PRESSURE INDUCED TRANSITIONS IN MnAs AND $MnAs_{0.80}Sb_{0.20}$

H. FJELLVÅG[1], H.D. HOCHHEIMER and W. HÖNLE
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, FRG

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The NiAs type phases of MnAs and $MnAs_{0.80}Sb_{0.20}$ were studied for at pressures up to 12 GPa using the energy dispersive X-ray diffraction technique. MnAs (at ~0.1 GPa) and $MnAs_{0.80}Sb_{0.20}$ (at ~4 GPa) transform from the NiAs into the MnP type structure, followed by strong volume reductions. The anomalous compressibility properties are probably correlated with changes in the electronic band structure and in this respect are related to the high to low spin conversion in $MnAs_{1-x}P_x$.

1. Introduction

The complex magnetic and structural properties of MnAs have motivated a large number of investigations, see e.g. refs. [1–21]. At ambient conditions MnAs crystallizes in the hexagonal NiAs type crystal structure and is ferromagnetic (F) [1–4,11,14,21]. The phases considered in this paper show metallic properties [10]. However, to a good approximation their magnetic moments can conveniently be understood and discussed in terms of high and low spin phases. The non-integer value $\mu_F = 3.6\mu_B$ of the ordered ferromagnetic moment in MnAs at low temperatures corresponds fairly well to what is expected for Mn^{3+}.

At $T_C = 317$ K (upon heating) MnAs undergoes a first order, combined magnetic (ferro (F) to paramagnetic (P)) and structural (NiAs to MnP type) phase transition [15]. In the particular case of MnAs, the MnP type structure (orthorhombic, space group Pnma) represents just a slightly distorted variant of the NiAs type. At higher temperatures, the distortion gradually diminishes, and at $T_D = 393$ K MnAs transforms back into the NiAs type structure via a second order (displacive) phase transition [14]. The magnetic susceptibility for $T > T_D$ agrees with high spin properties for manganese.

The properties of MnAs can be strongly changed by chemical substitution. Substitution of Mn by "smaller" atoms (V, Cr, Fe, Co, Ni) and of As by P [5–7,17,20,22,23], leads to a stabilisation of the MnP type structure over larger temperature intervals. For more than 1–5% substitution, the MnP type structure is stable at all $T < T_D$ [22]. For MnAs there seems to be a good equivalency between positive chemical (internal) pressure and applied (external) pressure [3,22]. The NiAs,F type phase can, similarly as by substitution, be transformed into an MnP,P or a helimagnetic MnP,H_a type phase (at $T < \sim 200$ K) by application of small external pressures ($p_D < \sim 0.4$ GPa) [2,3,22]. The substitution of larger atoms into MnAs, implies a volume expansion (negative chemical pressure) which stabilizes the NiAs type relative to the MnP type structure [22].

The magnetic and structural properties of the ternary derivatives of MnAs (e.g. $MnAs_{1-x}P_x$), are similar to those of MnAs only for $T > T_D$. At lower temperatures, the continuously increasing orthorhombic distortion (much larger than in MnAs itself) leads to strongly deformed octahedra and to two additional short metal–metal interatomic distances. The progressing deformation is accompanied by a significant reduction of the unit cell volume which cannot be understood only in terms of normal thermal expansion properties of related arsenides. The degree of distortion also increases for larger substitution levels. At $T < T_N \approx 200$ K, these phases commonly have a helimagnetic spin structure with an

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[1] Permanent address: Institute for Energy Technology, N-2007 Kjeller, Norway.

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Table 1
Properties of MnAs and ternary derivatives. P, paramagnetic; F, ferromagnetic; H, helimagnetic.

Structure type	Stabilizing factors	Magnetic properties
NiAs	– high temperatures	$P^{a,b)}$ $\mu_{eff} \sim 4.5\,\mu_B$
	– magnetic fields	$F^{a,b)}$ $\mu_F \sim 3.6\,\mu_B$
	– negative chemical pressure (Ti for Mn or Sb for As)	
MnP	– low temperatures	$P^{a,b)}$ not Curie–Weiss behaviour for the susceptibility
	– positive chemical pressure (V, Cr, Fe, Co, Ni for Mn or P	$F^{b)}$ $\mu_F \sim 1.7\,\mu_B$
	– external pressure	$H^{b,a)}$ $\mu_H \sim 1.8\,\mu_B$

a) In MnAs. b) In ternary derivatives.

ordered magnetic moment of $\sim 1.8\,\mu_B$ [4–7, 12, 17, 20]. The low value for the magnetic moment is here conveniently ascribed to low spin manganese atoms, and like the high spin phase also the low spin phase exhibits metallic conductivity [10]. A short compilation of properties of MnAs and its ternary derivatives is given in table 1.

