Structural and Magnetic Properties of Cr$_{1-t}$Ni$_t$As,
Mn$_{1-t}$Ni$_t$As, and Fe$_{1-t}$Ni$_t$As

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The pseudo-binary systems CrAs—NiAs, MnAs—NiAs, and FeAs—NiAs have been investigated by
X-ray and neutron diffraction and magnetic susceptibility measurements. All systems are characterized
by incomplete solid solubility. The structures of the ternary, random solid solution phases are either of
the MnP or NiAs type. The double, c axis helimagnetic ordering in CrAs extends slightly into the
ternary region (to 0.02 < t < 0.05) of Cr$_{1-t}$Ni$_t$As. Mn$_{0.95}$Ni$_{0.05}$As takes the double, a axis helimagnetic
ordering characteristic of other Mn rich Mn$_{1-t}$T$_t$As phases (T: V, Cr, Fe, Co).

The authors have earlier studied pseudo-binary
TAs — T'As (T, T': V, Cr, Mn, Fe, Co) system where
TAs and T'As both take the MnP type structure. In
the present paper we report the results of similar
studies on systems where T'As = NiAs has the
closely related NiAs type structure.

EXPERIMENTAL

The binary compounds CrAs, MnAs, and FeAs
were prepared as described in Refs. 3—5, and NiAs
[from 99.999 % Ni (Johnson, Matthey & Co.;
turnings from rods) and As (Koch-Light Laboratories)] by three heat treatments at 900 °C for one
week. Ternary T$_{1-t}$Ni$_t$As samples were made similarly from the binary compounds, and finally
either quenched (from 600—1000 °C) or slowly
cooled to room temperature. It proved difficult to
obtain thermodynamic equilibrium for Mn$_{1-t}$Ni$_t$As,
particularly in the region 0.6 < t < 0.8. The experi-
mental details concerning the X-ray and neutron
diffraction and magnetic susceptibility measure-
ments have been reported earlier.

RESULTS AND DISCUSSION

(i) Homogeneity ranges and atomic arrangements.
Isothermal cross-sections of Cr$_{1-t}$Ni$_t$As,
Mn$_{1-t}$Ni$_t$As, and Fe$_{1-t}$Ni$_t$As as derived for samples
quenched from 600 °C, show that the three systems
exhibit two-phase miscibility gaps for 0.50 ± 0.03 <
t < 0.68 ± 0.03, 0.07 ± 0.03 < t < 0.30 ± 0.05, 0.40 ±
0.05 < t < 0.60 ± 0.05, respectively. The limits of
the solubility ranges have been determined from the
variation in the unit cell dimensions with t (Fig. 1),
and further confirmed by application of the disap-
ppearing phase principle to the X-ray (Guinier) data.
From the variation of the unit cell dimensions
(particularly the volume V) with t it may be suggested
that complete miscibility can be obtained for
Cr$_{1-t}$Ni$_t$As and Mn$_{1-t}$Ni$_t$As at suitable experi-
mental conditions, whereas such a situation is not
expected for Fe$_{1-t}$Ni$_t$As. Samples with metal/non-
metal atomic ratios different from 1.00 have not
been studied.

Fig. 1a,c shows that the MnP type structure prevails at room temperature in the Cr and Fe rich
phases of Cr$_{1-t}$Ni$_t$As and Fe$_{1-t}$Ni$_t$As, whereas the
NiAs type is stable in the Ni rich phases. At room
temperature, Mn$_{1-t}$Ni$_t$As takes the NiAs type
structure in the Ni rich phase and in a narrow
region near MnAs. Throughout the rest of the Mn
rich phase the MnP type structure prevails (Fig. 1b).
A second or higher order MnP = NiAs type transition
is detected by high temperature, X-ray diffraction
measurements in Cr$_{1-t}$Ni$_t$As and Fe$_{1-t}$Ni$_t$As
(Fig. 2). The transformation in Mn$_{0.95}$Ni$_{0.05}$As is
more difficult to detect, but magnetic susceptibility
data (not presented here) suggest that it takes place
Fig. 1. Room temperature unit cell dimensions of (a) Cr$_{1-x}$Ni$_x$As, (b) Mn$_{1-x}$Ni$_x$As, and (c) Fe$_{1-x}$Ni$_x$As as functions of $t$. Open and filled symbols refer to NiAs and MnP type structures, respectively, both described in terms of space group $Pnma$.

