Structural Transformations in $Co_tNi_{1-t}As_2$, $NiAs_{2-x}S_x$, $NiAs_{2-x}Se_x$ and $CoAs_{1-x}Se_{1+x}$

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The structural transformations in $Co_tNi_{1-t}As_2$, $NiAs_{2-x}S_x$, $NiAs_{2-x}Se_x$ and $CoAs_{1-x}Se_{1+x}$ have been studied by X-ray and metallographic investigations on quenched samples. The structures of α-$NiAs_2$, α-CoAsSe (α-$NiAs_2$ type) and β-CoAsSe (FeS_2-m type with random As/Se distribution) have been determined by the powder neutron diffraction/profile refinement technique.

Very few phases have hitherto been assigned the pararammelsbergite type structure. The "low temperature" modification of $NiAs_2$ (*viz.* α-$NiAs_2$) is suggested [1,2] to be a member of this small family. However, Bennett and Heyding[1] point out that their powder X-ray diffraction pattern of α-$NiAs_2$ did not completely agree with that of the mineral pararammelsbergite. This uncertainty and the suggestion[2] that α-$NiAs_2$ should be isostructural with $AuSn_2$ have occasioned the present redetermination of the α-$NiAs_2$ structure. In order to shed some light on the cause of the restricted occurrence of this class of phases, we have also studied the substitutional solid solution phases $Co_tNi_{1-t}As_2$, $NiAs_{2-x}X_x$ (X = S,Se) and $CoAs_{1-x}Se_{1+x}$. [Long term (several years) annealing < 500 °C of the disordered $CoAs_{1-x}Se_{1+x}$ phase, with FeS_2-m (m = marcasite) type structure (As and Se distributed at random), has somewhat unexpectedly produced an α-$NiAs_2$ type arrangement rather than ordering according to a more FeS_2-m like structure.]

EXPERIMENTAL

The starting materials for the syntheses were 99.999 % Co and 99.995 % Ni (Johnson, Matthey & Co; turnings from rods), 99.999 + % S (American

Smelting and Refining Co.), 99.998 % Se (Bolidens Gruvaktiebolag) and 99.9999 % As (Koch-Light Laboratories). NiAs, $NiAs_2$ and $CoAs_2$ were made as described in Refs. 3 and 4. CoAs samples were also made according to the same procedure. (Samples with nominal compositions on both sides of stoichiometric $NiAs_2$ were prepared by heating the stoichiometric sample with NiAs or excess As.) CoAsSe, NiAsS and NiAsSe were synthesized from CoAs + Se, NiAs + S and NiAs + Se, respectively, by two successive annealings (intervening crushing) at 750 °C, followed by slow cooling to 400 °C, and then quenched to room temperature. $Co_tNi_{1-t}As_2$ is readily made from the binary end members by three successive annealings (intervening crushings) at 800 °C. To prepare $NiAs_{2-x}S_x$ and $NiAs_{2-x}Se_x$, NiAsS and NiAsSe, respectively, were mixed with appropriate amounts of $NiAs_2$, and heated at 750 °C (three annealings with intervening crushings; slow cooling). $CoAs_{1-x}Se_{1+x}$ was made from CoAsSe by adding desired amounts of either $CoAs_2$ or $CoSe_2$ (prepared as described in Ref. 5) and the use of three successive annealings at 800 °C.

The thus obtained β-modifications of $Co_{1-t}Ni_tAs_2$, $NiAs_{2-x}S_x$, $NiAs_{2-x}Se_x$ and $CoAs_{1-x}Se_{1+x}$ were subjected to long term (up to three years) annealings (intervening crushings) at temperatures from 300 to 600 °C followed by quenching to room temperature. All samples have been examined by the powder X-ray (Guinier) technique and most of them also by metallographic methods.

Powder neutron diffraction data for α-$NiAs_2$ and α- and β-CoAsSe were collected at room temperature (neutrons of wavelength 1.877 Å from the reactor JEEP II). The nuclear scattering lengths (b_{Co} = 0.278, b_{Ni} = 1.03, b_{As} = 0.64 and b_{Se} = 0.78; all × 10^{-12} cm) were taken from Ref. 6. The least squares profile refinement programme of Rietveld[7] was applied in the fitting of the variable parameters.

