

The Systems Rhenium-Arsenic, Rhenium-Antimony, Rhenium-Bismuth, Rhenium-Tellurium, and Niobium-Antimony-Tellurium

SIGRID FURUSETH and ARNE KJEKSHUS

Kjemisk Institutt A, Universitetet i Oslo, Blindern, Oslo 3, Norway

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

Re₃As₇; Ir₃Ge₇ type; $a = 8.7162 \pm 0.0007 \text{ \AA}$; $d_{\text{pycn}} = 10.77 \text{ g cm}^{-3}$.

ReTe₂; $a = 12.987 \pm 0.007 \text{ \AA}$, $b = 13.055 \pm 0.006 \text{ \AA}$, $c = 14.271 \pm 0.008 \text{ \AA}$; $d_{\text{pycn}} = 8.50 \text{ g cm}^{-3}$.

Nb₃(Sb,Te)₇; Ir₃Ge₇ type; $a = 9.8155 \pm 0.0008 \text{ \AA}$; $d_{\text{pycn}} = 8.16 \text{ g cm}^{-3}$.

Re₃As₇, ReTe₂, and Nb₃(Sb,Te)₇ have diamagnetic susceptibilities.

In continuation of the examination of transition metal chalcogenides and pnictides at this Institute, we present here data on the phase relationships in the systems Re-As, Re-Sb, Re-Bi, Re-Te, and Nb-Sb-Te.

Only one intermediate phase has previously been reported in the systems Re-As, Re-Sb, Re-Bi, and Re-Te. Wiechmann *et al.*¹ have established the existence of this phase by means of tensimetric analysis and powder X-ray diffraction measurements and have stated its composition to be approximately ReAs_{2.3}. The binary systems Nb-Sb and Nb-Te have recently been extensively studied at this Institute^{2,3} (references to further studies of these systems are given in these papers), but no study of the ternary system Nb-Sb-Te has as far as we are aware been carried out.

EXPERIMENTAL

The samples were prepared from 99.999 + % Re, As, Sb, and Te (Johnson, Matthey & Co., Ltd.), 99.98 % Nb (Johnson, Matthey & Co., Ltd.) and 99.99 + % Bi (American Smelting and Refining Co.) by heating weighed quantities of the components in different compositions in evacuated and sealed silica tubes for 20 days at 700°C and quenching in ice water. After crushing, portions of the samples were reannealed at various tempera-

tures between 500 and 1100°C, and quenching in ice water as well as slow cooling was applied.

X-Ray diffraction (oscillation, Weissenberg, precession, and Guinier photographs), density, and magnetic susceptibility measurements were carried out as described in the preceding papers.^{2,3}

RESULTS

The only intermediate phases found in this study are Re_3As_7 , ReTe_2 , and $\text{Nb}_3(\text{Sb},\text{Te})_7$. (The $\sim\text{ReAs}_{2.3}$ phase described by Wiechmann *et al.*¹ is undoubtedly identical with the present Re_3As_7 phase.*) There was no indication of a range of homogeneity for any of these phases. No intermediate phases have

Table 1. Guinier photograph data of Re_3As_7 and $\text{Nb}_3(\text{Sb},\text{Te})_7$, taken with strictly monochromatized $\text{CuK}\alpha_1$ -radiation.

$h^2+k^2+l^2$	$\sin^2\theta \times 10^5$ I_{obs}	
	Re_3As_7	$\text{Nb}_3(\text{Sb},\text{Te})_7$
2	1 560 vw	
4	3 127 st	2 455 w
6	4 688 vst	3 698 m
8	6 239 vw	
10	7 814 w	6 153 vst
12	9 365 vst	7 382 vst
14	10 921 st	8 617 vst
16	12 483 st	9 859 w
18	14 042 vst	11 082 vst
20	15 617 m	12 319 m
22	17 184 m	13 525 vw
24	18 728 st	14 781 st
26	20 304 vw	
30	23 426 m	18 466 vw
32	25 008 m	19 714 m
34	26 546 w	20 936 m
36	28 113 vst	22 153 m
38	29 703 st	23 404 m
40		24 619 w
42	32 821 st	25 855 m
44	34 387 m	27 106 w
46	35 946 st	
48		29 564 vw
54		33 260 st

* Note added in proof. The papers by Weglowski¹³ and Johnston *et al.*¹⁴ which independently confirm the existence of Re_3As_7 and ReTe_2 , respectively, have come to hand since this article was accepted for publication. The lattice dimension and observed density given by Weglowski for Re_3As_7 are: $a = 8.718 \text{ \AA}$; $d_{\text{pycn}} = 10.57 \text{ g cm}^{-3}$. The brief description of the phase relationships in the Re—Te system reported by Johnston *et al.* indicates that ReTe_2 is the only intermediate phase in this system, *i.e.* a result consistent with the present finding. Their characterization of ReTe_2 by the d -values of 7.8, 7.1, and 6.5 for three strong low-angle X-ray reflections confirms the identity with the present ReTe_2 phase (see Table 2).

Table 2. Guinier photograph data of ReTe₂ taken with 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	
vst	986	991	111	w	5569	5570	040
st	1161	1165	002	m	5730	5723	322
st	1392	1392	020	m	5916	{ 5919	{ 401
st	1402	1407	200	m		{ 5922	{ 140
vw	1514	1513	012	m	6105	6107	133
w	1692	{ 1683	{ 021	m	6141	6136	313
w		{ 1698	{ 201	w	6212	6213	141
w	1867	1865	112	st	6416	6416	214
w	2037	2035	121	w	6799	6793	402
vw	2560	2557	022	vw	6976	6977	240
w	2910	2909	122	w	7014	7020	420
w	3095	3090	221	w	7081	7087	142
vw	3769	3776	131	w	7142	7141	412
w	3814	3805	311	w	7173	7180	323
vw	4380	4377	213	m	7270	7268	241
vw	4562	4558	320	m	7466	7464	333
m	4655	4650	132	w	7793	7794	340
vw	4837	4831	231	w	7995	7983	115
vw	5020	5009	014	w	8157	8146	134
m	5428	5421	223				

been observed in the systems Re-Sb and Re-Bi. (Our investigation of the Re-Bi system was not entirely conclusive, and the result should therefore be regarded as somewhat tentative.) Solid solubility of metalloid in metal or *vice versa* is not noticeable in any of the systems under investigation.

