The Systems Molybdenum-Arsenic, Tungsten-Arsenic, Molybdenum-Antimony, Tungsten-Antimony, Niobium-Bismuth, Tantalum-Bismuth, Molybdenum-Bismuth, and Tungsten-Bismuth

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The phase relationships in the systems $Mo-As$, $W-As$, $Mo-Sb$, $W-Sb$, $Nb-Bi$, $Ta-Bi$, $Mo-Bi$, and $W-Bi$ have been studied by means of X-ray diffraction, density, thermal decomposition, and magnetic susceptibility measurements. The structure type, lattice dimensions, and observed densities of the only intermediate phases are:

Mo_5As_4; Ti_5Te_4 type; $a = 9.6005 \pm 0.0006$ Å, $c = 3.2781 \pm 0.0004$ Å; $d_{pycn} = 8.48$ g cm^{-3}.

Mo_2As_3; Mo_2As_3 type; $a = 16.061 \pm 0.002$ Å, $b = 3.2349 \pm 0.0004$ Å, $c = 9.643 \pm 0.001$ Å, $\beta = 136.74 \pm 0.02°$; $d_{pycn} = 8.07$ g cm^{-3}.

$MoAs_2$; $NbAs_2$ type; $a = 9.071 \pm 0.002$ Å, $b = 3.2994 \pm 0.0009$ Å, $c = 7.719 \pm 0.002$ Å, $\beta = 119.37 \pm 0.02°$; $d_{pycn} = 8.07$ g cm^{-3}.

W_2As_3; Mo_2As_3 type; $a = 15.966 \pm 0.001$ Å, $b = 3.2791 \pm 0.0004$ Å, $c = 9.599 \pm 0.001$ Å, $\beta = 136.648 \pm 0.006°$; $d_{pycn} = 11.32$ g cm^{-3}.

WAs_2; $NbAs_2$ type; $a = 9.078 \pm 0.002$ Å, $b = 3.3177 \pm 0.0006$ Å, $c = 7.686 \pm 0.001$ Å, $\beta = 119.42 \pm 0.02°$; $d_{pycn} = 10.89$ g cm^{-3}.

Mo_3Sb_7; Ir_3Ge_7 type; $a = 9.5713 \pm 0.0008$ Å, $d_{pycn} = 8.55$ g cm^{-3}.

The Mo_2As_3, $MoAs_2$, W_2As_3, and WAs_2 phases have diamagnetic susceptibilities, the Mo_3Sb_7 phase is paramagnetic, whereas the Mo_5As_4 phase changes its susceptibility from diamagnetic to paramagnetic at about 250°K. No intermediate phases have been found in the systems $W-Sb$, $Nb-Bi$, $Ta-Bi$, $Mo-Bi$, and $W-Bi$. There was no indication of a range of homogeneity for any of the phases.

In the course of continued studies of the transition metal chalcogenides and pnictides at this Institute, an investigation of the systems $Mo-As$, $W-As$, $Mo-Sb$, $W-Sb$, $Nb-Bi$, $Ta-Bi$, $Mo-Bi$, and $W-Bi$ has been carried out. Jensen and Kjekshus [1] have previously reported confirmation

of the $NbAs_2$ type crystal structure for the phase $MoAs_2$ (and the occurrence of phases with approximate compositions $MoAs_{0.8}$ and $MoAs_{1.4}$). The existence of the isostructural phase WAs_2 is mentioned in a paper by Furuseth et al.[2] Jensen et al.[3] have recently given a brief description of the crystal structures of the isostructural phases Mo_2As_3 and W_2As_3. The present paper concerns the phase relationships in the systems just referred to, whereas a more detailed discussion of the structural properties will be published elsewhere.

When this investigation was started, the only intermediate phases of these systems described in the literature [4,5] were MoAs, $MoAs_2$, WAs, and WAs_2. About one year later, when most of the results reported in this paper had been collected, two articles by Hulliger [6] and Boller and Nowotny [7] describing independent examinations of the systems Mo—As, W—As, Mo—Sb, and W—Sb came to hand. Hulligers paper is concerned only with the phases $MoAs_2$ and WAs_2, which are stated to have the $NbAs_2$ type structure and to show metallic conductivity. The intermediate phases noticed by Boller and Nowotny were Mo_5As_4, MoAs, $\sim MoAs_{1.04}$, $\sim Mo_4As_5$, $MoAs_2$, W_2As, $\sim W_4As_5$, and WAs_2. As some of Boller and Nowotny's results showed obvious disagreement with the findings of our study, a series of new experiments was carried out to confirm our data.

When these experiments were completed and the manuscript draft rewritten, a brief description of the crystal structures of $MoAs_2$, $Mo_{0.4}As_2$, and Mo_3Sb_7 was given by Brown [8] and at this time, one of the present authors (A.K.) was asked to referee the paper by Taylor et al.[9] which has now appeared in Can. J. Chem. These papers deal with the systems Mo—As, W—As, and Mo—Sb and give occasion for a further partial rewriting. Taylor et al. give an account of the crystallographic properties of the phases Mo_5As_4, Mo_2As_3, $MoAs_2$, W_2As_3, and WAs_2 which they find to be the only intermediate phases in the two systems. We concur with Taylor et al. regarding the phase relationships of these systems, and although the essence of the two studies is the same, the present treatment is justified because of the fact that independent methods are used in the phase analyses. The additional information thus obtained by us amplifies and completes the data presented by Taylor et al. and by comment and comparison it is hoped to make a useful contribution to the understanding of the chemistry of these systems.