RESULTS AND DISCUSSION

(i) NiAs₂. Structural data for β-NiAs$_2$ (FeS$_2$-m type) have been reported earlier.[3] As previously established,[4] the $\alpha \rightleftharpoons \beta$ conversion occurs at 580 ± 4 °C. On application of the disappearing phase principle (microscopic and X-ray powder examinations) of numerous small scale samples quenched from 520 °C, the composition of α-NiAs$_2$ was established as NiAs$_{2.00 \pm 0.05}$, the homogeneity range being very narrow.

The mineral pararammelsbergite is an NiAs$_2$ phase containing small amounts of Fe, Co, Cu, Sb and S.[8] Its structure has recently been redetermined by Fleet.[8] Our powder X-ray and neutron diffraction patterns for α-NiAs$_2$ could be indexed on an orthorhombic unit cell, and, assuming space group *Pbca* [Ni, As$_I$ and As$_{II}$ all in position 8(*c*)], the profile refinements of our neutron diffraction data were terminated at a reliability factor of 0.023. The deduced unit cell dimensions and positional parameters (Table 1) are in excellent agreement with those for pararammelsbergite.[8] Variation of occupation number parameters in the initial refinement cycles confirmed the 1:2.00 composition of our α-NiAs$_2$ sample, and comparison of the

Table 1. Structural data for α-NiAs$_2$. Distances in Å and angles in degrees.

a	5.7718(5)	As$_I$ – Ni – As$_I$	96.4(7)
b	5.8342(6)	As$_I$ – Ni – As$_I$	86.6(4)
c	11.4214(12)	As$_I$ – Ni – As$_I$	86.2(6)
x	0.9992(6)	As$_I$ – Ni – As$_{II}$	97.2(5)
y	0.1761(6)	As$_I$ – Ni – As$_{II}$	88.1(5)
z	0.3743(7)	As$_I$ – Ni – As$_{II}$	91.7(4)
x_I	0.1198(5)	As$_I$ – Ni – As$_{II}$	95.1(5)
y_I	0.0543(4)	As$_I$ – Ni – As$_{II}$	83.8(5)
z_I	0.1816(8)	As$_I$ – Ni – As$_{II}$	95.9(4)
x_{II}	0.3674(6)	As$_{II}$ – Ni – As$_{II}$	91.1(6)
y_{II}	0.3091(6)	As$_{II}$ – Ni – As$_{II}$	83.0(6)
z_{II}	0.4314(7)	As$_{II}$ – Ni – As$_{II}$	85.9(4)
Ni – As$_I$	2.398(10)	Ni – As$_I$ – Ni	117.7(5)
Ni – As$_I$	2.389(10)	Ni – As$_I$ – Ni	114.9(6)
Ni – As$_I$	2.415(22)	Ni – As$_I$ – Ni	115.5(6)
Ni – As$_{II}$	2.348(11)	Ni – As$_I$ – As$_{II}$	102.9(6)
Ni – As$_{II}$	2.355(12)	Ni – As$_I$ – As$_{II}$	104.4(6)
Ni – As$_{II}$	2.367(14)	Ni – As$_I$ – As$_{II}$	97.5(5)
As$_I$ – As$_{II}$	2.449(14)	Ni – As$_{II}$ – Ni	124.5(7)
As$_I$ – As$_I$	3.282(14)	Ni – As$_{II}$ – Ni	121.0(6)
As$_I$ – As$_I$	3.282(7)	Ni – As$_{II}$ – Ni	97.0(6)
As$_I$ – As$_{II}$	3.409(12)	Ni – As$_{II}$ – As$_I$	102.2(5)
As$_{II}$ – As$_{II}$	3.124(14)	Ni – As$_{II}$ – As$_I$	101.0(5)
As$_{II}$ – As$_{II}$	3.217(10)	Ni – As$_{II}$ – As$_I$	109.1(5)

observed (7.16 g/cm^3) and calculated (7.20 g/cm^3) densities lends additional confidence to this conclusion.

