Structural Properties of Co_3Sn_2, Ni_3Sn_2 and Some Ternary Derivatives

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The Co_3Sn_2 and Ni_3Sn_2 phases were studied as function of composition and temperature. The Ni_3Sn_2 type structures of the low temperature modifications were refined from powder neutron diffraction data. At higher temperatures the Co_3Sn_2 and Ni_3Sn_2 phases take the NiAs–Ni_2In type structure. The Ni_3Sn_2 to NiAs–Ni_2In type transition was studied by high temperature X-ray diffraction and differential scanning calorimetry. Complete solid solubility exists for the Co_3Sn_2–CoSb system while a two phase region is established for the Co_3Sn_2–CoAs system at room temperature.

The NiAs type atomic arrangement (*cf.*, *e.g.*, Ref. 1 and references therein) exhibits the remarkable feature that it can exist over the wide range of composition from T_2X to TX_2 (T and X denoting, respectively, metal and non-metal atoms). On the metal rich side T is taken up in trigonal bipyramidal holes until these are filled at the composition T_2X where the structural arrangement is converted to Ni_2In type. In the non-metal rich region T is omitted from alternate layers of metal atoms along the hexagonal c axis until the $Cd(OH)_2$ type structure is obtained at the TX_2 composition.

At (usually) higher temperatures some of the NiAs type phases exhibit appreciable ranges of homogeneity, and the variation in composition is normally absorbed without loss of the hexagonal crystal symmetry. At lower temperatures structural deformations often take place, either because the internal lattice stresses cannot be compensated without reduction in symmetry or due to ordering of the occupied and vacant sites within the metal sub-lattices.

The present paper concerns Co_3Sn_2 and Ni_3Sn_2 which have been reported to take extended homogeneity ranges with the intermediate NiAs–Ni_2In type structure above 800–900 K and superstructural ordering at lower temperatures.[2–9] Inspired by the findings[10] for the Ni_3Sn_2–NiSb system examination of the Co_3Sn_2–CoAs and Co_3Sn_2–CoSb systems were also included in this study.

Experimental

The pure elements used as starting materials for the syntheses were 99.99 + % Co, 99.995 % Ni and 99.99 % Sn (Johnson, Matthey & Co.; turnings from rods of Co and Ni, cuts from rods of Sn) and 99.999 % As and 99.9995 % Sb (Koch-Light Laboratories; lumps). The Co_3Sn_2 phase was prepared by heating weighed amounts of Co and Sn in evacuated sealed silica tubes at 900 °C for 3 d. After careful grinding the samples were reheated at 700 °C for 5 d followed by slow cooling to 300 °C, maintained there for 3 d and finally cooled to room temperature over 2 d. The Ni_3Sn_2 phase was prepared similarly, but in this case an additional heat treatment at 400 °C for 5 d was introduced before the final cooling to room temperature. CoAs and CoSb were synthesized as described in Ref. 11. Ternary Co_3Sn_2–CoAs or Co_3Sn_2–CoSb samples were made similarly from Co_3Sn_2 and CoAs or CoSb by two or three heat

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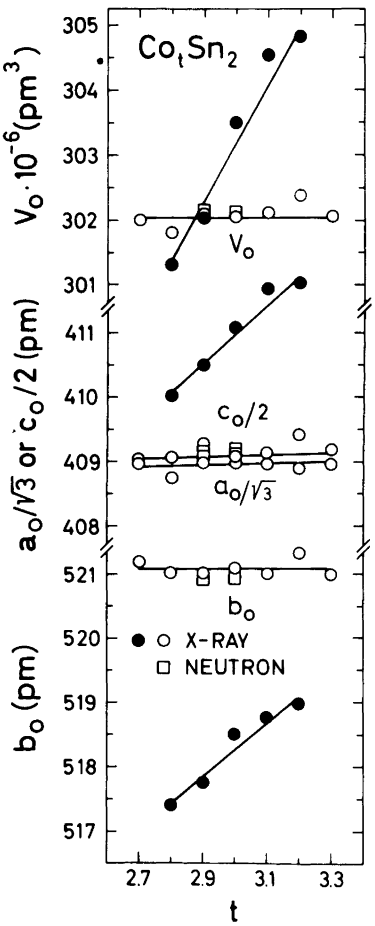
treatments at 900 °C for 5 d. The Co_3Sn_2 rich samples were subjected to an additional annealing at 400 °C for 5 d in order to promote the conditions for the formation of superstructural ordering.