EXPERIMENTAL

Materials. The molybdenum and tungsten metals used in this study were obtained from L. Light & Co., Ltd. Spectrographic analyses showed presence of the following impurities (in ppm): Na(3), Mg(30), Al($<$ 10), Si(100), K(1), Ca(10), Cr($<$ 1), Mn(1), Fe(30), Ni(10), Cu(1), Sb($<$ 1), and Pb($<$ 1) for the molybdenum, and B($<$ 10), Na(3), Mg(30), Al($<$ 10), Si(300), K(3), Ca(10), Cr(3), Mn(1), Fe($<$ 10), Ni(1), Cu(1), Sn(1), Sb(1), and Pb($<$ 1) for the tungsten. The niobium and tantalum metals were from Johnson, Matthey & Co., Ltd.; with reported impurities (in ppm): Mg(2), Si(100), Mn(1), Fe(500), Ta(100), and Pb(80) for the niobium, and Mg(1), Al(20), Si(100), Cr(20), Mn(5), Fe(300), Nb($<$ 200), and Sn(20) for the tantalum. The arsenic and antimony from Johnson, Matthey & Co., Ltd. contained (in ppm): Na(3), Mg($<$ 1), Si(2), Cu($<$ 1), and Ag($<$ 1) for the arsenic, and Mg($<$ 1), Si($<$ 1), Cu($<$ 1), and Ag($<$ 1) for the antimony. The bismuth from American Smelting and Refining Co. carried the analysis (in ppm): Fe(1), Cu(2), Ag(1), and Pb(1).

Preparation. Samples were prepared by heating weighed quantities of metal and pnigogen in evacuated and sealed silica tubes. In some cases crucibles of pure alumina were placed inside the silica tubes.

Samples with composition 20.00, 25.00, 33.33, 37.50, 40.00, 41.18, 42.86, 43.82, 44.44, 45.05, 45.95, 47.37, 50.00, 52.38, 54.55, 56.00, 56.52, 57.14, 58.33, 59.18, 59.51, 60.00, 60.47, 60.78, 61.54, 62.96, 64.29, 66.10, 66.67, 67.21, 67.74, 68.75, 75.00, and 80.00 atomic % As were made in the Mo−As system. All samples were first heated at 950°C for 5 days and quenched in ice water. After crushing, portions of these samples were reannealed at 650, 800, and 1100°C for periods of 14 days and finally quenched in ice water. A series of samples was slowly cooled from 800°C to room temperature over a period of 20 days.

Samples with composition 20.00, 25.00, 33.33, 37.50, 40.00, 44.44, 47.37, 50.00, 52.38, 54.55, 56.00, 56.52, 57.14, 58.33, 59.18, 59.51, 60.00, 60.47, 60.78, 61.54, 62.50, 62.96, 64.29, 64.66, 66.67, 67.74, 68.75, 71.43, 75.00, and 80.00 atomic % As were made in the W−As system. These samples were subjected to the same heat treatment as that already described for the molybdenum arsenide samples.

Samples with composition 33.33, 50.00, 60.00, 66.67, 67.74, 68.75, 69.70, 70.00, 70.15, 70.24, 70.58, 71.43, 72.73, 75.00, and 80.00 atomic % Sb were made in the Mo−Sb system and samples with 33.33, 50.00, 60.00, 66.67, 70.00, 75.00, and 80.00 atomic % Sb were made in the W−Sb system. All samples were first heated at 650°C for 5 days and quenched in ice water. The samples were afterwards crushed and reannealed at 850°C for 14 days and finally quenched in ice water. Portions of the samples with 50.00, 66.67, 70.00, and 75.00 atomic % Sb were also slowly cooled from 850°C to room temperature over a period of 14 days.

In the Nb−Bi, Ta−Bi, Mo−Bi, and W−Bi systems, samples with 33.33, 50.00, 60.00, 66.67, and 75.00 atomic % Bi were heated for 20 days at 800°C and quenched in ice water. The alloys were afterwards reheated to 800°C and then slowly cooled to room temperature over a period of a further 20 days.

Samples containing 25.00, 33.33, 40.00, and 50.00 atomic % pnigogen (from all of the eight alloy systems included in this study) were heated in a carbon resistance (Nernst-Tammann) furnace at approximately 1400°C. When the furnace reached the desired temperature, as measured with an optical pyrometer, the sample was removed and quenched in water. Samples with the same initial compositions were also prepared in an electric arc furnace by melting weighed amounts of the mixed and compacted components. A protecting atmosphere of argon gas was present in the furnace during the melting process.

