed.

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

The Ta_3Sb 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 Ta_3Sb phase, described by Nevitt.[8]

The purest samples of the Ta_3Sb phase were obtained by thermal decomposition of the $TaSb_2$ phase at 1150°C. After degradation the residuum was found to contain Ta_3Sb 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 Ta_3Sb phase (the purest sample judging from the Guinier photograph (Table 1)) is $a = 5.2646$ Å in close agreement with the value $a = 5.2595 \pm 0.0010$ Å reported by Nevitt.[8] According to the approximately constant a-axis for samples of different composition, the homogeneity range of the Ta_3Sb 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 Ta_3Sb-groups per unit cell. This discrepancy is readily explained by the contamination of the sample and gives no reason to reject the stoichiometric formula Ta_3Sb.

According to Nevitt [8] Ta_3Sb should be listed among substances having βW-type structure. A comparison of observed and calculated intensities of the

Table 1. Guinier photograph data of Ta_3Sb taken with strictly monochromatized $CuK\alpha_1$-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 Ta_3Sb are (in Å):

$$\text{Ta} \begin{array}{l} - \ 10 \ \text{Ta:} \ 2.632 \ (2); \ 3.224(8) \\ - \ \ 4 \ \text{Sb:} \ 2.943 \end{array}$$

$$\text{Sb} \begin{array}{l} - \ 12 \ \text{Ta:} \ 2.943 \\ - \ \ 8 \ \text{Sb:} \ 4.559 \end{array}$$

The shortest Ta—Ta distance is some 8 % shorter than in metallic tantalum (2.863 Å [11]). Similar short metal-metal distances observed in all phases with βW-type structure, are one of the most interesting features of this class of phases (see the discussion by Geller [12] and Pauling; [13] see also Nevitt [8]).

The Ta_5Sb_4 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 Ta_5Sb_4 taken with strictly monochromatized $CuK\alpha_1$-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
m	18 867	18 840	431	w	33 573	33 560	512
			501	st	34 670	34 656	721
		18 873	002	vw	36 134	36 152	800
w	19 193	19 206	530	vw	36 979	36 949	442
vw	20 010	20 003	112				

Table 3. Interatomic distances in Ta_5Sb_4 (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 $TaSb_2$ phase at 1000°C confirmed this composition and the phase was accordingly designated Ta_5Sb_4. Density measurements and structure determination proved the composition.

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

$a = 10.248$ Å, $c = 3.5460$ Å, $c/a = 0.3460$

The lattice constants of the stoichiometric Ta_5Sb_4 sample vary only slightly from the lattice constants of Ta_5Sb_4 in samples where the Ta_5Sb_4 phase is in equilibrium with the Ta_3Sb and $TaSb_2$ phases. This indicates that the homogeneity range of the Ta_5Sb_4 phase is rather narrow.

According to the pycnometric density 12.25 g cm^{-3} the unit cell contains 2 ($Z_c = 1.97$) Ta_5Sb_4-groups. The calculated density from the X-ray data is 12.41 g cm^{-3}.

The tetragonal structure of a phase Ti_5Te_4 has been described by Grønvold et al.[14] As it has been shown[1,2] that the compounds Nb_5Sb_4 and Ti_5Te_4 are isostructural, and as the Guinier photograph of Ta_5Sb_4 resembles that of Nb_5Sb_4 both with regard to line pattern and intensities, the possibility of Ta_5Sb_4 also being isostructural with Ti_5Te_4 was investigated.

In terms of the space group $I4/m$ the atomic arrangement in Ti_5Te_4 is as follows (the parameters have been rounded off):

2 Ti_I in (a) 0,0,0; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
8 Ti_{II} in (h) $\pm(x,y,0; \frac{1}{2}+x,\frac{1}{2}+y,\frac{1}{2}; \bar{y},x,0; \frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2})$
with $x_1 = 0.31$ and $y_1 = 0.38$
8 Te in (h) with $x_2 = 0.06$ and $y_2 = 0.28$

Table 4. Guinier photograph data of TaAs taken with strictly monochromatized $CuK\alpha_1$-radiation.

I_{obs}	$\sin^2\Theta \times 10^5$		hkl	I_{obs}	$\sin^2\Theta \times 10^5$		hkl
	obs	calc			obs	calc	
m	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$_6$	3.39$_1$	Boller and Parthé [5]
3.436 ± 0.002	11.644 ± 0.005	3.389	Saini *et al.* [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 Parthé [5] 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 Parthé [5] and Furuseth and Kjekshus.[3] In terms of space group $I4_1md$ 4 Ta and 4 As are in (*a*):

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

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 TaAs$_2$ taken with strictly monochromatized Cu$K\alpha_1$-radiation.