The homogeneity of the samples were checked from powder X-ray diffraction (Guinier technique, $CuK\alpha_1$-radiation, Si as internal standard) photographs taken at room temperature. High temperature X-ray diffraction photographs were obtained with an Enraf-Nonius Guinier Simon camera for temperatures between 300 and 1100 K. Differential scanning calorimetry (DSC) were performed with a Mettler TA 3000 system.

Powder X-ray diffraction intensity data were derived from the Guinier photographs by means of a Nicolet film scanning system L 18, and data reduction was made with the programme SCANPI.[12] Least squares refinements were performed with the programme SHELX[13] (using one common, isotropic temperature factor for all atoms and one scale factor in addition to the positional parameters as variables).

Powder neutron diffraction data were collected with the OPUS III spectrometer situated at the JEEP II reactor, Kjeller, using neutrons of wavelength 187.7 pm. The Hewat[14] version of the Rietveld[15] programme was used in the profile re-



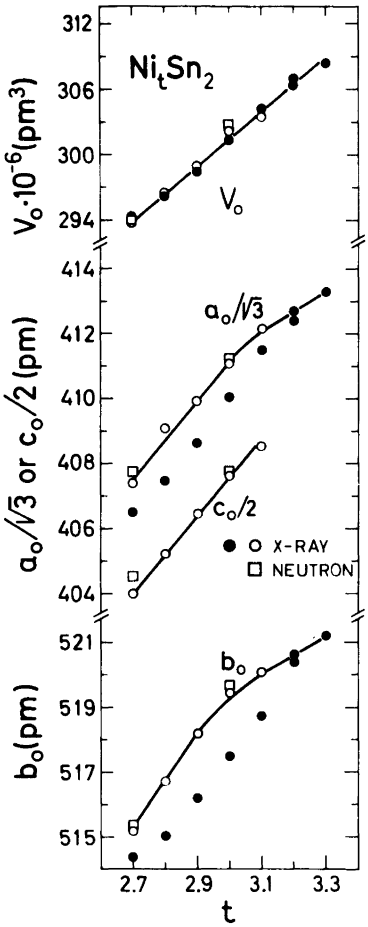


Fig. 1. Unit cell dimensions (at 293 K, using *Pnma* setting) *versus* composition (specified according to the gross formula T_tSn_2) for quenched and slowly cooled samples of the (a) Co_3Sn_2 and (b) Ni_3Sn_2 phases. Filled and open symbols refer to high (hexagonal) and low (orthorhombic) temperature modifications, respectively. *Calculated* error limits do not exceed the size of symbols.

finements of the powder diffraction data. The scattering lengths (in 10^{-12} cm) $b_{Co} = 0.253$, $b_{Ni} = 1.03$ and $b_{Sn} = 0.623$ were taken from Ref. 16.

Results and discussion

(i) Atomic arrangement of the Co_3Sn_2 and Ni_3Sn_2 phases

According to Ellner[9] the homogeneity ranges of the Co_3Sn_2 and Ni_3Sn_2 phases cover the ranges $Co_{2.76}Sn_2$–$Co_{3.26}Sn_2$ and $Ni_{2.70}Sn_2$–$Ni_{3.19}Sn_2$, respectively, for samples quenched from 1000–1050 K. The present results concur with these phase borders, although it should be noted that a critical re-evaluation of the limits was not intended.