Comparison of the bonding interatomic distances (using the averages for Ni – As) in α-NiAs$_2$ (Table 1) with those in β-NiAs$_2$,[3] shows good mutual agreement. The significantly smaller unit cell volume of α-NiAs$_2$ [$V/4 = 96.15(3)$ Å^3] than that of β-NiAs$_2$ [$V = 97.72(4)$ Å^3] should therefore imply a better packing in the former modification. An even smaller volume [$V/2 = 95.72(2)$ Å^3] is assigned[9] to the high pressure – high temperature induced FeS$_2$-p (p = pyrite) type modification (denoted hp) of NiAs$_2$. Following the trend from β- through α- to hp-NiAs$_2$ and guided by the packing idea, it is perhaps conceivable that another FeS$_2$-p like modification of NiAs$_2$ may be stabilized at low temperature conditions. [Such a (yet hypothetical) transition is expected to be difficult to detect, since already the $\beta \rightarrow \alpha$ transition is sluggish.] In this situation, it would also be more understandable why most of our previous searches for transitions from FeS$_2$-m to FeS$_2$-p type modifications by thermal means alone were unsuccessful.[10]

The hitherto only three examples of confirmed FeS$_2$-$m \rightarrow$ FeS$_2$-p type transitions[10,11] concern FeS$_2$ (marcasite mineral or hydrothermally synthesized samples), RuTe$_2$ and OsTe$_2$. However, these FeS$_2$-m type modifications appear to be metastable at all temperatures. The idea that FeS$_2$-p like structures (*viz.* not neccessarily cubic arrangements, but FeS$_2$-p like packing) could be "low" temperature polymorphs for some of the TX_2 (T = transition metal and X = pnigogen or chalcogen) compounds is, of course, a purely speculative hypothesis at present.

The As – As distances of 3.124(14) Å and larger (Table 1) should be considered as packing (not bonding) distances. The structure of α-NiAs$_2$ has earlier been described[2,8] as an intermediate between the FeS$_2$-m and FeS$_2$-p type structures based on the way the Ni – As$_6$ octahedra are linked together. An alternative, simple viewpoint is to start with the orientation pattern of the $X - X$ pairs and consider the differences in their packing modes. This approach is illustrated in Fig. 1. (Quantitative aspects of this way of looking at the relation between the FeS$_2$-m and FeS$_2$-p type structures will be discussed in a forthcoming paper.[12]) Here it should only be recorded that in α-NiAs$_2$, As$_I$ maintains an FeS$_2$-p like packing arrangement, whereas As$_{II}$ is packed in an FeS$_2$-m
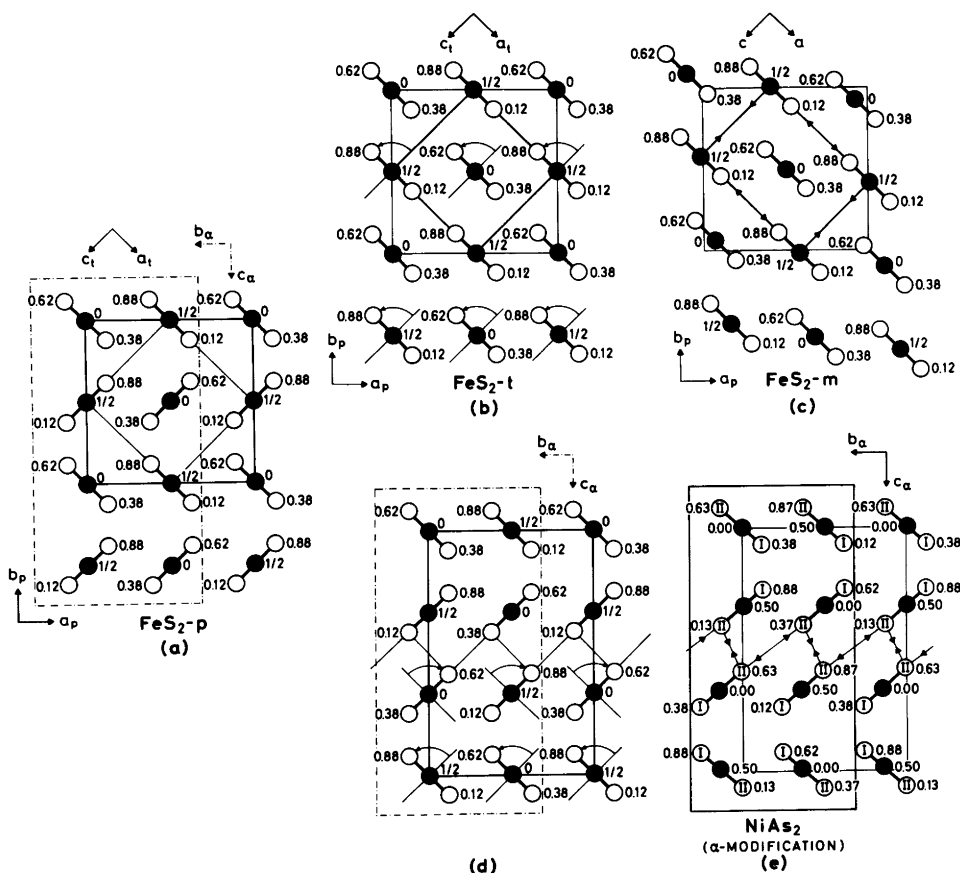
Fig. 1. Illustration showing how the FeS_2-*m* (c) and α-$NiAs_2$(e) type structures can be imagined derived from the FeS_2-*p* (a) type through change in orientation of the $X - X$ pairs. The intermediates in (b) and (d) are purely hypothetical atomic arrangements. Filled and open circles represent the T and X atoms, respectively.

