

## Structural and Magnetic Properties of $Mn_{1-t}Mo_tAs$

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The ternary MnAs–MoAs system has been investigated by X-ray and neutron diffraction and magnetic susceptibility measurements. Two regions of solid solution for  $Mn_{1-t}Mo_tAs$  were found, separated by a two-phase range for  $0.12 \pm 0.02 < t < 0.35 \pm 0.05$ . For  $t \leq 0.12 \pm 0.02$  the crystal structure is of the MnP type at and below room temperature except for a small range close to MnAs ( $t \sim 0.01$ ). At elevated temperatures a second order phase transition to the NiAs type structure was observed. The magnetic susceptibility follows the Curie-Weiss Law in the high temperature, NiAs type region. A helimagnetic spin structure of the  $H_a$  type appears at low temperatures. For  $0.35 \pm 0.05 \leq t < \sim 0.90$  another solid solution range with MnP type structure is found. No structural phase transition occurs at high temperatures. The Curie-Weiss Law is approximately fulfilled. For  $t > 0.90$  it was not possible to obtain single-phase samples.

The ternary systems  $Mn_{1-t}T_tAs$  ( $T=3d$  element) have been extensively studied during recent years.<sup>1–6</sup> The main purpose has been to see the effect of substitution on the magnetic and crystallographic properties of MnAs. MnAs is a ferromagnet with NiAs type structure at room temperature. However, MnAs transforms *via* a first order transition to a paramagnetic phase with MnP type structure at  $T_{C,h}=317$  K.<sup>7</sup> At an even higher temperature,  $T_D=393$  K, a second order phase transition back to the NiAs type structure occurs. By applying hydrostatic pressure on MnAs, the orthorhombic MnP type structure is retained down to 4.2 K.<sup>8</sup> This phase shows helimagnetic long range order.<sup>9</sup> In ternary systems of the types  $Mn_{1-t}T_tAs$  or  $MnAs_{1-x}X_x$  many of the characteristic features of MnAs are retained. However, the structural and magnetic

properties depend to some extent on the actual element  $T$  or  $X$ . The “size” of the substituting element seems to be an important factor in stabilizing the NiAs type or the MnP type structure for the ternary phases.

Only sparse information exists on  $Mn_{1-t}T_tAs$  phases where  $T$  is a  $4d$  or  $5d$  element. Guérin *et al.*<sup>10</sup> report partial solubility in the MnAs–MoAs ternary system. For phases with  $t < \sim 0.10$  they report the crystallographic space group to be  $C222_1$ . Further, they were not able to prepare single phase samples with  $t > \sim 0.90$ .

The present communication on  $Mn_{1-t}Mo_tAs$  includes some information on  $Mn_{1-t}W_tAs$ .

### EXPERIMENTAL

As starting materials for the preparation of ternary samples batches with nominal compositions MnAs, MoAs and WAs were prepared. MnAs was prepared as described in Ref. 1. The “MoAs” batch was synthesized by heating weighed amounts of Mo (powder, 99.99%, Koch-Light Laboratories) and As (lumps, 99.999%, Koch-Light Laboratories) in evacuated, sealed silica tubes. The temperature was increased  $3 \times 50$  °C/day up to 950 °C. After annealing for 7 d the sample was cooled to room temperature over 1 d. “WAs” was made similarly from W (powder, 99.99%, Koch-Light Laboratories) and As. A stoichiometric MoAs phase has been reported,<sup>11</sup> but, like Guérin *et al.*,<sup>10</sup> we were not successful in preparing it. The syntheses always resulted in two-phase samples of  $Mo_5As_4$  and  $Mo_2As_3$ . Neither was tin or lead flux (1300 K for 10 days, quenching from 1050 K) favourable for the preparation of MoAs. No 1:1 phase has been reported for the W–As binary system.

Powder X-ray photographs were obtained at room temperature with a Guinier camera

( $\text{CuK}\alpha_1$ -radiation, Si as internal standard). High- and low-temperature powder X-ray diffraction was performed with a Guinier-Simon camera between 100 and 900 K. Debye-Scherrer photographs were obtained between 293 and 1273 K. Magnetic susceptibility was registered with conventional equipment based on the Faraday method at temperatures between 80 and 1000 K.