Samples quenched from above 900 K are found to crystallize with the intermediate NiAs–Ni_2In type structure. In complete accordance with Ellner,[9] the atomic arrangement of these partly filled up NiAs type structures [space group $P6_3/mmc$: T_I in 2*a*, T_{II} in 2*d* (partly occupied by 0.76–1.26 Co for Co_3Sn_2 and 0.70–1.19 Ni for Ni_3Sn_2) and Sn in 2*c*] is confirmed by comparisons of observed and calculated powder X-ray diffraction structure factor data. The unit cell dimensions obtained for the quenched samples at room temperature (Fig. 1, the metal content being expressed in terms of *t* of the gross formula T_tSn_2) are also found to be in excellent agreement with those tabulated by Ellner,[9] and the properties of those samples will not be discussed further here.

Slowly cooled samples of the Co_3Sn_2 and Ni_3Sn_2 phases obtain orthorhombic symmetry. The variations in the unit cell dimensions (at 293 K) of the low temperature Co_3Sn_2 and Ni_3Sn_2 phases with the metal content are included in Fig. 1. The low temperature modification of Co_3Sn_2 is obtained as single phase only for the composition $Co_{2.9}Sn_2$. (CoSn occurs as minor phase in the $Co_{2.7}Sn_2$ and $Co_{2.8}Sn_2$ samples and Co in the samples with composition between $Co_{3.0}Sn_2$ and $Co_{3.3}Sn_2$.) The Ni_3Sn_2 phase, on the other hand, exhibits an appreciable range of homogeneity ($Ni_{2.7}Sn_2$ to $Ni_{3.1}Sn_2$, *cf.* Fig. 1b). It should be noted that the unit cell volumes coincide for the two modifications of the Co_3Sn_2 and Ni_3Sn_2 phases.

The systematic extinctions of reflections in the powder X-ray and neutron diffraction patterns are compatible with the space groups *Pnma* and $Pn2_1a$, and in accordance with Refs. 6–8 the former was adopted for the present structural refinements. Unit cell dimensions and positional parameters as derived through Rietveld[15] analyses of the room temperature, powder neutron diffraction data for $Co_{2.9}Sn_2$, $Ni_{2.7}Sn_2$, $Ni_{3.0}Sn_2$ and $Ni_{3.3}Sn_2$ are given in Table 1. [The results for $Co_{3.0}Sn_2$ (two phase; *vide supra*) which are not included in Table 1 match those listed for $Co_{2.9}Sn_2$.]

Structural refinements for the same and other

Table 1. Unit cell dimensions and positional parameters for $Ni_{2.7}Sn_2$, $Ni_{3.0}Sn_2$, $Ni_{3.3}Sn_2$ and $Co_{2.9}Sn_2$ obtained from Rietveld refinement of powder neutron diffraction data. (Space group *Pnma*, T_I in 8*d*, T_{II}, T_{III}, Sn_I and Sn_{II} in 4*c*; 60–70 reflections; $R_N = 0.04$–0.09.) Calculated standard deviations in parentheses.

Phase		$Ni_{2.7}Sn_2$	$Ni_{3.0}Sn_2$	$Ni_{3.3}Sn_2$[a]	$Co_{2.9}Sn_2$
a (pm)		706.15(8)	712.40(9)	715.89(9)	708.5(1)
b (pm)		515.30(4)	519.70(4)	521.18(4)	521.6(1)
c (pm)		809.03(12)	815.62(7)	[826.64(12)]	819.4(1)
T_I:	*x*	0.248(1)	0.2353(6)	1/4	0.231(2)
	y	0.000(1)	0.0040(8)	0	0.018(3)
	z	0.119(1)	0.1176(9)	1/8	0.120(3)
T_{II}:	*x*	0.909(1)	0.9077(11)	11/12	0.928(4)
	z	0.127(3)	0.1284(9)	1/8	0.135(4)
	n	0.67(1)	0.972(9)	1.0	0.846(9)
T_{III}[b]:	*n*	0.0	0.0	0.3	0.0
Sn_I:	*x*	0.593(3)	0.6022(19)	7/12	0.599(2)
	z	0.647(2)	0.6417(17)	5/8	0.653(2)
Sn_{II}:	*x*	0.576(3)	0.5657(15)	7/12	0.560(2)
	z	0.128(3)	0.0942(15)	1/8	0.104(2)

[a]Orthohexagonal values. [b]$x = 11/12$, $y = 1/4$, $z = 5/8$.

samples of the Co_3Sn_2, Ni_3Sn_2 phases were also made on the basis of powder X-ray diffraction data. However, although the values for the positional parameters thus obtained are entirely consistent with those in Table 1, the X-ray based values are considerably less accurate. (The *calculated* standard deviations in the X-ray based positional parameter for Sn_I and Sn_{II} are about three times larger than those for $Ni_{3.0}Sn_2$ in Table 1, whereas the disparities for T_I and T_{II} amount to approximately a factor of ten. Numerical values for the X-ray based positional parameters are therefore not included in this communication.)