The existence of the intermediate phases is established by the presence of their characteristic X-ray diffraction patterns (Tables 1 and 2) in the Guinier photographs. The unit cell dimensions are extracted from these data and listed in Table 3. The lattice dimensions are found to be invariant (within the limits of error stated in Table 3) for specimens with different initial proportions of the components.

The compositions as listed in Table 3 were estimated using the disappearing phase principle on the Guinier photograph data and by application of the thermal decomposition method. The Nb-Sb-Te phase was approached by first applying the thermal decomposition method to determine the sum of Sb and Te in the formula. Using a mean atomic weight of 125 for (Sb,Te) the composition was found to be Nb(Sb,Te)_{2.34}. The disappearing phase principle applied to the Guinier photographs of samples with different Sb/Te ratio suggested Nb₃Sb₂Te₅ as the most probable formula. (Indication of this composition was also obtained by analyses of single crystals using the electron microprobe analyser technique.) However, the present investigation was not entirely conclusive on this point and the formula Nb₃Sb₃Te₄, very probable from a structural point of view, cannot be excluded. The derived compositions were ascertained by comparison (Table 3) of the pycnometrically observed densities

Table 3. Structural data and densities of the phases Re_3As_7 , ReTe_2 , and $\text{Nb}_3(\text{Sb}_1\text{Te})_7$.

Phase	Space group	a (Å)	b (Å)	c (Å)	Z	d_{pycn} (g cm^{-3})	$d_{\text{X-ray}}$ (g cm^{-3})
Re_3As_7	$Im\bar{3}m$	8.7162 ± 0.0007			4	10.77	10.86
ReTe_2	*	12.987 ± 0.007	13.055 ± 0.006	14.271 ± 0.008	28	8.50	8.48
$\text{Nb}_3(\text{Sb}_1\text{Te})_7$	$Im\bar{3}m$	9.8155 ± 0.0008			4	8.16	8.09

* $Pna2_1$, $Fbca$, or $Pnma$.

with those calculated on the basis of the structural data assuming Z formula units per unit cell.

Single crystals of irregular polyhedral shape were obtained of the intermediate phases by means of chemical transport reactions ⁴ using traces of iodine as a transport agent. The identity of the samples prepared by the transport reactions with those described above was in each case established by oscillation, Weissenberg, and precession photographs of single crystals and Guinier photographs of crushed powders from each ingot.

Obvious relationships in composition, lattice dimensions, and possible space groups suggest very strongly that the structures of the Re_3As_7 and $\text{Nb}_3(\text{Sb},\text{Te})_7$ phases might be isostructural with the Mo_3Sb_7 phase⁵⁻⁷ (Ir_3Ge_7 type). The atomic arrangement in the Mo_3Sb_7 structure in terms of the space group $Im\bar{3}m$ is as follows:

Mo	in 12(e) with $x_1 = 0.344$
Sb _I	in 12(d)
Sb _{II}	in 16(f) with $x_2 = 0.163$

A reasonable agreement between observed and calculated intensities was obtained indicating that the proposed structure is correct. (Further refinement of the parameters will be carried out and published in a forthcoming paper.)

The available data for ReTe_2 does not indicate any similarity with the structures⁸⁻¹⁰ of ReS_2 and ReSe_2 .

The magnetic susceptibilities of the Re_3As_7 , ReTe_2 , and $\text{Nb}_3(\text{Sb},\text{Te})_7$ are, as shown in Fig. 1, smaller than the expected diamagnetism resulting

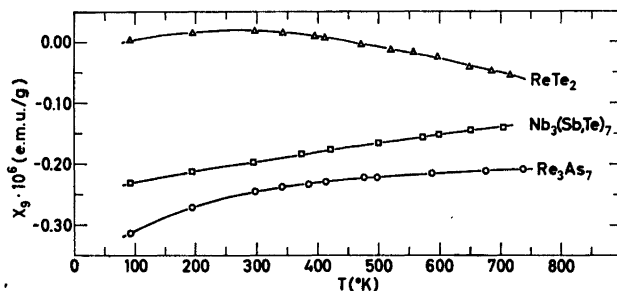


Fig. 1. The magnetic susceptibilities of Re_3As_7 , ReTe_2 , and $\text{Nb}_3(\text{Sb},\text{Te})_7$ as a function of temperature.

from the atomic cores. The core contributions are -0.50×10^{-6} e.m.u. per gram Re_3As_7 , -0.38×10^{-6} e.m.u. per gram ReTe_2 , and -0.52×10^{-6} e.m.u. per gram $\text{Nb}_3(\text{Sb},\text{Te})_7$ calculated from the diamagnetic corrections -28×10^{-6} e.m.u. per mole Re^{4+} and -9×10^{-6} e.m.u. per mole Nb^{5+} (according to Klemm¹¹) and -64.6×10^{-6} e.m.u. per mole As^{3-} , -94.4×10^{-6} e.m.u. per mole Sb^{3-} , and -70.6×10^{-6} e.m.u. per mole Te^{2-} (according to Angus¹²). By subtracting these values from the measured susceptibilities (Fig. 1) 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 metal atoms in any of these phases.

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