Fig. 2. Unit cell dimensions of (a) Cr_{0.90}Ni_{0.10}As, (b) Cr_{0.70}Ni_{0.30}As, (c) Fe_{0.80}Ni_{0.20}As, (d) Fe_{0.60}Ni_{0.40}As as functions of temperature.
Table 1. Unit cell dimensions and positional parameters with standard deviations for selected \( T_{1-}\text{NiAs} \) samples as derived by least squares profile refinements of neutron diffraction data. (Space group \( Pnma \); positions 4(c); overall profile reliability factors ranging between 0.021 and 0.038.)

<table>
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<th>( T )</th>
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<th>( T(K) )</th>
<th>( a(\text{Å}) )</th>
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just above room temperature. The two kinds of metal atoms are randomly distributed over the metal sub-lattices in the two types of atomic arrangement. The cell dimensions and positional parameters at and below room temperature for \( Cr_{0.98}Ni_{0.02}\text{As}, Cr_{0.95}Ni_{0.05}\text{As}, Cr_{0.90}Ni_{0.10}\text{As}, \) and \( Mn_{0.95}Ni_{0.05}\text{As} \) are listed in Table 1.

Among the quasi-binary MnAs—TAs systems those with \( T=V \) or Cr exhibit complete miscibility, whereas a two-phase region is found in the systems with \( T=Fe, Co \), or Ni. Since MnAs takes the NiAs type structure (except between \( ~50 \) and \( 120 \) °C), and VAs, CrAs, FeAs, and CoAs take the MnP type, a structural change must occur in MnAs—TAs with \( T=V, Cr, Fe, \) or Co. The miscibility gaps in MnAs—FeAs and MnAs—CoAs are directly associated with the structural change, and are therefore not unexpected. Similar considerations apply to the incomplete solid solubility in CrAs—NiAs and FeAs—NiAs. As MnAs and NiAs both take the same structure type, the change to the MnP type structure in MnAs—NiAs is, at first sight, surprising. However, the finding is less surprising when it is recalled that application of hydrostatic pressure or chemical substitution of either Mn with V, Cr, Fe, or Co, or As with P induce corresponding structural changes. Without taking up the question of cause and origin, it should be noted that both the application of pressure and chemical substitution lead to a reduction in the unit cell volume.

(ii) Magnetic susceptibility. The temperature characteristics of the reciprocal magnetic susceptibility show systematic variations with the composition parameter \( t \) for \( Cr_{1-}\text{NiAs} \) and \( Mn_{1-}\text{NiAs} \) (Fig. 3). The \( Fe_{1-}\text{NiAs} \) samples were contaminated by traces of ferromagnetic impurities, and the data for this system are not included here.

None of the \( \chi^{-1}(T) \) curves for \( Cr_{1-}\text{NiAs} \) (data for the two-phase sample with \( t=0.60 \) and the borderline sample with \( t=0.50 \) are included among the proper characteristics) follows the Curie-Weiss Law. For \( Mn_{1-}\text{NiAs} \) the one-phase samples with \( t=0.05, 0.30, \) and \( 0.40 \) show linear \( \chi^{-1}(T) \) curves to a very good approximation over the measured temperature intervals (Fig. 3). The values for \( \theta \) (paramagnetic Curie temperature in K), \( \mu_p \) (paramagnetic moment in \( \mu_B \)), \( 2S \) ("spin only" spin quantum number) for these samples are 270, 45, 3.6; 270, 4.4, 3.5; 210, 3.2, 2.4; and 160, 2.9, 2.1 (uncertainties 10, 0.3, 0.2) for \( t=0.05, 0.30, \) and 0.40, respectively. The \( \chi^{-1}(T) \) curves for \( 0.50 \leq t \leq 0.95 \) become gradually more convex towards the temperature axis. However, even for \( t=0.80 \) the Curie-Weiss Law represents a useful approximation below \( ~600 \) K, leading to \( \theta=75 \pm 10 \) K, \( \mu_p=1.7 \pm 0.2 \mu_B \), and \( 2S=1.0 \pm 0.2 \).