Samples of Mo_5As_4, Mo_2As_3, and W_2As_3 were also synthesized by thermal decomposition of $MoAs_2$ and WAs_2, respectively.

Single crystals of Mo_5As_4, Mo_2As_3, $MoAs_2$, W_2As_3, WAs_2, and Mo_3Sb_7 were prepared by chemical transport reactions.

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. Potassium chloride (Analar, The Britisch Drug Houses Ltd. $a = 6.2919$ Å [10]) was added to the specimen as an internal standard. Lattice dimensions, which are expressed in Ångström units on the basis of λ ($CuK\alpha_1$) = 1.54050 Å, were refined by applying the method of least squares to the Guinier photographic data.

X-Ray photographs were also taken with a Weissenberg camera of 57.3 mm diameter using $CuK\alpha$-radiation.

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 with kerosene under vacuum. 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 silica tubes of 3 mm internal diameter to a height of about 85 mm.

Table 1. Structural data and densities of the inter-
W—As, and

Phase	Structure type	Space group	Cell	a (Å)	b (Å)	c (Å)
Mo_5As_4	Ti_5Te_4	$I4/m$		9.60_0		3.27_8
	Ti_5Te_4	$I4/m$		9.595 ± 0.001		3.284 ± 0.002
	Ti_5Te_4	$I4/m$		9.6005 ± 0.0006		3.2781 ± 0.0004
$MoAs$	MnP	$Pnma$		5.98_9 Not confirmed	3.36_8	6.41_7
Mo_2As_3		$(C*/*)$	C	13.339 ± 0.002	3.240 ± 0.002	9.628 ± 0.002
			N	16.051 ± 0.002	3.240 ± 0.002	9.628 ± 0.002
	Mo_2As_3	$C2/m$	N	16.061 ± 0.002	3.2349 ± 0.0004	9.643 ± 0.001
			C	13.331 ± 0.002	3.2349 ± 0.0004	9.643 ± 0.001
$MoAs_2$	$NbAs_2$			9.064 ± 0.006	3.295 ± 0.002	7.715 ± 0.008
	$NbAs_2$	$C2$		9.067 ± 0.002	3.300 ± 0.001	7.718 ± 0.002
	$NbAs_2$	$C2$		9.07	3.30	7.73
	$NbAs_2$	$C2$		9.071 ± 0.002	3.2994 ± 0.0009	7.719 ± 0.002
$Mo_{0.4}As_2$	"$FeS_2(m)$"	$Pnnm$		5.299 ± 0.002 Not confirmed	5.983 ± 0.002	2.885 ± 0.001
W_2As_3			A	7.99	3.28	6.88
			C	13.76	3.28	9.67
			N	15.98	3.28	9.67
		$(C*/*)$	C	13.346 ± 0.002	3.278 ± 0.002	9.599 ± 0.002
			N	15.945 ± 0.002	3.278 ± 0.002	9.599 ± 0.002
	Mo_2As_3	$C2/m$	N	15.966 ± 0.001	3.2791 ± 0.0004	9.599 ± 0.001
			C	13.372 ± 0.001	3.2791 ± 0.0004	9.599 ± 0.001
WAs_2	$NbAs_2$			9.079 ± 0.005	3.318 ± 0.002	7.692 ± 0.005
	$NbAs_2$	$C2$		9.085 ± 0.002	3.318 ± 0.002	7.690 ± 0.002
	$NbAs_2$	$C2$		9.078 ± 0.002	3.3177 ± 0.0006	7.686 ± 0.001
Mo_3Sb_7	Ir_3Ge_7	$Im3m$		9.5688 ± 0.0001		
		$Im3m$		9.5713 ± 0.0008		

PHASE ANALYTICAL RESULTS

In a condensed form, the results of the phase analytical studies of the systems under investigation are as follows: The only intermediate phases are Mo_5As_4, Mo_2As_3, $MoAs_2$, W_2As_3, WAs_2, and Mo_3Sb_7. No extended ranges of homogeneity of these phases exist, and the compositions were unequivocally determined to be those stated above. Solid solubility of pnigogen in metal or *vice versa* is not noticeable in any of these systems.

All the intermediate phases have been described [1-4,6-9] earlier. (The existence of the phases MoAs, ~$MoAs_{1.04}$, $Mo_{0.4}As_2$, W_2As, and WAs, claimed

mediate phases reported in the systems Mo—As,
Mo—Sb.