like manner. Similarly, the $As_I - As_{II}Ni_3$ tetrahedra appear to resemble those of the FeS_2-*p* type structure and the $As_{II} - As_INi_3$ tetrahedra the more FeS_2-*m* like.

(ii) Transformations in $Co_tNi_{1-t}As_2$, $NiAs_{2-x}S_x$, and $NiAs_{2-x}Se_x$. The substitutional solid solution region of the $Co_tNi_{1-t}As_2$ phase is reported[13] to to cover the whole interval of t ($0 \leq t \leq 1$) at about 800 °C. At lower temperatures, we have only examined the Ni rich side from $t=0$ to 0.3 and found a single phase domain in this range for temperatures ≥ 300 °C. The extension of the substitutional solid solution regions for $NiAs_{2-x}S_x$ and $NiAs_{2-x}Se_x$ on the As rich sides are very limited; at 750 °C $0 \leq x \leq 0.05$ and $0 \leq x \leq 0.07$ for

$NiAs_{2-x}S_x$ and $NiAs_{2-x}Se_x$, respectively. The phase limits change only slightly with temperature and at 300 °C $0 \leq x \leq 0.04$ and $0 \leq x \leq 0.05$ for $NiAs_{2-x}S_x$ and $NiAs_{2-x}Se_x$, respectively.

Fig. 2 shows the variation of transformation temperature ($T_{trans.}$) for α-$Co_tNi_{1-t}As_2$ (α-$NiAs_2$ type $\rightleftarrows \beta$-$Co_tNi_{1-t}As_2$ (FeS_2-*m* type) with the compositional parameter t. Below 300 °C, the $\beta \rightarrow \alpha$ conversions are generally extremely sluggish and we have given up trying to obtain data below this temperature. As a rough estimate of maximum stability range of the α-$Co_tNi_{1-t}As_2$ phase, extrapolation to 0 K gives $t \approx 0.2$.

