Compounds with the Marcasite Type Crystal Structure

I. Compositions of the Binary Pnictides

HANS HOLSETH and ARNE KJEKSHUS

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

The compositions of the compounds $CrSb_2$, FeP_2, $FeAs_2$, $FeSb_2$, β-$NiAs_2$, $NiSb_2$, RuP_2, $RuAs_2$, $RuSb_2$, OsP_2, $OsAs_2$, and $OsSb_2$ are shown to be 1:2.00 by means of X-ray diffraction and density measurements. None of the compounds has any appreciable range of homogeneity. Inconsistencies between the previously reported compositions for some of the compounds are shown to result from the effects of kinetic hindrances in the associated reactions.

In all, 18 binary transition metal pnictides and chalcogenides are known to crystallize with the FeS_2-m (m=marcasite) type structure. Five of these compounds contain a chalcogen as one of the building elements, the others being pnictides. In addition, this structure type has also been suggested for some of the di-pnictides of Co, Rh, and Ir, but these suggestions appear to be incorrect since recent studies confirm only the monoclinic $CoSb_2$ type structure for these compounds.

The type of chemical bonding in compounds with the FeS_2-m type structure has been the subject of controversial discussions,[1-5] mainly concerning the question of whether the idealized ionic or covalent model applies. This problem and in particular its relation to the electrical properties of this class of compounds has recently been considered in detail in review articles by Hulliger and Mooser [6,7] and Pearson.[8] However, many of the arguments entering into their discussions were based on doubtful literature data and in some cases even speculative extrapolation of such data had to be utilized. Notably, the compositions of these compounds are frequently assumed to be stoichiometric (1:2) without proof, and in most cases insufficient attention has been paid to the possible occurrence of homogeneity ranges. Thus, bearing in mind that little value can be attached to the interpretation of chemical and physical properties measured on mixtures of two or more phases, the reliability of some of the previously reported data is somewhat doubtful and accordingly renders Hulliger and Mooser's and Pearson's interpretations meaningless in part.

A detailed research programme is being undertaken at this Institute in order to establish the properties of the compounds with the FeS_2-m type structure. The present article concerns the determination of the compositions of the binary pnictides by independent experimental techniques. Of the 13 compounds subjected to this study, five have previously been reported to assume a composition different from the ideal formula TX_2, $i.e.$ $CrSb_{1.86}$ $(Cr_{1.05}Sb_{1.95})$,[9] $Mo_{0.4}As_2$[10] (corrected to $Mo_{0.6}As_2$[11]), $FeP_{1.95}$—$FeP_{2.00}$,[12] $FeAs_{1.93}$ at 400°C [13] and $FeAs_{1.98}$—$FeAs_{2.00}$ at 800°C,[14] and $NiSb_{2.1}$—$NiSb_{2.2}$.[15]

EXPERIMENTAL

The pure elements used in this study were 99.999 % Cr (Koch-Light Laboratories, Ltd.), 99.99+ % Fe (Johnson, Matthey & Co., Ltd.; powder which was H_2 treated at 600°C for 8 h prior to use, or turnings from rods), 99.995 % Ni, 99.999 % Ru and Os (Johnson, Matthey & Co., Ltd.), 99.999 % P (Koch-Light Laboratories, Ltd.), and 99.999+ % As and Sb (Johnson, Matthey & Co., Ltd.). The samples were prepared by heating weighed quantities of the components in evacuated and sealed silica tubes. Several samples ($cf.$ Table 1) with different initial compositions were prepared of each phase, covering both sides of the stoichiometric 1:2 ratio. During the syntheses the temperature was slowly increased to the maximum value listed in Table 1, the samples were kept at this temperature for 8 days, and finally cooled slowly to room temperature over a period of 4 days. All samples were afterwards subjected to crushing and reannealing according to the scheme recorded in Table 1. The frequent opening of the capsules for crushing of the samples during the annealing process was found to be essential in order to avoid non-equilibrium conditions resulting from the kinetics of the reactions. The temperature of the furnaces surrounding the specimens was kept constant to within ±0.5°C during the annealing processes, using Getrosist (Philips) temperature regulators and a Frigistor reference chamber for the cold points of the Pt/Pt—Rh thermocouples (0.00 ±0.02°C). The recorded annealing temperatures (Table 1) were measured separately using a calibrated Pt/Pt—Rh thermocouple. The enclosing silica capsules were made as

Table 1. Heat treatment used in sample preparation.

Phase	Number of samples	Maximum temperature (°C)	Annealing temperature (°C)	Annealing period (days)	Number of intermediate crushings
$CrSb_2$	30	700	615	180	9
FeP_2	15	1000	800	30	1
$FeAs_2$	17	700	650	60	5
$FeSb_2$	30	700	615	180	9
α-$NiAs_2$	3	700	560	180	9
β-$NiAs_2$	18	700	650	60	5
$NiSb_2$	30	700	615	180	9
RuP_2	15	1000	800	25	1
$RuAs_2$	15	800	750	30	4
$RuSb_2$	15	1200	800	50	5
OsP_2	15	1000	800	25	1
$OsAs_2$	15	800	750	30	4
$OsSb_2$	15	1200	800	50	5

short as possible and furthermore surrounded by quartz sand in order to minimize the effects of thermal gradients in the furnaces.