$\beta(°)$		d_{pycn} (g cm^{-3})	$d_{X\text{-ray}}$ (g cm^{-3})	Reference
				Boller and Nowotny [7]
				Taylor et al.[9]
		8.48	8.56	Present
				Boller and Nowotny [7]
				Taylor et al. [9]; present
124.52	± 0.03	7.43	8.07	Taylor et al.[9]
136.78	± 0.03			Taylor et al.[9]
136.74	± 0.02	8.07	8.07	Jensen et al. [3]; present
124.70	± 0.02			Jensen et al. [3]; present
		8.07		Heinert and Biltz [4]
119.37	± 0.05			Hulliger [6]
119.35	± 0.02			Brown [8]
119.33				Taylor et al.[9]
119.37	± 0.02	8.07	8.11	Jensen and Kjekshus[1]; present
				Brown [8]
				Taylor et al. [9]; present
99.20				Boller and Nowotny [7]
125.35				Boller and Nowotny [7]
135.41				Boller and Nowotny [7]
124.80	± 0.03	11.28	11.41	Taylor et al.[6]
136.59	± 0.03			Taylor et al.[6]
136.648	± 0.006	11.32	11.41	Jensen et al. [3]; present
124.592	± 0.006			Jensen et al. [3]; present
119.43	± 0.05			Hulliger [6]
119.52	± 0.03	10.46	10.99	Taylor et al.[9]
119.42	± 0.02	10.89	10.99	Present
				Brown [9]
		8.55	8.63	Present

by Andrieux and Weiss,[5] Boller and Nowotny,[7] or Brown [8] could not be
confirmed.*) The present results and conclusions are indeed in this respect
similar to those of Taylor et al.[9] for the Mo—As and W—As systems and of
Brown [8] for the Mo—Sb system as was pointed out in the introductory section.
Rather than present our phase analytical results in a usual and direct manner,
with a risk of repeating relevant parts of the paper by Taylor et al., we have

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* Too little information regarding preparation and characterization is available for the
$Mo_{0.4}As_2$ (i.e. net composition $MoAs_5$) phase to justify a discussion of this discrepancy between
Brown [8] and the present study.

decided to take this opportunity of using our data to illustrate a more general discussion of phase analysis.

Phase analysis consists of establishing the existence of an unknown phase, of determining possible thermal conditions for its existence, of characterizing it for identificational purpose (this will normally involve measurements of its chemical or physical properties on a pure, homogeneous sample) and of stating its correct chemical composition. These may be treated as separate problems and solved independently, but by a suitable choice of method it is possible to collect several pieces of information at once.

A phase analytical survey of a system is performed by investigating changes in a chemical or physical property as a function of composition. (This common and convenient way of phase analysis is generally applicable to multicomponent systems, but the present discussion will be limited to binary systems.) Any property which differs from one phase to the other in a system may at least in principle be used for a phase analytical survey. The property most suitable for this survey is normally that showing the greatest variation from one phase to the next. The survey method has to be adjusted to the system; an approach which works well in one case may well be unsuitable in another. A special difficulty arises from the possible existence of ranges of homogeneity of the phases. The additional problem for the phase analyst is then the determination of phase limits, which requires attention as chemical and physical properties very often vary most unpredictably through a homogeneity range.

Some convenient and simple methods (commonly used at this Institute) have been applied in the phase analytical surveys of the examined systems; the results together with a brief discussion of the methods are presented below.

(i) The X-ray powder method

If thermodynamical equilibrium is attained, the maximum number of phases present in a sample is two, and the X-ray powder method relies on the fact that these two phases give non-identical diffraction patterns. The existence of a phase is established by its diffraction pattern and this pattern provides data for characterization (*e.g.* on the ASTM system). On the other hand, results obtained from samples after various heat treatments, or X-ray pictures taken with a high temperature camera are necessary in order to acquire information regarding the thermal conditions necessary for the existence of a given phase. The compositions of the phases are determined by the so-called disappearing phase principle. This principle is based on the fact that except at the exact composition of an occurring phase, two phases must invariably be present in the sample. The method is simple in application and the sensitivity is fairly high as the problem is limited to the detection of the presence of a second phase in the sample. (The use of the disappearing phase principle is indeed not limited to X-ray diffraction, it finds a versatile application in phase analysis by metallographic methods, thermal analysis, *etc.*) The accuracy of the determination of composition depends on the sensitivity by which the minor phase can be detected, which in turn depends on its crystal structure and its crystallinity in the samples as well as the sensitivity of the X-ray equipment.

The systems under investigation are favourable for phase analysis according to the X-ray powder method since the occurring phases are distinctly different crystallographically. Structural data for the intermediate phases are found in Table 1 and the corresponding data for the elements are listed by Pearson.[11] The existence of the intermediate phases is therefore easily established. The X-ray powder data for characterization of Mo_5As_4, Mo_2As_3, $MoAs_2$, W_2As_3, and WAs_2 are published elsewhere,[1,7,9] whereas the data for the phase Mo_3Sb_7 are given in Table 2. (Although the observations of diffraction angles made in the present study are more accurate than those of Hulliger [6] for $MoAs_2$ and WAs_2, of Boller and Nowotny [7] for Mo_5As_4, and of Taylor *et al.*[9] for Mo_2As_3,

Table 2. Guinier photograph data of Mo_3Sb_7 taken with strictly monochromatized $CuK\alpha_1$-radiation.