The relation between the orthorhombic, Ni_3Sn_2 and hexagonal, NiAs–Ni_2In type lattices is: $\mathbf{a}_O = \mathbf{a}_H + 2\mathbf{b}_H$, $\mathbf{b}_O = \mathbf{c}_H$, $\mathbf{c}_O = 2\mathbf{a}_H$; $V_O = 4V_H$ (where the subscripts O and H denote orthorhombic and hexagonal, respectively). The Ni_3Sn_2 type crystal structure is schematically shown in Fig. 2 as a projection on (010). The displacements of the T and Sn atoms relative to their positions in the undistorted NiAs–Ni_2In type atomic arrangement are illustrated by the arrows which depict direction and magnitude of the atomic shifts. In terms of a description based on space group *Pnma* the paramount distinction between the Ni_3Sn_2 and NiAs–Ni_2In type structures is that the T_{II} atoms of the former are confined to *one single* four-fold position (*cf.* Table 1 and Fig. 2) whereas they are distributed at random over two four-fold positions in the latter. On the other hand, the second four-fold position comes also into use in the Ni_3Sn_2 type atomic arrangement when the T: Sn atomic ratio exceeds 3 : 2 [but due to the small extension of the homogeneity range of the orthorhombic Ni_3Sn_2 phase on the metal rich side (*cf.* Fig. 1) the additional T atoms provide only a very low (random) occupancy in the second four-fold position (*cf.* Table 1)].

The calculated occupation numbers [as derived from neutron (*cf.* Table 1) and X-ray (not documented, *vide supra*) diffraction data] show that the T_I site is always fully occupied. The nominal variation in composition on going from $Ni_{2.7}Sn_2$ to $Ni_{3.0}Sn_2$ is nicely accounted for (*cf.* Table 1) by the calculated occupation numbers for the T_{II} site (70 % filled at $Ni_{2.7}Sn_2$, fully occupied at $N_{3.0}Sn_2$). At still higher metal contents the T_{III} site starts to be inhabited, but the homogeneity range of the orthorhombic Ni_3Sn_2 phase ceases before the phase limit of the corresponding hexagonal phase is reached.