It proved to be impossible to prepare homogeneous samples of the FeP_2 phase by a direct reaction from the elements using the fairly coarse turnings from iron rods as starting material. FeP_2 was, however, easily obtained from sufficiently powdered iron. For the syntheses of the α-$NiAs_2$ and β-$NiAs_2$ phases crucibles of pure alumina had to be placed inside the silica tubes in order to avoid crystallization of the quartz which appears to be catalysed by a mixture of these elements.

In addition to the phases listed in Table 1 attempts have also been made to prepare phases with the following compositions: CrP_2, $Cr_{0.667}P_2$, $CrAs_2$, $Cr_{0.667}As_2$, and $Mo_{0.667}As_2$. A variety of different thermal conditions were tried during these syntheses, but this endeavour failed. (All attempts to prepare the $Mo_{0.6}As_2$ phase reported by Brown [10,11] invariably led to a mixture of $MoAs_2$ and As in accordance with the results of Taylor et al.[16] and Jensen et al.[17]) It should be noted, however, that some of these phases may be obtainable, e.g. by application of the high pressure high temperature technique.

X-Ray powder photographs of all samples were taken in a Guinier type camera of 80 mm diameter with monochromatized $CuK\alpha_1$-radiation ($\lambda = 1.54050$ Å) using KCl ($a = 6.2919$ Å [18]) as internal standard. The lattice dimensions were refined by applying the method of least squares to the diffraction data.

The density measurements were made pycnometrically at 25.00°C with kerosene as displacement liquid. To remove gases adsorbed by the sample (weighing ~ 2 g), the pycnometer was filled with kerosene under vacuum.

RESULTS

(i) *Homogeneity ranges.* The X-ray powder method was used to investigate the possible existence of composition ranges for these phases, since a range of homogeneity is in most cases detectable by a corresponding change in the lattice dimensions. The lattice dimensions have been extracted from the primary diffraction data for a large number of samples with different initial proportions of the components. The values of a, b, and c obtained after least squares refinements are listed in Table 2 together with their corresponding standard deviations. As a, b, and c are found to be almost invariant for each phase, independent of the initial compositions of the specimens, consideration of average values appears to be justified. Weighed averages and corresponding standard deviations were accordingly calculated (Table 3), using standard statistical methods and weight factors based on the standard deviations in Table 2. On comparing the data in Tables 2 and 3 it will be appreciated that the numbers of observations in Table 2 are small from a statistical point of view and furthermore that the number of degrees of freedom in the problem is unknown. However, common statistical experience suggests that 68.3% of the observations in Table 2 should be within one standard deviation from the corresponding mean value in Table 3, 95.5% within two standard deviations, and 99.7% within three standard deviations from this value. These expectations are remarkably well borne out by the data in Tables 2 and 3, confirming that the unit cell dimensions of these phases are constant, independent of the composition of the investigated sample. Their homogeneity ranges must accordingly be rather narrow and they ought indeed to be considered as compounds with well defined compositions. The exact compositions of the compounds are, however, subjected to further considerations, *vide infra.*

Table 2. Unit cell dimensions with associated standard deviations for various samples of the TX_2 phases, as determined using least squares refinements.