I_{obs}	sin²Θ × 10⁵ obs	sin²Θ × 10⁵ calc	hkl	I_{obs}	sin²Θ × 10⁵ obs	sin²Θ × 10⁵ calc	hkl
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	402
m	4 525	4 532	$20\bar{2}$	w	29 619	29 624	$22\bar{3}$
vw	5 220	5 227	002	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	003	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	112	vw	35 653	35 657	$40\bar{6}$
m	14 420	14 425	400	w	36 638	36 620	$22\bar{4}$
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	$20\bar{4}$	vw	38 850	38 836	$42\bar{4}$
vw	17 811	17 825	311	vw	39 097	39 091	403
vw	18 125	18 126	$40\bar{4}$	vw	40 156	40 150	$71\bar{4}$
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			40 784	$60\bar{6}$
w	21 282	21 294	$31\bar{4}$	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	$02\bar{1}$			42 529	223
m	22 171	22 189	$51\bar{2}$	vw	43 136	43 133	$71\bar{1}$
vw	22 666	22 685	$11\bar{4}$	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	$80\bar{4}$
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			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	$51\bar{4}$	m	46 717	46 669	$11\bar{6}$
vw	27 285	27 311	$60\bar{1}$	vw	47 131	47 104	314
w	27 538	27 554	$60\bar{4}$	vw	47 374	47 352	$80\bar{5}$

As pointed out by Furuseth and Kjekshus[3] 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 TaSb$_2$ taken with strictly monochromatized Cu$K\alpha_1$-radiation.

I_{obs}	sin²Θ × 10⁵ obs	sin²Θ × 10⁵ calc	hkl	I_{obs}	sin²Θ × 10⁵ obs	sin²Θ × 10⁵ calc	hkl
w	1 160	1 160	001	w	25 641	25 643	22$\bar{3}$
m	2 312	2 309	20$\bar{1}$	w	26 054	26 051	31$\bar{5}$
vw	3 056	3 053	200	w	27 099	27 098	42$\bar{2}$
vw	3 885	3 884	20$\bar{2}$	vw	27 417	27 426 / 27 473	42$\bar{1}$ / 600
w	5 228	5 229	110	w	27 596	27 594	11$\bar{4}$
vw	5 434	5 437	11$\bar{1}$	w	27 905	27 911	60$\bar{5}$
vw	6 132	6 116	201	m	28 301	28 302	023
vst	7 341	7 341	111	w	29 087	29 089	42$\bar{3}$
m	7 774	7 779	20$\bar{3}$	w	29 464	29 464 / 29 465	511 / 11$\bar{5}$
st	7 965	7 965	11$\bar{2}$	m	30 075	30 074	420
w	9 228	9 234	40$\bar{2}$	vw	30 335	30 340	313
w	9 567	9 562	40$\bar{1}$	vw	31 112	31 118	40$\bar{6}$
m	9 631	9 638	31$\bar{1}$	vw	31 850	31 858	22$\bar{4}$
m	10 253	10 262	31$\bar{2}$	m	32 310	32 308	71$\bar{3}$
m	10 436	10 438	003	w	33 375	33 383 / 33 400	20$\bar{6}$ / 42$\bar{4}$
m	11 222	11 225	40$\bar{3}$	vw	34 073	34 072	403
st	11 330	11 334	310	vw	35 035	35 042	421
m	11 771	11 772	112	vw	36 432	36 421 / 36 433	024 / 80$\bar{3}$
m	12 204	12 210	400	m	36 743	36 740	51$\bar{6}$
w	12 808	12 812	11$\bar{3}$	m	37 072	37 067	223
m	13 201	13 205	31$\bar{3}$	vw	37 722	37 703	512
w	13 997	13 994	20$\bar{4}$	vw	38 239	38 249	80$\bar{2}$
vw	15 339	15 350	311	w	38 991	38 985	115
vw	17 171	17 178	401	vw	39 771	39 759	80$\bar{5}$
m	17 857	17 864	020	vw	40 019	40 031	425
w	18 446	18 468	31$\bar{4}$	vw	40 408	40 393	22$\bar{5}$
w	18 663	18 664	51$\bar{2}$	vw	40 807	40 785	62$\bar{1}$
w	19 203	19 203	203	vw	41 051	41 048	62$\bar{4}$
vw	19 704	19 704	51$\bar{3}$	w	41 275	41 272 / 41 315	11$\bar{6}$ / 314
vw	19 972	19 945 / 19 979	51$\bar{1}$ / 11$\bar{4}$	w	41 864	41 860	710
vw	20 164	20 172	22$\bar{1}$	vw	42 364	42 329 / 42 385 / 42 388	422 / 80$\bar{1}$ / 40$\bar{7}$
vw	20 681	20 689	60$\bar{2}$	w	43 076	43 069	131
w	21 676	21 685	312	w	43 655	43 632 / 43 692	71$\bar{6}$ / 13$\bar{2}$
vw	22 167	22 167	40$\bar{5}$				
vw	22 534	22 503 / 22 529	022 / 22$\bar{5}$				
vw	23 187	23 184	60$\bar{4}$				
vw	23 548	23 544	510				
vw	24 002	23 978	51$\bar{4}$				
vw	24 443	24 465	402				

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 $TaAs_2$ and $TaSb_2$.