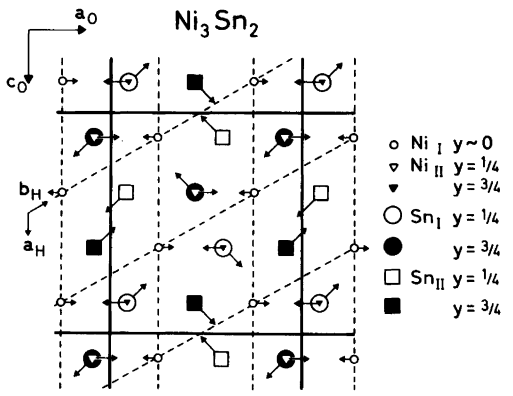


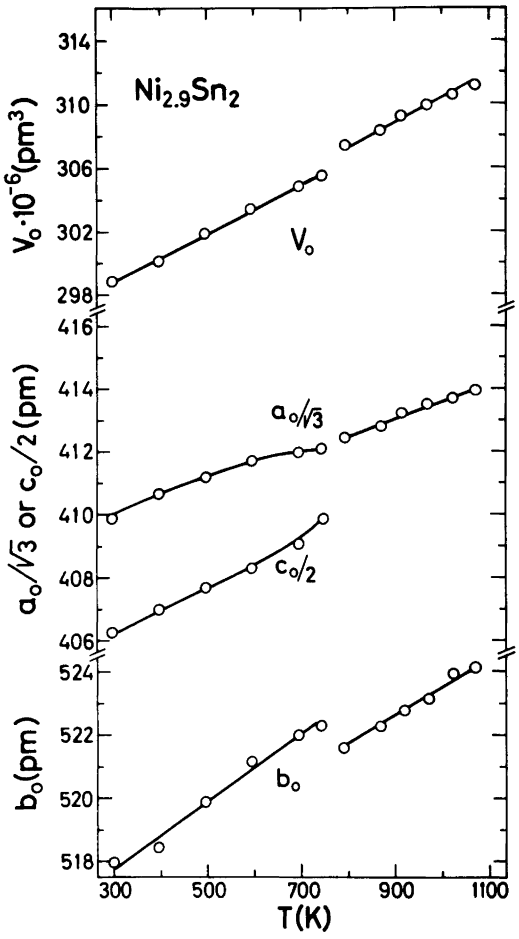
Fig. 2. Relationship between the NiAs–Ni_2In and Ni_3Sn_2 type structures. Legends to symbols are given on the illustration. Lengths and directions of arrows give displacements from former to latter type atomic arrangement. (The minor displacements of Ni_I parallel to projection axis are not shown.)

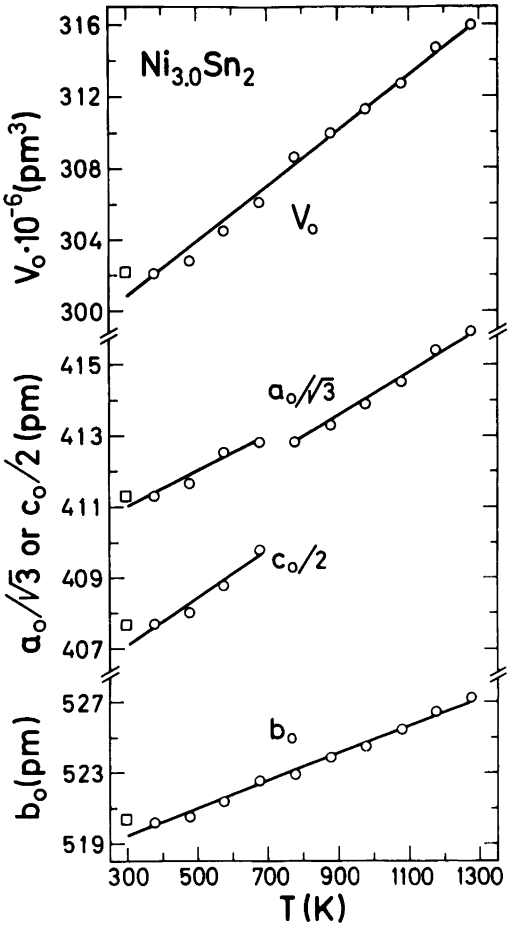
The structural data for the Co_3Sn_2 and Ni_3Sn_2 phases obtained in this study (*cf.* Fig. 1 and Table 1) differ to smaller or larger extent from the corresponding data in Refs. 6–8. (There is in fact only satisfactory agreement with Ref. 9.) Some of the discrepancies are too large to be explained away as due to compositional misfit or preparative peculiarities.