I_{obs}	$\sin^2 \Theta \times 10^5$		$h^2+k^2+l^2$	I_{obs}	$\sin^2 \Theta \times 10^5$		$h^2+k^2+l^2$
	obs	calc			obs	calc	
vw	2 589	2 590	4	m	24 612	24 609	38
w	3 883	3 886	6	vw	25 893	25 904	40
st	6 471	6 476	10	m	27 196	27 199	42
st	7 777	7 771	12	vw	28 494	28 495	44
st	9 065	9 067	14	vst	35 006	34 971	54
w	10 359	10 362	16	w	37 578	37 561	58
vst	11 664	11 657	18	m	40 168	40 152	62
w	12 945	12 952	20	vw	41 459	41 447	64
vw	14 231	14 247	22	st	42 735	42 742	66
m	15 532	15 543	24	w	44 062	44 037	68
m	20 731	20 724	32	w	46 656	46 628	72
w	22 019	22 019	34	m	49 236	49 218	76
m	23 312	23 314	36				

W_2As_3, and WAs_2 (see the error limits in Table 1) a presentation in this paper is hardly justified. Our diffraction data will be submitted to the editor of the ASTM index.) The compositions estimated using the disappearing phase principle are $MoAs_{0.80\pm0.02}$, $MoAs_{1.50\pm0.03}$, $MoAs_{2.00\pm0.05}$, $WAs_{1.50\pm0.03}$, $WA_{2.00\pm0.05}$, and $MoSb_{2.33\pm0.03}$ with the uncertainty in the determination indicated by the limits of error.

Contributing to the successful application of the X-ray powder method to the phase analyses of these systems is of course the fact that all reflections on the photographs can be accounted for by indexing. The crystallographic data listed in Table 1 are extracted from the primary diffraction data by applying the method of least squares in the fitting and refinement of the unit cell dimensions. The indicated error limits are obtained from these calculations by taking twice the standard deviations. The lattice dimensions are found to be almost invariant for specimens with different initial proportions of the components, and are normally well within the error, indicated by the limits in Table 1. As a range of homogeneity is in most cases detectable by a corresponding change in the lattice dimensions, it is deduced that the homogeneity ranges must be rather narrow. In a similar manner it is concluded that no indication of solid solubility of pnigogen in metal or *vice versa* is observed in any of the systems studied.

The lattice dimensions obtained in the independent studies by Hulliger,[6] Boller and Nowotny,[7] Brown,[8] and Taylor *et al.*[9] are also included in Table 1. Comparison of the data can immediately be performed for Mo_5As_4, $MoAs_2$, and WAs_2 whereas the Austrian [7] pseudo cell (A) and the Canadian [9] cell (C) for Mo_2As_3 and W_2As_3 have to be transformed in order to bring out the conformity with the Norwegian [3] cell (N). The transformation matrix for axes and indices from A to N is $\bar{2}00/010/101$ and similarly C is transformed to N by the matrix $102/010/00\bar{1}$. (A is accordingly transformed to C by the

matrix $00\bar{2}/010/101$.) The values obtained in the five studies must be said to be in reasonable accordance although some of the values fall beyond the limits of error stated in Table 1. In the paper by Boller and Nowotny the composition of the W_2As_3 phase has been mis-stated as $\sim W_4As_5$. Application of the data in Table 1 for identificational purposes clearly confirms the identity; the correct composition of the phase being W_2As_3 (cf. Taylor et al.[9]).

(ii) T h e   s p e c i f i c   v o l u m e   m e t h o d

Another convenient way of making a phase analytical survey of a binary system is to carry out measurements on a property whose quantitative variation with composition in a two phase region is well established. A linear relationship between the two quantities would, because of its simplicity, be desirable. The fortunate situation for phase analytical work is that many properties give a linear relationship between the measured quantity of the property and the composition in weight percent through a two phase region. Properties which should obey this relationship are, e.g., specific volume (i.e. reciprocal density), magnetic susceptibility, resistivity, etc.

In the absence of ranges of homogeneity of all of the phases in a system, a diagram of the measured quantity as function of composition in weight percent should be composed of linear sections. The point of intersection between two contiguous lines in the diagram establishes the existence and the composition of an intermediate phase. The corresponding angle of intersection determines the accuracy in the estimation of composition, i.e. this accuracy depends on the values of the investigated property for the two neighbour phases. As only two points are needed to establish the position of a straight line fewer samples are in principle necessary in order to perform a phase analytical survey according to this method compared with the use of the disappearing phase principle by which the composition of a phase is approached by successive approximations. If the angle of intersection between two of the linear sections is sufficiently small the corresponding phase might not be detectable by this method.
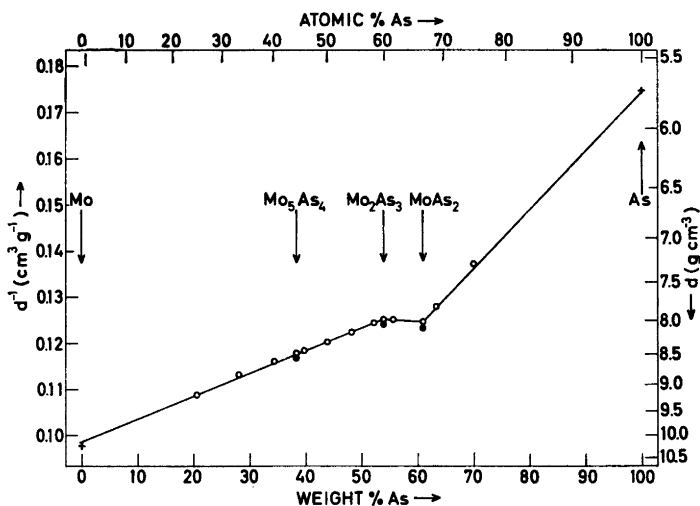