Powder neutron diffraction data were collected with the OPUS II spectrometer accommodated at the JEEP II reactor, Kjeller. Neutrons of wavelength 187.7 pm were used. The scattering lengths were taken from Ref. 12. The magnetic form factor for  $\text{Mn}^{2+}$  was chosen.<sup>13</sup> The Hewat version<sup>14</sup> of the Rietveld programme<sup>15</sup> was used in the profile refinements of the powder data.

## RESULTS AND DISCUSSION

(i) *Crystal structure.* The variations in unit cell dimensions of  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$  with  $t$  at room temperature are shown in Fig. 1. Two miscibility

gaps were found, for  $0.12 \pm 0.02 < t < 0.35 \pm 0.05$  (separating two MnP type solid solution phases) and for  $t > 0.90$  (separating at least three different phases). These results concur with the findings of Guérin *et al.*<sup>10,16</sup>

Both the powder X-ray and the neutron diffraction diagrams at 293 K could be indexed on an orthorhombic unit cell corresponding to the MnP type structure for  $0.01 < t \leq 0.10$ . This contrasts the results of Guérin *et al.*<sup>10</sup> who reported a larger unit cell with  $a' = a_{\text{MnP}}$ ,  $b' = 2b_{\text{MnP}}$ ,  $c' = 2c_{\text{MnP}}$  and space group  $C222_1$ .

The Rietveld analyses of the powder neutron diffraction data at and below room temperature were carried out according to space group  $Pnma$ . Mn and Mo were assumed to be randomly distributed over the metal sublattice. The derived values for the unit cell dimensions and the positional parameters for three different samples with  $t < 0.10$  are listed in Table 1. As seen from the table, a large contraction of the unit cell

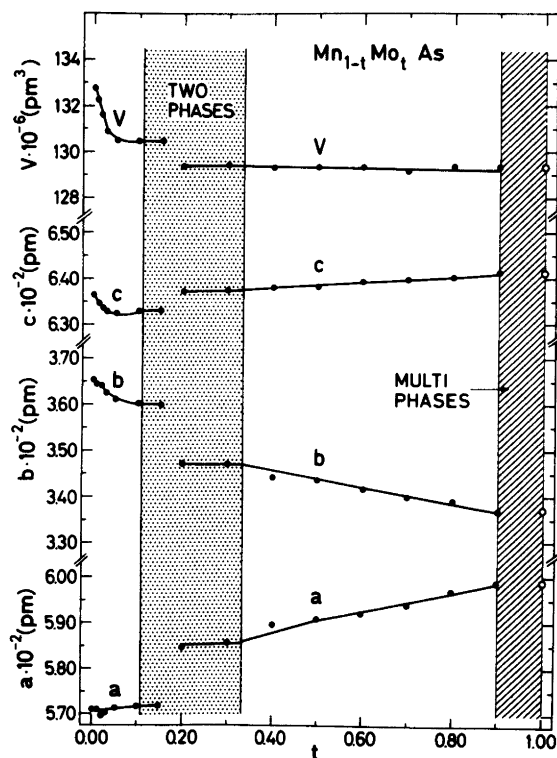


Fig. 1. Unit cell dimensions of ternary solid solution series  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$  as functions of compositional parameter  $t$ . Open symbols refer to values reported for  $\text{MoAs}$ .<sup>11</sup> Unit cell dimensions for  $\text{MnAs}$  are obtained by extrapolation of high-temperature data.<sup>7</sup>

Table 1. Unit cell dimensions and positional parameters for  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$ , space group  $Pnma$ , positions 4(c), standard deviations in parentheses (reliability factors:  $R_N=0.03-0.065$ ,  $R_P=0.10-0.13$ ).