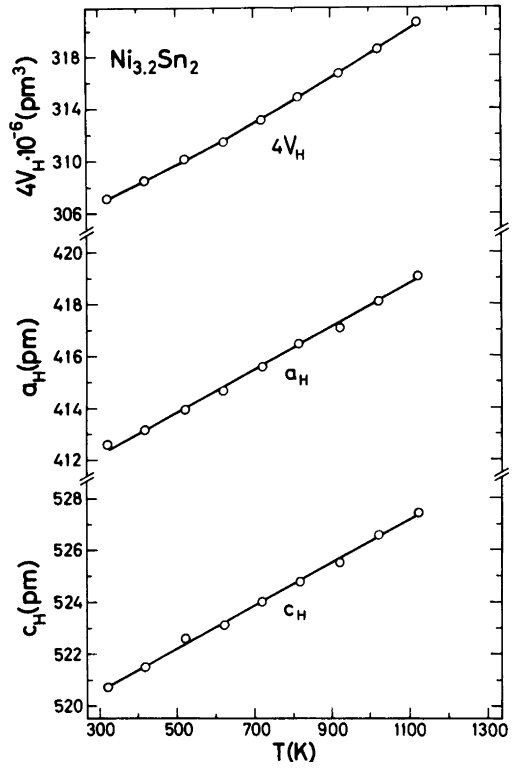
The fact that *Pnma* is a sub-group of $P6_3/mmc$ offers favourable conditions for a second order phase transition between the Ni_3Sn_2 and NiAs–Ni_2In type structures as function of temperature and composition. [The well-established continuous MnP ⇄ NiAs type transition (*cf.* Refs. 17, 18) may, to some extent, be imagined to serve as a model for such a transition.] However, the following three (intermingled) requirements must be satisfied if the Ni_3Sn_2 to NiAs–Ni_2In type conversion is to be of the continuous second order type:

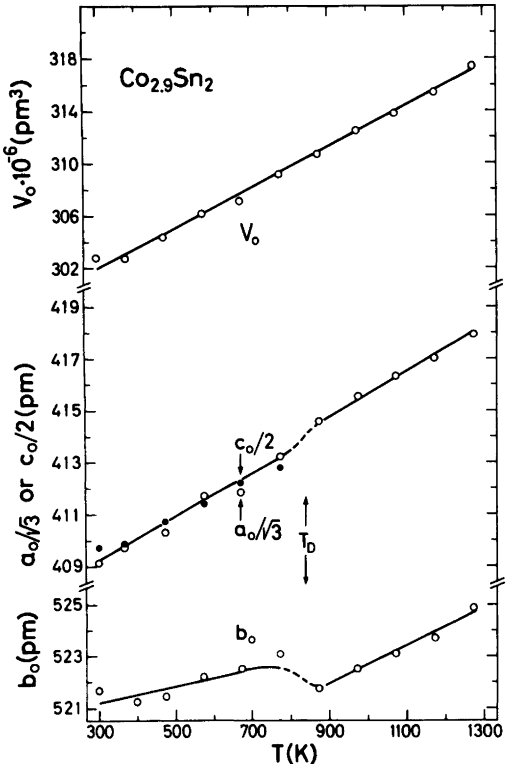
(A) The external proportions of the orthorhombic unit cell must through continuous changes obtain orthohexagonal shape at the transformation

Fig. 3. Unit cell dimensions *versus* temperature for (a) $Ni_{2.9}Sn_2$, (b) $Ni_{3.0}Sn_2$, (c) $Ni_{3.2}Sn_2$ and (d) $Co_{2.9}Sn_2$ between 300 and 1300 K. *Calculated* error limits do not exceed the size of symbol.


Ni2.9Sn2
V0·10-6(pm3)
V0
a0/√3 or c0/2 (pm)
a0/√3
c0/2
b0(pm)
b0
T(K)


Ni3.0Sn2
V0·10-6(pm3)
V0
a0/√3 or c0/2 (pm)
a0/√3
c0/2
b0(pm)
b0
T(K)


Ni3.2Sn2
4VH·10-6(pm3)
4VH
aH(pm)
aH
cH(pm)
cH
T(K)


Co2.9Sn2
V0·10-6(pm3)
V0
a0/√3 or c0/2(pm)
c0/2
a0/√3
TD
b0(pm)
b0
T(K)

temperature (T_D) or composition (t_D). In terms of $2a_O/c_O$ as indicator this implies that the ratio must take the value $\sqrt{3}$ at T_D or t_D. [$2a_O/c_O = \sqrt{3}$ is an insufficient condition for hexagonal symmetry. The real hexagonal structure demands in this case that some of the reflections characteristic of the orthorhombic structure are extinguished in the former.]

(B) The interior atomic rearrangement process must proceed gradually. The displacements of the atoms from their ideal orthohexagonal positions (*cf.* Table 1 and Fig. 2) must be continuously reduced to zero at T_D or t_D.

