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On the Structural and Magnetic Properties of $Co_{1-t}Ni_tAs$ and $CoAs_{1-x}Sb_x$

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The pseudo-binary CoAs–NiAs and CoAs–CoSb systems have been investigated by X-ray and neutron diffraction and magnetic susceptibility measurements. Both systems are characterized at room temperature by a very narrow miscibility gap around the compositions $Co_{0.88\pm0.02}Ni_{0.12\mp0.02}As$ and $CoAs_{0.92\pm0.02}Sb_{0.08\mp0.02}$, respectively. The compositions of the miscibility gaps are almost temperature independent. The CoAs-rich phases crystallize with MnP type structure at and below room temperature. Upon heating they transform to the NiAs type structure *via* a first order phase transition. For NiAs- and CoSb-richer samples the NiAs type structure prevails at all temperatures. All samples in the two systems show rather weak, almost temperature independent paramagnetism.

Transitions between MnP and NiAs type structures as a function of composition in pseudo-binary *T*As–NiAs and *T*As–*T*Sb systems (*T*: 3*d*-metal) have been observed earlier.[1–5] The aim of the present communication is to contribute to a more complete experimental knowledge on the phase relations in such systems.

EXPERIMENTAL

Samples were made from 99.998 % Co (Koch-Light Laboratories, turnings from rods), 99.998 % Ni (Johnson, Matthey & Co., turnings from rods), 99.9999 % As (Koch-Light Laboratories), and 99.9995 % Sb (Johnson, Matthey & Co.). CoAs and NiAs were made as described in Refs. 1 and 6, respectively. CoSb was prepared by heating equi-atomic quantities of Co and Sb at 1100 °C for 1 h followed by quenching to room temperature. Ternary samples were made from the binary compounds by 2–3 heat treatments at 900–950 °C for one week, followed by slow cooling to 600 °C and then quenching to room temperature.

Details of the experimental methods (powder X-ray and neutron diffraction, DTA, and magnetic susceptibility measurements) have been presented in earlier communications.[7,8] Nuclear scattering lengths were taken from Ref. 9.

RESULTS AND DISCUSSION

(i) Homogeneity ranges and atomic arrangements at room temperature. The room temperature unit cell dimensions of $Co_{1-t}Ni_tAs$ and $CoAs_{1-x}Sb_x$ as functions of the compositional parameters t or x are shown i Fig. 1a and 1b. The figures indicate that both ternary systems consist of two distinct solid solution phases separated by a very narrow two-phase region (within the composition limits $t=0.12\pm0.02$ and $x=0.08\pm0.02$ for $Co_{1-t}Ni_tAs$ and $CoAs_{1-x}Sb_x$, respectively).

The X-ray (Guinier) data show that the orthorhombic MnP type crystal structure prevails for the CoAs-rich solid solution phases (*i.e.* low values for t and x). The CoSb- and NiAs-rich solid solution phases take the hexagonal NiAs type crystal structure. The unit cell dimensions (orthohexagonal setting for NiAs type phases[10]) at the two ends of the miscibility gaps differ significantly for both systems, indicating that complete solid solubility can hardly be obtained even with a different preparational technique. Thus, the change from MnP to NiAs type

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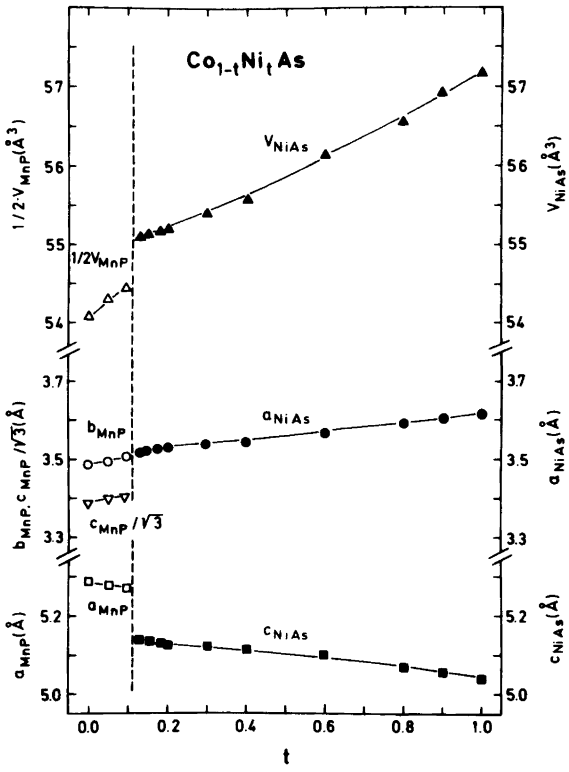