In this study, the changes in the crystal structure of MnAs caused by application of external pressures up to 12 GPa, have been studied by means of energy dispersive X-ray diffraction. Similar experiments were carried out for the negative chemical pressure phase $MnAs_{0.80}Sb_{0.20}$. In both samples, a transition from a high spin NiAs type to a low spin MnP,P type phase is expected. The specific unit cell volumes for the various phases discussed here, are related by $V(\text{NiAs,F-h.s.}) > V(\text{NiAs,P-h.s.}) \approx V(\text{MnP,P-h.s.}) > V(\text{MnP,P-l.s.}) \geqslant V(\text{MnP,F-l.s.}) \approx V(\text{MnP,H}_a\text{-l.s.})$.

2. Experimental

Powder samples of MnAs and of $MnAs_{0.80}Sb_{0.20}$ were synthesized from the elements (Mn, crushed flakes, 99.99%, Johnson, Matthey & Co.; As, lumps, 99.9999%, Koch-Light Laboratories, Sb, lumps, 99.9995%, Johnson, Matthey & Co.) by heating stoichiometric mixtures in sealed, evacuated silica tubes at 850°C for 5 d. After cooling to room temperature, the samples were crushed before subjected to a further annealing at 850°C for 5 d for MnAs, and at 800°C for 10 d for $MnAs_{0.80}Sb_{0.20}$, respectively. The crystalline state and the homogeneity of the samples were checked by means of room temperature powder X-ray diffraction (Guinier technique, $CuK\alpha_1$ radiation, Si as internal standard).

High pressure powder X-ray diffraction data were obtained using the energy dispersive technique [24]. Pressures up to 12 GPa were generated in a gasketed diamond anvil cell, and the pressures were determined with the ruby fluorescence technique [25]. The energies corresponding to the Bragg reflections were obtained using a curve fitting procedure. Powder X-ray diffraction intensities were calculated for various structure models with the LAZY-PULVERIX program [26], and used as aid for the indexing of the diffraction diagrams of the orthorhombic phases.

3. Results and discussion

MnAs and $MnAs_{0.80}Sb_{0.20}$ crystallize with the NiAs type crystal structure at ambient conditions ($a = 372.2 \pm 0.1$, $c = 570.2 \pm 0.1$ pm and $a = 376.1 \pm 0.1$ and $c = 576.2 \pm 0.1$ pm, respectively). The substitution of As by Sb leads to an increase of the unit cell volume per formula unit of 1.09×10^6 pm^3, which in turn favours the NiAs type structure.

The variation of the reduced unit cell volume V/V_0 of MnAs with applied pressure is shown in fig. 1. The first order NiAs,F to MnP,P type phase transition occurs already at very modest pressures. This transition has earlier carefully been examined by measurements of magnetic properties and conductivity, and it is found to take place at $p_D \sim 0.12$ GPa at 295 K (for increasing pressures) [2,3,22]. The same phase transition between NiAs,F and MnP,P type phases, occurs also as a function of the temperature, and it is accompanied by a discontinuous jump in the unit cell volume [17]. At T_C the ratio of the two volumes is $V(\text{MnP,P})/V(\text{NiAs,F}) = 0.978$. A similar jump is expected to occur at p_D, but it could not be resolved from the presently obtained data. The shaded region in fig. 1 corresponds to a jump of the relevant magnitude. For $p > p_D$ an extraordinary strong reduction

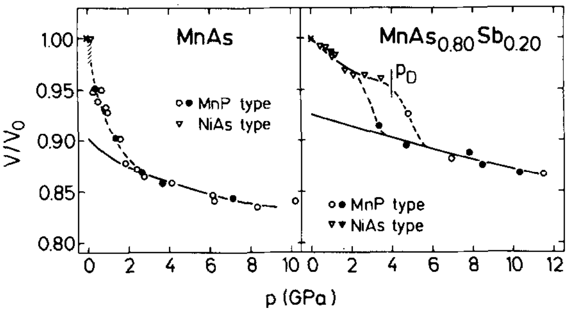

Fig. 1. Variation of reduced unit cell volume V/V_0 with external pressure (p) for MnAs and MnAs$_{0.80}$Sb$_{0.20}$. Open and filled symbols refer to increasing and decreasing pressures, respectively. Fully drawn lines refer to fits according to the Birch equation of state, see text. Dotted lines are guides for the eye.

of V/V_0 with pressure is observed, which levels out above 4 GPa.

The variation of V/V_0 with external pressure for MnAs$_{0.80}$Sb$_{0.20}$ is included in fig. 1. At ambient conditions MnAs$_{0.80}$Sb$_{0.20}$ crystallizes with the NiAs type structure and is paramagnetic. For MnAs$_{1-x}$Sb$_x$ T_C decreases with increasing x for $x<0.30$ [27–29]. Furthermore, since $\partial T_C/\partial p<0$ [3,22,27], one expects the NiAs type phase to be paramagnetic also at higher pressures. The V/V_0 versus p curve shows a pronounced change for $p>p_D\sim4$ GPa, and this probably reflects the onset of a NiAs,P to MnP,P type structural transition. The transition could well be of the continuous second order type (as found for related phases for temperature or composition as thermodynamical variables [30,31]), but the observed hysteresis (see fig. 1) implies a first order component. The enhanced V/V_0 reduction for $p>p_D$ is, although less clear, corresponding to the observations for MnAs, and it is believed that the same physical mechanism is responsible for the anomalous compressibility properties of both phases.