(C) The disordering of the T_{II} atoms (*vide supra*) must take place continuously and be completed at T_D or t_D. [Note that full parallelism between (B) and (C) is not required, but both processes have to be completed at T_D or t_D.]

In order to examine the structural transformation processes as a function of temperature, high temperature powder X-ray data were collected for various samples of the Co_3Sn_2 and Ni_3Sn_2 phases. The results show unequivocally that the reflections which are characteristic of the Ni_3Sn_2 type structure are retained right up to T_D (determined independently by DSC). Moreover, there are only minor intensity variations in the X-ray diffraction patterns between room temperature and T_D. (It may be worth emphasizing that this also applies to reflections which become extinguished for the NiAs–Ni_2In type atomic arrangement above T_D.) The inference is accordingly that the Ni_3Sn_2 to NiAs–Ni_2In type transitions in the Ni_3Sn_2 and (probably) Co_3Sn_2 phases are of first order and it appears that none of the above requirements (A)–(C) for a continuous process are met for these transformations. The typical thermal expansion curves for $Ni_{2.9}Sn_2$ and $Ni_{3.0}Sn_2$ shown in Fig. 3a, b also clearly bring out the first order character of the Ni_3Sn_2 to NiAs–Ni_2In type transition. This feature is masked for $Co_{2.9}Sn_2$

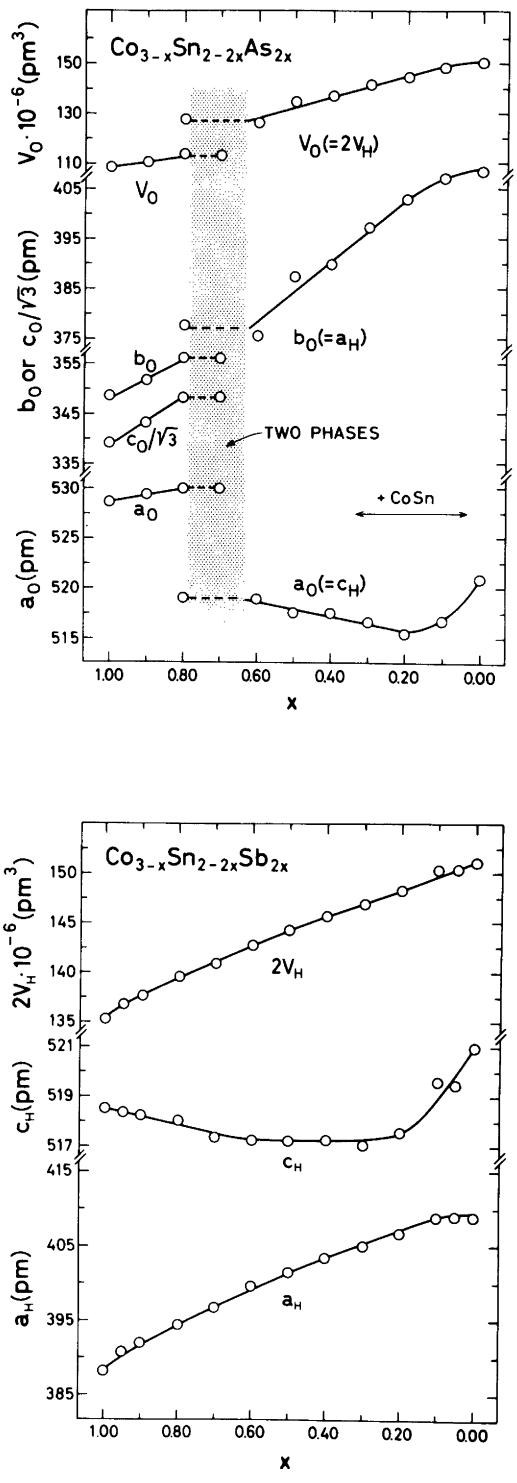


Fig. 4. Unit cell dimensions *versus* the compositional parameter x for (a) $Co_{3-x}Sn_{2-2x}As_{2x}$ and (b) $Co_{3-x}Sn_{2-2x}Sb_{2x}$. *Calculated* error limits do not exceed the size of symbols. CoSn is observed as an impurity phase for $0.10 < x < 0.30$ of $Co_{3-x}Sn_{2-2x}As_{2x}$. The index O in (a) refers to an MnP type unit cell.

