Phase Transitions in MnAs

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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 transitions 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 theoretical 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 experimental 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 measurements and the neutron diffraction measurements are given in Refs. 1 and 3.

RESULTS

Near room temperature MnAs [like the Mn-rich $Mn_{1-t}T_tAs$ (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 paramagnetic states with NiAs and MnP type structures, respectively. This combined crystallographic and

magnetic transition (conveniently abbreviated[1] as $NiAs,F \rightarrow MnP,P$ for increasing temperature) is only quasi-reversible, as demonstrated by the hysteresis loop in Fig. 1. The Curie temperatures for increasing ($T_{C,i}$) and decreasing ($T_{C,d}$) temperature in Fig. 1 are slightly higher than the values $T_{C,i} = 317$ K and $T_{C,d} = 306$ 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 $\Delta T \approx 10$ K. Apart from supplementary measurements with other techniques, 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 substantially higher Curie temperature than expressed above:
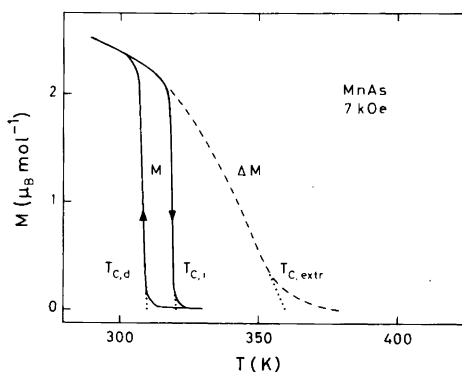

Fig. 1. Magnetization versus temperature for MnAs at 7 kOe (solid curves); magnetization increment versus temperature at the metamagnetic transition above $T_{C,i}$ (broken curve).

(*i*) The magnetization increment (ΔM) 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 ~360 K.

(*ii*) The relative magnetization ($M/M_{0\,K}$) for the NiAs,F type state of MnAs is known from magnetization[4] 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_P should be found close to the Curie temperature. The maxima in H_F and H_P (Fig. 2) occur at 360 and 365 K, respectively.

(*iv*) In an attempt to account for the thermodynamic properties of MnAs, Grønvold *et al.*[6] concluded that it was necessary to assume incomplete spin randomization above $T_{C,i}$. The observed MnP,$P \rightleftharpoons$ NiAs,F type transition can be looked upon as composed of two hypothetical transitions of the types MnP,$P \rightleftharpoons$ NiAs,P and NiAs,$P \rightleftharpoons$ 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 Grønvold *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 ~360 K. The energy associated with the hypothetical NiAs,$P \rightleftharpoons$ 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]

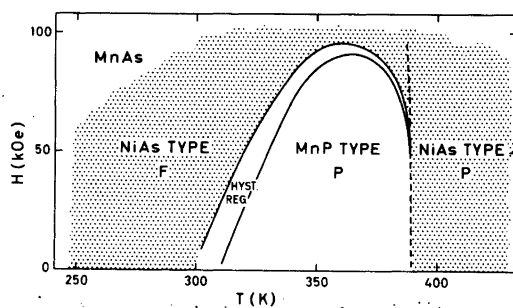The temperature *versus* applied magnetic field phase diagram for MnAs in Fig. 2 has the same general appearance as those for $Mn_{1-t}T_tAs$.[1] However, due to the fact that the NiAs,F type state exists at $H = 0$ kOe for MnAs, Fig. 2 is simpler below T_C than the corresponding diagrams in Ref. 1. The stability of the NiAs,F type state is also reflected in the shift of the phase borders H_P 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; $Mn_{0.99}Cr_{0.01}As$, 127; $Mn_{0.97}Cr_{0.03}As$, 154; $Mn_{0.97}Co_{0.03}As$, 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→MnP type transition at ~160 K as was indicated in Ref. 8.

The value $\mu_{F,tot.} = 3.3 \pm 0.1$ μ_B at 4.2 K obtained by neutron diffraction corresponds well with that (3.1 μ_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 $\mu_{F,tot.}$ 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 ($\mu_{F,tot.}, \mu_{F,\|c}, \mu_{F,\perp c}$ 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

Fig. 2. Phase diagram in T,H space for MnAs.

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.)

Structure type	NiAs			MnP		
T (K)	4.2	298	Temp. extrap. to 298	Conc. extrap.; 4.2	Temp. extrap. to 298	Conc. extrap.; 298
a (Å)	3.730	3.722	3.672	5.566	5.704	5.695
b (Å)				3.498	3.655	3.644
c (Å)	5.668	5.702	5.691	6.164	6.365	6.329
x_{Mn}				0.0003	0.005	0.0045
z_{Mn}				0.2141	0.222	0.2160
x_{As}				0.1963	0.224	0.2196
z_{Aa}				0.5828	0.582	0.5774
$(Mn-As)_{av.}$ (Å)	2.578	2.579	2.553	2.498	2.56	2.560
$Mn-Mn$ (Å)	2.834	2.851	2.846	2.815	2.87	2.883
$Mn-Mn$ (Å)	3.730	3.722	3.672	3.24	3.37	3.27
$2S_{Mn}$, magn. state	3.2 (av.), F^a	2.5, F^a	3.6, P	1.9, H^b	"low spin", P	"low spin", P

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

[b] $\alpha = 54°$, $\phi = 75°$, $\beta = 90°$ (fixed); $T_N \approx 210$ 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.[13] 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$_{0.1}$[14] and ~500 K in Mn$_{0.9}$Fe$_{0.1}$As.[15] Fig. 3 indicates that the stability range (~70 K) of the MnP type structure is much too narrow to obtain the "idealized"

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 $T_{C,extr.}$ 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.[1] 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.