(iii) Magnetic structures. NiAs is the only binary end member of the investigated systems which does not exhibit cooperative magnetism at low temperature.\(^6\) CrAs and FeAs both take helimagnetic arrangements of the double, \( c \) axis type below \( ~260-270 \) and \( 77 \pm 1 \) K,\(^3,4\) whereas MnAs is ferromagnetic below \( ~310-320 \) K.\(^7\) Since the cooperative magnetic states of FeAs\(^4\) and Fe\(_{1-}\text{CoAs}^8\) were difficult
Fig. 3. Reciprocal magnetic susceptibility versus temperature for (a) $\text{Cr}_{1-x}\text{Ni}_x\text{As}$ and (b) $\text{Mn}_{1-x}\text{Ni}_x\text{As}$. Data for $\text{Cr}_{0.40}\text{Ni}_{0.60}\text{As}$, $\text{Mn}_{0.90}\text{Ni}_{0.10}\text{As}$, and $\text{Mn}_{0.80}\text{Ni}_{0.20}\text{As}$ refer to two-phase samples.

to explore due to their low moments, Fe$_{1-x}$Ni$_x$As samples were not subjected to neutron diffraction examination.

The helimagnetic ordering in CrAs extends only slightly into the ternary composition range (to 0.02 < $t < 0.05$) of Cr$_{1-x}$Ni$_x$As. Comparatively small changes were observed in the variable parameters (angle between moment and spiral axis, $\beta$, fixed at 90°) on going from CrAs [80 K: $\mu$ = 1.70(5), $\mu_B$, $\tau/2\pi c^* = 0.353(1)$ (spiral propagation vector), $\phi = -133(1)^\circ$ (phase angle between independent spirals)]$^3$ to Cr$_{0.98}$Ni$_{0.02}$As (10 K: $\mu = 1.73(5)$, $\mu_B$, $\tau/2\pi c^*$ = 0.357(6), $\phi = -118(1)^\circ$; 80 K: $\mu = 1.68(5)$, $\mu_B$, $\tau/2\pi c^*$ = 0.351(7), $\phi = -126(1)^\circ$). However, the 2% substitution of CrAs by NiAs has led to an appreciable lowering of the Néel temperature ($T_N$) from $\sim 260 - 270$ to 170 - 208 K ($\pm 2$ K). Significant indications of reflections characteristic of the helimagnetic arrangement were not found for $t = 0.05$ and 0.10. The transition to the cooperative magnetic state in Cr$_{0.98}$Ni$_{0.02}$As is associated with hysteresis and involves two distinct MnP type phases. Thus, Cr$_{0.98}$Ni$_{0.02}$As fits nicely into the pattern of CrAs$^3$ and CrAs rich samples of V$_1-x$Cr$_x$As$^9$, Cr$_{1-x}$,Mn$_x$As$^{10}$, Cr$_{1-x}$Fe$_x$As$^{11}$, Cr$_{1-x}$Co$_x$As$^8$ and CrP$_{1-x}$As$_x$. The spiral parameters $\phi$ and $\tau$ vary little with temperature and composition for all these phases. In fact, the only magnetic parameter which changes rapidly is $T_N$, thus confirming our earlier suggestion$^8$ that the breakdown of the cooperative magnetism in Cr$_{1-x}$Ta$_x$As and CrP$_{1-x}$As$_x$ is associated with corresponding, rapid variations in the magnetic exchange interactions with $t$ or $x$.