Fig. 2 also shows the transformation temperature as a function of the compositional parameter x for
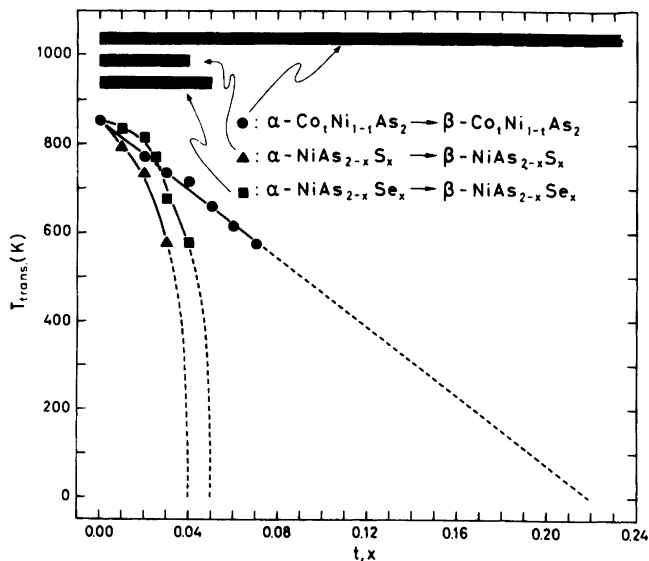
Fig. 2. $\alpha \rightleftarrows \beta$ transformation temperature, $T_{trans.}$, as a function of compositional parameters t and x for $Co_tNi_{1-t}As_2$ and $NiAs_{2-x}X_x$ ($X = S$, Se), respectively.

$NiAs_{2-x}S_x$ and $NiAs_{2-x}Se_x$. From the trends of $T_{trans.}$ *versus* x in Fig. 2 (and the only slight variation of maximum solubility with temperature between 300 and 750 °C, *vide supra*), it appears that $0 \leq x < 0.04$ and $0 \leq x < 0.05$ for $NiAs_{2-x}S_x$ and $NiAs_{2-x}Se_x$, respectively, represent the maximum extensions of these phases.

(iii) CoAsSe. CoAsSe has been reported[14] to crystallize with the FeS_2-p type structure. A more recent work[15] has led to an orthorhombic CoAsSe phase. The latter result is confirmed in this study,

Table 2. Structural data for β-CoAsSe (FeS_2-m type). Distances in Å and angles in degrees.

a	4.7562(3)	$4X-Co-X$	87.84(4)
b	5.7514(2)	$4X-Co-X$	92.16(4)
c	3.5628(3)	$2X-Co-X$	97.20(4)
x	0.2092(3)	$2X-Co-X$	82.80(4)
y	0.3706(2)		
		$2Co-X-Co$	122.03(3)
$4Co-X$	2.3749(9)	$1Co-X-Co$	97.20(4)
$2Co-X$	2.3523(12)	$2Co-X-X$	106.18(4)
$1X-X$	2.485(4)	$1Co-X-X$	101.77(6)
	$1X-X$	3.141(4)	
	$4X-X$	3.279(3)	

Table 3. Structural data for α-CoAsSe (α-NiAs$_2$ type; $X_1 =$ Se, $X_{II} =$ As). Distances in Å and angles in degrees.

|			
a	5.7285(8)	Se$-$Co$-$Se	96.5(7)
b	5.7741(7)	Se$-$Co$-$Se	85.8(4)
c	11.3653(15)	Se$-$Co$-$Se	85.8(6)
x	0.9989(7)	Se$-$Co$-$As	97.7(5)
y	0.1755(6)	Se$-$Co$-$As	89.2(5)
z	0.3740(8)	Se$-$Co$-$As	92.8(4)
x_1	0.1249(8)	Se$-$Co$-$As	94.5(6)
y_1	0.0505(6)	Se$-$Co$-$As	82.9(5)
z_1	0.1850(6)	Se$-$Co$-$As	95.8(4)
x_{II}	0.3661(6)	As$-$Co$-$As	90.9(7)
y_{II}	0.3083(5)	As$-$Co$-$As	83.2(6)
z_{II}	0.4312(7)	As$-$Co$-$As	85.6(4)
Co$-$Se	2.375(11)	Co$-$Se$-$Co	118.0(6)
Co$-$Se	2.358(13)	Co$-$Se$-$Co	116.1(6)
Co$-$Se	2.378(21)	Co$-$Se$-$Co	116.2(6)
Co$-$As	2.343(22)	Co$-$Se$-$As	102.0(5)
Co$-$As	2.331(12)	Co$-$Se$-$As	102.6(5)
Co$-$As	2.349(11)	Co$-$Se$-$As	96.7(5)
Se$-$As	2.482(14)		
		Co$-$As$-$Co	125.9(7)
Se$-$Se	3.223(14)	Co$-$As$-$Co	116.0(7)
Se$-$Se	3.223(14)	Co$-$As$-$Co	96.8(6)
Se$-$As	3.408(13)	Co$-$As$-$Se	101.4(5)
As$-$As	3.115(14)	Co$-$As$-$Se	101.2(5)
As$-$As	3.179(8)	Co$-$As$-$Se	109.4(5)
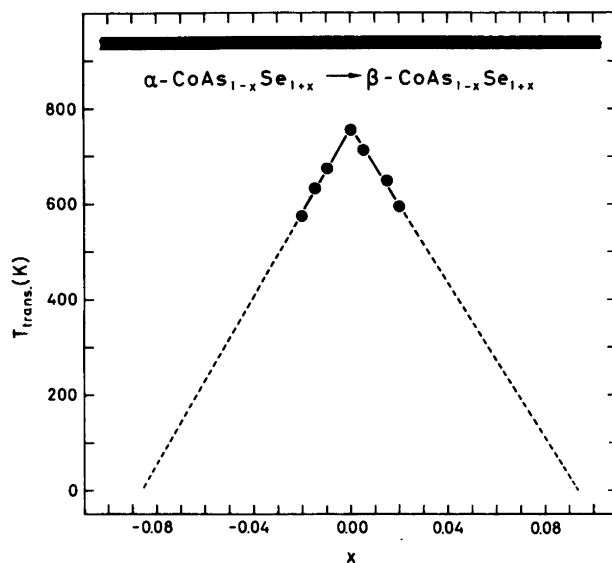
Fig. 3. Dependence of $\alpha \rightleftharpoons \beta$ transformation temperature, $T_{trans.}$, on compositional parameter x for $CoAs_{1-x}Se_{1+x}$.