Fig. 1. Reciprocal density as function of composition for a series of molybdenum-arsenic samples quenched from 650°C (O). The densities of Mo_5As_4, Mo_2As_3, and $MoAs_2$ (●), calculated from the X-ray data, are included.
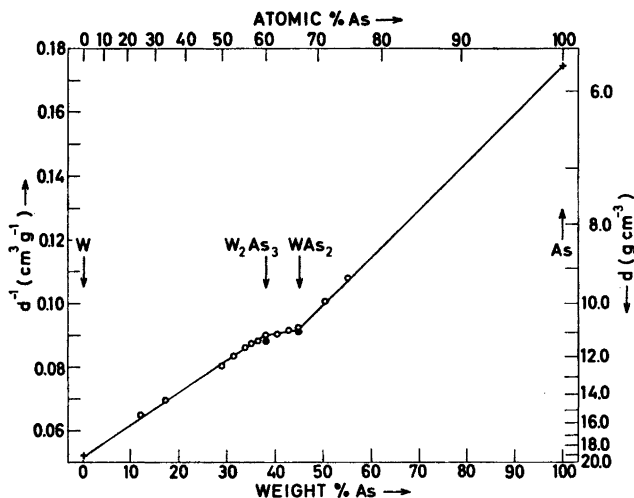
Fig. 2. Reciprocal density as function of composition for a series of tungsten-arsenic samples quenched from 650°C (O). The densities of W_2As_3 and WAs_2 (●), calculated from the X-ray data, are included.
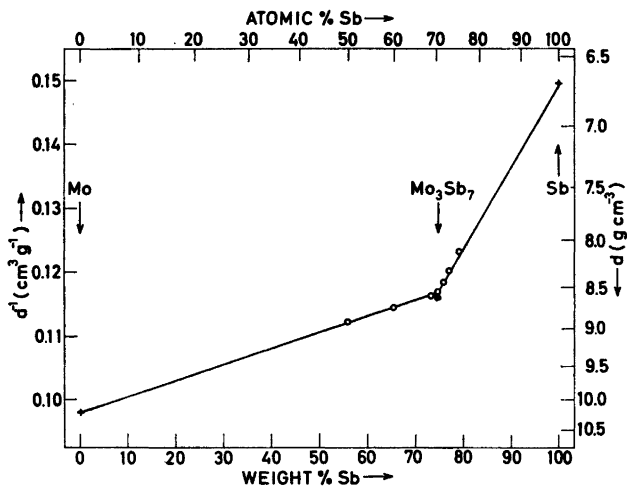

Fig. 3. Reciprocal density as function of composition for a series of molybdenum-antimony samples quenched from 650°C (O). The density of Mo_3Sb_7 (●), calculated from the X-ray data, is included.

The applicability of the specific volume method in phase analytical work is nicely illustrated in Figs. 1—3 by the results obtained in surveys of the systems Mo—As, W—As, and Mo—Sb. The existence of the phases Mo_2As_3, $MoAs_2$, W_2As_3, WAs_2, and Mo_3Sb_7 is clearly demonstrated in these diagrams.

As the specific volume, plotted in Fig. 1, was found to be an approximately linear function of weight % As in the concentration range from Mo to Mo_2As_3, this method is unable to establish the existence of the Mo_5As_4 phase. This case might serve as an example of the limitation of the method mentioned above. The fairly sharp intersection of the linear sections establishing the existence of the other intermediate phases gives no indication of ranges of homogeneity for the phases and their compositions were evaluated with good precision. Figs. 1—3 give a further confirmation of the absence of solid solubility of pnigogen in metal, and *vice versa*, in the three systems.

The derived compositions can be tested by comparison of the pycnometrically observed densities with those calculated for the assumed compositions on the basis of the structural data. It should be emphasized that this test is fairly sensitive as the two sets of data compared are obtained by completely independent experimental techniques. The densities of very carefully prepared samples of the intermediate phases are listed in Table 1 together with those calculated from the structural data. The comparison leaves no doubt about the correctness of the assumed compositions.

(iii) The thermal decomposition method

The thermal decomposition method represents a simplification of the method of tensimetric analysis, in which a controlled and gradual degradation of a sample is performed and vapour pressure isotherms of the volatile component as function of composition are simultaneously recorded. The application of tensimetric analysis to phase analytical surveys of binary metal—metalloid systems makes use of the thermodynamical fact that a rapid change in the vapour pressure of the metalloid component within a narrow composition range establishes the existence of a phase. The positions of these approximately vertical parts of the pressure-composition isotherms determine the compositions of the phases. In the simplified version of the method, a sample with well established composition is enclosed in an evacuated and sealed silica tube and heated in a furnace with a temperature gradient. The cooler end of the tube is kept at a temperature below the boiling point of the metalloid component. The temperature of the hotter end of the tube, where the sample is located, is gradually raised until the onset of decomposition is noticed by the deposition of metalloid at the cooler end. These experimental conditions are then retained until the degradation is completed, *i.e.* when no further sublimation occurs. The composition of the residuum, *i.e.* the composition of the phase, can be determined by chemical analysis and checked by weighing the sublimate. Following this method, phase analysis is conveniently carried out by starting with a sublimation of excess metalloid from a mixture of the most metalloid-rich phase and the metalloid component, and then performing a decomposition of the first residuum and repeating the process until the metal phase is obtained.