Fig. 1a. Room temperature unit cell dimensions of $Co_{1-t}Ni_tAs$ as functions of t.

structure with composition is a discontinuous process. This is consistent with the observation that no significant change in the axial ratio c/b (=1.682 for CoAs[10]) is found when going from pure CoAs to the composition limits of the MnP type phases. In the solid solution regions with NiAs type structure the unit cell dimensions vary almost linearly with t and x. The results obtained for $Co_{1-t}Ni_tAs$ are in good agreement with results reported by Heyding and Calvert.[2]

The samples $Co_{0.90}Ni_{0.10}As$, $Co_{0.85}Ni_{0.15}As$, $CoAs_{0.95}Sb_{0.05}$ and $CoAs_{0.90}Sb_{0.10}$, all with compositions very close to the phase limits, were examined by powder neutron diffraction. The variable positional parameters for the samples with MnP type structure ($Co_{0.90}Ni_{0.10}As$ and $CoAs_{0.95}Sb_{0.05}$) were refined by Rietveld analysis of the powder diffraction data, and the results at 293 K are given in Table 1. The corresponding values for CoAs[6] are not significantly different from the values in this table. For $Co_{0.85}Ni_{0.15}As$ and $CoAs_{0.90}Sb_{0.10}$ the NiAs type structure was confirmed. The Co and Ni atoms (and correspondingly As and Sb atoms) are randomly distributed over the metal (non-metal) sublattice for all the samples studied.

(ii) Low and high temperature results. Diffraction experiments were performed below and above room temperature in order to estimate the variation of the phase limits with temperature, and also to search for temperature induced structural phase transitions.

A number of binary and ternary compounds with MnP type structure at low temperatures, among these CoAs, are reported to transform by a second order phase transition (at T_D) to the NiAs type structure upon heating (*cf., e.g.*, Ref. 10). For CoAs T_D is reported to be 1250±20 K.[10] Similar behaviour is observed for CoAs-rich $Co_{1-t}T_tAs$ phases (T=Cr, Mn, Fe).[11,12] Hence, high temperature (Guinier-Simon) X-ray data were collected for selected $Co_{1-t}Ni_tAs$ and

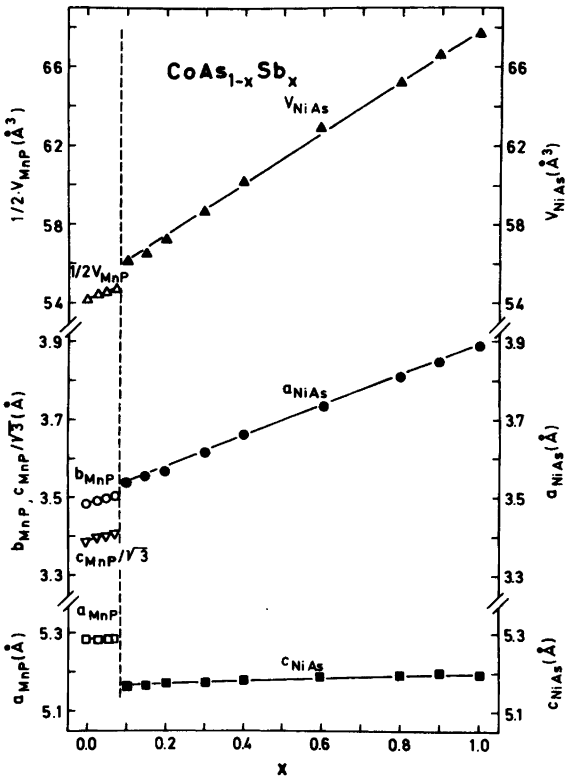

Fig. 1b. Room temperature unit cell dimensions of $CoAs_{1-x}Sb_x$ as functions of x.

$CoAs_{1-x}Sb_x$ samples. For $Co_{0.95}Ni_{0.05}As$ and $Co_{0.90}Ni_{0.10}As$ the phase transition was registered at 1210±20 K and 1040±20K, respectively. Similarly, T_D for $CoAs_{0.97}Sb_{0.03}$ is 1170±20 K and for $CoAs_{0.95}Sb_{0.05}$ 1150±20 K. The reported transition temperature for CoAs was confirmed. Thus, both Ni substitution for Co and Sb substitution for As lead to a slow, gradual descrease in T_D until the phase limits are reached.