Sample	a (Å)	b (Å)	c (Å)
$CrSb_{1.818}$	6.0274 ± 0.0007	6.8732 ± 0.0007	3.2712 ± 0.0007
$CrSb_{1.851}$	6.0273 ± 0.0006	6.8724 ± 0.0006	3.2714 ± 0.0004
$CrSb_{1.883}$	6.0269 ± 0.0007	6.8734 ± 0.0007	3.2705 ± 0.0004
$CrSb_{1.904}$	6.0266 ± 0.0004	6.8730 ± 0.0005	3.2707 ± 0.0003
$CrSb_{1.920}$	6.0279 ± 0.0005	6.8753 ± 0.0008	3.2718 ± 0.0004
$CrSb_{1.922}$	6.0286 ± 0.0007	6.8759 ± 0.0007	3.2721 ± 0.0004
$CrSb_{1.940}$	6.0271 ± 0.0007	6.8733 ± 0.0007	3.2706 ± 0.0005
$CrSb_{1.950}$	6.0281 ± 0.0007	6.8748 ± 0.0007	3.2721 ± 0.0004
$CrSb_{1.979}$	6.0271 ± 0.0006	6.8743 ± 0.0007	3.2719 ± 0.0004
$CrSb_{2.000}$	6.0281 ± 0.0005	6.8733 ± 0.0006	3.2722 ± 0.0004
$CrSb_{2.000}$	6.0281 ± 0.0007	6.8745 ± 0.0008	3.2719 ± 0.0004
$CrSb_{2.010}$	6.0285 ± 0.0006	6.8738 ± 0.0007	3.2700 ± 0.0006
$CrSb_{2.066}$	6.0271 ± 0.0006	6.8738 ± 0.0009	3.2713 ± 0.0005
$CrSb_{2.112}$	6.0272 ± 0.0006	6.8737 ± 0.0008	3.2711 ± 0.0006
$CrSb_{2.284}$	6.0273 ± 0.0005	6.8729 ± 0.0008	3.2718 ± 0.0004
$CrSb_{2.500}$	6.0283 ± 0.0005	6.8741 ± 0.0005	3.2720 ± 0.0005
$FeP_{1.796}$	4.9737 ± 0.0008	5.6575 ± 0.0008	2.7239 ± 0.0005
$FeP_{1.851}$	4.9734 ± 0.0007	5.6566 ± 0.0007	2.7235 ± 0.0004
$FeP_{1.902}$	4.9723 ± 0.0005	5.6563 ± 0.0006	2.7231 ± 0.0003
$FeP_{1.919}$	4.9732 ± 0.0005	5.6567 ± 0.0006	2.7234 ± 0.0003
$FeP_{1.935}$	4.9736 ± 0.0008	5.6579 ± 0.0009	2.7237 ± 0.0005
$FeP_{1.959}$	4.9737 ± 0.0006	5.6576 ± 0.0006	2.7233 ± 0.0003
$FeP_{1.978}$	4.9738 ± 0.0003	5.6571 ± 0.0003	2.7237 ± 0.0002
$FeP_{2.000}$	4.9727 ± 0.0005	5.6564 ± 0.0005	2.7240 ± 0.0003
$FeP_{2.000}$	4.9726 ± 0.0005	5.6565 ± 0.0006	2.7228 ± 0.0004
$FeP_{2.021}$	4.9736 ± 0.0006	5.6573 ± 0.0006	2.7238 ± 0.0004
$FeP_{2.046}$	4.9732 ± 0.0005	5.6569 ± 0.0005	2.7234 ± 0.0003
$FeP_{2.095}$	4.9730 ± 0.0006	5.6569 ± 0.0006	2.7236 ± 0.0004
$FeP_{2.200}$	4.9722 ± 0.0005	5.6572 ± 0.0005	2.7232 ± 0.0003
$FeAs_{1.852}$	5.2997 ± 0.0006	5.9853 ± 0.0007	2.8821 ± 0.0004
$FeAs_{1.900}$	5.3017 ± 0.0008	5.9866 ± 0.0008	2.8823 ± 0.0004
$FeAs_{1.922}$	5.3018 ± 0.0004	5.9867 ± 0.0004	2.8824 ± 0.0002
$FeAs_{1.938}$	5.3003 ± 0.0004	5.9854 ± 0.0005	2.8819 ± 0.0003
$FeAs_{1.961}$	5.3005 ± 0.0004	5.9851 ± 0.0004	2.8818 ± 0.0002
$FeAs_{1.979}$	5.3019 ± 0.0004	5.9862 ± 0.0004	2.8823 ± 0.0003
$FeAs_{2.000}$	5.3012 ± 0.0005	5.9868 ± 0.0005	2.8820 ± 0.0003
$FeAs_{2.000}$	5.3014 ± 0.0003	5.9852 ± 0.0003	2.8822 ± 0.0002
$FeAs_{2.038}$	5.3014 ± 0.0002	5.9861 ± 0.0003	2.8826 ± 0.0002
$FeAs_{2.059}$	5.3014 ± 0.0003	5.9857 ± 0.0004	2.8821 ± 0.0002
$FeAs_{2.099}$	5.3020 ± 0.0004	5.9866 ± 0.0005	2.8820 ± 0.0003
$FeAs_{2.199}$	5.3015 ± 0.0006	5.9862 ± 0.0006	2.8829 ± 0.0003
$FeSb_{1.819}$	5.8328 ± 0.0006	6.5376 ± 0.0009	3.1975 ± 0.0005
$FeSb_{1.899}$	5.8322 ± 0.0007	6.5367 ± 0.0009	3.1970 ± 0.0004
$FeSb_{1.920}$	5.8329 ± 0.0006	6.5384 ± 0.0007	3.1971 ± 0.0004
$FeSb_{1.942}$	5.8335 ± 0.0006	6.5376 ± 0.0007	3.1976 ± 0.0004
$FeSb_{1.950}$	5.8329 ± 0.0005	6.5376 ± 0.0006	3.1971 ± 0.0003
$FeSb_{1.960}$	5.8321 ± 0.0006	6.5369 ± 0.0007	3.1974 ± 0.0004
$FeSb_{1.981}$	5.8335 ± 0.0007	6.5379 ± 0.0009	3.1979 ± 0.0007
$FeSb_{2.000}$	5.8332 ± 0.0004	6.5378 ± 0.0005	3.1972 ± 0.0003

Table 2. Continued.