$t$	T (K)	a (pm)	b (pm)	c (pm)	$x_T$	$z_T$	$x_X$	$z_X$
0.03	293	573.04(5)	363.11(7)	633.11(8)	0.0072(29)	0.2275(29)	0.2190(10)	0.5841(16)
	10	561.42(4)	349.81(3)	619.61(6)	0.0100(12)	0.2101(15)	0.1976(7)	0.5808(7)
0.05	293	571.99(5)	362.04(6)	633.83(9)	0.0135(40)	0.2159(14)	0.2208(36)	0.5797(21)
	220	566.18(7)	356.74(5)	627.83(9)	0.0080(51)	0.2109(26)	0.2062(51)	0.5809(24)
	180	563.23(9)	353.26(5)	624.32(9)	0.0083(49)	0.2024(20)	0.2104(44)	0.5817(22)
0.075	10	558.83(9)	348.52(5)	617.17(9)	0.0062(39)	0.1991(18)	0.2096(44)	0.5830(22)
	293	571.27(5)	362.71(4)	633.92(9)	0.0041(28)	0.2220(32)	0.2161(10)	0.5808(12)
	10	558.59(7)	349.56(4)	617.63(9)	0.0021(25)	0.2107(26)	0.1953(10)	0.5846(10)

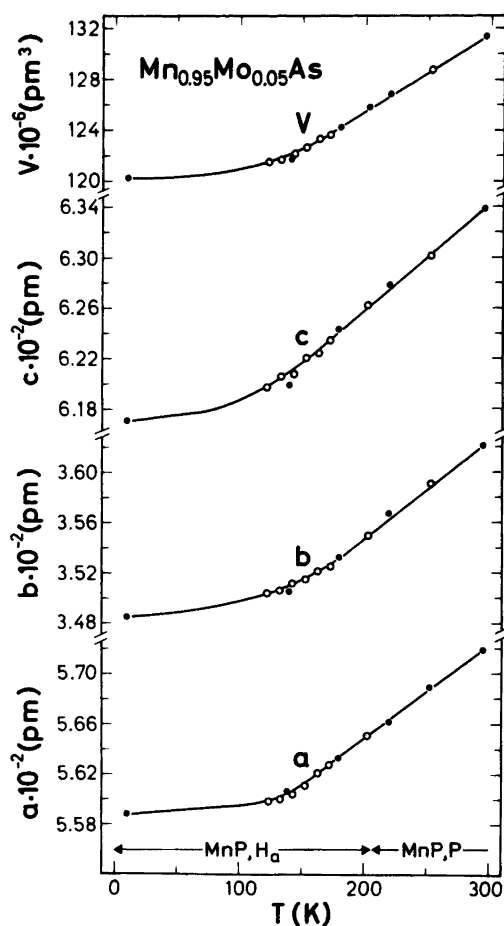


Fig. 2. Unit cell dimensions versus temperature for  $\text{Mn}_{0.95}\text{Mo}_{0.05}\text{As}$ . Open and filled symbols refer to results obtained by X-ray and neutron diffraction, respectively.

occurs upon cooling from 293 to 10 K. The changes in the positional parameters are less pronounced.

A low temperature X-ray diffraction study was performed for  $t=0.05$  between 120 and 300 K; see Fig. 2. The unit cell dimensions change uniformly, and no structural phase transition is detected in this temperature range. Thus, the magnetic phase transition between paramagnetic and helimagnetic states (at  $T_N=230$  K; see section on magnetic properties) is not reflected in the unit cell parameters. A combination of the results from neutron and X-ray diffraction experiments (Fig. 2) indicates that  $a$ ,  $b$  and  $c$  are almost constant below  $\sim 130$  K.