The variation in unit cell dimensions with temperature for $Co_{0.90}Ni_{0.10}As$ is shown in Fig. 2. This figure is representative for all the high temperature data. A characteristic feature of the figure is the change in the sign of the thermal expansion coefficient of a_{MnP} around T_D. Also a discontinuous change is observed at T_D for some of the unit cell parameters. The axial ratio c/b which for CoAs-rich MnP type phases is smaller than the orthohexagonal value of $\sqrt{3}$,[10] increases slowly with the temperature, but does not continuously approach $\sqrt{3}$. The phase transition is hence assumed to be of the first order, which

Table 1. Positional parameters with standard deviations for $Co_{0.90}Ni_{0.10}As$ and $CoAs_{0.95}Sb_{0.05}$ at 293 K (space group *Pnma*, positions 4(*c*)).

	Metal atoms		Non-metal atoms	
	x	*z*	*x*	*z*
$Co_{0.90}Ni_{0.10}As$	0.0111(3)	0.2049(8)	0.2117(3)	0.5700(8)
$CoAs_{0.95}Sb_{0.05}$	0.0051(1)	0.2009(3)	0.2026(4)	0.5849(5)

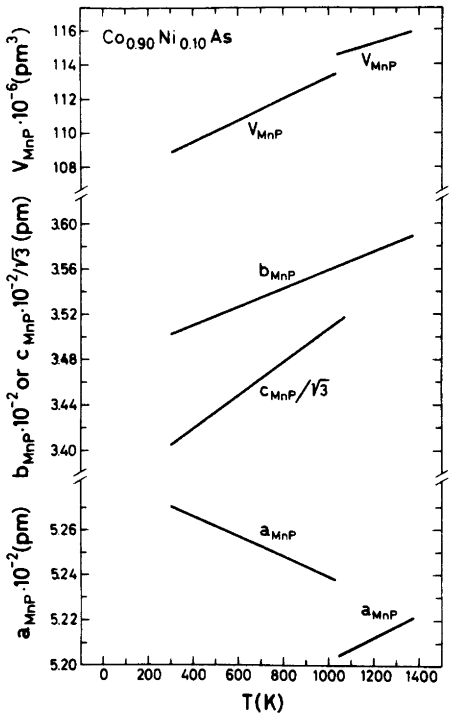

Fig. 2. Unit cell dimensions of $Co_{0.90}Ni_{0.10}As$ as functions of temperature (orthohexagonal setting for the NiAs type phase).

contrasts the earlier picture for CoAs.[10,11]

The transition temperatures observed by X-ray diffraction are reflected in the DTA measurements. Peaks in the DTA curves around T_D for all samples are consistent with first order transitions. In other systems showing transition from MnP to NiAs type structure (*e.g.* MnAs- or CrAs-rich phases[1,11-13]) the phase transitions certainly are of second (or higher) order. The different character of the transition in CoAs and CoAs-rich samples relative to other MnP type phases cannot be explained by the present measurements. The possibility that the high temperature and low temperature phases have different composition (*i.e.* the NiAs type phase not being stoichiometric in contrast to the MnP type phase) should not be ruled out. However, there is no experimental evidence for a deviation from stoichiometric metal/non-metal ratio for the hexagonal phases of $Co_{1-t}Ni_tAs$ and $CoAs_{1-x}Sb_x$ at room temperature.

$Co_{0.85}Ni_{0.15}As$ and $CoAs_{0.90}Sb_{0.10}$, which take the NiAs type structure at room temperature, were studied by powder neutron diffraction at 10 K. No indications of the existence of two phases nor of a structural change were found. Thus, it is reasonable to assume that samples of $Co_{1-t}Ni_tAs$ with $t \geqq 0.15$ and $CoAs_{1-x}Sb_x$ with $x \geqq 0.10$ take the NiAs type structure at all temperatures.

iii) Magnetic properties. Magnetic susceptibility measurements were performed for samples of $Co_{1-t}Ni_tAs$ and $CoAs_{1-x}Sb_x$ at temperatures between 80 and 1000 K. For all samples the measured susceptibilities were positive with χ varying between $\sim 1 \cdot 10^{-5}$ and $\sim 5 \cdot 10^{-7}$ e.m.u./g for different samples and different temperatures. Only a slight temperature dependence of χ was found. For $Co_{1-t}Ni_tAs$ samples χ generally increases with increasing temperature, whereas for $CoAs_{1-x}Sb_x$ χ generally decreases. None of the curves for the ternary phases reflect the Curie-Weiss Law. The results obtained for CoAs are in accordance with the results of Selte and Kjekshus.[6] However, the results for NiAs are not in accordance with the data published by Delphin *et al.*[1] The discrepancy between the two measurements may be caused by slight differences in the composition of the NiAs samples. The present (reproducible) measurements for NiAs give $\chi = 1.7 \cdot 10^{-6}$ e.m.u./g at 80 K decreasing gradually to $1.0 \cdot 10^{-6}$ at 400 K and a rather constant $\chi = 0.9 \cdot 10^{-6}$ e.m.u./g above 600 K.

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