and we have confirmed the FeS_2-m type structure by the powder neutron diffraction/profile refinement technique. In preliminary refinement cycles, various ordering schemes for As and Se were tried, without being confirmed. The assumption of space group *Pnnm* with Co in position $2(a)$, As and Se disordered in $4(g)$, gave a neutron diffraction reliability factor of 0.028, suggesting that the proposed structure with random As/Se distribution is essentially correct. Structural data for this FeS_2-m type modification (referred to as β) of CoAsSe are given in Table 2. The $X-X$ distances $\geq 3.141(4)$ Å are considered to reflect packing rather than bonding interatomic distances.

The $\alpha \rightleftharpoons \beta$ transition for CoAsSe occurs at 480 ± 5 °C. Whereas the $\alpha \rightarrow \beta$ reaction is comparatively fast (about five days at 560 °C), the opposite reaction is extremely slow and very dependent on temperature (the $\beta \rightarrow \alpha$ transition has not yet been detected below 300 °C), and the reaction is catalyzed by small amounts of the α-modification. When a few crystals of α-CoAsSe are present in the reaction vessel, the $\beta \rightarrow \alpha$ conversion proceeds comparatively fast (about two months for a 15 g sample at 460 °C). Starting with no α-phase, the conversion rate depends probably on minute amounts of impurities, and our first α-CoAsSe sample needed three years at 440 °C.

The structure of the α-CoAsSe phase was refined on the assumption that it takes the α-$NiAs_2$ type structure. The refinements converged to a neutron diffraction reliability factor of 0.032, structural data being given in Table 3. With reference to Fig. 1e, Se is X_I with FeS_2-p like packing, whereas As is X_{II} with FeS_2-m like packing.

The extension of the substitutional solid solution range of $CoAs_{1-x}Se_{1+x}$ covers at least $-0.12 \leq x \leq 0.12$ at 300 °C. (We have not yet examined samples outside this range. The $\beta \rightarrow \alpha$ conversion rate was speeded up by adding small amounts of α-CoAsSe to the β-$CoAs_{1-x}Se_{1+x}$ samples.) Fig. 3 shows the $\alpha \rightleftharpoons \beta$ transition temperature as a function of the compositional parameter x.