$\text{Mn}_{1-t}\text{Mo}_t\text{As}$  samples with  $t \leq 0.10$  transform by a second order phase transition to the NiAs type structure upon heating. Values of  $T_D$  as derived from Guinier-Simon high-temperature X-ray studies, are  $390 \pm 5$ ,  $435 \pm 10$ ,  $460 \pm 10$ , and  $500 \pm 10$  K for  $t = 0.00$ , 0.02, 0.05, and 0.10, respectively. These results concur with corresponding data for VAs-, CrAs-, and FeAs-substituted MnAs.<sup>2,4,17</sup>

In the compositional range  $0.35 \pm 0.05 \leq t < \sim 0.90$  another solid solution series with MnP type structure at room temperature is found. A significant distinction in the  $c/b$  (and also  $c/a$ ) axial ratio characterizes the two MnP type phases. Whereas  $c/b$  ratios for the MnAs-rich phase are very close to  $\sqrt{3}$  at room temperature,  $c/b$  in the MoAs richer solid solution phase varies from 1.837 ( $t = 0.35$ ) to 1.904 ( $t = 0.90$ ). In accordance with these high  $c/b$  ratios, no indication of a phase transition to a hexagonal structure was found at high temperatures for  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$  samples with  $0.40 \leq t \leq 0.90$ . The unit cell dimensions for  $\text{Mn}_{0.50}\text{Mo}_{0.50}\text{As}$  were found to increase almost linearly with temperature from  $a = 590.4 \pm 0.1$  pm,  $b = 343.9 \pm 0.1$  pm,  $c = 637.9 \pm 0.1$  pm at 293 K to  $a = 602.5 \pm 0.5$  pm,  $b = 350.0 \pm 0.5$  pm,  $c = 643.5 \pm 0.5$  pm at 1273 K.

For  $t > \sim 0.90$  it was not possible to obtain single phase samples. Three phases could be identified from the X-ray diffraction patterns,  $\sim \text{Mn}_{0.10}\text{Mo}_{0.90}\text{As}$ ,  $\text{Mo}_5\text{As}_4$  and  $\text{Mo}_2\text{As}_3$ . By extrapolating the unit cell dimensions for  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$  to  $t = 1.00$  one arrives at the values reported for MoAs by Boller *et al.*<sup>11</sup> Under favourable conditions for sample preparation it might be possible to obtain single-phase samples even for  $t > 0.90$ .

Different ways of synthesizing single phase samples of  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$ ,  $t > 0.90$  were tested. A slight P substitution for As was tried without any success. Neither were experiments using a Sn or Pb melt as flux medium successful.

The  $\text{Mn}_{1-t}\text{W}_t\text{As}$  system was only briefly studied. With the present sample preparational technique it was not possible to obtain any ternary  $\text{Mn}_{1-t}\text{W}_t\text{As}$  phases. Several different annealing temperatures as well as quenches were tried.

(ii) *Magnetic properties.* Magnetic susceptibility was measured for a series of  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$  samples. All samples showed paramagnetic behaviour.

For  $t \leq 0.10$  the Curie-Weiss Law is not valid in

Table 2. Effective paramagnetic moment ( $\mu_{\text{eff}}$ ), spin ( $S$ ) and paramagnetic  $\theta$  temperature for  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$  (estimated uncertainties in parentheses).

$t$	$\mu_{\text{eff}}(\mu_B)$	$S$	$\theta$ (K)
0.02	4.8(2)	1.9(1)	220(10)
0.03	5.0(2)	2.0(1)	170(10)
0.05	4.7(2)	1.9(1)	180(10)
0.10	4.8(2)	1.9(1)	100(10)
0.50	2.8(2)	1.0(1)	130(30)
0.60	2.5(2)	0.9(1)	170(20)
0.80	1.9(2)	0.6(1)	150(20)

temperature regions where the MnP type structure prevails. However, a linear relation between inverse susceptibility and temperature indicates that the Curie-Weiss Law applies to the high temperature, NiAs type phase ( $t \leq 0.10$ ). Values for  $\mu_{\text{eff}}$ ,  $S$  ("spin only") and  $\theta$  are given in Table 2. Corresponding values for MnAs are  $\mu_{\text{eff}} = 4.5\mu_B$ ,  $S = 1.8$  and  $\theta = 270$  K.<sup>6</sup> Hence, only minor changes are observed on going from  $t = 0.00$  to  $t = 0.10$ . It was not possible to obtain values for  $T_D$  from the inverse susceptibility *versus* temperature curves.