The results obtained using the thermal decomposition method on the systems Mo—As, W—As, and Mo—Sb are listed in Table 3. Only the intermediate phases described above were confirmed as indicated by the penultimate column of the table. The compositions of these phases, as determined from the residua, are in good agreement with those found by the other methods used in this study.

Table 3. Phase analysis by the thermal decomposition method.

Original phase	Degradation temperature (°C)	Composition of residuum	Residual phase
$MoAs_2$ + As	420 ± 20	$MoAs_{2.01}$	$MoAs_2$
$MoAs_2$	720 ± 20	$MoAs_{1.47}$	Mo_2As_3
Mo_2As_3	800 ± 20	$MoAs_{0.78}$	Mo_5As_4
Mo_5As_4	1050 ± 20	Mo	Mo
WAs_2 + As	420 ± 20	$WAs_{1.98}$	WAs_2
WAs_2	580 ± 20	$WAs_{1.50}$	W_2As_3
W_2As_3	720 ± 20	W	W
Mo_3Sb_7 + Sb	650 ± 20	$MoSb_{2.32}$	Mo_3Sb_7
Mo_3Sb_7	800 ± 20	Mo	Mo

(iv) The magnetic susceptibility method

The magnetic susceptibilities of the phases Mo_5As_4, Mo_2As_3, $MoAs_2$, Mo_3Sb_7, W_2As_3, and WAs_2 were measured at temperatures between 90 and 725°K, the results being shown in Figs. 4 and 5. Diamagnetic susceptibilities are found
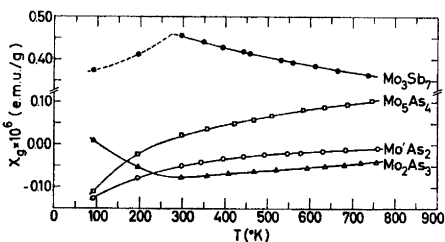

Fig. 4. The magnetic susceptibilities of Mo_5As_4, Mo_2As_3, $MoAs_2$, and Mo_3Sb_7 as a function of temperature.
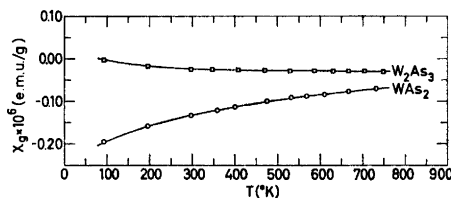
Fig. 5. The magnetic susceptibilities of W_2As_3 and WAs_2 as a function of temperature.

for Mo_2As_3, $MoAs_2$, W_2As_3, and WAs_2, whereas Mo_3Sb_7 shows paramagnetic susceptibility and Mo_5As_4 changes sign of the susceptibility at about 250°K. (Field strength dependent susceptibilities were not observed, and mean values of the susceptibilities at the different field strengths are therefore shown in Figs. 4 and 5.)

The experimental curves in Figs. 4 and 5 have not been corrected for induced diamagnetism. The expected diamagnetism resulting from the atomic cores was calculated from the diamagnetic corrections -7.5×10^{-6} e.m.u. per mole Mo^{6+} and -13×10^{-6} e.m.u. per mole W^{6+} according to Klemm [12] 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.[13] The corresponding core contributions are -0.38×10^{-6}, -0.50×10^{-6}, -0.56×10^{-6}, -0.60×10^{-6}, -0.37×10^{-6}, and -0.40×10^{-6} e.m.u. per gram Mo_5As_4, Mo_2As_3, $MoAs_2$, Mo_3Sb_7, W_2As_3,

and WAs_2, respectively. By subtracting these values from the measured susceptibilities, the total susceptibilities of localized, non-bonding electrons, valence electrons and conduction electrons are obtained. It is ascertained that no unpaired d-electrons are present on the metal atoms in Mo_5As_4, Mo_2As_3, $MoAs_2$, W_2As_3, and WAs_2. Mo_5As_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. The Curie-Weiss Law is approximately satisfied for Mo_3Sb_7 above room temperature while at temperatures below $\sim 275°K$ the curve indicates a transition to an antiferromagnetic state. A magnetic moment of about 2.9 B.M. per Mo atom is obtained on application of the diamagnetic correction stated above, whereas the value 1.2 B.M. is found when no correction is used. The probable inaccuracy in the diamagnetic correction hardly justifies a detailed discussion as to whether the observation indicates one or two unpaired electrons per magnetic atom. A more comprehensive treatment of the magnetic properties in relation to the structural properties of the phases will be published elsewhere.