In complete accordance with our neutron diffraction results, the temperature dependence of the $Mn-As$ and $Mn-Mn$ distances gives no evidence
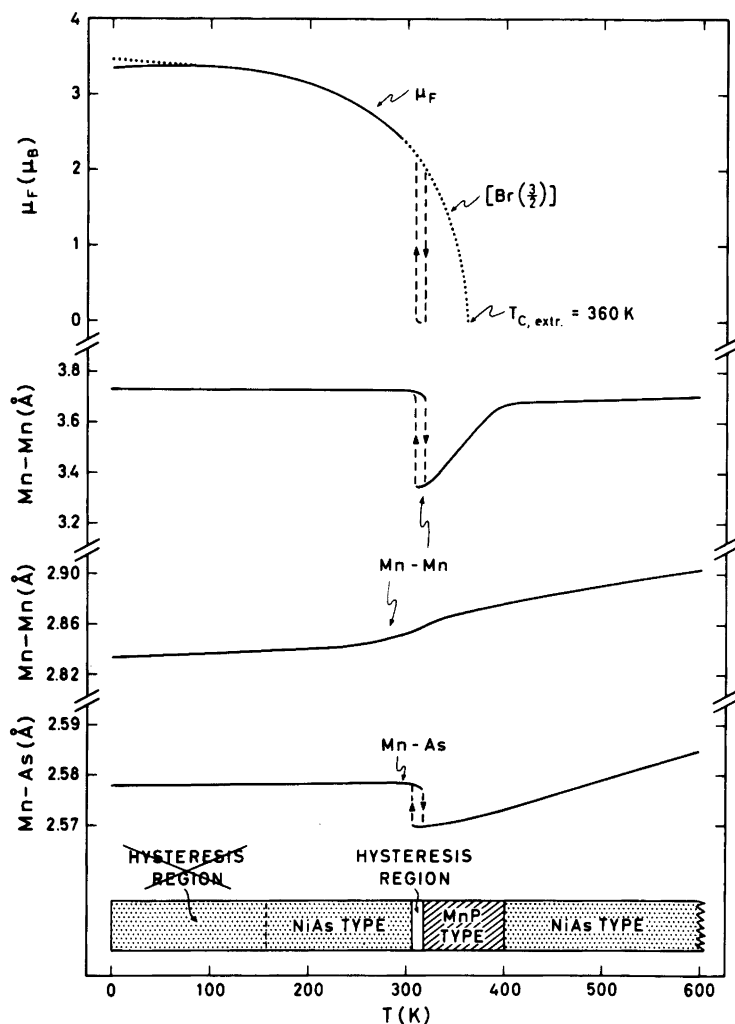
Fig. 3. Structural changes with temperature in MnAs quoted from Ref. 1. Temperature dependence of Mn−As (averaged for MnP type) and Mn−Mn distances according to this study and data from Refs. 9−12. μ_F *versus* T as observed by neutron diffraction.

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.

REFERENCES

1. Selte, K., Kjekshus, A., Andresen, A. F. and Zięba, A. *J. Phys. Chem. Solids 38* (1977) 719.
2. Selte, K., Kjekshus, A. and Andresen, A. F. *Acta Chem. Scand. A 28* (1974) 61.

3. Selte, K., Kjekshus, A. and Andresen, A. F. *Acta Chem. Scand. 26* (1972) 3101.
4. Bean, C. P. and Rodbell, D. S. *Phys. Rev. 126* (1962) 104.
5. Smart, J. S. *Effective Field Theories of Magnetism*, Sanders, Philadelphia – London 1966.
6. Grønvold, F., Snildal, S. and Westrum, E. F. *Acta Chem. Scand. 24* (1970) 285.
7. Bacon, G. E. and Street, R. *Nature 175* (1955) 518.
8. Menyuk, N., Kafalas, J. A., Dwight, K. and Goodenough, J. B. *Phys. Rev. 177* (1969) 942.
9. Willis, B. T. M. and Rooksby, H. P. *Proc. Phys. Soc. London Sect. B 67* (1954) 290.
10. Kornelsen, R. O. *Can. J. Phys. 39* (1961) 1728.
11. Wilson, R. H. and Kasper, J. S. *Acta Crystallogr. 17* (1964) 95.
12. Kjekshus, A. and Pearson, W. B. *Prog. Solid State Chem. 1* (1964) 83.
13. Endresen, K., Furuseth, S., Selte, K., Kjekshus, A., Rakke, T. and Andresen, A. F. *Acta Chem. Scand. A 31* (1977) 249.
14. Hall, E. L., Schwartz, L. H., Felcher, G. P. and Ridgley, D. H. *J. Appl. Phys. 41* (1970) 939.
15. Selte, K., Kjekshus, A. and Andresen, A. F. *Acta Chem. Scand. 27* (1973) 3607.
16. Yoshie, H. and Hihara, T. *J. Phys. Soc. Jpn. 40* (1976) 427.
17. Selte, K., Kjekshus, A., Valde, G. and Andresen, A. F. *Acta Chem. Scand. A 30* (1976) 8.
18. Selte, K., Kjekshus, A., Valde, G. and Andresen, A. F. *Acta Chem. Scand. A 30* (1976) 468.
19. Selte, K., Kjekshus, A., Peterzéns, P. G. and Andresen, A. F. *Acta Chem. Scand. In press.*