FeSb$_{2.000}$	5.8325 ± 0.0005	6.5383 ± 0.0008	3.1969 ± 0.0003
FeSb$_{2.045}$	5.8327 ± 0.0006	6.5375 ± 0.0009	3.1975 ± 0.0004
FeSb$_{2.092}$	5.8328 ± 0.0005	6.5373 ± 0.0006	3.1975 ± 0.0003
NiAs$_{1.850}$	4.7593 ± 0.0004	5.7966 ± 0.0006	3.5453 ± 0.0004
NiAs$_{1.900}$	4.7596 ± 0.0003	5.7966 ± 0.0004	3.5454 ± 0.0003
NiAs$_{1.920}$	4.7586 ± 0.0004	5.7946 ± 0.0004	3.5442 ± 0.0003
NiAs$_{1.941}$	4.7590 ± 0.0004	5.7965 ± 0.0005	3.5449 ± 0.0004
NiAs$_{1.960}$	4.7582 ± 0.0006	5.7956 ± 0.0007	3.5447 ± 0.0004
NiAs$_{1.980}$	4.7574 ± 0.0004	5.7954 ± 0.0005	3.5446 ± 0.0004
NiAs$_{2.000}$	4.7571 ± 0.0005	5.7950 ± 0.0007	3.5442 ± 0.0004
NiAs$_{2.000}$	4.7581 ± 0.0003	5.7956 ± 0.0004	3.5452 ± 0.0003
NiAs$_{2.041}$	4.7579 ± 0.0003	5.7952 ± 0.0004	3.5448 ± 0.0003
NiAs$_{2.060}$	4.7587 ± 0.0004	5.7958 ± 0.0005	3.5452 ± 0.0004
NiAs$_{2.095}$	4.7593 ± 0.0005	5.7954 ± 0.0005	3.5454 ± 0.0003
NiAs$_{2.098}$	4.7576 ± 0.0003	5.7947 ± 0.0003	3.5446 ± 0.0003
NiAs$_{2.199}$	4.7579 ± 0.0004	5.7952 ± 0.0005	3.5450 ± 0.0003
NiSb$_{1.806}$	5.1837 ± 0.0009	6.3204 ± 0.0009	3.8393 ± 0.0010
NiSb$_{1.851}$	5.1829 ± 0.0004	6.3181 ± 0.0006	3.8410 ± 0.0004
NiSb$_{1.892}$	5.1845 ± 0.0006	6.3197 ± 0.0007	3.8410 ± 0.0006
NiSb$_{1.954}$	5.1845 ± 0.0005	6.3176 ± 0.0009	3.8413 ± 0.0005
NiSb$_{1.963}$	5.1838 ± 0.0005	6.3198 ± 0.0007	3.8415 ± 0.0005
NiSb$_{2.000}$	5.1839 ± 0.0004	6.3189 ± 0.0005	3.8408 ± 0.0004
NiSb$_{2.000}$	5.1834 ± 0.0003	6.3174 ± 0.0005	3.8403 ± 0.0004
NiSb$_{2.000}$	5.1843 ± 0.0005	6.3186 ± 0.0006	3.8414 ± 0.0005
NiSb$_{2.000}$	5.1833 ± 0.0005	6.3175 ± 0.0008	3.8407 ± 0.0005
NiSb$_{2.036}$	5.1840 ± 0.0004	6.3184 ± 0.0005	3.8404 ± 0.0004
NiSb$_{2.080}$	5.1826 ± 0.0004	6.3173 ± 0.0005	3.8400 ± 0.0004
NiSb$_{2.102}$	5.1840 ± 0.0005	6.3182 ± 0.0005	3.8407 ± 0.0004
NiSb$_{2.146}$	5.1839 ± 0.0006	6.3199 ± 0.0008	3.8422 ± 0.0006
NiSb$_{2.156}$	5.1843 ± 0.0004	6.3179 ± 0.0005	3.8403 ± 0.0004
NiSb$_{2.211}$	5.1839 ± 0.0005	6.3189 ± 0.0007	3.8412 ± 0.0004
NiSb$_{2.246}$	5.1841 ± 0.0006	6.3198 ± 0.0009	3.8423 ± 0.0006
RuP$_{1.710}$	5.1165 ± 0.0004	5.8933 ± 0.0004	2.8706 ± 0.0002
RuP$_{1.870}$	5.1171 ± 0.0006	5.8931 ± 0.0008	2.8710 ± 0.0003
RuP$_{1.900}$	5.1168 ± 0.0008	5.8931 ± 0.0008	2.8712 ± 0.0004
RuP$_{1.920}$	5.1172 ± 0.0006	5.8925 ± 0.0008	2.8710 ± 0.0003
RuP$_{1.960}$	5.1177 ± 0.0009	5.8942 ± 0.0009	2.8709 ± 0.0004
RuP$_{1.978}$	5.1173 ± 0.0004	5.8926 ± 0.0005	2.8711 ± 0.0002
RuP$_{2.000}$	5.1166 ± 0.0005	5.8929 ± 0.0005	2.8712 ± 0.0003
RuP$_{2.000}$	5.1168 ± 0.0006	5.8930 ± 0.0005	2.8711 ± 0.0003
RuP$_{2.029}$	5.1180 ± 0.0004	5.8924 ± 0.0005	2.8715 ± 0.0002
RuP$_{2.060}$	5.1175 ± 0.0008	5.8939 ± 0.0010	2.8708 ± 0.0004
RuP$_{2.090}$	5.1185 ± 0.0006	5.8939 ± 0.0006	2.8712 ± 0.0003
RuP$_{2.190}$	5.1184 ± 0.0008	5.8942 ± 0.0008	2.8725 ± 0.0004
RuP$_{2.270}$	5.1174 ± 0.0006	5.8941 ± 0.0006	2.8714 ± 0.0003
RuAs$_{1.848}$	5.4305 ± 0.0006	6.1845 ± 0.0006	2.9719 ± 0.0004
RuAs$_{1.889}$	5.4301 ± 0.0006	6.1832 ± 0.0006	2.9718 ± 0.0004
RuAs$_{1.926}$	5.4306 ± 0.0005	6.1836 ± 0.0005	2.9715 ± 0.0003
RuAs$_{1.938}$	5.4296 ± 0.0007	6.1833 ± 0.0007	2.9706 ± 0.0004
RuAs$_{1.950}$	5.4314 ± 0.0006	6.1838 ± 0.0006	2.9713 ± 0.0003
RuAs$_{1.975}$	5.4306 ± 0.0006	6.1820 ± 0.0007	2.9710 ± 0.0004
RuAs$_{2.000}$	5.4309 ± 0.0004	6.1839 ± 0.0004	2.9717 ± 0.0002
RuAs$_{2.000}$	5.4303 ± 0.0006	6.1828 ± 0.0007	2.9713 ± 0.0003
RuAs$_{2.017}$	5.4303 ± 0.0005	6.1835 ± 0.0005	2.9716 ± 0.0002

Table 2. Continued.