As it was not possible to obtain a good fit with reasonable results for all data points of the V/V_0 versus p curves to a single Birch equation of state [32], it is believed, that the curves must be separated into various regions, which can be attributed to phases with particular structural and magnetic characteristics. The NiAs,P high spin phase is found for MnAs$_{0.80}$Sb$_{0.20}$ with $p<p_D$, and the MnP,P low spin phase probably exists for MnAs at $p>\sim3$ GPa as well as for MnAs$_{0.80}$Sb$_{0.20}$ at $p>\sim5$ GPa. Therefore only data points in selected parts of the V/V_0 versus p plots were fitted to a Birch equation of state [32]. In order to settle a reasonable V_0 value for the MnP,P low spin phase of MnAs, crystal structure data (composition and temperature dependence) for ternary derivatives of MnAs [5–7,17,20,22,23] were considered, and rescaling was performed according to V_0(MnP,P-l.s.)/V_0(NiAs,F)$=0.904$. The somewhat higher ratio of 0.925 was more arbitrarily adopted for the corresponding situation in MnAs$_{0.80}$Sb$_{0.20}$. For the NiAs,P type phase of MnAs$_{0.80}$Sb$_{0.20}$ $B_0=73$ GPa and $B_0'=3.0$ were obtained, while for the MnP,P type phase $B_0=106$ GPa and $B_0'=8$. For the NiAs,F type phase of MnAs no parameter values could be deduced, but for the MnP,P type phase $B_0=24$ GPa and $B_0'=40$ were found. The latter value for B_0' most probably does not reflect physical realities.

The compressibility properties of MnAs and MnAs$_{0.80}$Sb$_{0.20}$ shown in fig. 1, are believed to be connected with electronic changes induced by the strong orthorhombic distortion of the crystal structure. The feature is quite similar to the so-called high to low spin conversion, that is particularly well developed and hence also studied for samples of the MnAs$_{1-x}$P$_x$ solid solution phase ($\sim0.03<x<\sim0.20$) [10,12,15,16,18,20,33,34]. In the latter phase the phenomenon is studied as function of temperature, and the "transition temperature (T_{hl})" has been obtained from peaks in $c_p(T)$ curves [33, 34]. The $c_p(T)$ peaks correspond approximately to the temperature where the thermal expansion coefficients take maximal values [34] and where a considerable reduction of the unit cell volume is found. The elastic bulk modulus is reported to decrease significantly upon approaching T_{hl} [18, 33]. The variation in reduced volume V/V_0 as funtion of composition x for MnAs$_{1-x}$P$_x$ and as function of reduced temperature T/T_D for MnAs$_{0.90}$P$_{0.10}$ is shown in fig. 2. It is seen that the functional dependence shows clear resemblance with the V/V_0 versus p curves in fig. 1. For MnAs$_{1-x}$P$_x$ these anomalous variations in the unit cell volume are believed to result from continuous changes in the electronic band structure induced by the progressing MnP type distortion. The V/V_0 variations can be understood by a larger specific volume for manganese atoms with a high number of unpaired electrons (although not necessarily local-

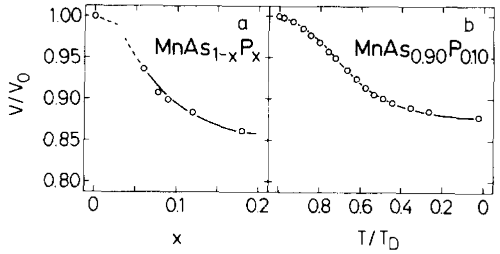

Fig. 2. Variation of reduced unit cell volume V/V_0 for (a) $MnAs_{1-x}P_x$ as function of composition x and (b) $MnAs_{0.90}P_{0.10}$ as function of reduced temperature T/T_D.

ized) than for manganese atoms with lower magnetic moments. Considering the present compressibility data, at least those for MnAs, it is reasonable to conclude that a similar high to low spin conversion also can be induced by application of external pressure.

Compressibility data are available for some related NiAs and MnP type phases. The lower compressibility for the antimony substituted sample agrees with the results reported for MnSb (which, when fitted with the Birch equation of state, yield the parameters $B_0 = 46$ GPa and $B_0' = 8$) [35]. The obtained B_0 value for the MnP,P low spin phase of MnAs agrees surprisingly well with values for the compressibility of MnAs determined by other methods [1,21,36,37], although the latter values refer to the NiAs high spin phase. The MnP type arsenides FeAs and CoAs [38] are much less compressible (having $B_0 = 118$ GPa, $B_0' = 7.2$ and $B_0 = 123$ GPa, $B_0' = 8.8$ from least-squares fit to the Birch and Murnaghan equation of state, respectively), which may be understood by the fact that the orthorhombic MnP type distortion of these compounds is completed at room temperature and that no electronic instabilities occur.

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