Phase Transitions in MnAs

ANDRZEJ ZIEBA, a KARI SELTE, b ARNE KJEKSHUS b and ARNE F. ANDRESEN c

a Institute of Nuclear Physics and Techniques, Academy of Mining and Metallurgy, 30-059 Kraków, Poland, 
b Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway and c Institutt for Atomenergi, 
N-2007 Kjeller, Norway

The transformation properties of MnAs are studied 
by magnetization measurements in external 
magnetic fields up to 250 kOe and by neutron diffraction 
measurements between 4.2 and 400 K. The results 
are used to propose a qualitative explanation of the 
phase transitions in this compound.

The peculiar and apparently unique phase transi-
tions in MnAs 1 are, although certainly recognized 
among solid state specialists, perhaps not commonly 
appreciated outside this limited sphere. A probable 
reason for this lack of general appreciation is that the 
thoretical understanding of the behaviour of MnAs 
is rather poor.

The object of this communication is to present a 
qualitative basis for a theoretical model for the 
transition properties of MnAs, using fresh exper-
imental results as well as facts summarized in Ref. 1.

EXPERIMENTAL

The samples were prepared as described in Ref. 2, 
their homogeneity being ascertained from powder 
X-ray (Guinier) photographs. Experimental details 
concerning the pulsed field magnetization measure-
ments and the neutron diffraction measurements are 
given in Refs. 1 and 3.

RESULTS

Near room temperature MnAs [like the Mn-rich 
Mn 1−x,Mn x P (T: V, Cr, Fe, or Co) samples discussed 
in Ref. 1] exhibits, as shown in Fig. 1, a first-order 
phase transition between ferromagnetic and paramag-
magnetic states with NiAs and MnP type structures, 
respectively. This combined crystallographic and 
magnetic transition (conveniently abbreviated 1 as 
NiAs,F → MnP,P for increasing temperature) is 
only quasi-reversible, as demonstrated by the 
hysteresis loop in Fig. 1. The Curie temperatures 
for increasing (T cr,i ) and decreasing (T cr,d ) tempera-
ture in Fig. 1 are slightly higher than the values 
T cr,i = 317 K and T cr,d = 306 K obtained in weak 
sinusoidal fields. This discrepancy is a consequence 
of the experimental conditions which give rise to 
the magnetocalorimetric effect outlined in Ref. 1. 
The maximum magnetocalorimetric effect occurs 
in the vicinity of T c and amounts to ΔT ≈ 10 K. Apart 
from supplementary measurements with other tech-
niques, no attempt has been made to correct the 
present data for this deficiency.

Several parallel evidences suggest that the NiAs,F 
type state of MnAs should be assigned a substan-
tially higher Curie temperature than expressed 
above:

\[ M(\mu_0 \text{mol}^{-1}) \]

\[ T_\text{cr,i} \quad T_\text{cr,d} \quad T_\text{c, crit} \]

\[ 300 \quad 350 \quad 400 \quad T (K) \]

**Fig. 1.** Magnetization versus temperature for MnAs 
at 7 kOe (solid curves); magnetization increment versus 
temperature at the metamagnetic transition 
above T cr,i (broken curve).
(i) The magnetization increment ($\Delta M$) at the metamagnetic transition above $T_{C, i}$ (Fig. 1) joins nicely to the magnetization $M(T)$ curve. The $\Delta M(T)$ curve gives an extrapolated Curie temperature ($T_{C, extr}$) of $\sim 360$ K.

(ii) The relative magnetization ($M/M_{0,K}$) for the NiAs,$F$ type state of MnAs is known from magnetization and neutron diffraction (vide infra) measurements. Assuming that MnAs behaves like a typical ferromagnet (say Fe or Ni) $T_{C,extr} \approx 360$ K would result, whereas the extrapolation of $M/M_{0,K}$ according to a Brillouin function gives a slightly higher value.$^5$

(iii) The Clausius-Clapeyron equation may be used to predict that maximum values of the transition fields $H_F$ and $H_F$ should be found close to the Curie temperature. The maxima in $H_F$ and $H_F$ (Fig. 2) occur at 360 and 365 K, respectively.

(iv) In an attempt to account for the thermodynamic properties of MnAs, Grenvold et al.$^6$ concluded that it was necessary to assume incomplete spin randomization above $T_{C, i}$. The observed MnP,$P \leftrightarrow$NiAs,$F$ type transition can be looked upon as composed of two hypothetical transitions of the types MnP,$P \leftrightarrow$NiAs,$P$ and NiAs,$P \leftrightarrow$NiAs,$F$. The splitting of the total energy into the contributions from these two processes is difficult to assess on an experimental basis. However, extrapolation of the data of Grenvold et al.$^6$ suggests that the internal energy of the MnP,$P$ type state lies between the energies of the NiAs,$P$ and NiAs,$F$ type states below $\sim 360$ K. The energy associated with the hypothetical NiAs,$P \leftrightarrow$NiAs,$F$ type transition can be estimated by means of the molecular field theory.$^5$