RuAs$_{2.044}$	5.4297 ± 0.0006	6.1830 ± 0.0005	2.9718 ± 0.0003
RuAs$_{2.065}$	5.4310 ± 0.0004	6.1841 ± 0.0005	2.9715 ± 0.0002
RuAs$_{2.098}$	5.4291 ± 0.0003	6.1824 ± 0.0004	2.9706 ± 0.0002
RuAs$_{2.200}$	5.4298 ± 0.0007	6.1838 ± 0.0006	2.9712 ± 0.0003
RuSb$_{1.851}$	5.9525 ± 0.0005	6.6740 ± 0.0006	3.1805 ± 0.0003
RuSb$_{1.874}$	5.9524 ± 0.0004	6.6729 ± 0.0005	3.1798 ± 0.0003
RuSb$_{1.901}$	5.9532 ± 0.0004	6.6739 ± 0.0005	3.1804 ± 0.0004
RuSb$_{1.941}$	5.9520 ± 0.0006	6.6735 ± 0.0006	3.1800 ± 0.0004
RuSb$_{1.961}$	5.9512 ± 0.0006	6.6723 ± 0.0006	3.1797 ± 0.0004
RuSb$_{2.000}$	5.9529 ± 0.0006	6.6756 ± 0.0007	3.1810 ± 0.0004
RuSb$_{2.000}$	5.9529 ± 0.0006	6.6736 ± 0.0007	3.1810 ± 0.0004
RuSb$_{2.016}$	5.9521 ± 0.0005	6.6742 ± 0.0005	3.1803 ± 0.0003
RuSb$_{2.052}$	5.9524 ± 0.0006	6.6746 ± 0.0007	3.1810 ± 0.0004
RuSb$_{2.104}$	5.9518 ± 0.0006	6.6728 ± 0.0007	3.1801 ± 0.0004
OsP$_{1.390}$	5.1006 ± 0.0007	5.9021 ± 0.0008	2.9178 ± 0.0006
OsP$_{1.850}$	5.1002 ± 0.0005	5.9020 ± 0.0005	2.9185 ± 0.0004
OsP$_{1.876}$	5.0988 ± 0.0009	5.9028 ± 0.0008	2.9182 ± 0.0003
OsP$_{1.912}$	5.1008 ± 0.0006	5.9017 ± 0.0007	2.9191 ± 0.0004
OsP$_{1.926}$	5.0995 ± 0.0007	5.9003 ± 0.0008	2.9171 ± 0.0005
OsP$_{1.930}$	5.1011 ± 0.0007	5.9016 ± 0.0009	2.9180 ± 0.0004
OsP$_{1.940}$	5.1017 ± 0.0004	5.9029 ± 0.0005	2.9189 ± 0.0002
OsP$_{1.983}$	5.0993 ± 0.0006	5.8992 ± 0.0008	2.9170 ± 0.0004
OsP$_{2.000}$	5.0998 ± 0.0006	5.9000 ± 0.0008	2.9181 ± 0.0004
OsP$_{2.000}$	5.1010 ± 0.0008	5.9018 ± 0.0007	2.9184 ± 0.0003
OsP$_{2.048}$	5.0997 ± 0.0005	5.9000 ± 0.0006	2.9173 ± 0.0004
OsP$_{2.076}$	5.0981 ± 0.0006	5.8990 ± 0.0006	2.9170 ± 0.0003
OsP$_{2.109}$	5.0983 ± 0.0007	5.8993 ± 0.0008	2.9170 ± 0.0004
OsP$_{2.221}$	5.1003 ± 0.0008	5.9026 ± 0.0007	2.9187 ± 0.0002
OsAs$_{1.800}$	5.4129 ± 0.0006	6.1908 ± 0.0007	3.0122 ± 0.0003
OsAs$_{1.844}$	5.4135 ± 0.0006	6.1902 ± 0.0005	3.0121 ± 0.0003
OsAs$_{1.903}$	5.4138 ± 0.0007	6.1920 ± 0.0007	3.0127 ± 0.0004
OsAs$_{1.912}$	5.4137 ± 0.0007	6.1917 ± 0.0008	3.0130 ± 0.0003
OsAs$_{1.948}$	5.4130 ± 0.0006	6.1906 ± 0.0005	3.0127 ± 0.0002
OsAs$_{1.956}$	5.4115 ± 0.0007	6.1902 ± 0.0007	3.0120 ± 0.0005
OsAs$_{1.985}$	5.4120 ± 0.0008	6.1899 ± 0.0008	3.0125 ± 0.0004
OsAs$_{2.000}$	5.4128 ± 0.0006	6.1913 ± 0.0006	3.0130 ± 0.0003
OsAs$_{2.013}$	5.4136 ± 0.0006	6.1921 ± 0.0007	3.0132 ± 0.0005
OsAs$_{2.042}$	5.4140 ± 0.0005	6.1920 ± 0.0005	3.0127 ± 0.0002
OsAs$_{2.047}$	5.4118 ± 0.0009	6.1900 ± 0.0008	3.0120 ± 0.0004
OsAs$_{2.058}$	5.4116 ± 0.0009	6.1920 ± 0.0008	3.0126 ± 0.0005
OsAs$_{2.097}$	5.4128 ± 0.0008	6.1914 ± 0.0007	3.0128 ± 0.0003
OsAs$_{2.200}$	5.4113 ± 0.0007	6.1891 ± 0.0007	3.0123 ± 0.0005
OsSb$_{1.873}$	5.9396 ± 0.0007	6.6877 ± 0.0008	3.2109 ± 0.0004
OsSb$_{1.908}$	5.9411 ± 0.0005	6.6891 ± 0.0006	3.2114 ± 0.0003
OsSb$_{1.940}$	5.9429 ± 0.0004	6.6873 ± 0.0005	3.2112 ± 0.0003
OsSb$_{1.960}$	5.9412 ± 0.0003	6.6889 ± 0.0003	3.2116 ± 0.0003
OsSb$_{1.985}$	5.9405 ± 0.0006	6.6879 ± 0.0007	3.2111 ± 0.0004
OsSb$_{1.990}$	5.9407 ± 0.0005	6.6877 ± 0.0005	3.2110 ± 0.0003
OsSb$_{2.000}$	5.9403 ± 0.0006	6.6889 ± 0.0005	3.2114 ± 0.0004
OsSb$_{2.000}$	5.9403 ± 0.0005	6.6868 ± 0.0006	3.2107 ± 0.0004
OsSb$_{2.010}$	5.9397 ± 0.0005	6.6871 ± 0.0005	3.2108 ± 0.0003
OsSb$_{2.020}$	5.9409 ± 0.0004	6.6881 ± 0.0005	3.2113 ± 0.0003
OsSb$_{2.032}$	5.9410 ± 0.0006	6.6872 ± 0.0008	3.2113 ± 0.0003
OsSb$_{2.150}$	5.9403 ± 0.0005	6.6871 ± 0.0006	3.2110 ± 0.0003