The MnP type phase for  $0.35 \leq t < \sim 0.90$  fulfills approximately the Curie-Weiss Law. The paramagnetic data for some selected samples are given in Table 2. This behaviour is not typical for MnP type phases. Nevertheless, it has been reported in some cases (*cf.*, *e.g.*, Ref. 18).

The neutron diffraction patterns for  $t = 0.03$ , 0.05 and 0.075 at 10 K all show the presence of extra reflections (satellites) which is attributed to a helimagnetic structure. The positions and intensity relations between the different satellites strongly suggest that the magnetic structure is of the  $H_a$  type found in other  $\text{Mn}_{1-t}\text{T}_t\text{As}$  phases (*cf.*, *e.g.*, Refs. 2, 3). The Néel-temperature ( $T_N$ ) was determined from the temperature dependence of the integrated intensity of the (strong)  $000^\pm$  satellite reflection.  $T_N$  was found to be approximately the same in the three samples studied (Table 3), and thus it is assumed that helimagnetic order prevails through the whole MnAs-rich solid solution range up to the beginning of the two-phase region. Samples with  $t > 0.10$  were not studied by neutron diffraction.

The parameters describing the  $H_a$  type helimagnetic structure are the magnetic moment  $\mu_H$

Table 3. Helimagnetic parameters for some  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$  samples (estimated uncertainties in parentheses).

$t$	T (K)	$\tau_a/2\pi a^*$	$\mu_H$ ( $\mu_B$ )	$\phi_{1,2}$ ( $^\circ$ )	$T_N$ (K)
0.03	10	0.139(3)	1.9(1)	63(5)	228(5)
	100	0.157(3)			
0.05	10	0.133(3)	1.6(1)	72(5)	230(5)
	140	0.152(3)			
0.75	10	0.140(3)	1.5(1)	76(5)	232(5)

(in the  $bc$ -plane), the spiral propagation vector  $\tau_a$  (the spiral propagates parallel to the  $a$ -axis), and the phase difference  $\phi_{1,2}$  between the independent spirals (*cf.* Refs. 2,3). A slight increase in  $\phi_{1,2}$  and a significant decrease in  $\mu_H$  is found on going from  $t=0.03$  to 0.075, while  $\tau_a$  remains approximately constant (Table 3). The  $\tau_a$ -value reported for metastable, orthorhombic  $\text{MnAs}^9$  ( $0.137 \cdot 2\pi a^*$ ) agrees well with the findings for  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$ . The temperature dependence of  $\tau_a$  for  $t=0.05$  is shown in Fig. 3. Analogous curves were obtained for  $t=0.03$  and 0.075. This kind of temperature dependence is typical for  $H_a$ -type spirals ( $\tau_a$  increases with increasing temperature).<sup>2,3</sup>

In order to establish the borderline between low temperature orthorhombic (helimagnetic) and hexagonal (ferromagnetic)  $\text{Mn}_{1-t}\text{Mo}_t\text{As}$ , a low temperature X-ray study of  $\text{Mn}_{0.99}\text{Mo}_{0.01}\text{As}$  was performed. However, for all  $T < \sim 310$  K two

phases were present, one of the NiAs type and one of the MnP type. Hence,  $\text{Mn}_{0.99}\text{Mo}_{0.01}\text{As}$  is inside the small two-phase region separating the ferro- and helimagnetic phases.

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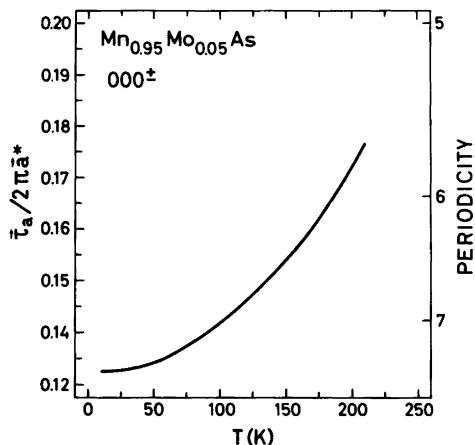


Fig. 3. Temperature dependence of propagation vector  $\tau_a$  for  $\text{Mn}_{0.95}\text{Mo}_{0.05}\text{As}$ .

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