(iv) Comments on the α-$NiAs_2$ type family. CoPSe was first synthesized by Nahigian *et al.*[15] and assigned the α-$NiAs_2$ type structure. We have presently confirmed their proposal as far as powder X-ray data can be stretched: $a = 5.5475(6)$, $b = 5.6588(7)$ and $c = 11.1848(12)$ Å, with Se as X_I and P as X_{II}, our positional parameters being so approximate that there is no point in quoting them here. Also CoSbS (and the mineral paracostibite[16]) shows[15] X-ray powder patterns similar to α-$NiAs_2$. Our preliminary X-ray investigations leave not much doubt that this is essentially correct [$a = 5.8351(7)$, $b = 5.9600(8)$ and $c = 11.6632(16)$ Å]. Further in-

Table 4. Survey of $CoXY$ and NiX_2 ($X = P$, As, Sb and $Y = S$, Se, Te) phases according to means of synthesis. (Data are taken from Refs. 1, 4, 9, 15, 19−23, and this work.)

Phase	Sealed silica capsule technique	High pressure − high temperature technique
CoPS	Tetragonal (a new structure type). FeS_2-p like?	−
CoPSe	α-$NiAs_2$ type. Disordering of P and Se not possible?	FeS_2-p type (disordered P and Se)
CoPTe	−	−
CoAsS	Ordered $\rightleftarrows$ disordered FeS_2-p like structures	−
CoAsSe	α-$NiAs_2$ type $\rightleftarrows$ FeS_2-m type (disordered As and Se)	FeS_2-p like
CoAsTe	−	−
CoSbS	α-$NiAs_2$ type. Disordering of Sb and S not possible?	NiSbS (ullmannite) type
CoSbSe	FeS_2-m type. Ordering of Sb and Se not possible?	No transformation
CoSbTe	−	−
NiP_2	NiP_2 type	FeS_2-p type
$NiAs_2$	α-$NiAs_2$ type $\rightleftarrows$ FeS_2-m type	FeS_2-p type
$NiSb_2$	FeS_2-m type	−

vestigations of $CoP_{1-x}Se_{1+x}$ and $CoSb_{1-x}S_{1+x}$ have been started.

The structure of $AuSn_2$ [17] is related to the α-$NiAs_2$ type [the same space group *Pbca*; Au, Sn_I and Sn_{II} in position 8(c)], but lacks the property of distinct $Sn_I - Sn_{II}$ pairs. Thus, $AuSn_2$ may be said to be in a similar relation to the α-$NiAs_2$ type as the $CuAl_2$ type phases are with respect to the $TiSb_2$ type structure.[18] The α-$NiAs_2$ type structure should therefore best be regarded as a separate structure type.

The limited occurrence of the α-$NiAs_2$ type phases appears to suggest that the guideline for this type may be associated with a formal d^6 (non-bonding) manifold on T. This would make other $CoXY$ ($X = P$, As, Sb and $Y = S$, Se, Te) phases interesting candidates for long-term annealings at lower temperatures than hitherto tried. A survey of $CoXY$ (and NiX_2) phases is given in Table 4. Among these, CoSbSe, which is reported to take the FeS_2-m type structure, is a particularly interesting candidate. On the other hand, $NiSb_2$ has previously[4] been subjected to long-term annealings at temperatures ≥ 300 °C without showing any sign of an α-$NiAs_2$ type modification.

Other phases of interest are $Ni_{1-t}Pd_tAs_2$ and $Ni_{1-t}Pt_tAs_2$ which already have been examined to some extent by Bennett and Heyding.[1] $Ni_{1-t}Pt_tAs_2$ appears to show virtually no solid solubility. For $Ni_{1-t}Pd_tAs_2$, on the other hand, Bennett and Heyding report extended ranges of solid solubility. The FeS_2-p type structure is stabilized for $0.433 \leq t \leq 1$, followed by a two-phase field for $t < 0.433$.

The Ni rich side was unfortunately not examined systematically. However, Bennett and Heyding's results suggest that $Ni_{0.9}Pd_{0.1}As_2$ and $Ni_{0.8}Pd_{0.2}As_2$ may well be stabilized with the α-$NiAs_2$ type structure at 650 and 750 °C, respectively. (The quoted temperatures represent preparation rather than transformation temperatures.) Thus, $Ni_{1-t}Pd_tAs_2$ appears to provide an example of increased stability of the α-$NiAs_2$ type modification with increasing degree of substitution (*viz.* opposite to the trends in Figs. 2 and 3).

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