(Fig. 3d) due to its axial relation $a_O/\sqrt{3} \approx c_O/2$. The thermal expansion curves for (hexagonal) $Ni_{3.2}Sn_2$ (Fig. 3c) are included for comparison. T_D for the Ni_3Sn_2 phase varies only little with the composition ($\Delta T_D \approx 50$ K) and goes through a broad maximum at $T_D = 750 \pm 10$ K for $Ni_{2.9}Sn_2$–$Ni_{3.0}Sn_2$ ($T_D = 840 \pm 10$ K being obtained for $Co_{2.9}Sn_2$).

(ii) On the systems Co_3Sn_2–CoAs and Co_3Sn_2–CoSb

In order to gain some insight into solid solution systems where the end phases take different structure types and compositions, the systems Co_3Sn_2–CoAs and Co_3Sn_2–CoSb were examined. (CoAs and CoSb take,[19,20] respectively, the MnP and NiAs type structures at room temperature.) To arrive at rational formulae for these phases, the non-metal sublattices for the end phases should be used as the common reference. On this basis one obtains the formulae $Co_{3-x}Sn_{2-2x}As_{2x}$ [$\equiv (Co_3Sn_2)_{1-x}(Co_2As_2)_x$] and $Co_{3-x}Sn_{2-2x}Sb_{2x}$. No attempts have been made to vary the composition at the Co_3Sn_2 end phase in these series. The stability ranges of the different structure types in terms of the compositional parameter x are shown in Fig. 4 together with the unit cell dimensions *versus* composition relationships.

Complete miscibility is found for the Co_3Sn_2–CoSb system (Fig. 4b), and all reflections on the X-ray diffraction diagrams can be accounted for as due to an NiAs–Ni_2In type structure. This implies that a gradual emptying of the trigonal bipyramidal sites takes place as x increases from 0.00 to 1.00. The Ni_3Sn_2 type ordering within the trigonal bipyramidal sublattice (*vide supra*) is only observed for $0.00 \leqq x \leqq 0.10$ (*viz.* close to Co_3Sn_2).

In the Co_3Sn_2–CoAs system there is a two phase region for $0.61 \pm 0.05 \leqq x \leqq 0.82 \pm 0.05$ (Fig. 4a) which separates the domains ruled by the NiAs–Ni_2In and MnP type structures. The fact that the systems CoSb–CoAs[11] and NiAs–CoAs[11] also exhibit two phase regions show that the miscibility gaps in the three systems do not have a common simple origin like atomic size, interstitial atoms, valence electron concentration *etc.*

The MnP type structure has hitherto only been unequivocally associated with phases which have a $T:X$ atomic ratio 1 : 1. However, for $x = 0.80$ of $Co_{3-x}Sn_{2-2x}As_{2x}$ the 10 % extra Co atoms (relative to the $T:X$ atomic ratio 1 : 1) are assumed to be accommodated in interstitial positions. There is only a slight increase in c_O/b_O from 1.682 for $x = 1.00$ (CoAs) to 1.695 for $x = 0.80$. This may indicate that there is a corresponding slight decrease in the MnP to NiAs type transition temperature when Co_3Sn_2 is substituted into CoAs ($T_D = 1248 \pm 20$ K[17]).

Within the domain of the NiAs–Ni_2In type phase there is a range ($0.10 < x < 0.30$) where the X-ray diffraction photographs demonstrate that small amounts of CoSn are present in the samples. It proved impossible to get rid of this impurity by repeated annealings, prolonged annealing periods, slow cooling or rapid quenching. No attempts have been made to correct the unit cell dimension *versus* composition relationships in Fig. 4a for this slight deficiency.

The structural data for the $Co_{3-x}Sn_{2-2x}As_{2x}$ and $Co_{3-x}Sn_{2-2x}Sb_{2x}$ phases comply with the valence electron concentration and atomic size considerations of Ellner.[9]

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