Table 3. Mean values of lattice dimensions for TX_2 phases, together with their corresponding standard deviations. (See text.)

Phase	a (Å)	b (Å)	c (Å)
$CrSb_2$	6.0275 ± 0.0006	6.8738 ± 0.0009	3.2715 ± 0.0007
FeP_2	4.9732 ± 0.0005	5.6570 ± 0.0005	2.7235 ± 0.0003
$FeAs_2$	5.3013 ± 0.0007	5.9859 ± 0.0006	2.8822 ± 0.0003
$FeSb_2$	5.8328 ± 0.0005	6.5376 ± 0.0005	3.1973 ± 0.0003
$\beta\text{-}NiAs_2$	4.7583 ± 0.0008	5.7954 ± 0.0007	3.5449 ± 0.0004
$NiSb_2$	5.1837 ± 0.0006	6.3184 ± 0.0010	3.8408 ± 0.0006
RuP_2	5.1173 ± 0.0006	5.8932 ± 0.0007	2.8711 ± 0.0005
$RuAs_2$	5.4302 ± 0.0007	6.1834 ± 0.0007	2.9714 ± 0.0004
$RuSb_2$	5.9524 ± 0.0006	6.6737 ± 0.0009	3.1803 ± 0.0005
OsP_2	5.1001 ± 0.0010	5.9012 ± 0.0014	2.9182 ± 0.0008
$OsAs_2$	5.4129 ± 0.0010	6.1910 ± 0.0010	3.0126 ± 0.0004
$OsSb_2$	5.9409 ± 0.0009	6.6880 ± 0.0008	3.2112 ± 0.0003

It is also proposed that the mean values (with the appropriate error limits, *e.g.* twice the standard deviation) listed in Table 3 give very good values for the lattice dimensions of these compounds. (The data in Table 3 agree reasonably well with most of those found in the literature [9,13-15,19-36] within the limited accuracies of the various studies.)

(ii) *Determination of the composition of the compounds.* Several methods are available for the determination of the composition of a binary compound. Every method has a certain limiting accuracy, however, which introduces error limits in the determination, but such error limits must be distinguished from the limits of composition ranges.

Four different methods have been used to determine the compositions of the compounds subjected to this study. Two of the methods concentrate on the minor phases in mixtures and the others on the major phases. The two former (here referred to as the visual and X-ray powder methods) are based on qualitative measurements and use of the disappearing phase principle. The two methods concentrating on the major phases are based on quantitative measurements of densities and X-ray diffraction intensities and comparisons with calculated data for these parameters.

Table 4 presents the limits which the various methods give for the compositions of the compounds. These limits vary somewhat according to the sensitivity and limitations of the method. Visual inspection of the samples is in this case only suitable for determinations of the upper composition limits, whereas the X-ray powder method leaves the upper limits undetermined for the phosphides and arsenides.

Table 4. Compositions of the phases, as determined by the various methods described in the text. The numbers give extreme outer limits for the compositions.