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 $TaAs_2$ and $TaSb_2$ phases. The phases $TaAs_2$ and $TaSb_2$ were easily achieved by heating mixtures of the elements. Guinier photographs (Tables 6 and 7) of the stoichiometric $TaAs_2$ and $TaSb_2$ samples were indexed mono-clinically. The unit cell dimensions will be seen from Table 8, where also the values previously determined for $TaAs_2$ 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} ($TaAs_2$) and 10.53 g cm^{-3} ($TaSb_2$) the unit cells contain 4 TaX_2-groups ($Z_c = 3.97$ for $TaAs_2$ and $Z_c = 3.98$ for $TaSb_2$). The calculated densities from the X-ray data are 10.33 g cm^{-3} ($TaAs_2$) and 10.58 g cm^{-3} ($TaSb_2$).

Guinier photographs of $TaAs_2$ and $TaSb_2$ 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 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 $NbAs_2$-type.[1,4] To confirm this suggestion, a set of calculated structure factors (based on the parameter values (rounded off) from $NbAs_2$ and $NbSb_2$) 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 $NbAs_2$-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:

$TaAs_2$: $\quad x_{Ta} = 0.34, \; y_{Ta} = \frac{1}{2}, \quad z_{Ta} = 0.30$
$\qquad\qquad x_{AsI} = 0.09, \; y_{AsI} = 0.49, \; z_{AsI} = 0.39$
$\qquad\qquad x_{AsII} = 0.14, \; y_{AsII} = 0.07, \; z_{AsII} = 0.03$

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

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$_5$Sb$_4$, TaAs, TaAs$_2$, and TaSb$_2$ were measured at temperatures between 90 and 725°K. (The Ta$_3$Sb
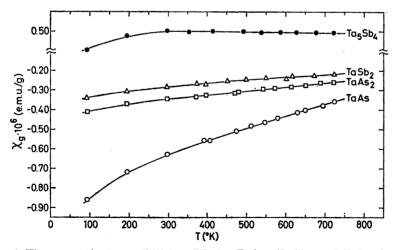

Fig. 1. The magnetic susceptibilities of TaAs, TaAs$_2$, Ta$_5$Sb$_4$, and TaSb$_2$ as a function of temperature.

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, $TaAs_2$, and $TaSb_2$ 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, $TaAs_2$, and $TaSb_2$, respectively. (These values were calculated from the diamagnetic corrections -14×10^{-6} e.m.u. per mole Ta^{5+} according to Klemm [22] and -64.6×10^{-6} e.m.u. per mole As^{3-} and -94.4×10^{-6} e.m.u. per mole Sb^{3-} 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, $TaAs_2$, and $TaSb_2$.

The core contribution is -0.32×10^{-6} e.m.u. per gram Ta_5Sb_4. Ta_5Sb_4 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 Ta_3Sb 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 Ta_3Sb and Ta_5Sb_4 must await further experimental data.

The bonding in TaAs, $TaAs_2$, and $TaSb_2$ is conveniently discussed in terms of the general (8—N) rule:[24-27]

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

where per formula unit n_e 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 NbAs [2]) and each tantalum atom must consequently contribute 5, 3, or 1 electron to n_e. 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_e/n_a	b_a/n_a	b_c/n_a	Anion substructure	Reference
TiSb₂, ZrAs₂, HfAs₂	CuAl₂ PbCl₂	7 7	1 1½	$-\frac{1}{2}$	X–X pairs X–X pairs	Pearson[28] Trzebiatowski et al.[29]
ThAs₂, ThSb₂	Cu₂Sb	7		-1	between I–I	Jeitschko and Nowotny[30] Pearson[28]
VSb₂ NbAs₂, NbSb₂, TaAs₂, TaSb₂	CuAl₂ NbAs₂	7½ 7½	1 1½	$\frac{1}{2}$	X–X pairs X–X pairs between II–II	Pearson[28] Furuseth and Kjekshus[4]
CrSb₂, MoP₂, WP₂	Marcasite MoP₂	8 8	1 1	1 1	X–X pairs X–X pairs between I–II	Pearson[28] Rundqvist and Lundström[31]
MoAs₂, WAs₂	NbAs₂	8	½	½	X–X pairs between II–II	Jensen and Kjekshus[20] Skansen and Kjekshus[21]
UP₂, UAs₂, USb₂, UBi₂	Cu₂Sb	8				Pearson[28]

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 pnigogen phases with composition MX_2, M being a transition metal from subgroup IV, V, or VI.[4] Table 10 (which is quoted from Furuseth and Kjekshus [4] with some additions) shows the partition of n_e/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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