It may be taken as a reasonable proof of selfconsistency that $T_C = T_{C,extr} = 360$ K and $S = 3/2$ leads to a somewhat higher transition energy than observed.$^6$

The temperature versus applied magnetic field phase diagram for MnAs in Fig. 2 has the same general appearance as those for Mn$_{1-x}$Fe$_x$As.$^1$ However, due to the fact that the NiAs,$F$ type state exists at $H = 0$ kOe for MnAs, Fig. 2 is simpler below $T_C$ than the corresponding diagrams in Ref. 1. The stability of the NiAs,$F$ type state is also reflected in the shift of the phase borders $H_F$ and $H_F$ to lower fields in MnAs. (The situation may be illustrated by quoting the critical field $H_{F,max,}$ (in kOe) for a few samples: MnAs, 97; Mn$_{0.95}$Cr$_{0.05}$As, 127; Mn$_{0.95}$Cr$_{0.05}$As, 154; Mn$_{0.95}$Co$_{0.05}$As, 176; Mn$_{0.95}$Co$_{0.05}$As, $> 250$.) This, together with comparison of Fig. 2 with Figs. 7–10 of Ref. 1, serves to emphasize that a pure, good quality sample is required in any attempt to establish the intrinsic properties of MnAs.

The neutron diffraction data show that on cooling, MnAs retains the NiAs type crystal structure down to 4.2 K. This is in complete accordance with earlier findings (see Refs. 6 and 7), and there is no evidence for a partial NiAs$\rightarrow$MnP transition at $\sim 160$ K as was indicated in Ref. 8.

The value $\mu_{F,rot} = 3.3 \pm 0.1 \mu_B$ at 4.2 K obtained by neutron diffraction corresponds well with that (3.1 $\mu_B$) obtained by magnetization measurements, and is also reasonably consistent with the value $2S_{Mn} = 3.6 \pm 0.2$ derived for the NiAs,$P$ type state (using the "spin only" approximation). The temperature dependence of $\mu_{F,rot}$ over the interval 4.2–297 K follows nicely the Brillouin function for $S = 3/2$ assuming a Curie temperature of 360 K, thus supporting the conclusion drawn from the magnetization data (vide supra). The present work concurs with the results of Bacon and Street$^7$ apart from a somewhat temperature-dependent deviation of the moment from the direction perpendicular to c ($\mu_{F,rot}, \mu_{F,1c}, \mu_{F,1c}$ are 3.31(10), 1.31(13), 3.03(11) and 2.46(16), 0.81(42), 2.32(20) at 4.2 and 298 K, respectively; as derived by least squares profile refinement of the neutron diffraction data; standard deviations in brackets).

**DISCUSSION**

The present data shed new light on the peculiar transformation properties of MnAs, which are summarized in the bottom part of Fig. 3. In order to illustrate our points, Fig. 3 also shows a sketch of the temperature variations in the shortest (bonding) Mn – As (averaged in MnP type state) and Mn – Mn distances. In addition, Table 1 gives a comparison between the NiAs,$P$ NiAs,$F$ and MnP,$P$ type states.

---

Table 1. Structural and magnetic parameters for real and hypothetical states of MnAs at 4.2 and 298 K. (NiAs and MnP type structures are referred to space groups $P6_3/mmc$ and $Pnma$, respectively. Extrapolations are based on data from Refs. 1, 2, 10–12, 15, 17–19.)

<table>
<thead>
<tr>
<th>Structure type</th>
<th>NiAs</th>
<th>MnP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (K)</td>
<td>4.2</td>
<td>298</td>
</tr>
<tr>
<td>Temp. extrap. to 298</td>
<td>3.672</td>
<td>5.704</td>
</tr>
<tr>
<td>Conc. extrap.;</td>
<td>5.566</td>
<td>5.695</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>3.730</td>
<td>3.722</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>3.722</td>
<td>3.672</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.668</td>
<td>5.702</td>
</tr>
<tr>
<td>$x_{Mn}$</td>
<td>6.164</td>
<td>6.365</td>
</tr>
<tr>
<td>$x_{As}$</td>
<td>3.498</td>
<td>3.655</td>
</tr>
<tr>
<td>$z_{Mn}$</td>
<td>0.0003</td>
<td>0.005</td>
</tr>
<tr>
<td>$z_{As}$</td>
<td>0.2141</td>
<td>0.222</td>
</tr>
<tr>
<td>$(Mn-As)_{av}$ (Å)</td>
<td>0.1963</td>
<td>0.224</td>
</tr>
<tr>
<td>Mn–Mn (Å)</td>
<td>2.578</td>
<td>2.579</td>
</tr>
<tr>
<td>2S$_{Mn}$, magn. state</td>
<td>2.575</td>
<td>2.553</td>
</tr>
<tr>
<td>Mn–Mn (Å)</td>
<td>2.834</td>
<td>2.851</td>
</tr>
<tr>
<td>2S$_{Mn}$, magn. state</td>
<td>2.846</td>
<td>2.866</td>
</tr>
<tr>
<td>2S$_{Mn}$, magn. state</td>
<td>3.730</td>
<td>3.722</td>
</tr>
<tr>
<td>2S$_{Mn}$, magn. state</td>
<td>3.722</td>
<td>3.672</td>
</tr>
<tr>
<td>2S$_{Mn}$, magn. state</td>
<td>3.6, P</td>
<td>2.5, $F^a$</td>
</tr>
<tr>
<td>2S$_{Mn}$, magn. state</td>
<td>1.9, $H^b$</td>
<td>“low spin”, P</td>
</tr>
</tbody>
</table>