Phase	Minor phase examined		Major phase examined	
	visually	by X-rays	by density measurements	by X-rays
$CrSb_2$	u — 2.05	1.95 — 2.05	1.94 — 2.02	1.94 — 2.08
FeP_2	u — 2.07	1.90 — u	1.91 — 2.02	1.96 — 2.04
$FeAs_2$	u — 2.05	1.86 — u	1.95 — 2.03	1.94 — 2.08
$FeSb_2$	u — 2.05	1.95 — 2.05	1.95 — 2.02	1.94 — 2.08
$\beta\text{-}NiAs_2$	u — 2.05	1.94 — u	1.93 — 2.02	1.94 — 2.08
$NiSb_2$	u — 2.06	1.96 — 2.04	1.94 — 2.02	1.94 — 2.08
RuP_2	u — 2.08	1.90 — u	1.88 — 2.03	1.96 — 2.04
$RuAs_2$	u — 2.07	1.85 — u	1.92 — 2.02	1.94 — 2.08
$RuSb_2$	u — 2.07	1.90 — 2.02	1.95 — 2.03	1.94 — 2.08
OsP_2	u — 2.09	1.93 — u	1.83 — 2.07	1.96 — 2.08
$OsAs_2$	u — 2.08	1.95 — u	1.90 — 2.03	1.96 — 2.04
$OsSb_2$	u — 2.06	1.97 — 2.03	1.93 — 2.04	1.94 — 2.08

u = undetermined

Comparison (Table 5) of the pycnometrically determined densities with those calculated from the unit cell dimensions in Table 3 and an assumed formula TX_2, confirm an agreement of within 1 %. (This agreement is good, since the two sets of data compared are obtained by completely independent experimental techniques.) In order to be able to judge upper and lower limits for the compositions of the compounds according to the density data the model for the defects in the crystal lattice has to be introduced as a new variable.

Table 5. Comparisons of observed and calculated densities (for compositions TX_2).

Phase	d_{pycn} (g cm^{-3})	d_{X-ray} (g cm^{-3})	Phase	d_{pycn} (g cm^{-3})	d_{X-ray} (g cm^{-3})
$CrSb_2$	7.16	7.24	RuP_2	6.19	6.25
FeP_2	5.05	5.11	$RuAs_2$	8.28	8.35
$FeAs_2$	7.43	7.47	$RuSb_2$	9.01	9.06
$FeSb_2$	8.09	8.15	OsP_2	9.47	9.53
$\beta\text{-}NiAs_2$	7.02	7.08	$OsAs_2$	11.10	11.19
$NiSb_2$	7.90	7.98	$OsSb_2$	11.23	11.29

The limits listed in Table 4 refer to the assumption of a general formula $T_{1\pm t}X_2$, i.e. interstitial T-atoms or vacant T-sites are allowed in the crystal lattices. (This appears to be the only reasonable physical and/or chemical defect model in this case.)

The good agreement obtained on comparing observed and calculated X-ray intensities (powder diffractometer data; see the succeeding paper [37]) suggest that the compositions of the compounds are very close to TX_2. In order to obtain upper and lower composition limits from these data the above defect model has been utilized with the additional specification that the interstitial T-atoms occupy randomly the octahedral holes in the FeS_2-m type crystal structure. (The vacant T-sites were also assumed to be randomly distributed.) Sets of calculated intensities were evaluated for all compounds for $0.00 \leq |t| \leq 0.08$ using the values for the structural x and y parameters of the X atoms listed in the succeeding paper. Any value $|t| > 0.00$ leads to an increase of the structural correlation factor $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. The limits given in Table 4 have been extracted from these data on the assumption that a relative increase of R by 10 % is significant.

It is seen from Table 4 that all the four independent methods give results which group around a common composition 1:2.00. The conclusion is accordingly that TX_2 is the correct formula for all these compounds.

(iii) *On the formation of $CrSb_2$, $FeSb_2$, and $NiSb_2$.* $CrSb_2$ and $NiSb_2$ have previously been reported [9,15] to adopt compositions significantly different from 1:2.00 (see Introduction). This discrepancy is consistent with the fact that the nature of the starting material of the metal component is of fundamental importance in the formation of these compounds. Control experiments in which the intermediate crushings of the samples (see Experimental) during the annealing processes were omitted, showed that such samples failed to reach equilibrium states.

Another factor which greatly influences the reaction rate is the temperature. The maximum reaction temperatures for $CrSb_2$, $FeSb_2$, and $NiSb_2$ are limited by their eutectic temperatures, which ought to be approached as closely as possible without being exceeded. Differential thermal analysis verified the previously reported [38-40] eutectic temperatures, their redetermined values being 619.8 ± 0.5, 627.9 ± 0.5, and $615.7 \pm 0.5°C$ for $CrSb_2$, $FeSb_2$, and $NiSb_2$, respectively.

Reaction kinetical experiments on the formation of $CrSb_2$, $FeSb_2$, and $NiSb_2$ at 605°C were carried out using sheets of the three metals as starting materials. (For a description of the experimental technique used, reference is made to Furuseth and Kjekshus.[41]) Transverse metallographic sections of the specimens were studied at different lengths of the reaction period, showing firmly adherent coatings which did not spall from the metal nucleus during or after cooling of the specimens to room temperature. The coatings consisted of two layers, i.e. inner layers of the mono-antimonide phases CrSb, FeSb, and NiSb (identified according to Kjekshus and Walseth [42]) which separate the metal nuclei from the corresponding di-antimonides. After initial reaction periods of about 10 days the thickness of the layers were found to be essentially constant, showing that the reactions had reached apparent equilibrium states. The completion of the reactions are obviously being hindered by low

diffusion of the atoms within the layers. This result emphasizes the importance of the intermediate crushings during the annealing processes.