Although the magnetic susceptibility measurements were not carried out with the intention of using the results in phase analytical surveys, we would like to comment on their possible application for this purpose. As neither the magnetic data presented above nor the corresponding data for the elements given in Landolt Börnstein [14] indicate that any of the phases can occur in a ferro- or ferri-magnetic state, the application of the disappearing phase principle (see section i) is excluded. A magnetic susceptibility (at constant temperature, *e.g.* T = 293°K) *versus* weight percent pnigogen plot (see section ii) should nevertheless, according to the available data, (see Figs. 4—5 and Ref. 14) be able to establish the existence and composition of the intermediate phases in the systems Mo—As, W—As, and Mo—Sb.

(v) Single crystal methods

Single crystals of the intermediate phases have been obtained by means of chemical transport reactions.[15] Traces of one of the elements chlorine, bromine, and iodine have been successfully applied as transport agents (*cf.* Boller and Nowotny [7] and Taylor *et al.*[9]). (In the absence of the transport agents we have been unable to detect visible growth of enlarged crystals under comparable experimental conditions.) Single crystals of the phases are obtained in good yield and selective preparation of only one phase is possible under suitable experimental conditions. (The successful preparative separations of these phases by chemical transport reactions are partly a result of careful adjustment and control of the furnace temperature, but a helpful contribution also results from the fact that some of the compounds migrate into the hotter and some into the cooler zone of the reaction space.) A detailed discussion of the application of chemical transport reactions to these systems will be published in a forthcoming paper.

As it is possible to prepare comparatively large quantities of the pure phases by the transport reactions, this might be utilized in phase analysis. The existence of the phases is of course immediately established and the compositions may be determined by chemical analysis. The identity of the samples prepared by the transport reactions was in each case established by oscillation and Weissenberg photographs of single crystals and Guinier photo-

graphs of crushed powders from each ingot (see Table 1). The single crystals of Mo_2As_3, $MoAs_2$, W_2As_3, and WAs_2 are needle-shaped with the diad axes along the needle axes, the cross-sections being of parallelogram-form. Needle-shaped single crystals of approximately square cross-section and having [001] parallel to the needle axis were also obtained of Mo_5As_4. The single crystals of Mo_3Sb_7 were of approximately spherical shape.

The intermediate phases can also be assigned a further characterization by their detailed crystal structure (as determined from our single crystal X-ray data). The structural types are listed in Table 1, but the details of the structure analyses and discussions of the results are presented in forthcoming papers.* In connection with the present discussion of the phase analytical results it must nevertheless be emphasized that the structure determinations provide accurate confirmation of the compositions stated in Table 1 for these phases.

(vi) Systems with no intermediate phases

The non-occurrence of intermediate phases in the systems W—Sb, Nb—Bi, Ta—Bi, Mo—Bi, and W—Bi is easily verified by the X-ray powder method (see section i). These negative findings do not result from non-equilibrium conditions of a kinetic character, since all the metals used in this study were finely powdered. Furthermore, one would expect to detect a trace of a new phase in the Guinier photographs even for samples prepared from coarse-grained metal powder. A technique which has been frequently used at this Institute to investigate the effects of kinetic hindrance in reactions of this type is to use sheets as starting material of the metals and study their surface after "reaction". Application of this technique to the investigation of the systems W—Sb, Nb—Bi, Ta—Bi, Mo—Bi, and W—Bi confirmed the non-occurrence of intermediate phases in these systems.

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* Two comments regarding the structural relationships suggested by Taylor *et al.*[9] seem nevertheless to be appropriate in this connection:

(1) A structural classification in relation to the NiAs type structure has been proposed for Mo_2As_3 (W_2As_3) on the basis of similarities in unit cell dimensions. Geometrical considerations of unit cell dimensions alone are, however, often only of limited value in the determination of structure. We are therefore not surprised to find that the only obvious relationship between the Mo_2As_3 (W_2As_3) type structure[3] and NiAs and closely-related structures[16] is the octahedral coordination of the metal atoms. Each of the structure types may be regarded as being built up of metalloid octahedra, but the stacking of these octahedra and the fitting of the metal atoms into the octahedral interstices are different.

(2) Structural relationships exist between the $NbAs_2$, FeS_2 (marcasite), and FeAsS (arseno-pyrite) type structures (see also Furuseth and Kjekshus[17]). The resemblance between the FeS_2 (marcasite) and FeAsS (arsenopyrite) type structures is fairly close, whereas the similarity between the $NbAs_2$ and FeS_2 (marcasite) type structures is less marked. The structural dissimilarity between the latter types may easily be noticed on looking at the coordination of the metal atoms in the two types of structure. In the $NbAs_2$ type structure, each metal atom is surrounded by six metalloid atoms at the corners of a triangular prism and by two other metalloid atoms outside the rectangular faces of the prism. The coordination polyhedron in the FeS_2 (marcasite) type structure is that of an octahedron. Thus, fairly large shifts of the atoms are necessary in order to derive the FeS_2 (marcasite) type structure from the $NbAs_2$ type structure.

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