$^a$ Magn. moments 67° (4.2 K) and 71° (298 K) off c; $T_{ce,extr} \approx 360$ K.

$^b$ $\alpha = 54^\circ$, $\phi = 75^\circ$, $\beta = 90^\circ$ (fixed); $T_x \approx 210$ K (Refs. 1 and 19).

at 298 K and the NiAs,F and MnP,H type states at 4.2 K, including data extrapolated according to temperature or concentration.

The situation in the NiAs,P type state may conveniently be chosen as the starting point for the following brief considerations. At, say, 600 K the atomic arrangement of MnAs is of the “typical” NiAs type with two short Mn–Mn distances of 2.90 Å along the hexagonal axis and six longer Mn–Mn distances of 3.70 Å within the basal plane. As the temperature is lowered towards 400 K, these distances, as well as the Mn–As distances, decrease slightly. At 393 K the structure changes to the MnP type, and a marked shrinkage of the second shortest Mn–Mn distance is observed as the temperature is lowered to ~ 320 K.

The driving force of the NiAs→MnP type transformation is considered to be the “strive” to establish four close metal–metal contacts. The bonding nature of these metal–metal contacts is still essentially unknown. The transformation from NiAs type to “idealized” MnP type structure [Ref. 13; inter alia characterized by four (2+2) short metal–metal distances of virtually equal lengths] proceeds continuously over an appreciable temperature interval which amounts to ~200 K in MnAs$_{0.9}$P$_{0.1}$ and ~500 K in Mn$_{0.9}$Fe$_{0.1}$As. As seen from Table 1, there is a dissimilarity between the shortest and the second shortest Mn–Mn distances also in the hypothetical MnP,H type mode of MnAs.

In complete accordance with our neutron diffraction results, the temperature dependence of the Mn–As and Mn–Mn distances gives no evidence

MnP type atomic arrangement for MnAs.

When the temperature is lowered to ~310 K, the atomic arrangement of MnAs converts back to the NiAs type. The driving force of this transformation is almost certainly the magnetic exchange interactions. Due to the marked dissimilarity between the two pairs of short Mn–Mn distances (2.86 versus ~3.3 Å), the exchange interactions corresponding to the closest Mn–Mn contacts will dominate. Hence, the structural rearrangement to the NiAs type is a natural consequence of this imbalance.

The fact that $T_{ce,extr}$ is substantially higher than the observed transformation temperature (~310–~320 K), may be explained by the competition between the two direct magnetic exchange paths. The extrapolated Néel temperature for the hypothetical MnP,H type mode of MnAs is ~210 K. The NiAs,F and hypothetical MnP,H type modes have in common notable similarities in magnetic arrangements, since the spin directions are (approximately) perpendicular to a common direction in the two structure types ($c_{NiAs}$ and $a_{MnP}$). As seen from Table 1, there is a dissimilarity between the shortest and the second shortest Mn–Mn distances also in the hypothetical MnP,H type mode of MnAs.
Fig. 3. Structural changes with temperature in MnAs quoted from Ref. 1. Temperature dependence of Mn—As (averaged for MnP type) and Mn—Mn distances according to this study and data from Refs. 9–12. \( \mu_F \) versus T as observed by neutron diffraction.

for the indicated,\(^8\) partial NiAs,\(F\rightarrow\)MnP,\(H\) type transition at \(\sim 160\) K. Such a transition can, however, be induced by the application of a comparatively small external pressure\(^{16}\) or by small substitutions of another transition metal for Mn\(^{1,2,17-19}\). The fact that the application of an external pressure on MnAs is able to decrease the second shortest Mn—Mn distance, is consistent with expectation, and the pressure induced MnP,\(H\) mode\(^{16}\) thus provides additional support for the above considerations.

Acknowledgements. The authors are grateful to cand.mag. P. G. Peterzéns for help in the neutron diffraction experiments. This work has received financial support from The Norwegian Research Council for Science and the Humanities.

REFERENCES


Received September 19, 1977.