(iv) *The α-NiAs₂ phase*. In accordance with the results of Bennett and Heyding,[36] annealing experiments at 560°C confirmed the existence of the "low" temperature modification α-NiAs₂. The exact composition of this phase could not, however, be determined during this study, since all our samples turned out to contain β-NiAs₂ and/or NiAs in addition to α-NiAs₂.

The unit cell dimensions (with the corresponding standard deviations) $a=5.7717\pm0.0005$, $b=5.8380\pm0.0006$, and $c=11.4264\pm0.0013$ Å found in this study are in good agreement with those previously reported for α-NiAs₂.

REFERENCES

1. Huggins, M. L. *J. Am. Chem. Soc.* **44** (1922) 1841.
2. Pauling, L. and Huggins, M. L. *Z. Krist.* **87** (1934) 205.
3. Huggins, M. L. *Z. Krist.* **96** (1937) 384.
4. Buerger, M. J. *Z. Krist.* **97** (1937) 504.
5. Haraldsen, H. *Avhandl. Norske Videnskaps-Akad. Oslo I, Mat. Naturv. Kl.* **1947** No. 4.
6. Hulliger, F. and Mooser, E. *Progr. Solid State Chem.* **2** (1965) 330.
7. Hulliger, F. and Mooser, E. *J. Phys. Chem. Solids* **26** (1965) 429.
8. Pearson, W. B. *Z. Krist.* **121** (1965) 449.
9. Haraldsen, H., Rosenqvist, T. and Grønvold, F. *Archiv Math. Naturvidensk.* **1948** No. 4.
10. Brown, A. *Nature* **206** (1965) 502.
11. Brown, A. *Private communication*.
12. Franke, W., Meisel, K. and Juza, R. *Z. anorg. allgem. Chem.* **218** (1934) 346.
13. Heyding, R. D. and Calvert, L. D. *Can. J. Chem.* **38** (1960) 313.
14. Roseboom, E. H. *Am. Mineralogist* **48** (1963) 271.
15. Rosenqvist, T. *Acta Met.* **1** (1953) 761; *N.T.H.-Trykk* Trondheim 1953.
16. Taylor, J. B., Calvert, L. D. and Hunt, M. R. *Can. J. Chem.* **43** (1965) 3045.
17. Jensen, P., Kjekshus, A. and Skansen, T. *Acta Chem. Scand.* **20** (1966) 403.
18. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
19. de Jong, W. F. *Physica* **6** (1926) 325.
20. Hägg, G. *Nova Acta Reg. Soc. Sci. Upsaliensis (Ser. 4)* **7** (1929) No. 1.
21. Buerger, M. J. *Z. Krist.* **82** (1932) 165.
22. Meisel, K. *Z. anorg. allgem. Chem.* **218** (1934) 360.
23. Fürst, U. and Halla, F. *Z. phys. Chem.* **B 40** (1938) 285.
24. Peacock, M. A. *Trans. Roy. Soc. Can. Sect. III* **35** (1941) 105.
25. Ôsawa, A. and Sibata, N. *Sci. Rept. Tohoku Univ. First Ser.* **30** (1942) 234.
26. Kaiman, S. *Univ. Toronto Studies Geol. Ser.* **51** (1946) 49.
27. Swanson, H., Cook, M. I., Evans, E. H. and de Groot, J. H. *Natl. Bur. Std. (U.S.) Circ.* **539** (1960) p. 21.
28. Rundqvist, S. *Nature* **185** (1960) 31.
29. Kuz'min, R. N., Zhuravlev, N. N. and Losievskaya, S. A. *Soviet Phys. Cryst.* **5** (1960) 202.
30. Zhuravlev, N. N., Zhdanov, G. S. and Kuz'min, R. N. *Soviet Phys. Cryst.* **5** (1961) 532.
31. Heyding, R. D. and Calvert, L. D. *Can. J. Chem.* **39** (1961) 955.
32. Johnston, W. D. *J. Inorg. Nucl. Chem.* **22** (1961) 13.
33. Rundqvist, S. *Acta Chem. Scand.* **16** (1962) 1.
34. Berry, L. G. and Thompson, R. M. *Geol. Soc. Am. Mem.* **85** (1962) 14.
35. Hulliger, F. *Nature* **198** (1963) 1081.
36. Bennett, S. L. and Heyding, R. D. *Can. J. Chem.* **44** (1966) 3017.

37. Holseth, H. and Kjekshus, A. *Acta Chem. Scand.* **22** (1968) 3284.
38. Williams, R. S. *Z. anorg. allgem. Chem.* **55** (1907) 7.
39. Kurnakow, N. S. and Konstantinow, N. S. *Z. anorg. allgem. Chem.* **58** (1908) 1.
40. Lossew, K. *J. russ. phys.-chem. Ges.* **43** (1911) 375.
41. Furuseth, S. and Kjekshus, A. *J. Less-Common Metals* **7** (1964) 227.
42. Kjekshus, A. and Walseth, K. P. *To be published.*

Received April 6, 1968.