The hystereses in structural and cooperative magnetic parameters around $T_N$ show that the transition in Cr$_{0.98}$Ni$_{0.02}$As is of a combined first and second (or higher) order. [To denote this type of quasi-reversible crystallographic and magnetic transition we suggest the abbreviation MnP(I), $H \rightarrow$ MnP(II), $P$.] The transition has been most extensively studied for CrAs itself, for which it has been demonstrated that changes in unit cell dimensions, positional parameters, sub-lattice magnetizations, specific heat, and electrical resistivity are associated with the transition, whereas no significant changes hitherto have been detected for magnetic susceptibility, Hall coefficient and thermoelectric power. Despite the distinct changes in unit cell dimensions and positional parameters at the MnP(II), $P \rightarrow$ MnP(I), $H$ transition, it is difficult to detect a clear-cut pattern for the variation of the bonding interatomic distances in the systems studied. The only systematic trend we have found so far is that the shortest metal—metal contact shrinks 1 – 2% during the transition. No such shrinkage has been observed for samples lacking this cooperative magnetic behaviour, but with almost the same substitution of VAs, CoAs, and NiAs for CrAs. The origin of the quasi-reversible MnP(I), $H \rightleftharpoons$ MnP(II), $P$ transition of CrAs is virtually unknown. Boile and Kalles$^{13}$ have suggested that the first order contribution is due to an electronic transition between localized and collective states. Although this interpretation appeared to be satisfactory in view of the structural data provided by these authors, it seems less likely on the basis of the structural data given here and in Refs. 3, 8, and 9.

The cooperative magnetic state of the Mn rich Mn$_{1-x}$Ni$_x$As phase follows the pattern found in other Mn rich Mn$_{1-x}$Ta$_x$As phases (T: V, Cr, Fe, Co) by associating a ferromagnetic mode with the low temperature, NiAs type structure and a double, a axis helimagnetic mode with the MnP type structure. Although the NiAs,F state (0 $\leq t < 0.05$) has not been experimentally studied for Mn$_{1-x}$Ni$_x$As, experience$^7,17$ suggests that its magnetic parameters differ only insignificantly from those of MnAs itself.

At $T_N =$ 202 $\pm$ 3 K Mn$_{0.95}$Ni$_{0.05}$As undergoes a second (or higher) order MnP,$P \rightleftharpoons$ MnP,$H$ type transition, and below this temperature it takes a similar helimagnetic arrangement to that in Mn$_{1-x}$V$_x$As (0.05 $\leq t \leq 0.40$),$^{14}$ Mn$_{1-x}$Ta$_x$As (0.10 $\leq t \leq 0.35$),$^{15}$ Mn$_{1-x}$Fe$_x$As (0.01 $\leq t \leq 0.12$),$^{5,18}$ and Mn$_{1-x}$Co$_x$As (0.05 $\leq t \leq 0.15$).$^{15}$ The parameters specifying the magnetic structure are: $\mu = 1.6(1)$, $\mu_B$, $\tau = 0.155(3) \times 2\pi a^*$, $\phi = 92(2)^\circ$ at 10 K and $\mu = 1.6(1)$, $\mu_B$, $\tau = 0.155(3) \times 2\pi a^*$, $\phi = 98(2)^\circ$ at 80 K ($\beta = 90^\circ$; fixed). The constraint $\beta = 90^\circ$ was relaxed in the preliminary refinements since the magnetic susceptibility measurements had given indication of a ferromagnetic component in Mn$_{0.95}$Ni$_{0.05}$As. However, by far the best agreement between the observed and calculated intensity data was found for $\beta = 90^\circ$.

The spiral parameters and $T_N$ for Mn$_{0.95}$Ni$_{0.05}$As fit in with corresponding data for the other Mn$_{1-x}$Ta$_x$As phases. The temperature dependence of the relative (integrated) intensity for the strongest satellites 000± and 001± (Fig. 4) also show marked similarities with corresponding observations for the other Mn$_{1-x}$Ta$_x$As phases, and the spiral parameters of Mn$_{0.95}$Ni$_{0.05}$As vary with temperature as found.
Fig. 4. Relative intensities of satellite reflections 000 and 001 as functions of temperature for Mn$_{0.95}$Ni$_{0.05}$As.

earlier. Probably, the chemical and magnetic phase boundary of Mn$_1$Ni$_x$As coincide at $t = 0.07$ ± 0.03. Thus, among the Mn$_1$-$T_x$ phases, the MnP$_x$H state of Mn$_1$-$T_x$Ni$_x$As is characterized by the narrowest compositional stability range. For further discussions on the cooperative magnetic and associated transformational properties of MnAs and Mn$_1$-$T_x$As reference is made to earlier communications.

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REFERENCES


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